Title	THE STRUCTURAL STUDIES ON ASYMMETRIC SELECTIVE POLYMERIZATION OF RACEMIC METHACRYLATES CATALYZED BY GRIGNARD REAGENT- (-) -SPARTEINE DERIVATIVE COMPLEXES
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（メタクリル酸エステルのグリニャール試薬-
(—)-スパルテイン誘導体錯体による不斉選択重合の構造化学的研究）

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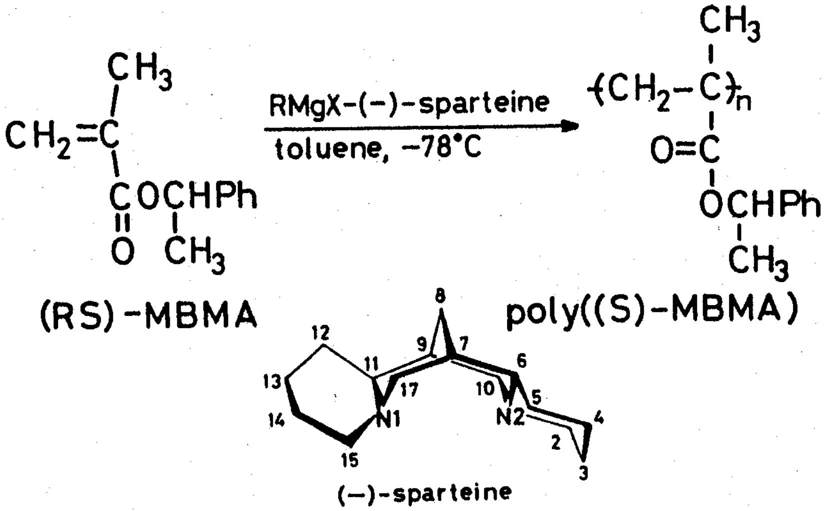
CONTENTS

GENERAL INTRODUCTION

The molecular structure determination by means of X-ray diffraction has been established and likely has become a routine work in these years. This afford us the X-ray diffraction as one of the most effective tools for the analysis of the reation systems of complicated compounds because the X-ray crystal structure analysis gives the three-dimensional, exact structures of these complex compounds if they can be crystallized.

Recently Okamoto *et al.* have studied the asymmetric selective polymerization of racemic α-methylbenzyl methacrylate(MBMA) with Grignard reagent-(–)-sparteine as initiators.$^{1-5)}$ In this reaction, the (*S*)-MBMA molecules are polymerized preferentially over the (*R*)-antipodes, which is proved by the high optical purity of the polymer produced and the unreacted (*R*)-monomer(Scheme 1).



Scheme 1.

The reaction activity of the initiators for the asymmetric selective polymerization of methacrylates is attained by modifying the environment of the Mg atom in Grignard reagents with a chiral bidentate ligand, (−)-sparteine. The detailed studies on the mechanism of the enantiomer selection in this reaction will probably give us useful informations for the design of new catalyst systems for optical resolution. In this thesis, the structural-chemical approach has been described in order to elucidate the catalytic reaction mechanism of the asymmetric selective polymerization of methacrylates mainly from two sides: One is concerned with the molecular structures of initiators and the other concerned with that of methacrylate monomers.

This thesis consists of three chapters. In Chapter I molecular structures of initiators, Grignard reagent-(−)-sparteine derivative complexes have been determined by means of X-ray diffraction, and the structures determined have been compared in order to find correlation with thier reactivity. Chapter II deals with the X-ray determination and description of the molecular structures of methacrylates with bulky ester substituents, and also deals with discussions on the relationship between molecular conformation and enantiomer selectivity. In Chapter III, based on the molecular structures of initiator complexes and of methacrylates determined, discussions about the mechanism of this asymmetric selective polymerization of racemic methacryalte is described by referring and considering the chemical evidences.

CHAPTER I

The Molecular Structure of Grignard Reagent-(−)-Sparteine Derivative Complexes

Introduction

In this chapter the X-ray structure determination of some Grignard reagent-(−)-sparteine derivative complexes is described, and the relationship between the molecular structure and the reactivity of these molecules as the initiator for the asymmetric selective polymerization of racemic α-methylbenzyl methacrylate is discussed.

Brief History of Asymmetric Selective Polymerization

The usage of the Ziegler-Natta catalyst(1955) to obtain isotactic polypropylene made an epoch in the polymer chemistry. The specified polymerizations have been first developed to control the tacticity of the polymer obtained by using a metal salt or an organometallic compound as a catalyst in polymerization reaction system, which made much contribution to the later development of the polymer chemistry and polymer industry. The specified polymerization has widely developed in the fields of stereospecific polymerization, stereoselective polymerization, asymmetric selective polymerization, and so forth.

The asymmetric selective polymerization is a polymerization that one enantiomer from a racemic mixture of monomers are polymerized preferentially over the antipode monomers by enantio-differentiating function of the chiral initiators or catalyst added to the polymerization reaction system. Optical resolution performed in these polymerizations, is a kinetic resolution that utilized different ratios in polymerization of enatiomers. These asymmetric selective polymerizations in the early time are, for example, the polymerization of α-olefins with (+)-bis[(*S*)-2-methylbutyl]zinc/$TiCl_4$ catalyst initiated by Pino *et al.*(1963)$^{6)}$, and the polymerization of methyloxirane with Et_2Zn-(+)-borneol initiator reported by Tsuruta *et al.*(1962)$^{7)}$. But the optical purity obtained in these polymerizations were not so high, and therefore these could not be used as practical method for optical resolution. During period from 1979 to 1980 several asymmetric selective polymerizations of high selectivity were published; they are, for example, the polymerization of racemic methylthiirane with (*S*)-2,2'-dihydroxy-1,1'-binaphtyl/Et_2Zn initiator by Spassky *et al.*(1981)$^{8)}$, the polymerization of α-methylbenzyl methacrylate with (*R*)-2,2'-diamino-6,6'-dimethylbiphenyl/Grignard reagent by Suda *et al.*(1981).

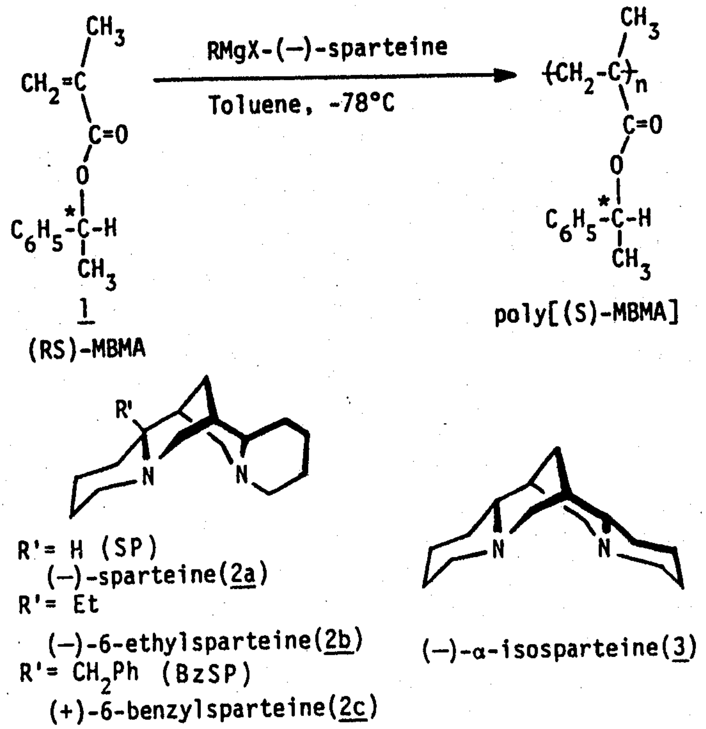
Among them, polymerization of racemic methacrylates with Grignard reagent-(—)-sparteine initiator by Yuki, Okamoto *et al.* has specially high enatiomer selectivity with the optical putity greater than 90%. Surprisingly, the monomer in this polymerization reaction system has a chiral center on the γ-site from the reaction site, although in the other asymmetric selective polymerization system the monomer has a chiral center on the α-position from the reaction site and all of them indicated low enatiomer selectivity. Much interest about the mechanism of the enantiomer selection promoted the present author to undertake the present study in order to obtain informations to explain the whole behavior of the asymmetric selective polymerization of methacrylates, which based on the molecular structures, determined by means of X-ray diffraction, of some Grignard reagent-(−)-sparteine derivative complexes and several racemic methacrylates with chiral carbon atom at α-position of alcohol.

The Studies on Initiators of The Asymmetric Selective Polymerization of Racemic Methacrylates, Grignard Reagent-(−)-Sparteine Derivative Complexes

The studies on the asymmetric selective polymerization of racemic α-methylbenzyl methacrylate with Grignard reagent-(−)-sparteine complexes has been begun by the discovery of highly active initiators, *c*-HexMgCl- and *c*-HexMgBr-(−)-sparteine. In these cases the initiator system polymerizes preferentially (*S*)-monomers over (*R*)-monomers in toluene at -78°C, where the optical purity of the unreacted monomer was more than 90% at about 65% yield of the polymer(Scheme 2).

Thereafter the studies on the catalyst system have been widely developed in two directions: One is that the polymerization reaction with the initiator systems of which Grignard reagents were altered systematically against the (−)-sparteine, and the other is that with the initiator system of which (−)-sparteine derivatives were changed against a Grignard reagent, EtMgBr(Scheme 2). The results of polymerization experiments by Okamoto *et al.* are given in Table 1.

Remarkable result of the former series of experiments is



Scheme 2.

Table 1.

Polymerization with Grignard reagent-(–)-sparteine and Grignard reagent-(–)-sparteine derivative systems (toluene, -78°C)

Grignard reagent	Time hr	Yield %	$[\alpha]_D^{20}$ (O.P.) of polymer	$[\alpha]_D^{20}$ (O.P.) of monomer	Tacticity(%)			
					I	H	S	
(–)-sparteine								
EtMgBr	1	41.4	-102.2(82)	+30.4(57.4)	94	5	1	(4a)
i-PrMgBr	1	31.7	-106.1(85)	+20.7(39.4)	-	-	-	(4b)
i-BuMgBr	6	32.0	-106.6(85)	+20.4(39.0)	-	-	-	(4c)
c-HexMgBr	2	51.8	-95.5(76)	+43.8(82.7)	-	-	-	(4d)
n-BuMgCl	1	52.6	-93.9(75)	+45.0(84.8)	-	-	-	(4e)
c-HexMgCl	4	48.1	-101.3(81)	+40.5(75.1)	92	5	3	(4f)
t-BuMgCl	96	0.4	0 (0)	0 (0)	-	-	-	(4g)
BzMgCl	123	0.6	-87.2(70)	+0.3(0.6)	-	-	-	(4h)
PhMgBr	192	0	- (-)	- (-)	-	-	-	(4i)
c-HexMgI	115	32.6	-34.7(28)	+6.9(13.1)	70	18	12	(4j)
(–)-α-isosparteine								
EtMgBr	22	0	- (-)	- (-)	-	-	-	(5)
(–)-6-ethylsparteine								
EtMgBr	264	0	- (-)	- (-)	-	-	-	(6)
(+)-6-benzylsparteine								
EtMgBr	99.0	14.1	-82.9(66)	+6.2(11.7)	77	14	9	(7)

that the initiators consist of a primary or secondary Grignard reagent indicate high activity and selectivity for the asymmetric selective polymerization, however those with tertiary or bulky Grignard reagents show no activity. On the other hand, in the latter series of experiments resulted in that the initiators which has (+)-6-benzylsparteine as a ligand has low activity and selectivity, and those have (–)-6-ethylsparteine and (–)-α-isosparteine as ligands show no activity.

The systematic studies on the molecular structure of these initiator complexes by X-ray structure determination, were planed and carried out. However only four complexes, highly active EtMgBr-(–)-sparteine(4a), inactive *t*-BuMgCl-(–)-sparteine(4g), inactive EtMgBr-(–)-α-isosparteine(5), and poorly selective EtMgBr-(+)-6-benzylsparteine(7) could be crystallized suitably for X-ray diffraction measurement because of the difficulty in crystallization as mentioned below. In this chapter the molecular structure of these four complexes and other related complexes, which easily crystallized during the course of crystallization is described.

1.1. X-Ray Experiment and Structure Determination

Each complex was prepared in the manner that a solution of the corresponding Grignard reagent was added to a (–)-sparteine derivative in toluene at room temperature under dry nitrogen(for (+)-6-benzylsparteine crystal itself, Scheme 3).

Preparation

EtMgBr/ether + (–)-sparteine/toluene $\xrightarrow{\text{r.t.}}$ 4a
t-BuMgCl/ether + (–)-sparteine/toluene $\xrightarrow{\text{r.t.}}$ 4g
EtMgBr/ether + (–)-α-isosparteine/toluene $\xrightarrow{\text{r.t.}}$ 5
EtMgBr/ether + (+)-6-benzylsparteine $\xrightarrow{\text{r.t.}}$ 7

By-products Schlenk equilibrium $2RMgX \rightleftarrows R_2Mg + MgX_2$
R= *i*-Pr, X= Br, L= (–)-sparteine
i-PrMgBr-L(4b), $(i\text{-Pr})_2$Mg-L, and $MgBr_2$-L(4b')
R= *t*-Bu, X= Cl, L= (–)-sparteine
t-BuMgCl-L(4g), $(t\text{-Bu})_2$Mg-L, and $MgCl_2$-L(4g')
R= Et, X= Br, L= (+)-6-benzylsparteine
EtMgBr-L(7), Et_2Mg-L, and $MgBr_2$-L(7')

Scheme 3.

Crystals used in X-ray experiment were obtained by recrystallization from toluene under nitrogen, but in some cases by-products expected from Schlenk equilibrium(mainly dihalogeno[(–)-sparteine derivative]magnesium(II) complexes) crystallized(Scheme 3). For example, only dibromo[(–)-sparteine]magnesuim(II) crystallized when *i*-PrMgBr was used as Grignard reagent. This difficulty in the crystallization of the target complexes limited the number of crystals used in the X-ray experiment. In this chapter, the molecular structures of $MgCl_2$-(–)-sparteine(4g'), $MgBr_2$-(+)-6-benzylsparteine(7') were also described. The molecular structure of (+)-6-benzylsparteine(2c) has also been determined in order to know the conformation of un-coordinated (–)-sparteine derivative ligands. Crystals of (+)-6-benzylsparteine was recrystallized from methanol.

X-ray Experiment

Crystals of the above-mentioned complexes(from 4a to 7') are all sensitive to moisture in air, and they were all sealed in glass capillary tubes under nitrogen. Each crystal was mounted on a Rigaku automated, four-circle diffractometer. Zirconium-filtered Mo*K*α radiation(λ=0.7107 Å) was used for 4a, graphite monochromatized Mo*K*α radiation for 4a-7', and nickel-filtered Cu*K*α radiation(λ=1.5418 Å) for 2c, respectively. Unit-cell dimensions of each crystal were determined by the least-squares fit of 2θ values of 25 high order, strong reflections. Crystal data of each crystal are summarized in Table 2.

Reflection intensities were measured by the θ-2θ scan technique. Backgrounds were counted for 7.5 s at both ends of a scan. Four standard reflections were measured after every 60 reflections(in the case of 4a after 27 reflections), which showed less than 5% fluctuations throughout the data collection except for 4g'. For 4g', the intensities of the four standard reflections decreased; as they did so uniformly with time, the observed intensities were corrected linearly. Generally the reflection profiles were not so sharp, and in some case only the observed reflections were used for the structure analysis. Usual Lp corrections were applied but corrections for absorption and extinction were ignored. Conditions of the intensity measurement were listed in Table 3.

Structure Solution and Refinement

The structures of 4a, 5, and 7 were solved by the heavy atom method. The Br atom was located by three-dimensional Patterson function. Positions of the Mg, N, and C atoms were determined by the subsequent Fourier synthesis. The structures of 4g, 4g' and 7' were solved by the heavy atom method with the aid of the direct method(*MULTAN* 78[9]). The positions of the Br, Cl and Mg atoms were confirmed by three-dimensional Patterson function. Positions of the N and C atoms were determined in same manner. The structure of 2c was solved by the direct method(*MULTAN* 78).

The refinement of the structures were carried out by block-diagonal least-squares procedure(*HBLS* V[10]). The function minimized was $\Sigma w(\Delta F)^2$. Generally hydrogen atoms were located and fixed at the calculated positions(C-H=1.08 Å) with equal isotropic temperature factors while non-hydrogen atoms were refined anisotropically. At the final stage of the refinement the anomalous dispersion of all the non-hydrogen atoms were considered. Details of the refinement and final R and R_w values were summarized in Table 3. The final atomic parameters of 4a, 4g, 4g', 5, 7, 7', and 2c are listed in Tables 4, 5, 6, 7, 8, 9, and 10, respectively.

Atomic scattering factors and coefficients of anomalous dispersion[11] used were taken from International Tables for X-Ray Crystallography, Vol. IV. All the computations were done on an ACOS 700 or 900 computer at the Computation Center, and an ACOS 700 or 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Table 2.

Crystal Data

Compound	(4a)	(4g)	(4g')	(5)	(7)	(7')	(2c)
Formula	$C_{17}H_{31}N_2MgBr$	$C_{19}H_{35}N_2MgCl$	$C_{15}H_{26}N_2MgCl_2$	$C_{17}H_{31}N_2MgBr$	$C_{24}H_{37}N_2MgBr$	$C_{22}H_{32}N_2MgBr_2 \cdot C_7H_8$	$C_{22}H_{32}N_2$
F.W.	367.7	351.3	329.6	367.7	457.8	600.8	324.5
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a[Å]	11.278(2)	25.689(6)	11.180(4)	10.646(4)	11.020(4)	16.654(3)	10.711(1)
b[Å]	14.112(3)	10.030(2)	11.957(4)	14.491(4)	23.660(10)	19.723(4)	25.868(4)
c[Å]	11.746(2)	7.942(2)	12.573(5)	11.857(3)	8.666(6)	8.637(2)	6.804(1)
V[Å^3]	1869.5(5)	2046.3(7)	1680.7(10)	1829.1(9)	2260(2)	2836.8(9)	1885.1(4)
Z	4	4	4	4	4	4	4
D_c[gcm^{-3}]	1.31	1.14	1.30	1.34	1.35	1.41	1.14
μ(Mo$K\alpha$)[cm^{-1}]	23.6	2.22	4.18	24.1	19.7	30.7	-
μ(Cu$K\alpha$)[cm^{-1}]	-	-	-	-	-	-	5.07

Table 3.

Summary of Experimental Conditions, Structure Solution and Refinement

Compound	(4a)	(4g)	(4g')	(5)	(7)	(7')	(2c)
Radiation	Mo *K*α Zr-filter	Mo *K*α graphite monochromator	Mo *K*α graphite monochromator	Mo *K*α graphite monochromator	Mo *K*α graphite monochromator	Mo *K*α graphite monochromator	Cu *K*α Ni-filter
Crystal Size[mm^3]	0.50×0.50×0.38	0.40×0.20×0.18	0.20×0.18×0.50	0.55×0.38×0.30	0.68×0.33×0.25	0.13×0.25×0.50	0.38×0.25×0.23
Scan Technique	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
Scan Range $\Delta 2\theta$[°]	$2.0+0.7\tan\theta$	$2.4+0.7\tan\theta$	$2.4+0.7\tan\theta$	$2.4+0.7\tan\theta$	$2.4+0.7\tan\theta$	$2.4+0.7\tan\theta$	$2.0+0.3\tan\theta$
Backgrounds Count[s]	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Scan Speed(in 2θ)	4°/min	4°/min	4°/min	4°/min	4°/min	4°/min	4°/min
$2\theta_{max}$[°]	50.5	46.0	50.5	50.5	50.5	50.5	110
Number of Reflections							
Measured	1937	1678	1763	1914	2369	2942	1408
Observed a)	1272 b)	1199 b)	1347	1235	1445	1501	1346 b)
Used for Refinement	1272	1678	1347	1235	1445	1501	1404
Solution Method c)	H.A.M.	H.A.M., D.M.	H.A.M., D.M.	H.A.M.	H.A.M.	H.A.M., D.M.	D.M.
Hydrogen Atoms	not located	included	included	included	not located	not located	refined
Final *R* Value d)							
for Measured Reflections	-	0.206	-	-	-	-	0.059
for Observed Reflections	0.100	0.098	0.091	0.074	0.169	0.118	0.055
Final R_w Value	0.103	0.124	0.104	0.078	0.188	0.126	0.092
Weighting Scheme e)	-f)				-f)	-f)	
a		0.03251	0.	0.06889			0.
b	-	0.00231	0.10124	0.00110	-	-	0.01024
c	-	0.02855	-	-	-	-	0.63654

a) $|F_o| \geq 3\sigma(F_o)$.. b) $|F_o|>0$. C) H.A.M.; heavy atom method, D.M.; direct method(*MULTAN* 78).

d) The block-diagonal least-squares procedures(*HBLS* V) was used for the refinement.

e) The weighting scheme $w = \{\sigma^2(F_o) + a\cdot|F_o| + b\cdot|F_o|^2\}^{-1}$ for $|F_o|>0$, and $w = c$ for $|F_o|=0$.

f) $w = 1$ for all reflections used for the refinement.

(4a). The C(10) and C(17) atoms, and the C(16) atom which was located by the subsequent Fourier synthesis, were refined isotropically. Hydrogen atoms could not be located on the difference Fourier map.

(4g and 4g'). The isotropic temperature factors *B*'s were fixed to 3.3 $\mathring{A}^2$.

(5). The isotropic temperature factors *B*'s were fixed to 4.0 $\mathring{A}^2$.

(7). The isotropic temperature factors of the C(1) atom was fixed as B=4.67 $\mathring{A}^2$ which was derived from the Wilson statistics of structure amplitudes. The C(16) could be located on a difference Fourier map and fixed at the position. The C(3) atom was refined isotropically. Hydorgen atoms could not be located on the difference Fourier map.

(7'). Hydrogen atoms could not be located on a difference Fourier map.

(2c). Hydrogen atoms were located on a difference Fourier map, which were refined isotropically. During the course of the refinement four strong reflections(200, 230, 031 and 160), which were considered largely affected by the extiction, were excluded.

Table 4. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s$^{12)}$ of 4a with their estimated standard deviations in parentheses.

Atom	x	y	z	B_{eq} (or B) [$\mathrm{\AA}^2$]
Br	-0.0481(3)	0.5669(2)	0.4195(2)	5.4
Mg	-0.0501(7)	0.4081(5)	0.3286(6)	4.0
N(1)	0.090(2)	0.403(2)	0.206(2)	4.6
N(2)	-0.161(2)	0.428(2)	0.181(2)	5.1
C(1)	-0.041(3)	0.285(2)	0.450(2)	5.4
C(2)	-0.290(2)	0.447(2)	0.220(3)	7.0
C(3)	-0.332(3)	0.365(2)	0.285(3)	6.5
C(4)	-0.336(3)	0.277(3)	0.213(3)	8.5
C(5)	-0.198(3)	0.261(2)	0.164(3)	6.4
C(6)	-0.162(3)	0.346(2)	0.101(2)	6.3
C(7)	-0.033(2)	0.333(2)	0.049(2)	5.0
C(8)	-0.011(3)	0.418(2)	-0.024(2)	5.8
C(9)	-0.004(3)	0.505(2)	0.057(3)	7.1
C(10)$^{a)}$	-0.126(2)	0.520(2)	0.120(2)	4.8(5)
C(11)	0.100(3)	0.494(2)	0.139(3)	6.3
C(12)	0.221(3)	0.508(2)	0.080(3)	7.5
C(13)	0.326(3)	0.495(3)	0.167(3)	8.7
C(14)	0.319(2)	0.399(3)	0.218(3)	7.1
C(15)	0.198(2)	0.388(2)	0.281(3)	6.2
C(16)$^{a)}$	-0.080(4)	0.296(3)	0.543(4)	12.7(13)
C(17)$^{a)}$	0.069(2)	0.319(2)	0.131(2)	4.2(5)

a) Refined isotropically.

Table 5. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of 4q with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[$Å^2$]
Cl	0.04219(14)	0.0720(4)	0.0861(5)	4.4
Mg	0.1037(2)	0.0490(4)	0.3000(6)	2.7
N(1)	0.1347(4)	0.2502(10)	0.3113(12)	2.7
N(2)	0.0784(4)	0.0905(10)	0.5561(12)	3.0
C(1)	0.1570(5)	-0.1191(14)	0.2685(21)	5.0
C(2)	0.0522(6)	-0.0317(14)	0.6271(17)	4.5
C(3)	-0.0009(6)	-0.0534(14)	0.5246(18)	4.9
C(4)	-0.0345(6)	0.0665(15)	0.5460(19)	5.3
C(5)	-0.0070(5)	0.1945(12)	0.4890(17)	3.7
C(6)	0.0441(5)	0.2093(12)	0.5822(16)	3.5
C(7)	0.0741(5)	0.3374(12)	0.5315(17)	3.3
C(8)	0.1187(5)	0.3553(14)	0.6599(19)	4.7
C(9)	0.1567(5)	0.2412(13)	0.6174(15)	3.3
C(10)	0.1281(5)	0.1091(12)	0.6602(17)	3.8
C(11)	0.1780(5)	0.2510(13)	0.4395(15)	3.1
C(12)	0.2152(6)	0.3681(13)	0.4197(20)	4.4
C(13)	0.2377(6)	0.3759(15)	0.2402(19)	4.8
C(14)	0.1931(6)	0.3911(13)	0.1188(18)	4.5
C(15)	0.1563(5)	0.2664(14)	0.1402(16)	4.3
C(16)	0.1599(9)	-0.139(3)	0.081(3)	10.4
C(17)	0.0933(5)	0.3472(13)	0.3514(16)	3.6
C(18)	0.2118(7)	-0.107(2)	0.330(4)	11.0
C(19)	0.1320(8)	-0.242(2)	0.339(3)	8.8

Table 5. (continued)

b) Hydrogen atoms*

Atom	x	y	z
H(2a)	0.0439	-0.017	0.759
H(2b)	0.0772	-0.118	0.613
H(3a)	0.0076	-0.068	0.393
H(3b)	-0.0209	-0.140	0.572
H(4a)	-0.0449	0.076	0.677
H(4b)	-0.0695	0.054	0.473
H(5a)	0.0003	0.190	0.355
H(5b)	-0.0316	0.279	0.515
H(6)	0.0340	0.217	0.714
H(7)	0.0463	0.418	0.535
H(8a)	0.1045	0.346	0.787
H(8b)	0.1373	0.451	0.645
H(9)	0.1917	0.247	0.692
H(10a)	0.1180	0.109	0.792
H(10b)	0.1540	0.027	0.636
H(11)	0.2010	0.163	0.415
H(12a)	0.2468	0.357	0.508
H(12b)	0.1946	0.459	0.447
H(13a)	0.2592	0.286	0.212
H(13b)	0.2636	0.460	0.230
H(14a)	0.2076	0.396	-0.009
H(14b)	0.1719	0.482	0.146
H(15a)	0.1782	0.178	0.109
H(15b)	0.1243	0.276	0.053
H(16a)	0.1215	-0.160	0.033
H(16b)	0.1857	-0.221	0.053
H(16c)	0.1745	-0.049	0.023
H(17a)	0.0608	0.330	0.268
H(17b)	0.1082	0.447	0.331
H(18a)	0.2120	-0.107	0.466
H(18b)	0.2343	-0.191	0.285
H(18c)	0.2288	-0.016	0.284
H(19a)	0.1362	-0.243	0.474
H(19b)	0.0912	-0.243	0.307
H(19c)	0.1506	-0.330	0.287

* Isotropic temperature factors B's were fixed as 3.3 Å^2.

Table 6. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s[12] of 4g' with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	$B_{eq}[\mathring{A}^2]$
Cl(1)	0.2110(4)	0.1164(3)	0.0138(3)	4.4
Cl(2)	0.1761(4)	0.4379(3)	0.0491(3)	5.0
Mg	0.1941(4)	0.2655(3)	0.1245(3)	2.4
N(1)	0.0535(7)	0.2304(7)	0.2364(7)	2.0
N(2)	0.3045(7)	0.2883(7)	0.2637(7)	2.5
C(2)	0.4269(10)	0.3228(9)	0.2285(10)	3.1
C(3)	0.4870(10)	0.2277(12)	0.1643(12)	4.4
C(4)	0.4951(12)	0.1249(12)	0.2267(12)	4.9
C(5)	0.3706(11)	0.0927(10)	0.2696(10)	3.8
C(6)	0.3131(10)	0.1923(9)	0.3313(9)	3.0
C(7)	0.1912(10)	0.1645(10)	0.3825(9)	3.2
C(8)	0.1487(11)	0.2595(12)	0.4476(9)	4.1
C(9)	0.1321(10)	0.3544(10)	0.3769(9)	3.3
C(10)	0.2521(11)	0.3816(10)	0.3246(10)	3.8
C(11)	0.0296(10)	0.3308(9)	0.2979(8)	2.5
C(12)	-0.0933(11)	0.3261(10)	0.3540(10)	3.5
C(13)	-0.1945(10)	0.3024(10)	0.2780(10)	3.3
C(14)	-0.1689(11)	0.1950(11)	0.2237(11)	4.1
C(15)	-0.0496(10)	0.1987(11)	0.1636(11)	3.7
C(17)	0.0889(10)	0.1354(9)	0.3016(10)	3.2

Table 6. (continued)

b) Hydrogen atoms*

Atom	x	y	z
H(2a)	0.4808	0.3419	0.2975
H(2b)	0.4202	0.3966	0.1794
H(3a)	0.5759	0.2536	0.1414
H(3b)	0.4352	0.2117	0.0934
H(4a)	0.5557	0.1375	0.2924
H(4b)	0.5289	0.0583	0.1771
H(5a)	0.3793	0.0219	0.3224
H(5b)	0.3134	0.0698	0.2039
H(6)	0.3720	0.2104	0.3971
H(7)	0.2085	0.0907	0.4297
H(8a)	0.2138	0.2796	0.5081
H(8b)	0.0650	0.2383	0.4856
H(9)	0.1046	0.4282	0.4201
H(10a)	0.3145	0.4055	0.3861
H(10b)	0.2393	0.4514	0.2714
H(11)	0.0255	0.3999	0.2428
H(12a)	-0.1095	0.4055	0.3925
H(12b)	-0.0910	0.2612	0.4137
H(13a)	-0.2778	0.2964	0.3211
H(13b)	-0.2014	0.3689	0.2202
H(14a)	-0.1655	0.1290	0.2822
H(14b)	-0.2399	0.1774	0.1679
H(15a)	-0.0322	0.1174	0.1296
H(15b)	-0.0559	0.2594	0.1002
H(17a)	0.1195	0.0690	0.2501
H(17b)	0.0119	0.1065	0.3456

* Isotropic temperature factors B's were fixed as 3.3 $Å^2$.

Table 7. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of 5 with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
Br	0.01848(17)	0.04953(11)	0.07701(14)	5.1
Mg	0.0110(5)	-0.1001(3)	0.1827(4)	3.5
N(1)	-0.1161(10)	-0.1246(8)	0.3221(10)	3.3
N(2)	0.1490(11)	-0.0749(8)	0.3167(10)	3.6
C(1)	-0.0094(12)	-0.2206(9)	0.0680(11)	3.4
C(2)	0.2708(13)	-0.0437(12)	0.2696(13)	4.8
C(3)	0.3221(16)	-0.1173(12)	0.1921(17)	6.4
C(4)	0.3404(16)	-0.2086(13)	0.2542(16)	6.5
C(5)	0.2223(14)	-0.2362(10)	0.3099(15)	4.8
C(6)	0.1693(13)	-0.1595(10)	0.3894(11)	3.8
C(7)	0.0549(13)	-0.1850(10)	0.4530(12)	4.1
C(8)	0.0235(18)	-0.1097(12)	0.5375(13)	5.6
C(9)	-0.0120(18)	-0.0250(11)	0.4664(12)	5.5
C(10)	0.0966(16)	0.0035(11)	0.3907(13)	5.0
C(11)	-0.1341(14)	-0.0476(11)	0.4034(12)	4.6
C(12)	-0.1939(16)	0.0374(13)	0.3437(16)	6.4
C(13)	-0.3178(17)	0.0107(14)	0.2885(16)	6.8
C(14)	-0.3002(16)	-0.0722(12)	0.2173(14)	5.2
C(15)	-0.2410(15)	-0.1514(12)	0.2752(15)	5.2
C(16)	0.0752(23)	-0.2166(15)	-0.0211(25)	11.0
C(17)	-0.0621(13)	-0.2061(10)	0.3823(13)	4.2

Table 7. (continued)

b) Hydrogen atoms*

Atom	x	y	z
H(1a)	0.0068	-0.2832	0.1152
H(1b)	-0.1038	-0.2218	0.0347
H(2a)	0.2763	0.0236	0.2307
H(2b)	0.3217	-0.0423	0.3484
H(3a)	0.2575	-0.1275	0.1230
H(3b)	0.4114	-0.0947	0.1587
H(4a)	0.3681	-0.2614	0.1948
H(4b)	0.4134	-0.2010	0.3167
H(5a)	0.1531	-0.2515	0.2460
H(5b)	0.2394	-0.2977	0.3591
H(6)	0.2368	-0.1472	0.4557
H(7)	0.0788	-0.2493	0.4937
H(8a)	0.1037	-0.0948	0.5903
H(8b)	-0.0541	-0.1304	0.5904
H(9)	-0.0295	0.0348	0.5184
H(10a)	0.0648	0.0584	0.3361
H(10b)	0.1717	0.0292	0.4433
H(11)	-0.1999	-0.0693	0.4676
H(12a)	-0.1301	0.0629	0.2801
H(12b)	-0.2104	0.0912	0.4050
H(13a)	-0.3509	0.0672	0.2370
H(13b)	-0.3868	-0.0036	0.3530
H(14a)	-0.2420	-0.0534	0.1464
H(14b)	-0.3911	-0.0937	0.1867
H(15a)	-0.2289	-0.2073	0.2159
H(15b)	-0.3013	-0.1743	0.3430
H(16a)	0.0952	-0.1454	-0.0410
H(16b)	0.0352	-0.2502	-0.0940
H(16c)	0.1612	-0.2512	0.0025
H(17a)	-0.0375	-0.2576	0.3203
H(17b)	-0.1333	-0.2339	0.4375

* Isotropic temperature factors B's were fixed as 4.0 Å^2.

Table 8. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of 7 with their estimated standard deviations in parentheses.

Atom	x	y	z	B_{eq}[Å^2]
Br	0.3580(4)	0.3635(2)	-0.0705(6)	5.3
Mg	0.536(2)	0.3805(6)	0.1038(15)	4.0
N(1)	0.458(3)	0.3966(11)	0.325(4)	3.2
N(2)	0.639(3)	0.3164(11)	0.231(3)	2.8
C(1)a)	0.674(4)	0.4436(16)	-0.007(5)	4.67
C(2)	0.714(3)	0.2910(13)	0.102(5)	3.5
C(3)b)	0.650(4)	0.2698(14)	-0.021(4)	4.0(8)
C(4)	0.549(4)	0.2211(16)	0.056(6)	5.3
C(5)	0.483(4)	0.2481(16)	0.182(5)	3.7
C(6)	0.567(4)	0.2722(16)	0.308(4)	3.6
C(7)	0.494(3)	0.2996(14)	0.442(5)	3.2
C(8)	0.579(3)	0.3263(14)	0.567(6)	4.4
C(9)	0.649(4)	0.3747(14)	0.467(6)	6.0
C(10)	0.712(3)	0.3490(13)	0.334(4)	2.1
C(11)	0.560(4)	0.4291(17)	0.420(6)	5.5
C(12)	0.509(4)	0.4547(13)	0.566(6)	4.0
C(13)	0.423(4)	0.5041(18)	0.513(5)	4.7
C(14)	0.312(4)	0.4710(16)	0.448(6)	5.5
C(15)	0.359(4)	0.4440(15)	0.287(5)	4.3
C(16)c)	0.765	0.4218	-0.100	15(3)
C(17)	0.397(4)	0.3451(16)	0.401(6)	5.6
C(18)	0.640(4)	0.2246(16)	0.373(5)	4.8
C(19)	0.584(3)	0.1763(14)	0.459(4)	2.6
C(20)	0.575(3)	0.1737(14)	0.621(5)	3.9
C(21)	0.532(4)	0.1274(15)	0.703(5)	4.8
C(22)	0.489(4)	0.0796(17)	0.613(6)	5.4
C(23)	0.490(4)	0.0803(16)	0.456(6)	5.0
C(24)	0.542(4)	0.1261(12)	0.373(5)	3.5

a) The isotropic tempearture factor was fixed as B=4.67 Å^2.
b) Refined isotropically.
c) The positional parameters were fixed.

Table 9. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s$^{12)}$ of 7' with their estimated standard deviations in parentheses.

Atom	x	y	z	B_{eq}[Å^2]
Br(1)	0.4524(3)	0.1648(3)	-0.4109(6)	6.7
Br(2)	0.3287(3)	0.1758(3)	-0.8188(6)	7.2
Mg	0.3250(7)	0.1949(5)	-0.5359(12)	3.9
N(1)	0.235(2)	0.141(2)	-0.422(3)	3.3
N(2)	0.247(2)	0.282(2)	-0.507(3)	3.0
C(2)	0.289(2)	0.336(2)	-0.594(5)	5.0
C(3)	0.374(3)	0.351(2)	-0.526(4)	4.8
C(4)	0.372(2)	0.362(2)	-0.336(4)	3.8
C(5)	0.317(2)	0.308(2)	-0.269(4)	3.7
C(6)	0.238(2)	0.301(2)	-0.336(4)	3.8
C(7)	0.181(2)	0.245(2)	-0.263(3)	2.6
C(8)	0.099(2)	0.237(2)	-0.338(4)	3.7
C(9)	0.118(2)	0.211(2)	-0.513(4)	4.2
C(10)	0.174(2)	0.268(2)	-0.594(4)	3.8
C(11)	0.163(2)	0.139(2)	-0.512(4)	3.3
C(12)	0.093(2)	0.088(2)	-0.461(5)	5.4
C(13)	0.136(2)	0.016(2)	-0.447(4)	4.3
C(14)	0.207(2)	0.018(2)	-0.342(6)	5.9
C(15)	0.270(2)	0.071(2)	-0.389(5)	4.1
C(17)	0.226(2)	0.172(2)	-0.259(4)	4.5
C(18)	0.188(3)	0.371(2)	-0.328(5)	5.4
C(19)	0.161(2)	0.389(2)	-0.157(4)	3.1
C(20)	0.085(2)	0.382(2)	-0.117(4)	3.7
C(21)	0.055(3)	0.402(2)	0.027(5)	7.4
C(22)	0.114(3)	0.433(2)	0.132(5)	6.4
C(23)	0.189(3)	0.444(2)	0.087(5)	6.1
C(24)	0.218(3)	0.422(2)	-0.072(5)	5.8
C(25)	-0.055(4)	0.023(3)	-0.102(6)	11.6
C(26)	-0.017(4)	0.077(3)	-0.045(6)	11.5
C(27)	0.060(3)	0.069(3)	0.015(6)	9.1
C(28)	0.098(4)	0.124(3)	0.072(6)	10.9
C(29)	0.059(4)	0.198(3)	0.072(7)	12.6
C(30)	-0.006(3)	0.199(4)	0.010(5)	10.4
C(31)	-0.057(3)	0.139(2)	-0.053(5)	6.4

Table 10. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of 2c with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
N(1)	0.9110(3)	0.4216(2)	0.0795(6)	3.9
N(2)	0.6163(3)	0.3744(2)	-0.1125(5)	3.0
C(2)	0.4936(4)	0.3781(2)	-0.2008(6)	3.9
C(3)	0.4005(4)	0.4050(2)	-0.0636(8)	4.8
C(4)	0.3965(4)	0.3785(2)	0.1376(7)	4.1
C(5)	0.5299(4)	0.3734(2)	0.2187(6)	3.2
C(6)	0.6218(4)	0.3464(2)	0.0767(6)	2.9
C(7)	0.7575(4)	0.3515(2)	0.1553(6)	3.0
C(8)	0.8493(4)	0.3273(2)	0.0108(6)	3.5
C(9)	0.8424(4)	0.3592(2)	-0.1764(6)	3.4
C(10)	0.7103(4)	0.3581(2)	-0.2558(6)	3.5
C(11)	0.8921(4)	0.4150(2)	-0.1343(7)	3.5
C(12)	1.0145(4)	0.4246(2)	-0.2409(8)	4.4
C(13)	1.0676(5)	0.4777(2)	-0.1915(10)	6.0
C(14)	1.0763(5)	0.4856(2)	0.0296(10)	6.0
C(15)	0.9518(5)	0.4740(2)	0.1277(9)	5.1
C(17)	0.7964(4)	0.4091(2)	0.1882(6)	3.7
C(18)	0.5837(4)	0.2878(2)	0.0541(6)	3.2
C(19)	0.5941(4)	0.2549(2)	0.2381(6)	3.0
C(20)	0.6943(4)	0.2214(2)	0.2642(7)	3.7
C(21)	0.7019(5)	0.1902(2)	0.4323(7)	4.3
C(22)	0.6103(5)	0.1923(2)	0.5734(7)	4.4
C(23)	0.5101(4)	0.2246(2)	0.5475(7)	4.1
C(24)	0.5009(4)	0.2552(2)	0.3801(7)	3.7

Table 10. (continued)

b) Hydrogen atoms

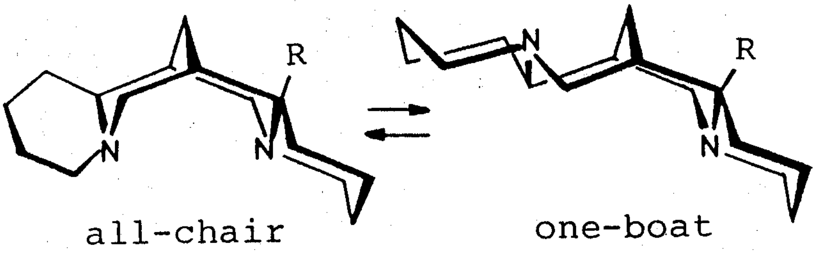
Atom	x	y	z	B[Å^2]
H(2a)	0.464(5)	0.341(2)	-0.226(8)	3.4(11)
H(2b)	0.497(4)	0.401(2)	-0.327(7)	2.7(10)
H(3a)	0.316(5)	0.405(2)	-0.123(8)	3.0(10)
H(3b)	0.427(4)	0.442(2)	-0.047(8)	3.3(11)
H(4a)	0.353(5)	0.344(2)	0.122(8)	3.0(10)
H(4b)	0.349(5)	0.400(2)	0.234(9)	3.8(11)
H(5a)	0.527(4)	0.353(2)	0.343(7)	2.9(10)
H(5b)	0.562(5)	0.409(2)	0.249(8)	2.7(10)
H(7)	0.761(4)	0.333(2)	0.283(7)	2.0(9)
H(8a)	0.825(4)	0.290(2)	-0.017(6)	1.8(9)
H(8b)	0.938(4)	0.328(2)	0.067(7)	2.3(9)
H(9)	0.898(5)	0.345(2)	-0.282(8)	3.6(11)
H(10a)	0.706(5)	0.385(2)	-0.368(8)	3.3(11)
H(10b)	0.691(4)	0.322(2)	-0.298(7)	2.7(10)
H(11)	0.826(4)	0.441(2)	-0.178(7)	2.3(10)
H(12a)	1.002(5)	0.422(2)	-0.390(9)	3.5(11)
H(12b)	1.077(5)	0.398(2)	-0.197(8)	3.5(11)
H(13a)	1.005(5)	0.504(2)	-0.256(8)	4.7(13)
H(13b)	1.151(6)	0.482(2)	-0.264(8)	4.5(12)
H(14a)	1.103(5)	0.523(2)	0.063(8)	3.5(11)
H(14b)	1.141(5)	0.461(2)	0.087(9)	3.9(11)
H(15a)	0.887(5)	0.501(2)	0.076(8)	3.5(11)
H(15b)	0.957(6)	0.478(2)	0.281(9)	4.6(13)
H(17a)	0.722(4)	0.430(2)	0.139(8)	2.6(10)
H(17b)	0.815(5)	0.419(2)	0.332(9)	3.9(12)
H(18a)	0.637(5)	0.271(2)	-0.059(9)	3.5(11)
H(18b)	0.493(4)	0.286(2)	0.003(7)	2.4(10)
H(20)	0.763(4)	0.221(2)	0.156(7)	1.5(9)
H(21)	0.779(4)	0.166(2)	0.449(7)	3.2(11)
H(22)	0.618(4)	0.171(2)	0.698(7)	2.5(10)
H(23)	0.445(5)	0.226(2)	0.647(9)	3.2(11)
H(24)	0.420(5)	0.278(2)	0.369(8)	3.0(10)

1.2. Results

Molecular Structure

Perspective views(*ORTEP* II[13]) of 2c, 4a, 4g, 4g', 5, 7, and 7' are depicted in Figures 1, 2, 3, 4, 5, 6, and 7, respectively. Bond lengths and bond angles in these compounds are given in Figures 8, 9, 10, 11, 12, 13, and 14, respectively. Comparison of the coordination geometry around the Mg atom is summarized in Table 11.

It is known that (–)-sparteine derivative can take two types of conformation: the "one-boat" form[14] for free (–)-sparteine and the "all-chair" form[15] for that coordinated to a metal(Scheme 4).



R = H, Et, CH_2Ph

Scheme 4.

It is confirmed that (+)-6-benzylsparteine(2c) takes a one-boat form in free situation in crystal. It is also observed in all the complexes in this study except for 5 that (–)-sparteine derivative coordinate to the Mg atom of Grignard reagent takes an all-chair form. All the Mg atoms in these complexes are tetrahedrally coordinated by the N atoms of (–)-sparteine derivative, and the C atom of alkyl group and the

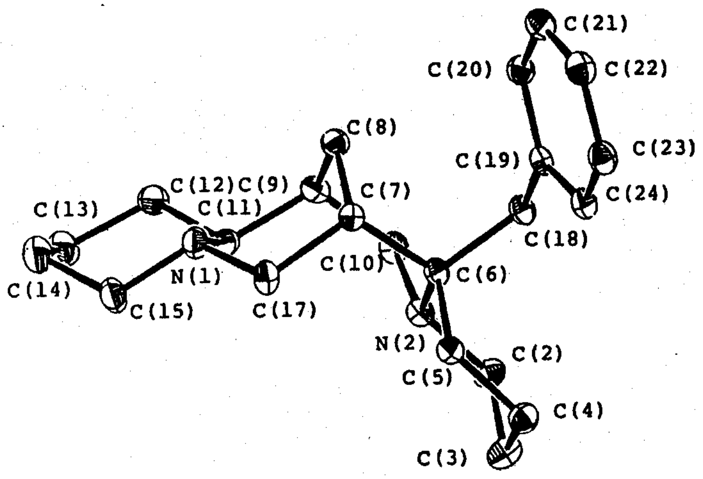


Figure 1. A perspective view(*ORTEP* II) of 2c

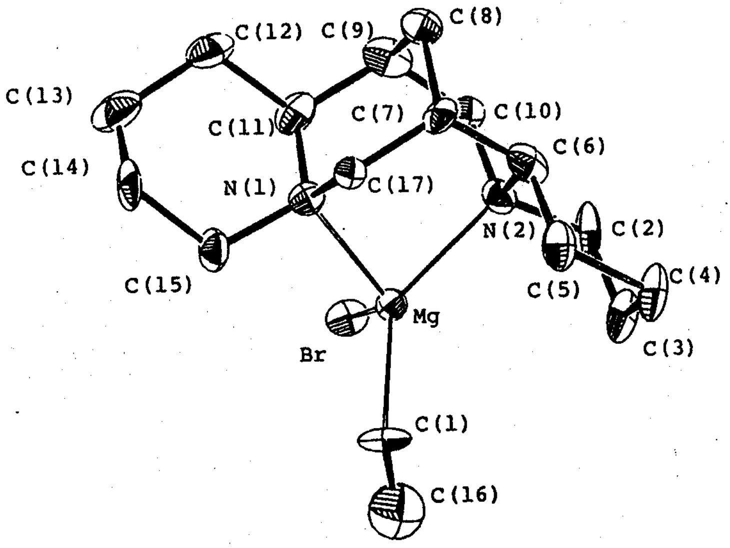


Figure 2. A perspective view(*ORTEP* II) of 4a

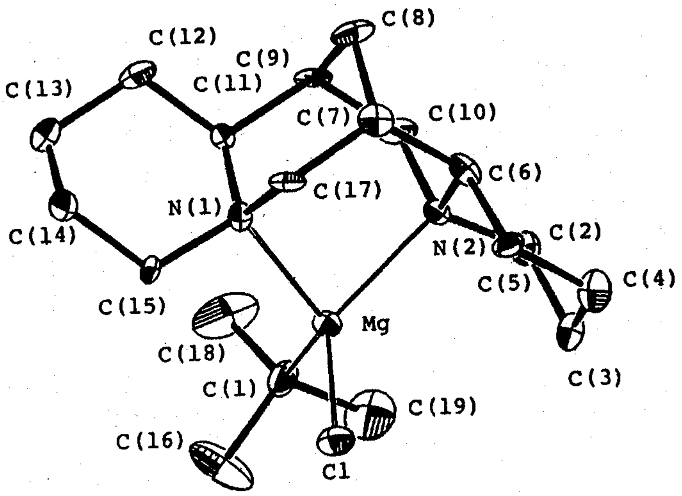


Figure 3. A perspective view(*ORTEP* II) of 4g

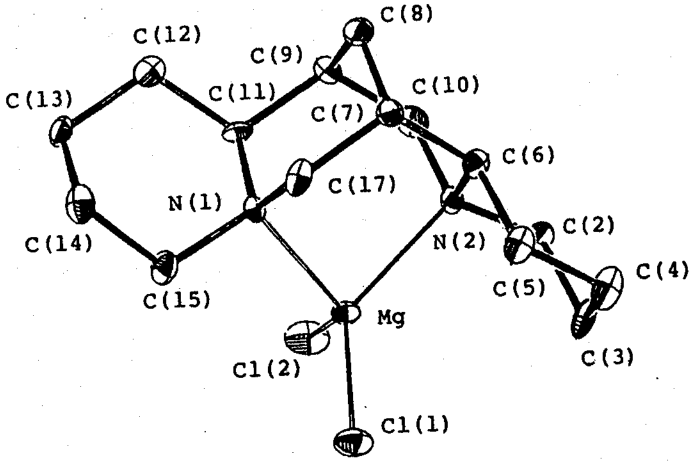


Figure 4. A perspective view(*ORTEP* II) of 4g'

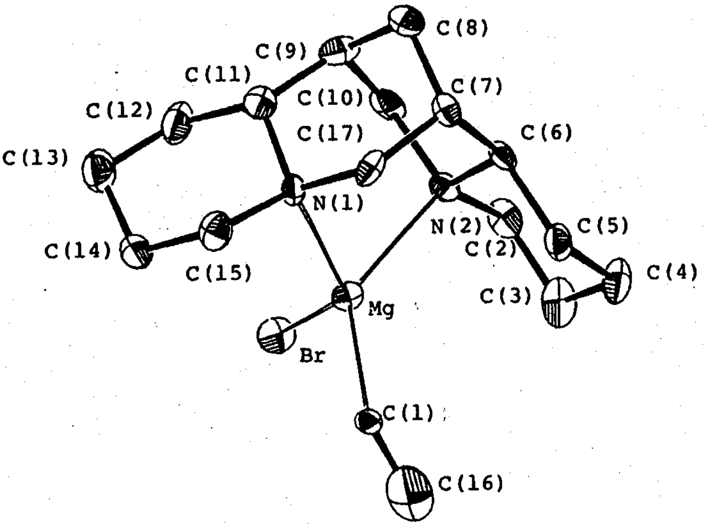


Figure 5. A perspective view(*ORTEP* II) of 5

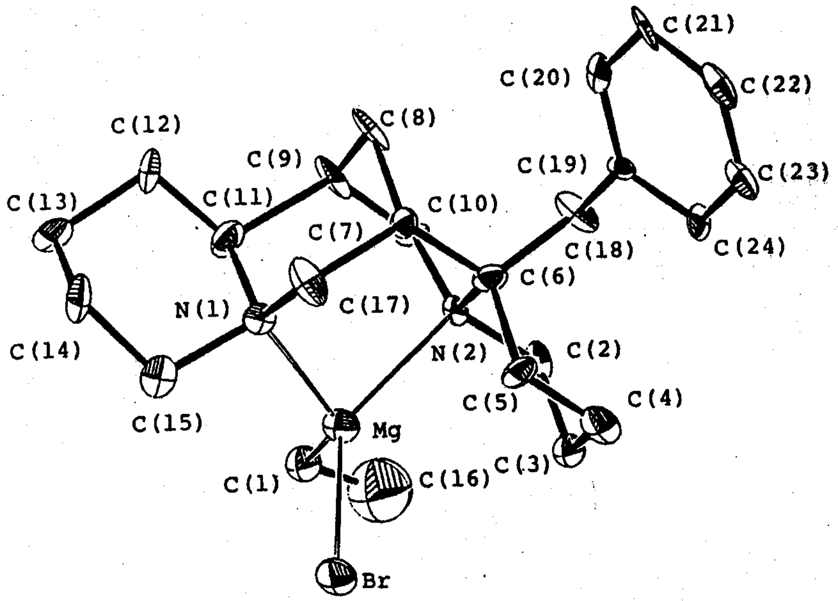


Figure 6. A perspective view(*ORTEP* II) of 7

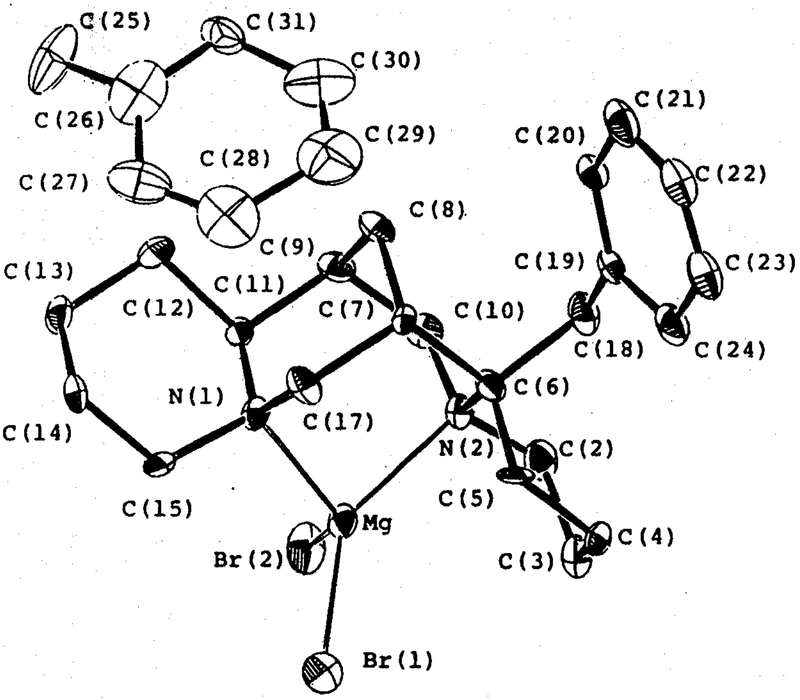
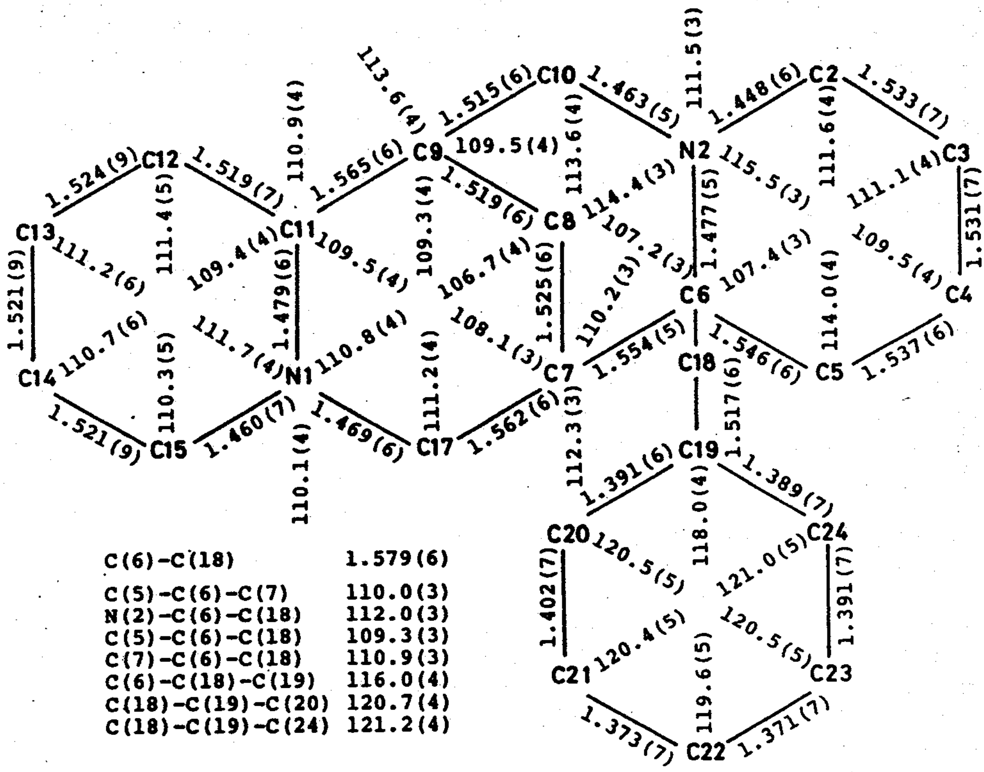


Figure 7.

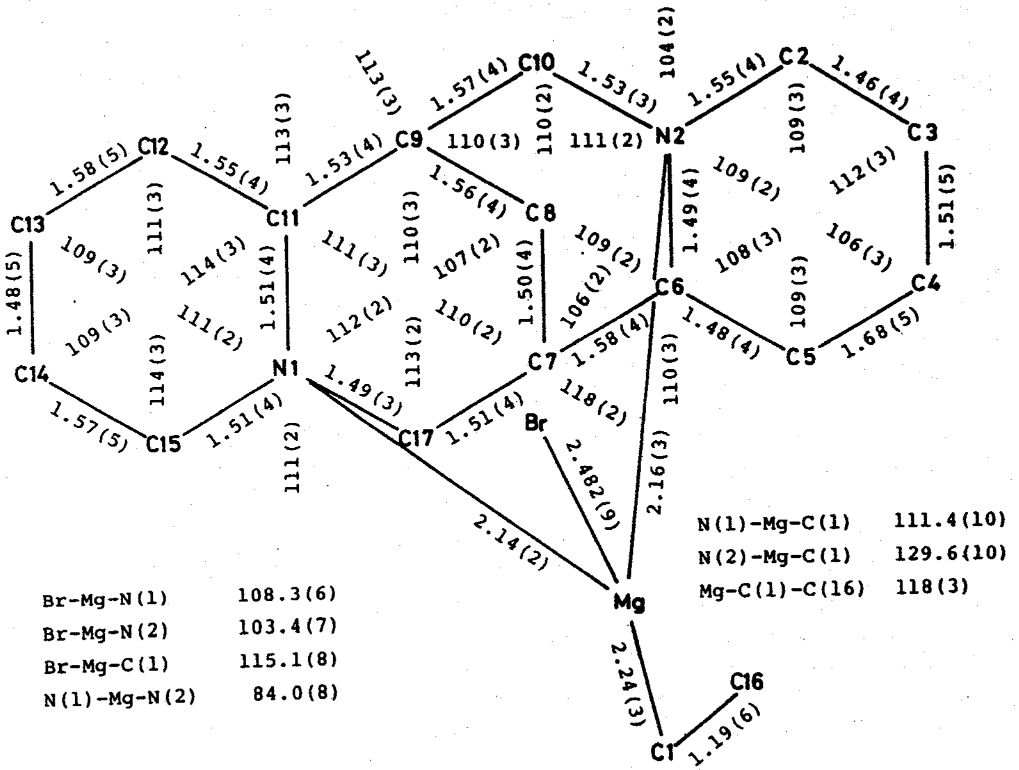
Perspective views(*ORTEP* II) of 7' and crystalline toluene

Figure 8. Bond lengths[Å] and bond angles[°] in 2c



C(6)-C(18)	1.579(6)
C(5)-C(6)-C(7)	110.0(3)
N(2)-C(6)-C(18)	112.0(3)
C(5)-C(6)-C(18)	109.3(3)
C(7)-C(6)-C(18)	110.9(3)
C(6)-C(18)-C(19)	116.0(4)
C(18)-C(19)-C(20)	120.7(4)
C(18)-C(19)-C(24)	121.2(4)

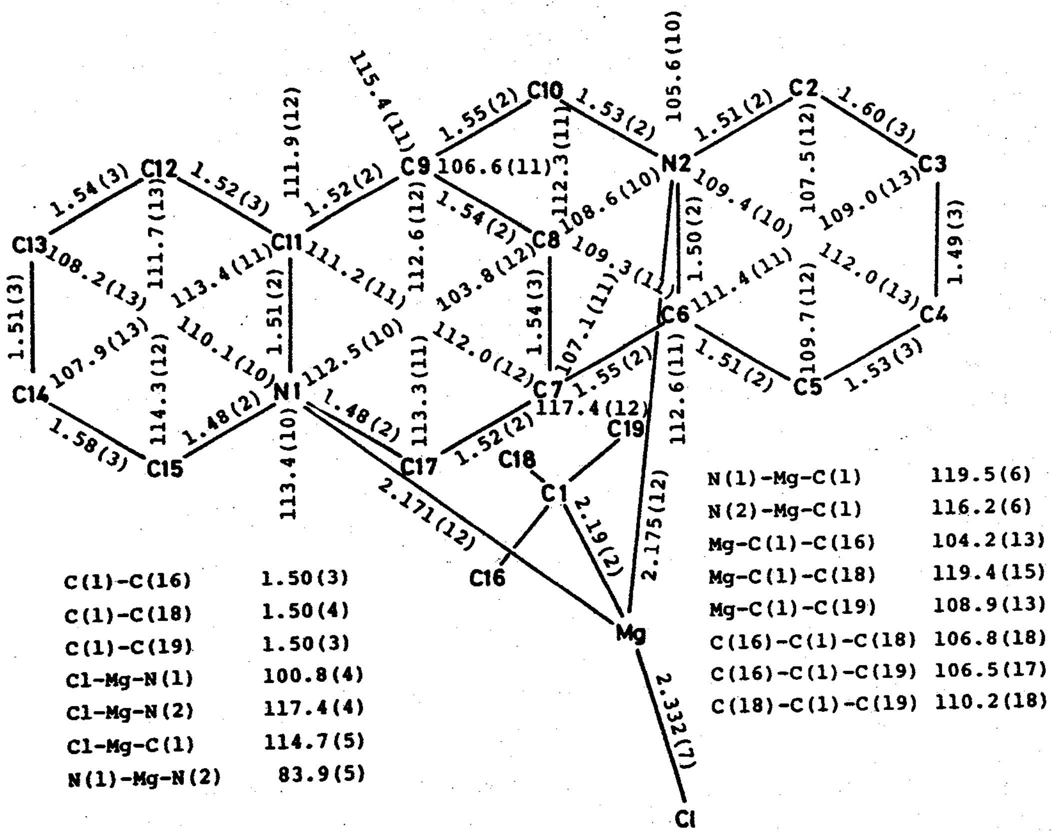
Figure 9. Bond lengths[Å] and bond angles[°] in 4a



Br-Mg-N(1)	108.3(6)
Br-Mg-N(2)	103.4(7)
Br-Mg-C(1)	115.1(8)
N(1)-Mg-N(2)	84.0(8)

N(1)-Mg-C(1)	111.4(10)
N(2)-Mg-C(1)	129.6(10)
Mg-C(1)-C(16)	118(3)

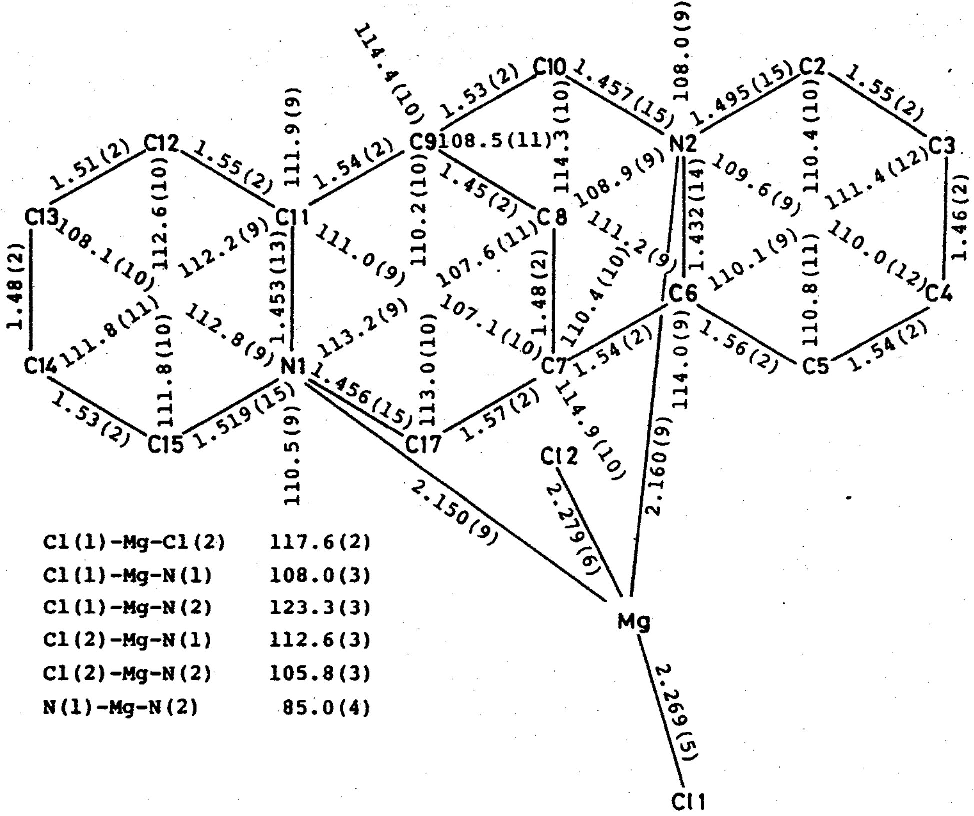
Figure 10. Bond lengths[Å] and bond angles[°] in 4g



C(1)-C(16)	1.50(3)
C(1)-C(18)	1.50(4)
C(1)-C(19)	1.50(3)
Cl-Mg-N(1)	100.8(4)
Cl-Mg-N(2)	117.4(4)
Cl-Mg-C(1)	114.7(5)
N(1)-Mg-N(2)	83.9(5)

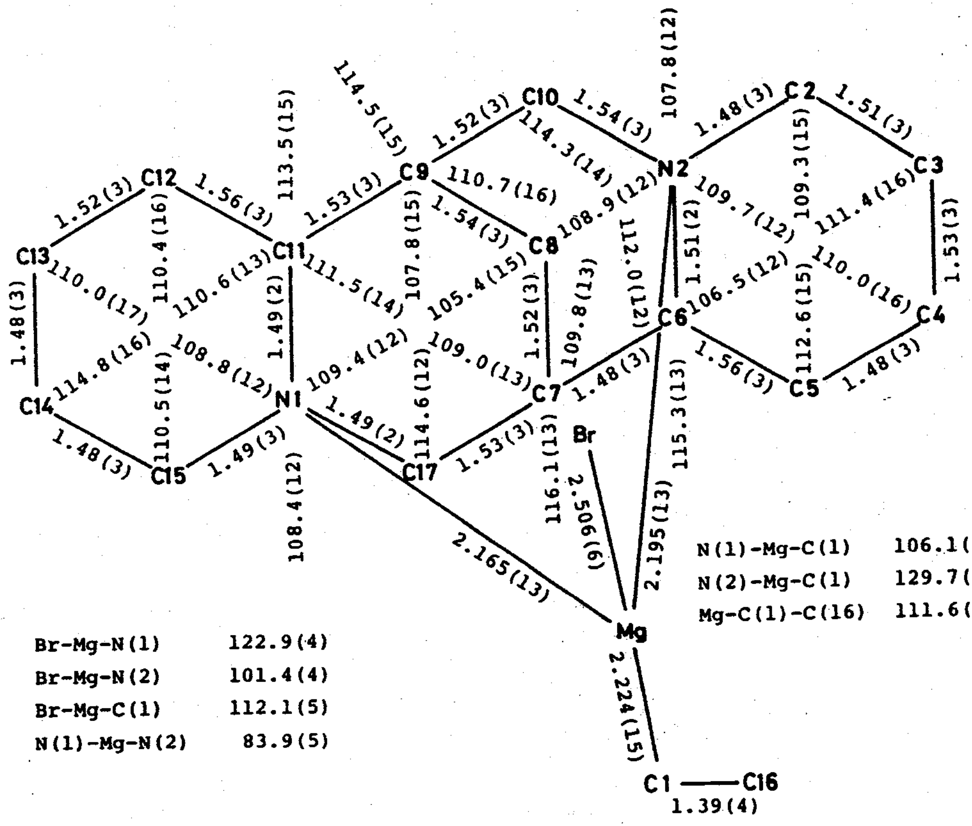
N(1)-Mg-C(1)	119.5(6)
N(2)-Mg-C(1)	116.2(6)
Mg-C(1)-C(16)	104.2(13)
Mg-C(1)-C(18)	119.4(15)
Mg-C(1)-C(19)	108.9(13)
C(16)-C(1)-C(18)	106.8(18)
C(16)-C(1)-C(19)	106.5(17)
C(18)-C(1)-C(19)	110.2(18)

Figure 11. Bond lengths[Å] and bond angles[°] in <u>4g'</u>



Cl(1)-Mg-Cl(2)	117.6(2)
Cl(1)-Mg-N(1)	108.0(3)
Cl(1)-Mg-N(2)	123.3(3)
Cl(2)-Mg-N(1)	112.6(3)
Cl(2)-Mg-N(2)	105.8(3)
N(1)-Mg-N(2)	85.0(4)

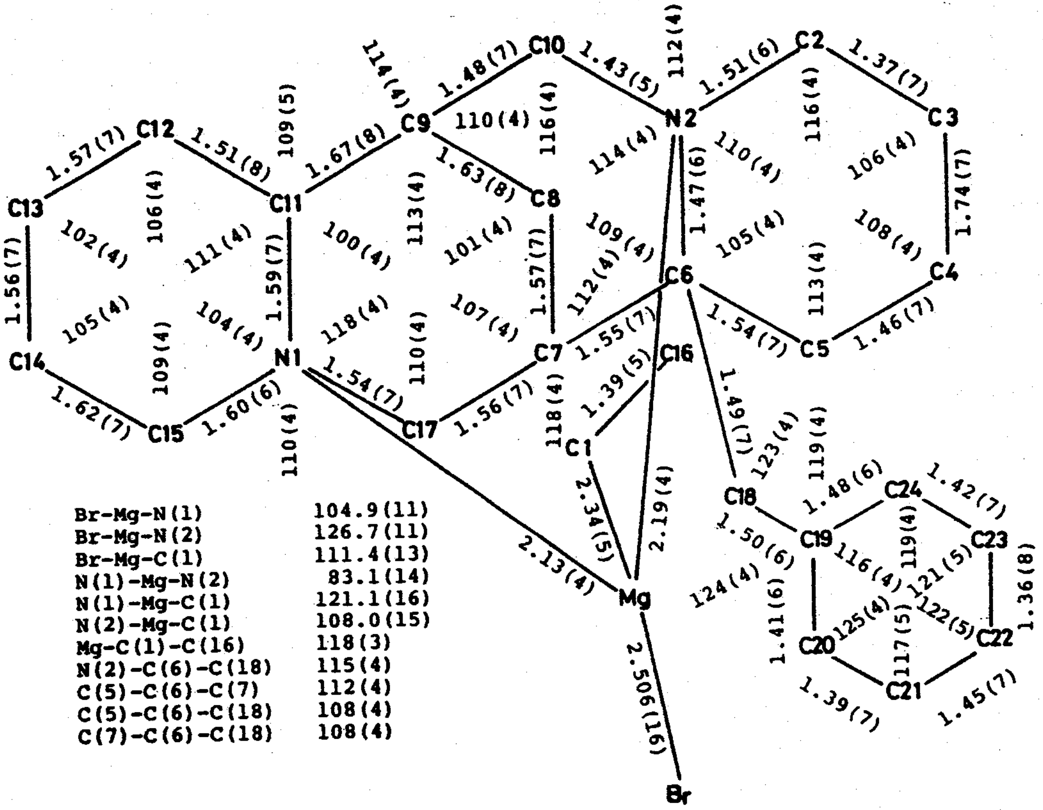
Figure 12. Bond lengths[Å] and bond angles[°] in 5



N(1)-Mg-C(1)	106.1(6)
N(2)-Mg-C(1)	129.7(6)
Mg-C(1)-C(16)	111.6(15)

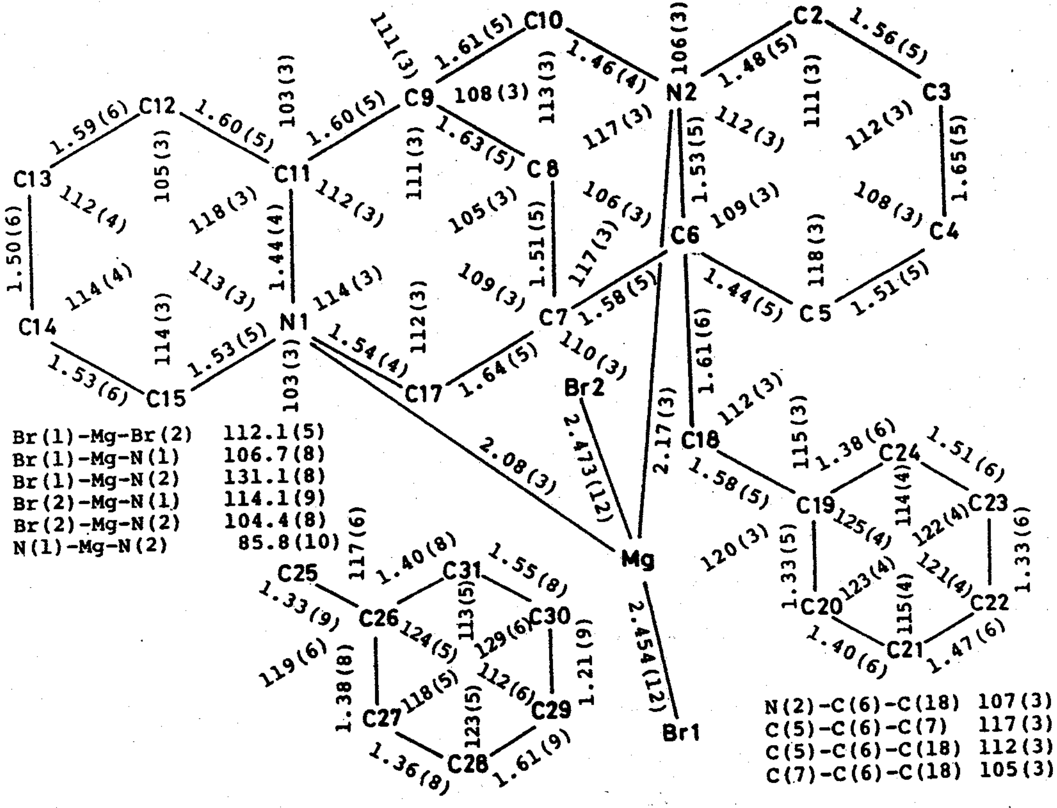
Br-Mg-N(1)	122.9(4)
Br-Mg-N(2)	101.4(4)
Br-Mg-C(1)	112.1(5)
N(1)-Mg-N(2)	83.9(5)

Figure 13. Bond lengths[Å] and bond angles[°] in 7



Br-Mg-N(1)	104.9(11)
Br-Mg-N(2)	126.7(11)
Br-Mg-C(1)	111.4(13)
N(1)-Mg-N(2)	83.1(14)
N(1)-Mg-C(1)	121.1(16)
N(2)-Mg-C(1)	108.0(15)
Mg-C(1)-C(16)	118(3)
N(2)-C(6)-C(18)	115(4)
C(5)-C(6)-C(7)	112(4)
C(5)-C(6)-C(18)	108(4)
C(7)-C(6)-C(18)	108(4)

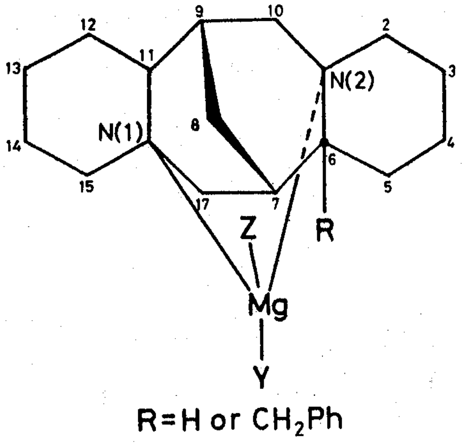
Figure 14. Bond lengths[Å] and angles[°] in 7' and crystalline toluene



Br(1)-Mg-Br(2)	112.1(5)
Br(1)-Mg-N(1)	106.7(8)
Br(1)-Mg-N(2)	131.1(8)
Br(2)-Mg-N(1)	114.1(9)
Br(2)-Mg-N(2)	104.4(8)
N(1)-Mg-N(2)	85.8(10)

N(2)-C(6)-C(18)	107(3)
C(5)-C(6)-C(7)	117(3)
C(5)-C(6)-C(18)	112(3)
C(7)-C(6)-C(18)	105(3)

halogen atom, or two halogen atoms. In the following discussion these complexes are expressed as the Scheme below (Scheme 5).



Scheme 5.

The remarkable difference between structures of these complexes of Grignard reagents and (–)-sparteine derivatives is the spatial arrangement of the alkyl and halogen ligands to the sparteine skeleton through the Mg atom. The Y ligand (Scheme 5) is alkyl group in 4a(designated as "type A"), whereas the Z ligand is alkyl group in 4g or 7(designated as "type B"). For 5 this classification can not be applied since (–)-α-isosparteine ligand has C_2 symmetry.

The coordination geometry around the Mg atom is distorted tetrahedral. As shown in Table 11, two Mg-N bond lengths are equal[av. 2.15 Å], and the N-Mg-N angle is sharp and solid[83.1-85.8°, av. 84.3°]. Regardless the geometrical relation of the alkyl and halogen ligands to the sparteine skeleton mentioned before, the Y-Mg-N(2) angle is larger than the Y-Mg-N(1), whereas the Z-Mg-N(2) angle is smaller than the Z-Mg-N(1). The Y-Mg-Z angle is slightly larger than the

Table 11.

Comparison of the coordination geometry around the Mg atom with estimated standard deviations in parentheses

(a) Bond lengths[l/Å]

Complex	Mg-N(1)	Mg-N(2)	Mg-Y Mg-C	Mg-Y Mg-Cl	Mg-Y Mg-Br	Mg-Z Mg-C	Mg-Z Mg-Cl	Mg-Z Mg-Br
(4a)	2.14(2)	2.16(3)	2.24(3)					2.482(9)
(4g)	2.171(12)	2.175(12)		2.332(7)		2.19(2)		
(4g')	2.150(9)	2.160(9)		2.269(5)			2.279(6)	
(5)	2.165(13)	2.195(13)	2.224(15)					2.506(6)
(7)	2.13(4)	2.19(4)			2.506(16)	2.34(5)		
(7')	2.08(3)	2.17(3)			2.452(12)			2.473(12)

(b) Bond angles[ϕ/°]

Complex	N(1)-Mg-N(2)	Y-Mg-N(1)	Y-Mg-N(2)	Z-Mg-N(1)	Z-Mg-N(2)	Y-Mg-Z
(4a)	84.0(8)	111.4(10)	129.6(10)	108.3(6)	103.4(7)	115.1(8)
(4g)	83.9(5)	100.8(4)	117.4(4)	119.5(6)	116.2(6)	114.7(5)
(4g')	85.0(4)	108.0(3)	123.3(3)	112.6(3)	105.8(3)	117.6(2)
(5)	83.9(5)	106.1(6)	129.7(6)	122.9(4)	101.4(4)	112.1(5)
(7)	83.1(14)	104.9(11)	126.7(11)	121.1(16)	108.0(15)	111.4(13)
(7')	85.8(10)	106.7(8)	131.1(8)	114.1(9)	104.4(8)	112.1(5)

tetrahedral angle. The Mg-C bond lengths in four complexes are equal[2.19(2)-2.34(5), av. 2.25 Å] within the range of error.

Crystal Structure

The packing of molecules in crystal of 2c, 4a, 4g, 4g', 5, 7, and 7' are drawn in Figures 15, 16, 17, 18, 19, 20, and 21. The dimeric association of molecules, observed in the crystal structures of Grignard reagents, $[EtMgBr, Et_3N]_2$ 16) and $[EtMgBr, (i\text{-}Pr)_2O]_2$ 17) is not observed. The molecular packing in crystals of 2c and 7 is determined by the van der Waals contacts between carbon atom of the benzyl group in one molecule to those of sparteine skeleton in other molecule, while that in crystals of 4a, 4g, 4g' and 5 is determined by the contacts between the sparteine skeletons. In the crystal of 7' the Mg complexes are loosely bound by crystalline toluene molecules by van der Waals forces.

1.3. Discussion

In the Grignard reagent-(−)-sparteine derivative system species, which can be considered to have initiator activity are RMgX-(−)-sparteine and R_2Mg-(−)-sparteine that are expected from Schlenk equilibrium(Scheme 6).

$$2RMgX\text{-}L(A,B) \rightleftarrows R_2Mg\text{-}L + MgX_2\text{-}L$$

L = (−)-sparteine derivative

Scheme 6.

The results of the polymerization experiments indicated that R_2Mg-L(L=(−)-sparteine) has no activity. The RMgX-L

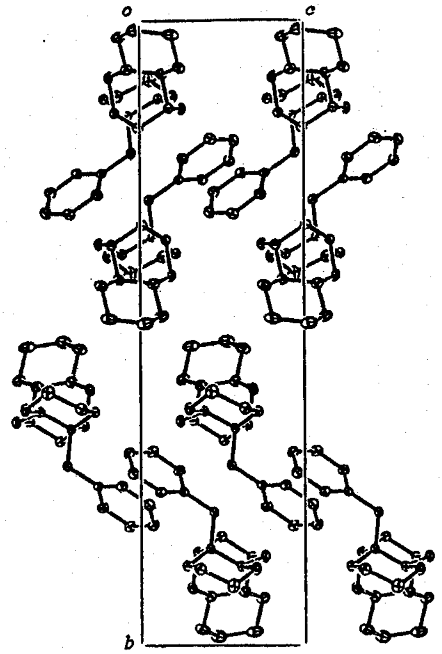


Figure 15. The crystal structure of 2c(*ORTEP* II)

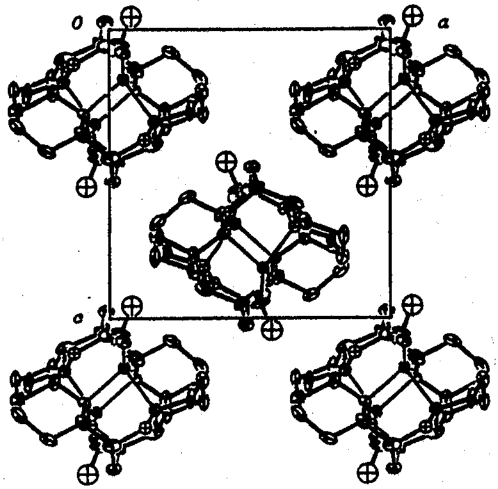


Figure 16. The crystal structure of 4a(*ORTEP* II)

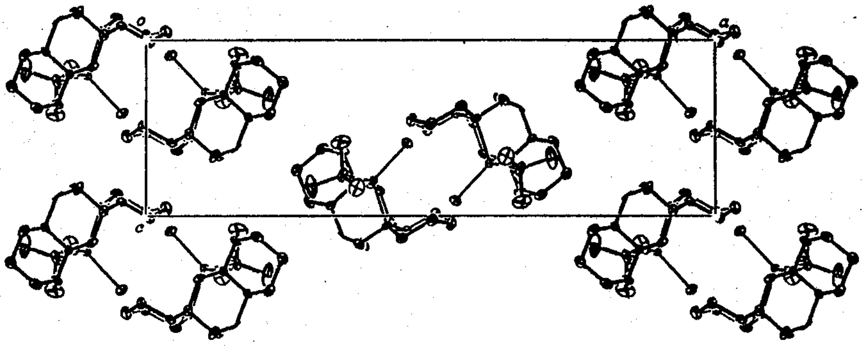


Figure 17. The crystal structure of 4g(*ORTEP* II)

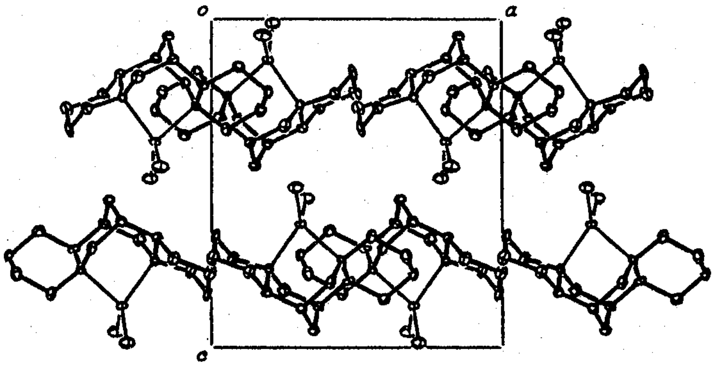


Figure 18. The crystal structure of 4g'(*ORTEP* II)

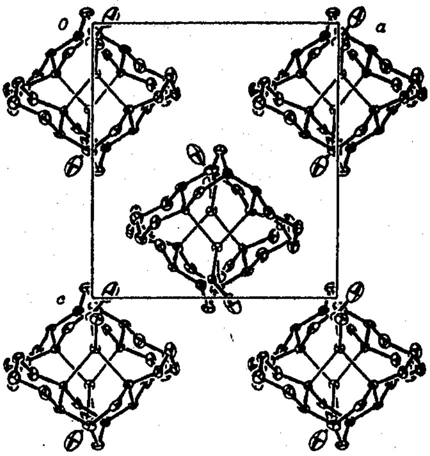


Figure 19. The crystal structure of 5(*ORTEP* II)

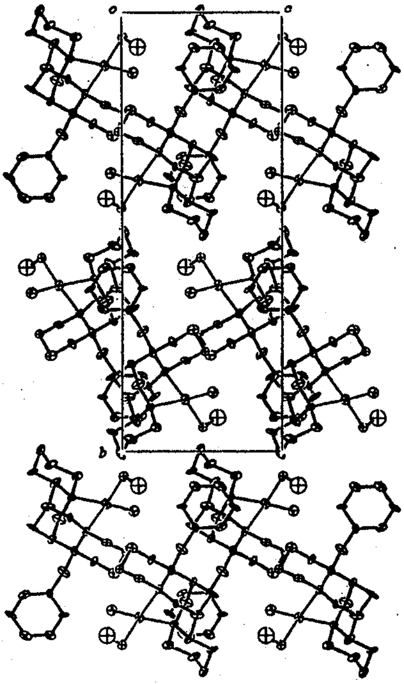


Figure 20. The crystal structure of 7(*ORTEP* II)

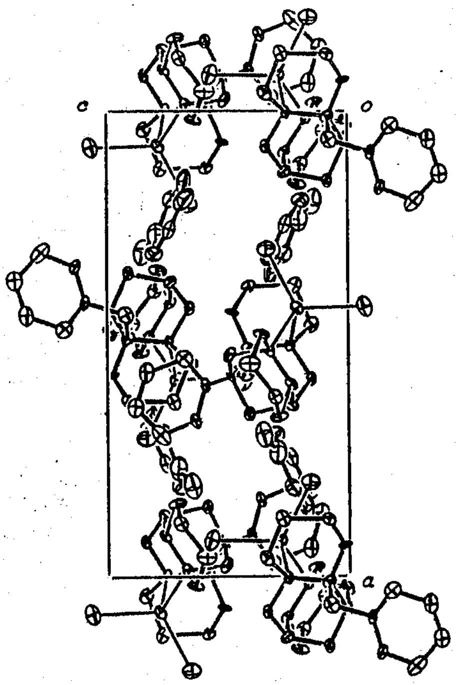
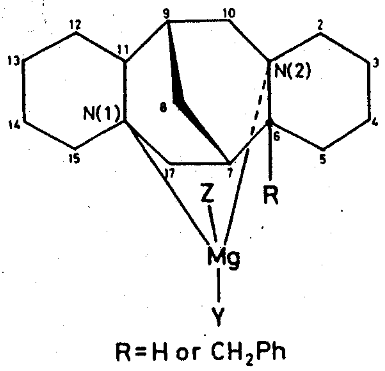


Figure 21. The crystal structure of 7'(*ORTEP* II)

Table 12.

Comparison of the structure in crystal and in solution



Complex	(4a)	(4g)	(5)	(7)
Crystal				
A$^{a)}$	○	X	-	X
B$^{b)}$	X	○	-	○
Solution$^{c)}$				
A	Major	minor	-	X
B	minor	Major	-	○
Activity	high	no	no	poor

a) Type A: Y = alkyl group, Z = halogen atom.
b) Type B: Y = halogen atom, Z = alkyl group.
c) In toluene-d_8 (^{1}H and ^{13}C NMR).

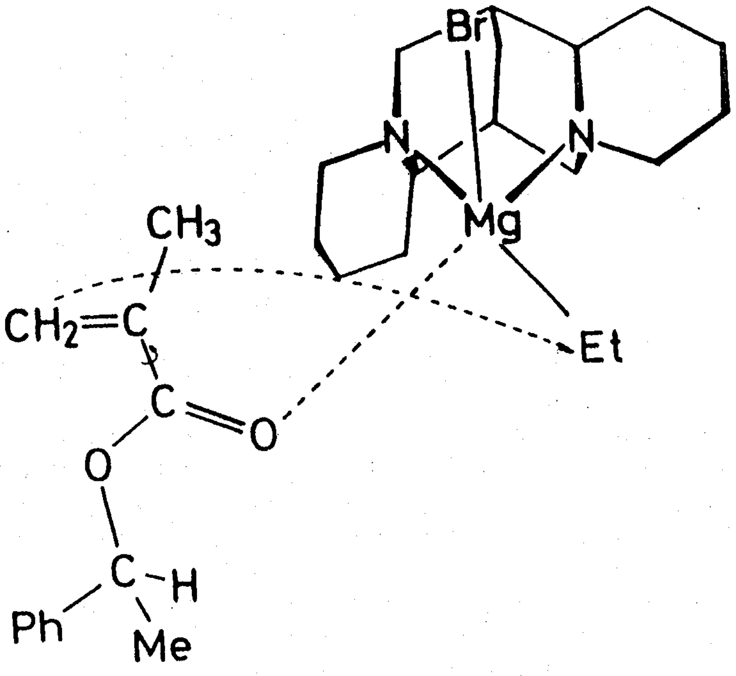
species are divided into two groups, type A and B as mentioned above. In Table 12 given are existence of two types in crystal and that in solution which were detected by ^1H and ^{13}C NMR spectra of complexes in toluene-d_8, and the asymmetric selective polymerization activity.

The complex 7 which takes type B structure in solution and in crystal has low activity whereas the complex 4a which takes type A predominantly in solution and crystal has high activity. Therefore, the RMgX-L in type A is considered to be active form. The other reason is considered for low reactivity of complex 4g which has type A in solution, and complex 5 which can not be divided into two types.

The kinetic studies of the polymerization reaction of MBMA suggested that the polymerization proceeds in a coordination mechanism. The initial stage of the polymerization is considered to be coordination of the carbonyl oxygen of a monomer(MBMA) to the Mg atom of a Grignard reagent-(—)-sparteine complex(Scheme 7).

Therefore, the complexes which has a sufficient space to access the monomer to the Mg atom in its neighborhood can only initiate the polymerization. The space-filling models (*PLUTO*[18)]) of complexes 4a, 7, 4g and 5, which are drawn in Figures 22, 23, 24 and 25, respectively, show the spatial room around the Mg atom(viewed directions of these models are from the Mg atom down to the C(8) atom).

In catalytically active EtMgBr-(—)-sparteine(4a), the Et group coordinates to the Mg atom at the spatially less opened C(7)-side(Y=Et) whereas the bulky Br ligand at the more opened C(9)-side. The Et group is not so large. The Mg atom, therefore, has a sufficient space to accommodate the MBMA in



Scheme 7.

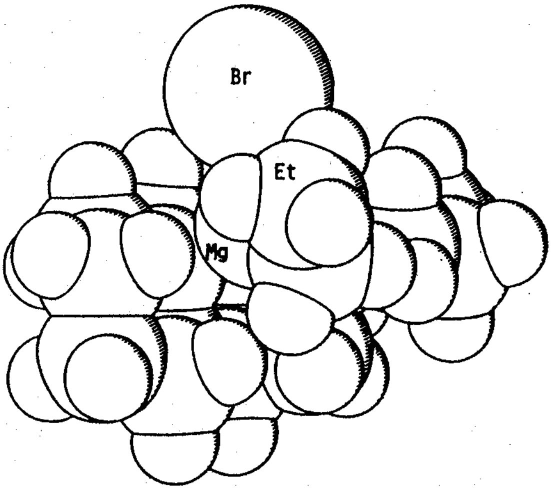


Figure 22. The space-filling model of 4a(*PLUTO*)

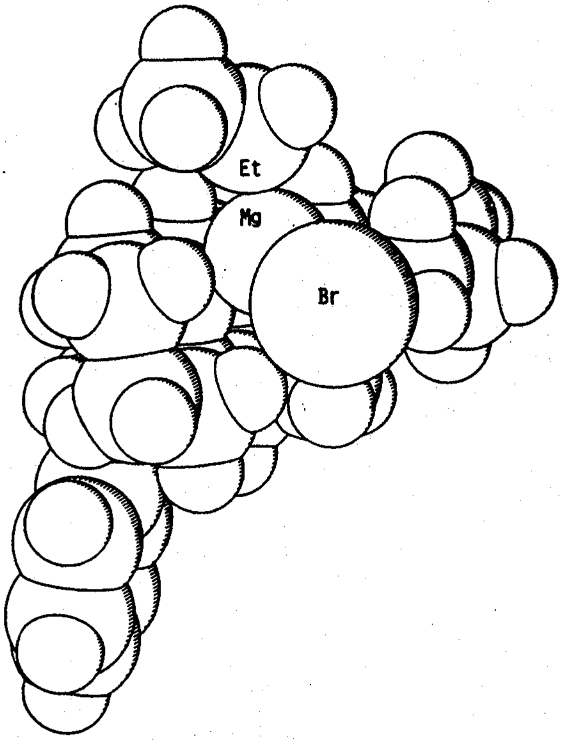


Figure 23. The space-filling model of 7(*PLUTO*)

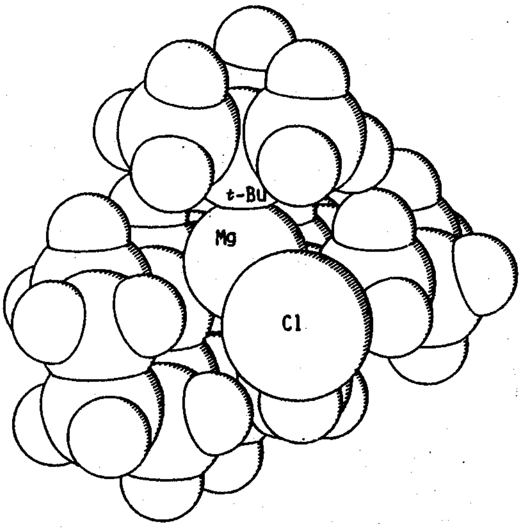


Figure 24. The space-filling model of 4g(*PLUTO*)

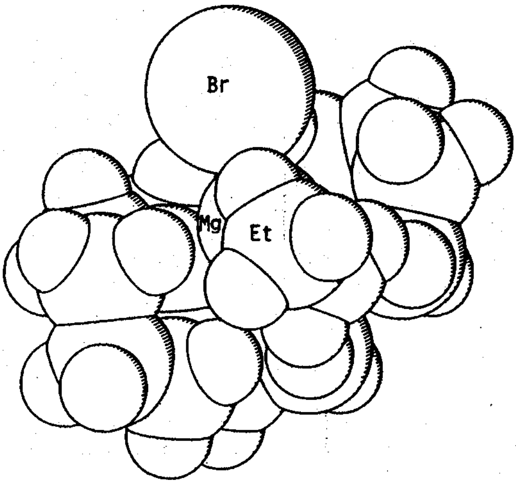
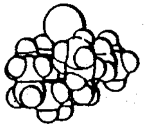
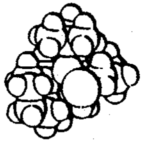
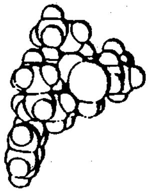
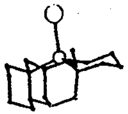
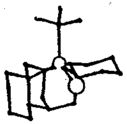
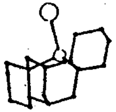
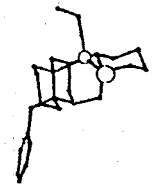


Figure 25. The space-filling model of $\underline{5}$(*PLUTO*)

its neighborhood. In the poorly active EtMgBr-(+)-6-benzylsparteine($\underline{7}$), the Et ligand coordinates to the Mg atom at the more opened C(9)-side of the cavity but the benzyl group substituted on the C(6) atom, pushes the six-membered ring(N(2), C(2), C(3), C(4), C(5) and C(6) atoms) toward the Mg atom. The spatial room around the Mg atom, therefore, is less opened than $\underline{4a}$. In the inactive *t*-BuMgCl-(−)-sparteine($\underline{4g}$), the bulky *t*-Bu ligand covers the Mg atom. This limits the spatial room around the Mg atom and may lead to the inactivity of this complex. In EtMgBr-(−)-α-isosparteine($\underline{5}$), the cavity of (−)-α-isosparteine is less opened than that of (−)-sparteine. The Mg atom coordinates deep in the cavity covered with Et and Br ligands, which leads to inactivity of this complex too.

Table 13.

Structure and reactivity of RMgX-(−)-sparteine derivative complexes

Complex	(4a)	(4g)	(5)	(7)
Molecular structure				
Space-filling model				
Solid ball and spoke model				
Substrate-accomodation in the neighborhood of Mg atom	Sufficiently large	No	No	Small
Reactivity for the enantiomer selective polymerization of (*RS*)-MBMA(Ref. Tab. 1)	Good	No	No	Poor

1.4. Conclusion

The structure of initiator complexes and reactivity for the asymmetric selective polymerization are summarized in Table 13.

At first, it can be concluded that the polymerization activity relates with the free space around the Mg atom in complexes. Secondly, the enantiomer selectivity is high in complexes of type A(the lower ligand in the Figure is alkyl group) and low in complexes of type B(the upper ligand in the Figure is alkyl group).

CHAPTER II

The Molecular Structure of Methacrylates with Bulky Ester Substituents

Introduction

In this chapter, the X-ray structure determination of several methacrylates with bulky ester substituents is described because the molecular structure of these methacrylate monomers is also one of the important factors that effects the high selectivity of this asymmetric selective polymerization.

The Asymmetric Selective Polymerization of Various α-Substituted Benzyl Methacrylates with Active Grignard Reagent-(—)-Sparteine Complexes

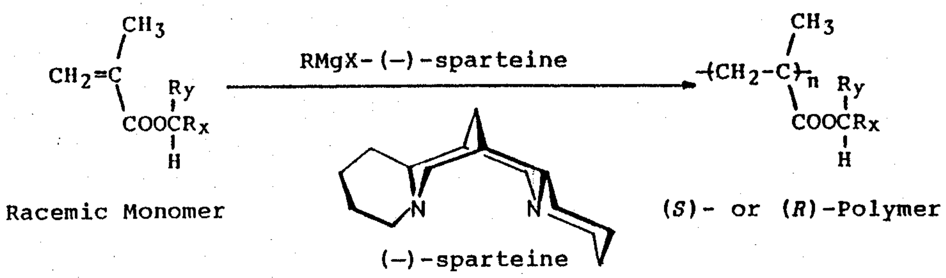
The influence of substituents of α-substituted benzyl methacrylates on the enantiomer selectivity of these monomers by active Grignard reagent-(—)-sparteine complexes, has been investigated in order to elucidate the mechanism of the enantiomer selection. A part of the results summarized in Table 14[19)].

It is demonstrated that the asymmetric selective polymerization of racemic methacrylates with Grignard reagent-(—)-sparteine catalyst in toluene at -78°C can be treated as a copolymerization of *R* and *S* monomers(Scheme 8).

In this Scheme $PC{\sim}S^-$ and $PC{\sim}R^-$ are polymer chains which have (*S*)- and (*R*)-monomer units at the growing terminals,

Table 14.

Enantiomer selectivity ratios, r_S and r_R in the polymerization of methacrylate monomers with Grignard reagent-(−)-sparteine in toluene at -78°C



Monomer	R_x	R_y	RMgX	r_S	r_R
MBMA	Ph	Me	*c*-HexMgCl	33.7	0.27
i-PBMA	Ph	*i*-Pr	*c*-HexMgBr	50	0.09
t-BBMA	*t*-Bu	Ph	*c*-HexMgBr	<1	1>
DPEMA-1,2	Ph	CH_2Ph	EtMgBr	45	0.45
TrBzMA	CPh_3	Ph	EtMgBr	1>	<1

Abbreviations: MBMA, (*RS*)-α-methylbenzyl methacrylate; *i*-PBMA, (*RS*)-α-isopropylbenzyl methacrylate; *t*-BBMA, (*RS*)-α-*t*-butylbenzyl methacrylate; DPEMA-1,2, (*RS*)-1,2-diphenylethyl methacrylate; TrBzMA, (*RS*)-1,2,2,2-tetraphenylethyl methacrylate

$$PC\sim S^-C^+ + S \overset{K_{SS}}{\rightleftarrows} PC\sim S^-C^+S \overset{k_{SS}}{\rightleftarrows} PC\sim S^-C^+$$

$$PC\sim S^-C^+ + R \overset{K_{SR}}{\rightleftarrows} PC\sim S^-C^+R \overset{k_{SR}}{\rightleftarrows} PC\sim R^-C^+$$

$$PC\sim R^-C^+ + S \overset{K_{RS}}{\rightleftarrows} PC\sim R^-C^+S \overset{k_{RS}}{\rightleftarrows} PC\sim S^-C^+$$

$$PC\sim R^-C^+ + R \overset{K_{RR}}{\rightleftarrows} PC\sim R^-C^+R \overset{k_{RR}}{\rightleftarrows} PC\sim R^-C^+$$

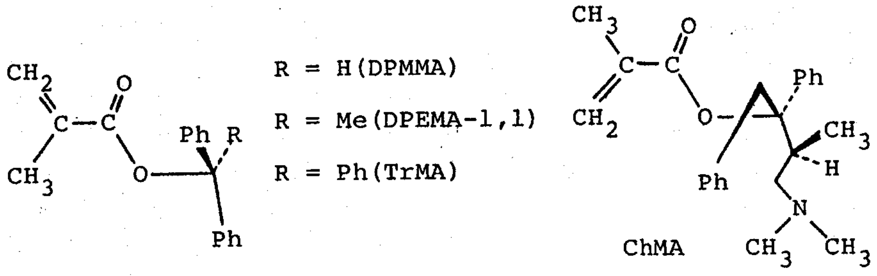
Scheme 8.

respectively. And C^+ is the counter ion, $[MgX\text{-}(-)\text{-sparteine}]^+$. Values of enantiomer selectivity ratios, $r_S(=k_{SS}K_{SS}/k_{SR}K_{SR})$ and $r_R(=k_{RR}K_{RR}/k_{RS}K_{RS})$, mean that enantiomer selection depends on the configuration of ester group of the growing end. In case of racemic α-methylbenzyl methacrylate ((*RS*)-MBMA), the *S* end polymerizes preferentially *S* monomer over *R* monomer by a factor 33.7 and the *R* end also prefers *S* monomer only about fourfold. Therefore, this monomer belongs to "(*S*)-selected monomer". On the other hand in case of racemic α-*t*-butylbenzyl methacrylate(*t*-BBMA), the *S* end polymerizes preferentially *R* monomer over *S* monomer and *R* end also prefers *R* monomer. Therefore this monomer belongs to "(*R*)-selected monmer". Of examples listed in Table 14 only *t*-BBMA is the (*R*)-selected monomer. This reason will be discuss later (Chapter III).

From the results above it recognized that either the structure of monomer molecules and that of growing end units take an important role in enantiomer selection mechanism. In this chapter the general features of the molecular structure and conformation of methacrylates are discussed from the results of the X-ray structure determination of several α-substituted benzyl methacrylates.

The Methacrylates Used for the X-Ray Structure Determination

Of the methacrylates used in the asymmetric selective polymerization with Grignard reagent-(−)-sparteine, no monomer was suitable for X-ray measurement at the beginning of the present study because these monomers have low melting points and sublimes easily even if they could be crystallized. The present study first was started to determine the molecular structure of some achiral methacrylates which could be crystallized.



Scheme 9.

These, shown in Scheme 9, are diphenylmethyl methacrylate(DPMMA), 1,1-diphenylethyl methacrylate(DPEMA-1,1), and triphenylmethyl methacrylate(TrMA).

Some novel, chiral methacrylates, which are found able to be crystallized and the polymerization of these monomers have been studied. They are 1,2-diphenylethyl methacrylate(DPEMA-1,2), α-*t*-butylbenzyl methacrylate(*t*-BBMA), 1,2,2,2-tetraphenylethyl methacrylate(TrBzMA), and (2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butyl methacrylate(ChMA, Scheme 9), all of which have a chiral carbon atom at the α-position of alcohol part. This chapter describes the molecular structures of these seven methacrylates determined by means of X-ray diffraction.

2.1. X-Ray Experiment and Structure Determination

Crystals of DPMMA, DPEMA-1,2, and ChMA were respectively obtained from their hexane solution by slow cooling. The crystal of *t*-BBMA was obtained from a hexane solution by slow evaporation. Crystals of TrMA and TrBzMA were recrystallized from a benzene solution. The DPEMA-1,1 crystals were crystallized from petroleum ether solution by slow evaporation.

X-Ray Experiment

Crystals of DPEMA-1,1 and *t*-BBMA sublime easily, and they were sealed in glass capillary tubes. Each crystal was mounted on a Rigaku automated, four-circle diffractometer. Nickel-filtered Cu*K*α radiation(λ=1.5418 Å) was used for DPMMA, DPEMA-1,2, *t*-BBMA, TrBzMA, and ChMA. Graphite monochromatized Mo*K*α radiation(λ=0.7107 Å) was used for DPEMA-1,1 and TrMA. Unit-cell dimensions of each crystal were determined by the least-squares fit using 2θ values of 25 high order, strong reflections. Crystal data of each compound is listed in Table 15.

Reflection intensities were measured by the θ-2θ scan technique, where backgrounds were counted at both ends. Four standard reflections were measured after every 60 reflections. They showed less than 2% deterioration throughout the data collection except for DPEMA-1,1 and DPEMA-1,2. For DPEMA-1,1 they remained approximately constant for about half a day, but suddenly fell down to about 60% of the initial values. After that they fell so gradually, as if they were constant, that the intensities collected under this condition were used for the subsequent structure solution. For DPEMA-1,2 four standard reflections decreased by about 15% at the end of measurement because the effect of sublimation has been underestimated before the experiment and crystal was not sealed in glass capillary: as the decrease did so uniformly with time, a linear correction factor was applied. Usual Lp corrections were applied but corrections for absorption and extinction were ignored. Conditions of the intensity measurement are listed in Table 16.

Structure Solution and Refinement

The structures of all methacrylates were solved by the direct method(*MULTAN* 74[20)] for DPMMA, and *MULTAN* 78 for other six compounds). Positions of the O, N and C atoms was located on an *E*-map. Hydrogen atoms were located on the difference Fourier map. The refinements of the structures were carried out by the block-diagonal least-squares procedure(*HBLS* V); where the function minimized being $\Sigma w(\Delta F^2)$. In general, non-hydrogen atoms were refined anisotropically whereas hydrogen atoms isotropically. Conditions of the refinement and final R and R_w values are given in Table 16. The final atomic parameters of DPMMA, DPEMA-1,1, TrMA, DPEMA-1,2, *t*-BBMA, TrBzMA, and ChMA are listed in Tables 17, 18, 19, 20, 21, 22, and 23, respectively.

Atomic scattering factors used were taken from International Tables for X-Ray Crystallography, Vol. IV. All the computations were done on an ACOS 700 or 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

(DPMMA). During the course of the refinement five strong reflections(602, 110, $\bar{3}11$, $\bar{1}12$, and 512), which were considered largely affected by the extinction, were excluded.

(DPEMA-1,1). Hydrogen atoms were fixed at the calculated positions with equal isotropic thermal parameters(B=4.89 Å^2) derived from the Wilson statistics. During the course of the

Table 15.

Crystal data

Compound	DPMMA	DPEMA-1,1	TrMA	DPEMA-1,2	*t*-BBMA	TrBzMA	ChMA
Formula	$C_{17}H_{16}O_2$	$C_{18}H_{18}O_2$	$C_{23}H_{20}O_2$	$C_{18}H_{18}O_2$	$C_{15}H_{20}O_2$	$C_{30}H_{26}O_2\cdot$ $0.5C_6H_6$	$C_{23}H_{29}O_2N$
F.W.	252.3	266.3	328.4	266.3	232.3	457.6	351.5
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space Group	$C2/c$	$P2_1/a$	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1$
a[Å]	29.177(2)	9.666(6)	17.349(3)	33.341(3)	6.028(1)	9.271(2)	12.482(1)
b[Å]	6.017(1)	19.94(2)	9.487(2)	5.916(1)	31.009(3)	33.965(4)	9.184(1)
c[Å]	16.110(1)	8.132(6)	11.254(2)	15.911(2)	15.207(1)	9.167(2)	9.246(1)
α[°]	-	-	-	-	-	90.26(2)	-
β[°]	96.840(5)	104.49(7)	102.30(2)	106.42(1)	96.780(8)	118.80(2)	93.49(1)
γ[°]	-	-	-	-	-	88.03(2)	-
V[Å^3]	2808.0(3)	1517(2)	1809.8(5)	3010.5(5)	2822.5(4)	2527.8(7)	1057.8(2)
Z	8	4	4	8	8	4	2
D_c[gcm^{-3}]	1.194	1.166	1.205	1.175	1.093	1.202	1.104
D_m[gcm^{-3}]	-	1.17	1.19	-	-	1.22	1.11
μ(Mo*K*α)[cm^{-1}]	-	0.81	0.82	-	-	-	-
μ(Cu*K*α)[cm^{-1}]	6.21	-	-	6.04	5.67	5.79	5.51

Table 16.

Summary of Experimental Conditions, Structure Solution and Refinement

Compound	DPMMA	DPEMA-1,1	TrMA	DPEMA-1,2	*t*-BBMA	TrBzMA	ChMA
Radiation	Cu*K*α Ni-filter	Mo*K*α graphite monochromator	Mo*K*α graphite monochromator	Cu*K*α Ni-filter	Cu*K*α Ni-filter	Cu*K*α Ni-filter	Cu*K*α Ni-filter
Crystal Size[mm^3]	0.20×0.20×0.40	0.30×0.38×0.63	0.25×0.50×0.63	0.20×0.20×0.10	0.12×0.12×0.50	0.43×0.25×0.13	0.25×0.30×0.38
Scan Technique	θ-2θ	θ-2θ	θ-2θ	θ-2θ	θ-2θ	θ-2θ	θ-2θ
Scan Range Δ2θ[°]	2.0+0.3tanθ	2.0+0.7tanθ	2.0+0.7tanθ	2.0+0.3tanθ	2.0+0.3tanθ	2.0+0.3tanθ	2.0+0.3tanθ
Backgrounds Count[s]	7.5	3.25	7.5	7.5	7.5	3.25	7.5
Scan Speed(in 2θ)	4°/min	4°/min	4°/min	4°/min	4°/min	4°/min	4°/min
$2\theta_{max}$[°]	110	50	50	110	110	110	110
Number of Reflections							
Measured	1773	2674	3193	1900	3012	6329	1416
Observed[a]	1565	1265[b]	2272[b]	1103[b]	2208	5229	1387
Used for Refinement	1768	1264	2272	1100	2206	6329	1416
Solution Method	*MULTAN* 74	*MULTAN* 78	*MULTAN* 78	*MULTAN* 78	*MULTAN* 78	*MULTAN* 78	*MULTAN* 78
Hydrogen Atoms	refined	included	refined	refined	refined[c]	refined	refined
Final R Value[d]							
for Measured Reflections	0.071	-	-	-	0.133	0.079	0.059
for Observed Reflections	0.060	0.171	0.056	0.113	0.081	0.054	0.057
Final R_w Value	0.091	0.175	0.073	0.118	0.112	0.072	0.086
Weighting Scheme[e]							
a	0.06443	-[f]	0.	-[f]	0.08650	0.	0.
b	0.00154	-	0.00182	-	0.00011	0.00164	0.00571
c	0.27604	-	-	-	0.16543	0.23314	2.01781

a) $|F_o|>0$. b) $|F_o|\geq 3\sigma(F_o)$. c) The hydrogen atoms attached to the methacryl group of mol. 2 were excluded.

d) The block-diagonal least-squares procedures(*HBLS* V) was used for the refinement.

e) The weighting scheme $w = (\sigma^2(F_o) + a\cdot|F_o| + b\cdot|F_o|^2)^{-1}$ for $|F_o|>0$, and $w = c$ for $|F_o|=0$.

f) $w = 1$ for all reflections used for the refinement.

Table 17. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of DPMMA with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
O(1)	0.58723(7)	0.5651(4)	0.2664(2)	4.8
O(2)	0.57659(9)	0.2130(4)	0.3026(2)	6.2
C(1)	0.56703(10)	0.4052(5)	0.3071(2)	4.2
C(2)	0.53135(10)	0.4952(6)	0.3571(2)	4.5
C(3)	0.52634(13)	0.7132(6)	0.3668(3)	6.4
C(4)	0.50303(13)	0.3281(7)	0.3933(3)	6.7
C(5)	0.62579(10)	0.5003(5)	0.2220(2)	4.3
C(6)	0.62414(9)	0.6437(5)	0.1450(2)	3.9
C(7)	0.60345(10)	0.8485(6)	0.1385(2)	4.8
C(8)	0.60332(12)	0.9762(6)	0.0660(2)	5.5
C(9)	0.62488(12)	0.8952(6)	-0.0001(2)	5.7
C(10)	0.64623(12)	0.6936(7)	0.0068(2)	6.2
C(11)	0.64601(11)	0.5648(6)	0.0782(2)	5.1
C(12)	0.66992(10)	0.5242(5)	0.2809(2)	4.2
C(13)	0.70163(12)	0.3521(6)	0.2891(3)	5.9
C(14)	0.74253(12)	0.3776(8)	0.3426(3)	7.5
C(15)	0.75122(13)	0.5672(8)	0.3878(3)	7.7
C(16)	0.72014(14)	0.7374(7)	0.3796(3)	6.9
C(17)	0.67915(12)	0.7163(6)	0.3258(2)	5.4

b) Hydrogen atoms

Atom	x	y	z	B[Å^2]
H(3a)	0.4952(15)	0.767(8)	0.394(3)	11.4(13)
H(3b)	0.5434(17)	0.808(8)	0.344(3)	13.1(15)
H(4a)	0.4764(12)	0.399(6)	0.411(3)	8.4(10)
H(4b)	0.4902(14)	0.201(7)	0.340(3)	10.5(12)
H(4c)	0.5205(18)	0.254(9)	0.432(4)	13.1(15)
H(5)	0.6230(9)	0.342(5)	0.208(2)	5.2(7)
H(7)	0.5834(18)	0.894(9)	0.177(4)	13.7(16)
H(8)	0.5810(14)	1.123(7)	0.061(3)	9.9(11)
H(9)	0.6207(14)	1.000(7)	-0.058(3)	10.9(12)
H(10)	0.6585(15)	0.635(7)	-0.031(3)	11.1(13)
H(11)	0.6632(11)	0.406(6)	0.085(2)	7.1(8)
H(13)	0.6933(11)	0.218(6)	0.258(2)	7.3(9)
H(14)	0.7632(13)	0.233(7)	0.350(3)	9.2(10)
H(15)	0.7841(15)	0.581(8)	0.428(3)	11.0(12)
H(16)	0.7278(13)	0.878(7)	0.408(3)	9.2(11)
H(17)	0.6557(12)	0.837(6)	0.324(3)	7.8(9)

Table 18. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of DPEMA-1,1 with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
O(1)	0.3969(11)	0.4184(5)	-0.284(2)	6.3
O(2)	0.4180(13)	0.3076(6)	-0.328(2)	8.2
C(1)	0.464(2)	0.3617(9)	-0.312(3)	7.5
C(2)	0.618(2)	0.3822(9)	-0.329(3)	7.9
C(3)	0.694(3)	0.3289(11)	-0.371(5)	12.5
C(4)	0.666(2)	0.4497(11)	-0.297(4)	10.1
C(5)	0.247(2)	0.4104(8)	-0.261(3)	5.6
C(6)	0.213(2)	0.4869(8)	-0.232(3)	5.9
C(7)	0.085(2)	0.4984(9)	-0.180(3)	6.1
C(8)	0.049(2)	0.5646(9)	-0.156(3)	7.0
C(9)	0.132(2)	0.6177(9)	-0.167(4)	8.2
C(10)	0.256(2)	0.6060(8)	-0.216(4)	8.7
C(11)	0.296(2)	0.5420(9)	-0.247(3)	6.9
C(12)	0.248(2)	0.3721(7)	-0.114(2)	4.1
C(13)	0.143(2)	0.3196(8)	-0.125(3)	6.0
C(14)	0.150(2)	0.2867(8)	0.032(3)	7.3
C(15)	0.249(3)	0.2968(10)	0.187(3)	7.7
C(16)	0.348(2)	0.3484(10)	0.191(3)	7.6
C(17)	0.343(2)	0.3813(8)	0.040(2)	4.9
C(18)	0.153(2)	0.3918(9)	-0.440(3)	6.3

b) Hydrogen atoms*

Atom	x	y	z
H(3a)	0.654	0.282	-0.385
H(3b)	0.795	0.336	-0.385
H(4a)	0.687	0.460	-0.169
H(4b)	0.593	0.483	-0.357
H(4c)	0.758	0.458	-0.331
H(7)	0.022	0.459	-0.160
H(8)	-0.046	0.574	-0.128
H(9)	0.104	0.665	-0.140
H(10)	0.317	0.646	-0.233
H(11)	0.389	0.535	-0.284
H(13)	0.069	0.308	-0.237
H(14)	0.074	0.251	0.031
H(15)	0.249	0.267	0.290
H(16)	0.423	0.361	0.305
H(17)	0.420	0.417	0.043
H(18a)	0.051	0.385	-0.440
H(18b)	0.189	0.349	-0.484
H(18c)	0.158	0.429	-0.525

* Isotropic temperature factor B's were fixed as 4.89 Å^2.

Table 19. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s$^{12)}$ of TrMA with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	$B_{eq}[\mathrm{\AA}^2]$
O(1)	0.11040(10)	0.1973(2)	-0.2979(2)	3.49
O(2)	0.20838(12)	0.3401(2)	-0.3302(2)	5.30
C(1)	0.1659(2)	0.2404(3)	-0.3581(3)	3.80
C(2)	0.1666(2)	0.1457(3)	-0.4646(3)	4.36
C(3)	0.2037(2)	0.1950(4)	-0.5500(3)	6.04
C(4)	0.1283(3)	0.0093(4)	-0.4701(4)	6.53
C(5)	0.0951(2)	0.2776(3)	-0.1941(3)	3.08
C(6)	0.0740(2)	0.4290(3)	-0.2368(3)	3.23
C(7)	0.0041(2)	0.4501(3)	-0.3210(3)	4.57
C(8)	-0.0170(2)	0.5830(4)	-0.3676(4)	5.68
C(9)	0.0310(2)	0.6969(3)	-0.3302(3)	5.29
C(10)	0.1010(2)	0.6774(3)	-0.2477(3)	4.87
C(11)	0.1226(2)	0.5438(3)	-0.2015(3)	4.00
C(12)	0.0235(2)	0.2021(3)	-0.1627(3)	3.30
C(13)	0.0080(2)	0.0616(3)	-0.1910(3)	4.39
C(14)	-0.0558(2)	-0.0066(4)	-0.1590(3)	5.39
C(15)	-0.1037(2)	0.0651(4)	-0.0971(3)	5.99
C(16)	-0.0885(2)	0.2036(4)	-0.0664(3)	5.82
C(17)	-0.0252(2)	0.2733(4)	-0.0987(3)	4.62
C(18)	0.1641(2)	0.2613(3)	-0.0849(3)	3.28
C(19)	0.1635(2)	0.3349(3)	0.0221(3)	4.42
C(20)	0.2228(2)	0.3136(4)	0.1258(3)	5.31
C(21)	0.2819(2)	0.2165(4)	0.1234(3)	5.69
C(22)	0.2824(2)	0.1436(4)	0.0190(3)	5.20
C(23)	0.2237(2)	0.1634(3)	-0.0846(3)	4.07

b) Hydrogen atoms

Atom	x	y	z	$B[\mathrm{\AA}^2]$
H(3a)	0.230(2)	0.292(4)	-0.540(3)	4.7(8)
H(3b)	0.207(2)	0.137(4)	-0.625(3)	4.5(8)
H(4a)	0.132(2)	-0.044(4)	-0.548(3)	4.8(8)
H(4b)	0.070(2)	0.019(4)	-0.469(4)	4.9(8)
H(4c)	0.153(2)	-0.048(4)	-0.398(3)	5.0(9)
H(7)	-0.031(2)	0.368(4)	-0.352(3)	4.1(8)
H(8)	-0.069(2)	0.596(4)	-0.429(3)	4.3(8)
H(9)	0.015(2)	0.795(4)	-0.364(3)	4.1(8)
H(10)	0.137(2)	0.761(4)	-0.222(3)	4.2(8)
H(11)	0.175(2)	0.529(4)	-0.141(3)	4.1(8)
H(13)	0.044(2)	0.007(4)	-0.236(3)	4.2(8)
H(14)	-0.067(2)	-0.110(4)	-0.182(3)	4.5(8)
H(15)	-0.151(2)	0.015(4)	-0.074(3)	4.8(8)
H(16)	-0.124(2)	0.256(4)	-0.021(3)	4.6(8)
H(17)	-0.014(2)	0.377(4)	-0.076(3)	4.1(8)
H(19)	0.119(2)	0.407(4)	0.024(3)	3.8(7)
H(20)	0.222(2)	0.369(4)	0.202(3)	4.4(8)
H(21)	0.325(2)	0.201(4)	0.199(3)	4.5(8)
H(22)	0.327(2)	0.071(4)	0.016(3)	4.4(8)
H(23)	0.224(2)	0.106(4)	-0.162(3)	4.0(7)

Table 20. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of DPEMA-1,2 with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
O(1)	0.9109(3)	0.203(2)	0.1440(6)	6.8
O(2)	0.9293(3)	-0.159(2)	0.1610(6)	6.8
C(1)	0.9368(4)	0.030(3)	0.1460(7)	5.0
C(2)	0.9757(4)	0.104(2)	0.1251(8)	4.9
C(3)	0.9830(5)	0.322(3)	0.1163(12)	8.7
C(4)	1.0049(5)	-0.074(3)	0.1188(9)	7.1
C(5)	0.8726(4)	0.154(3)	0.1705(8)	5.3
C(6)	0.8383(4)	0.299(3)	0.1047(8)	5.5
C(7)	0.7955(4)	0.245(3)	0.1161(7)	5.3
C(8)	0.7760(4)	0.398(3)	0.1569(8)	5.9
C(9)	0.7364(4)	0.348(3)	0.1673(9)	6.8
C(10)	0.7159(4)	0.150(3)	0.1343(8)	6.1
C(11)	0.7352(4)	-0.004(3)	0.0950(8)	6.4
C(12)	0.7750(4)	0.042(3)	0.0849(8)	6.3
C(13)	0.8801(4)	0.219(2)	0.2653(8)	5.3
C(14)	0.8976(4)	0.429(3)	0.2981(8)	5.7
C(15)	0.9046(4)	0.482(3)	0.3861(8)	6.3
C(16)	0.8927(4)	0.339(3)	0.4426(9)	7.0
C(17)	0.8748(4)	0.131(3)	0.4076(9)	7.4
C(18)	0.8686(4)	0.071(3)	0.3198(8)	5.9

b) Hydrogen atoms

Atom	x	y	z	B[Å^2]
H(3a)	0.964(4)	0.44(3)	0.124(7)	6(4)
H(3b)	1.009(4)	0.37(3)	0.105(8)	7(4)
H(4a)	1.034(4)	-0.01(2)	0.118(7)	5(3)
H(4b)	0.993(4)	-0.16(2)	0.068(7)	5(4)
H(4c)	1.011(4)	-0.17(2)	0.172(7)	6(4)
H(5)	0.862(4)	-0.02(3)	0.162(7)	6(4)
H(6a)	0.839(3)	0.25(2)	0.041(6)	3(3)
H(6b)	0.846(3)	0.48(2)	0.116(6)	4(3)
H(8)	0.792(4)	0.55(3)	0.184(8)	6(4)
H(9)	0.721(3)	0.46(2)	0.206(7)	4(3)
H(10)	0.687(4)	0.09(3)	0.143(7)	6(4)
H(11)	0.721(4)	-0.14(3)	0.074(8)	7(4)
H(12)	0.788(4)	-0.05(2)	0.045(7)	6(4)
H(14)	0.905(4)	0.53(3)	0.259(7)	6(4)
H(15)	0.919(3)	0.62(2)	0.410(7)	4(3)
H(16)	0.897(4)	0.38(3)	0.507(7)	6(4)
H(17)	0.866(4)	0.03(2)	0.452(7)	6(4)
H(18)	0.855(3)	-0.08(2)	0.292(6)	4(3)

Table 21. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s$^{12)}$ of t-BBMA with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
MOLECULE 1				
O(1)	-0.0875(6)	0.3693(2)	0.1565(3)	5.7
O(2)	-0.4375(7)	0.3448(2)	0.1345(3)	6.6
C(1)	-0.2589(10)	0.3491(2)	0.1093(4)	4.7
C(2)	-0.2029(10)	0.3329(2)	0.0229(4)	5.2
C(3)	0.0086(12)	0.3365(3)	0.0013(5)	8.1
C(4)	-0.3837(12)	0.3122(3)	-0.0363(5)	7.3
C(5)	-0.1199(9)	0.3827(2)	0.2455(4)	4.6
C(6)	-0.0285(10)	0.3482(2)	0.3096(4)	4.9
C(7)	0.1705(11)	0.3263(2)	0.2983(4)	6.1
C(8)	0.2481(12)	0.2946(3)	0.3589(5)	7.6
C(9)	0.1359(14)	0.2852(3)	0.4297(5)	8.3
C(10)	-0.0642(13)	0.3064(3)	0.4399(5)	7.8
C(11)	-0.1438(11)	0.3372(2)	0.3794(4)	6.1
C(12)	-0.0138(10)	0.4279(2)	0.2606(4)	5.0
C(13)	-0.1353(12)	0.4592(3)	0.1915(5)	7.5
C(14)	-0.0515(11)	0.4436(2)	0.3531(4)	6.3
C(15)	0.2366(10)	0.4278(2)	0.2527(5)	6.3
MOLECULE 2				
O(1')	0.5500(6)	0.0874(2)	0.2658(3)	5.0
O(2')	0.2400(8)	0.1009(2)	0.3250(3)	9.9
C(1')	0.4257(10)	0.0860(2)	0.3314(4)	5.3
C(2')	0.5310(11)	0.0636(2)	0.4107(4)	5.6
C(3')	0.3996(12)	0.0592(3)	0.4827(5)	7.6
C(4')	0.7523(11)	0.0481(3)	0.4119(5)	7.7
C(5')	0.4707(9)	0.1111(2)	0.1861(4)	4.3
C(6')	0.5715(9)	0.1562(2)	0.1948(4)	4.4
C(7')	0.7894(10)	0.1630(2)	0.2335(4)	5.5
C(8')	0.8786(12)	0.2043(3)	0.2398(5)	7.2
C(9')	0.7471(14)	0.2385(3)	0.2087(5)	8.2
C(10')	0.5321(13)	0.2325(2)	0.1710(5)	7.8
C(11')	0.4411(11)	0.1909(2)	0.1635(4)	6.1
C(12')	0.5290(9)	0.0844(2)	0.1065(4)	4.8
C(13')	0.4121(12)	0.0403(2)	0.1095(5)	7.3
C(14')	0.4423(11)	0.1072(3)	0.0224(4)	6.5
C(15')	0.7793(11)	0.0768(3)	0.1089(4)	6.6

Table 21. (continued)

b) Hydrogen atoms

Atom	x	y	z	B[Å^2]
MOLECULE 1				
H(3a)	0.025(11)	0.327(3)	-0.063(4)	7(2)
H(3b)	0.125(11)	0.348(3)	0.048(5)	8(2)
H(4a)	-0.343(11)	0.302(2)	-0.101(4)	7(2)
H(4b)	-0.451(11)	0.292(2)	-0.004(4)	6(2)
H(4c)	-0.493(14)	0.336(3)	-0.059(5)	11(3)
H(5)	-0.299(8)	0.385(2)	0.250(3)	2(2)
H(7)	0.238(10)	0.330(2)	0.238(4)	6(2)
H(8)	0.396(11)	0.277(2)	0.350(4)	7(2)
H(9)	0.193(12)	0.262(3)	0.473(5)	9(3)
H(10)	-0.135(11)	0.303(3)	0.499(5)	7(2)
H(11)	-0.291(11)	0.354(2)	0.382(5)	7(2)
H(12)	-0.079(11)	0.490(3)	0.205(5)	8(2)
H(13)	-0.100(11)	0.449(3)	0.130(5)	7(2)
H(14)	-0.299(13)	0.458(3)	0.189(5)	10(3)
H(15)	0.011(10)	0.473(2)	0.369(4)	5(2)
H(16)	-0.222(11)	0.445(3)	0.363(5)	8(2)
H(17)	0.009(10)	0.425(2)	0.406(4)	6(2)
H(18)	0.257(10)	0.416(2)	0.191(4)	5(2)
H(19)	0.309(11)	0.458(2)	0.269(4)	7(2)
H(20)	0.324(10)	0.407(2)	0.299(4)	6(2)
MOLECULE 2				
H(5')	0.288(9)	0.115(2)	0.180(3)	4(2)
H(7')	0.886(10)	0.137(2)	0.261(4)	6(2)
H(8')	1.031(10)	0.210(2)	0.270(4)	5(2)
H(9')	0.800(12)	0.267(3)	0.216(5)	8(2)
H(10')	0.423(10)	0.257(2)	0.146(4)	7(2)
H(11')	0.270(11)	0.186(2)	0.137(4)	7(2)
H(12')	0.238(11)	0.042(3)	0.101(5)	7(2)
H(13')	0.460(10)	0.027(2)	0.168(4)	6(2)
H(14')	0.443(11)	0.022(2)	0.052(4)	7(2)
H(15')	0.284(9)	0.112(2)	0.012(4)	5(2)
H(16')	0.510(11)	0.136(3)	0.019(5)	7(2)
H(17')	0.465(11)	0.087(2)	-0.035(4)	7(2)
H(18')	0.872(11)	0.104(2)	0.105(4)	7(2)
H(19')	0.834(9)	0.061(2)	0.166(4)	5(2)
H(20')	0.812(9)	0.060(2)	0.052(4)	5(2)

Table 22. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s[12] of TrBzMA with estimated standard deviations in parentheses.

a) Non-hydrogen atoms of MOLECULE 1 refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
O(1)	0.5713(2)	0.38540(5)	0.1717(2)	3.2
O(2)	0.5548(3)	0.43370(6)	0.3320(3)	4.3
C(1)	0.6356(4)	0.41384(8)	0.2874(3)	3.2
C(2)	0.8151(4)	0.41715(8)	0.3499(4)	3.7
C(3)	0.8961(4)	0.44446(10)	0.4723(4)	5.1
C(4)	0.8955(4)	0.39199(11)	0.2840(5)	5.9
C(5)	0.3975(3)	0.37794(8)	0.1075(3)	3.0
C(6)	0.3830(4)	0.34544(8)	0.2134(3)	3.4
C(7)	0.2470(4)	0.34518(9)	0.2393(4)	4.6
C(8)	0.2341(5)	0.31607(11)	0.3364(5)	5.7
C(9)	0.3559(5)	0.28737(10)	0.4110(4)	5.4
C(10)	0.4912(4)	0.28708(10)	0.3873(4)	5.2
C(11)	0.5045(4)	0.31605(9)	0.2874(4)	4.2
C(12)	0.3300(3)	0.36788(7)	-0.0815(3)	2.9
C(13)	0.1402(3)	0.36480(8)	-0.1653(3)	3.1
C(14)	0.0570(4)	0.33777(9)	-0.2890(4)	4.1
C(15)	-0.1134(4)	0.33591(10)	-0.3663(4)	4.9
C(16)	-0.2053(4)	0.36129(10)	-0.3247(4)	4.6
C(17)	-0.1272(4)	0.38971(10)	-0.2084(4)	4.5
C(18)	0.0444(4)	0.39170(9)	-0.1299(4)	4.0
C(19)	0.3561(3)	0.40222(8)	-0.1760(3)	3.0
C(20)	0.3486(4)	0.39481(8)	-0.3298(4)	3.7
C(21)	0.3687(4)	0.42502(9)	-0.4200(4)	4.2
C(22)	0.3935(4)	0.46302(9)	-0.3602(4)	4.6
C(23)	0.3962(4)	0.47082(9)	-0.2118(4)	4.7
C(24)	0.3785(4)	0.44075(8)	-0.1197(4)	3.8
C(25)	0.4214(3)	0.32985(8)	-0.0894(3)	3.1
C(26)	0.3688(4)	0.29244(8)	-0.0771(4)	3.9
C(27)	0.4587(4)	0.25866(8)	-0.0772(4)	4.7
C(28)	0.6013(5)	0.26141(9)	-0.0875(4)	5.1
C(29)	0.6576(4)	0.29795(9)	-0.0934(4)	4.7
C(30)	0.5689(4)	0.33167(8)	-0.0943(4)	3.8

Table 22. (continued)

b) Non-hydrogen atoms of MOLECULE 2 refined anisotropically

Atom	x	y	z	B_{eq} [Å^2]
O(1')	0.9204(2)	0.11502(5)	0.6062(3)	3.3
O(2')	0.9374(3)	0.06636(6)	0.7796(3)	4.5
C(1')	0.8562(4)	0.08603(8)	0.6556(4)	3.2
C(2')	0.6787(4)	0.08170(8)	0.5396(4)	3.7
C(3')	0.5968(4)	0.05507(10)	0.5814(5)	5.3
C(4')	0.5991(4)	0.10621(11)	0.3920(5)	5.9
C(5')	1.0933(3)	0.12294(8)	0.7117(3)	3.1
C(6')	1.1068(4)	0.15568(8)	0.8297(4)	3.6
C(7')	1.2366(5)	0.15469(10)	0.9921(4)	5.1
C(8')	1.2517(5)	0.18458(12)	1.1020(5)	7.0
C(9')	1.1371(6)	0.21568(12)	1.0507(5)	7.1
C(10')	1.0073(5)	0.21687(10)	0.8905(5)	6.1
C(11')	0.9920(4)	0.18689(9)	0.7800(4)	4.7
C(12')	1.1609(3)	0.13257(7)	0.5871(3)	3.0
C(13')	1.3503(3)	0.13637(8)	0.6882(4)	3.2
C(14')	1.4310(4)	0.16200(8)	0.6360(4)	4.0
C(15')	1.6012(4)	0.16511(9)	0.7242(4)	4.8
C(16')	1.6947(4)	0.14239(10)	0.8649(5)	5.1
C(17')	1.6186(4)	0.11545(11)	0.9140(4)	5.4
C(18')	1.4480(4)	0.11236(9)	0.8252(4)	4.4
C(19')	1.1356(3)	0.09778(7)	0.4684(3)	3.0
C(20')	1.1351(4)	0.10462(8)	0.3184(4)	3.9
C(21')	1.1175(4)	0.07416(9)	0.2096(4)	4.5
C(22')	1.1037(4)	0.03600(9)	0.2504(4)	4.8
C(23')	1.1091(4)	0.02835(9)	0.4016(4)	4.7
C(24')	1.1245(4)	0.05918(8)	0.5096(4)	3.8
C(25')	1.0664(4)	0.17000(8)	0.4904(4)	3.2
C(26')	1.1193(4)	0.20774(8)	0.5482(4)	3.8
C(27')	1.0224(5)	0.24084(9)	0.4672(4)	4.9
C(28')	0.8704(5)	0.23744(10)	0.3280(5)	5.7
C(29')	0.8151(4)	0.20043(9)	0.2707(4)	5.1
C(30')	0.9126(4)	0.16732(8)	0.3499(4)	3.9

Table 22. (continued)

c) Non-hydrogen atoms of the benzene refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
C(31)	0.6574(5)	-0.00212(14)	0.0279(7)	8.1
C(32)	0.6236(6)	0.01497(13)	0.1419(5)	7.7
C(33)	0.4646(6)	0.01719(14)	0.1138(6)	8.3
C(34)	0.1588(5)	0.49741(13)	0.1249(6)	7.3
C(35)	0.0367(6)	0.48342(13)	0.1494(5)	7.6
C(36)	-0.1241(5)	0.48580(12)	0.0224(6)	7.0

d) hydrogen atoms of MOLECULE 1

Atom	x	y	z	B[Å^2]
H(3a)	0.839(5)	0.4598(11)	0.518(5)	5.2(9)
H(3b)	1.008(5)	0.4461(11)	0.517(5)	5.7(10)
H(4a)	1.021(5)	0.3962(11)	0.339(5)	5.7(10)
H(4b)	0.845(6)	0.3973(14)	0.157(6)	9.6(14)
H(4c)	0.870(6)	0.3612(15)	0.283(7)	10.1(14)
H(5)	0.341(3)	0.4046(7)	0.121(3)	1.3(6)
H(7)	0.157(4)	0.3684(9)	0.183(4)	3.9(8)
H(8)	0.131(5)	0.3143(10)	0.351(5)	4.9(9)
H(9)	0.342(4)	0.2653(10)	0.478(4)	4.2(8)
H(10)	0.584(4)	0.2636(9)	0.440(4)	4.0(8)
H(11)	0.611(4)	0.3162(9)	0.267(4)	2.9(7)
H(14)	0.122(4)	0.3190(8)	-0.329(4)	2.4(6)
H(15)	-0.169(4)	0.3146(9)	-0.454(4)	3.8(8)
H(16)	-0.327(4)	0.3595(9)	-0.378(4)	3.1(7)
H(17)	-0.197(4)	0.4105(9)	-0.179(4)	3.8(8)
H(18)	0.094(4)	0.4157(9)	-0.051(4)	3.1(7)
H(20)	0.326(4)	0.3684(9)	-0.376(4)	3.7(8)
H(21)	0.363(4)	0.4181(9)	-0.527(4)	2.9(7)
H(22)	0.412(4)	0.4852(9)	-0.425(4)	3.3(7)
H(23)	0.414(4)	0.4999(9)	-0.166(4)	3.8(8)
H(24)	0.373(4)	0.4494(10)	-0.013(4)	4.3(8)
H(26)	0.264(4)	0.2892(9)	-0.065(4)	3.2(7)
H(27)	0.415(4)	0.2324(10)	-0.071(4)	4.2(8)
H(28)	0.665(4)	0.2359(9)	-0.089(4)	3.9(8)
H(29)	0.766(4)	0.3012(9)	-0.098(4)	3.8(8)
H(30)	0.615(3)	0.3592(8)	-0.097(3)	1.5(6)

Table 22. (continued)

e) Hydrogen atoms of MOLECULE 2

Atom	x	y	z	B[$\mathrm{\AA}^2$]
H(3a')	0.659(4)	0.0406(10)	0.688(4)	4.7(9)
H(3b')	0.482(4)	0.0523(10)	0.509(4)	4.7(9)
H(4a')	0.471(5)	0.1016(10)	0.317(5)	5.2(9)
H(4b')	0.647(6)	0.1008(12)	0.317(6)	8.0(12)
H(4c')	0.622(5)	0.1354(12)	0.409(6)	7.3(11)
H(5')	1.153(4)	0.0970(8)	0.780(4)	1.9(6)
H(7')	1.320(4)	0.1300(10)	1.032(4)	4.6(8)
H(8')	1.346(5)	0.1854(12)	1.222(5)	7.0(11)
H(9')	1.152(5)	0.2399(12)	1.135(5)	6.9(11)
H(10')	0.923(4)	0.2409(10)	0.846(4)	4.4(8)
H(11')	0.893(4)	0.1880(8)	0.658(4)	2.9(7)
H(14')	1.367(4)	0.1787(9)	0.532(4)	3.1(7)
H(15')	1.659(4)	0.1860(9)	0.685(4)	3.3(7)
H(16')	1.815(4)	0.1478(10)	0.927(4)	4.3(8)
H(17')	1.685(5)	0.0957(10)	1.014(5)	5.3(9)
H(18')	1.400(4)	0.0898(9)	0.864(4)	2.9(7)
H(20')	1.145(4)	0.1328(8)	0.287(4)	2.3(6)
H(21')	1.112(5)	0.0788(10)	0.103(5)	5.7(10)
H(22')	1.092(4)	0.0128(9)	0.170(4)	3.9(8)
H(23')	1.099(4)	-0.0009(9)	0.432(4)	3.7(8)
H(24')	1.130(4)	0.0516(9)	0.621(4)	3.5(7)
H(26')	1.233(4)	0.2114(8)	0.658(4)	2.7(7)
H(27')	1.064(4)	0.2683(9)	0.512(4)	3.4(7)
H(28')	0.803(5)	0.2627(11)	0.274(5)	5.7(9)
H(29')	0.705(5)	0.1966(10)	0.170(5)	4.9(9)
H(30')	0.871(4)	0.1413(8)	0.302(4)	2.7(7)

f) Hydrogen atoms of the benzene molecule

Atom	x	y	z	B[$\mathrm{\AA}^2$]
H(31)	0.771(5)	-0.0031(13)	0.044(6)	7.5(12)
H(32)	0.719(5)	0.0273(11)	0.249(5)	6.4(10)
H(33)	0.439(5)	0.0321(12)	0.203(5)	7.3(11)
H(34)	0.271(5)	0.4976(11)	0.214(5)	6.6(11)
H(35)	0.055(5)	0.4725(12)	0.259(5)	7.1(11)
H(36)	-0.216(5)	0.4751(11)	0.045(5)	6.8(11)

Table 23. Fractional atomic positional parameters and equivalent temperature factors B_{eq}'s12) of ChMA with their estimated standard deviations in parentheses.

a) Non-hydrogen atoms refined anisotropically

Atom	x	y	z	B_{eq}[Å^2]
O(1)	0.2091(2)	0.3280(4)	0.6993(3)	4.2
O(2)	0.3240(3)	0.4384(4)	0.5537(3)	5.6
N(1)	0.0203(3)	0.0285(7)	0.8649(4)	6.9
C(1)	0.2421(4)	0.4371(5)	0.6158(4)	4.6
C(2)	0.1606(5)	0.5577(6)	0.6064(5)	6.3
C(3)	0.0608(6)	0.5373(10)	0.6617(10)	10.5
C(4)	0.1914(6)	0.6879(7)	0.5379(7)	8.5
C(5)	0.2772(3)	0.2001(5)	0.7293(4)	4.0
C(6)	0.2973(3)	0.1206(5)	0.5883(4)	4.2
C(7)	0.2248(3)	0.1289(6)	0.4706(4)	4.8
C(8)	0.2396(4)	0.0518(6)	0.3420(5)	5.6
C(9)	0.3323(5)	-0.0334(6)	0.3372(6)	6.6
C(10)	0.4039(4)	-0.0427(7)	0.4510(6)	6.9
C(11)	0.3871(4)	0.0334(6)	0.5767(5)	5.7
C(12)	0.3843(3)	0.2501(5)	0.8105(4)	4.5
C(13)	0.3738(3)	0.3496(5)	0.9378(4)	4.4
C(14)	0.3712(4)	0.4995(6)	0.9206(5)	6.0
C(15)	0.3629(4)	0.5912(6)	1.0397(6)	7.5
C(16)	0.3575(4)	0.5340(7)	1.1757(6)	6.5
C(17)	0.3633(4)	0.3857(7)	1.1975(5)	6.6
C(18)	0.3707(4)	0.2956(6)	1.0773(5)	5.5
C(19)	0.2065(3)	0.1097(5)	0.8305(4)	4.5
C(20)	0.0969(3)	0.0729(6)	0.7595(4)	4.9
C(21)	-0.0671(5)	-0.0575(8)	0.7997(8)	8.2
C(22)	-0.0260(7)	0.1613(14)	0.9322(9)	12.7
C(23)	0.2602(4)	-0.0318(6)	0.8866(5)	6.1

Table 23. (continued)

b) Hydrogen atoms

Atom	x	y	z	B[Å^2]
H(3a)	0.041(5)	0.440(8)	0.720(7)	6.2(14)
H(3b)	0.006(5)	0.623(9)	0.657(6)	6.5(14)
H(4a)	0.191(5)	0.686(8)	0.423(6)	6.3(14)
H(4b)	0.260(5)	0.724(7)	0.567(5)	4.8(11)
H(4c)	0.130(4)	0.756(7)	0.573(5)	5.0(12)
H(7)	0.156(4)	0.196(6)	0.472(5)	3.5(10)
H(8)	0.180(4)	0.061(6)	0.258(5)	4.0(10)
H(9)	0.344(5)	−0.089(7)	0.245(6)	5.1(12)
H(10)	0.474(4)	−0.112(7)	0.448(5)	4.3(11)
H(11)	0.446(3)	0.026(6)	0.664(4)	3.0(9)
H(12a)	0.434(3)	0.303(5)	0.736(4)	2.2(8)
H(12b)	0.425(4)	0.175(5)	0.840(4)	2.6(8)
H(14)	0.384(4)	0.542(7)	0.823(5)	4.2(11)
H(15)	0.360(4)	0.701(8)	1.025(6)	5.4(12)
H(16)	0.346(5)	0.603(8)	1.265(6)	5.8(13)
H(17)	0.363(4)	0.343(7)	1.296(5)	4.8(11)
H(18)	0.378(4)	0.196(6)	1.093(5)	3.8(10)
H(19)	0.195(4)	0.179(6)	0.918(5)	3.5(10)
H(20a)	0.103(4)	−0.011(6)	0.687(5)	3.9(10)
H(20b)	0.068(4)	0.166(6)	0.701(5)	3.4(10)
H(21a)	−0.126(4)	−0.095(7)	0.870(6)	4.7(11)
H(21b)	−0.039(4)	−0.155(8)	0.755(6)	5.5(12)
H(21c)	−0.112(4)	−0.003(7)	0.721(5)	4.4(11)
H(22a)	−0.084(5)	0.145(9)	1.003(6)	6.7(14)
H(22b)	−0.073(6)	0.225(9)	0.851(7)	7.3(15)
H(22c)	0.021(5)	0.230(8)	0.975(6)	6.1(14)
H(23a)	0.214(4)	−0.097(7)	0.950(6)	4.7(11)
H(23b)	0.329(4)	−0.022(6)	0.935(5)	4.0(10)
H(23c)	0.272(4)	−0.102(6)	0.808(5)	4.0(10)

refinement one strong reflection(020), which was considered largely affected by the extinction, were excluded.

(DPEMA-1,2). Three reflections(600, $\bar{1}14$, and 004), which were considered to be affected by extinction, were excluded at the final stage of the refinement.

(*t*-BBMA). Two molecules are contained in an asymmetric unit. The hydrogen atoms attached to the methacryl group of MOLECULE 2 could not be located because there was ambiguity about the conformation of two double bonds, C=C and C=O in the methacryl group. Two reflections(040 and 002), which were considered to be affected by extinction were excluded from the refinement.

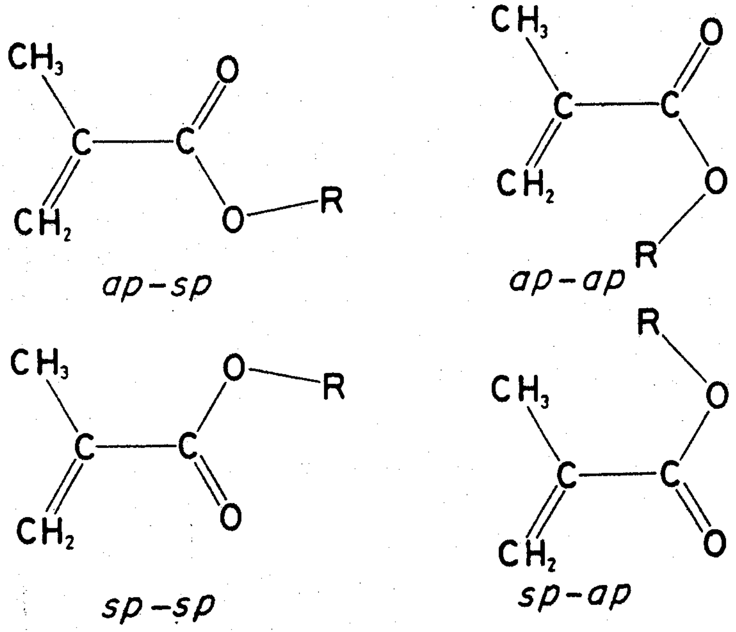
(TrBzMA). Two molecules and two halves of the benzene molecule(each benzene molecule lies on a symmetry center) are contained in an asymmetric unit.

2.2. Results and Discussion

Molecular Structure

Molecular structures with the numbering scheme of atoms in DPMMA, DPEMA-1,1, TrMA, DPEMA-1,2, *t*-BBMA, TrBzMA, and ChMA(*ORTEP* II) are depicted in Figures 26, 27, 28, 29, 30, 31, and 32, respectively. Selected bond lengths and bond angles of DPMMA, DPEMA-1,1, TrMA, DPEMA-1,2, *t*-BBMA, TrBzMA, and ChMA are listed in Tables 24, 25, 26, 27, 28, 29, and 30, respectively. Selected least-squares planes and dihedral angles between the planes of these monomers are also listed in Tables 31, 32, 33, 34, 35, 36, and 37, respectively.

One of the interest on the structure of methacrylate derivatives is the conformation about the C(1)-C(2) and C(1)-O(1) bonds. Four possible structures are shown in Scheme 10.



Scheme 10.

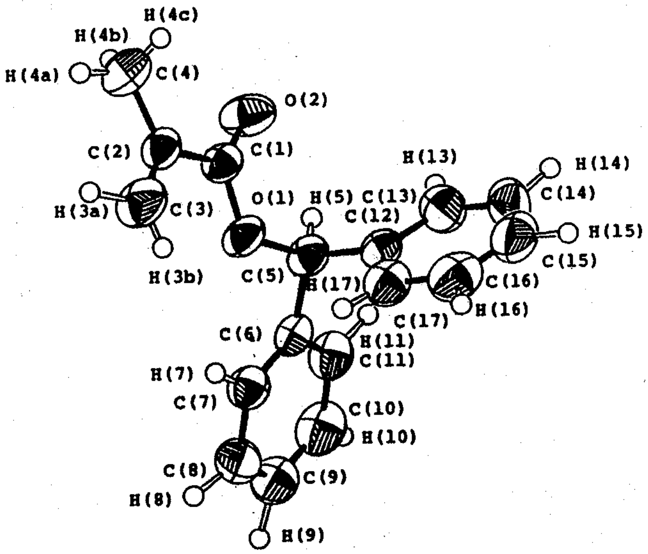


Figure 26. The molecular structure of DPMMA(*ORTEP* II)

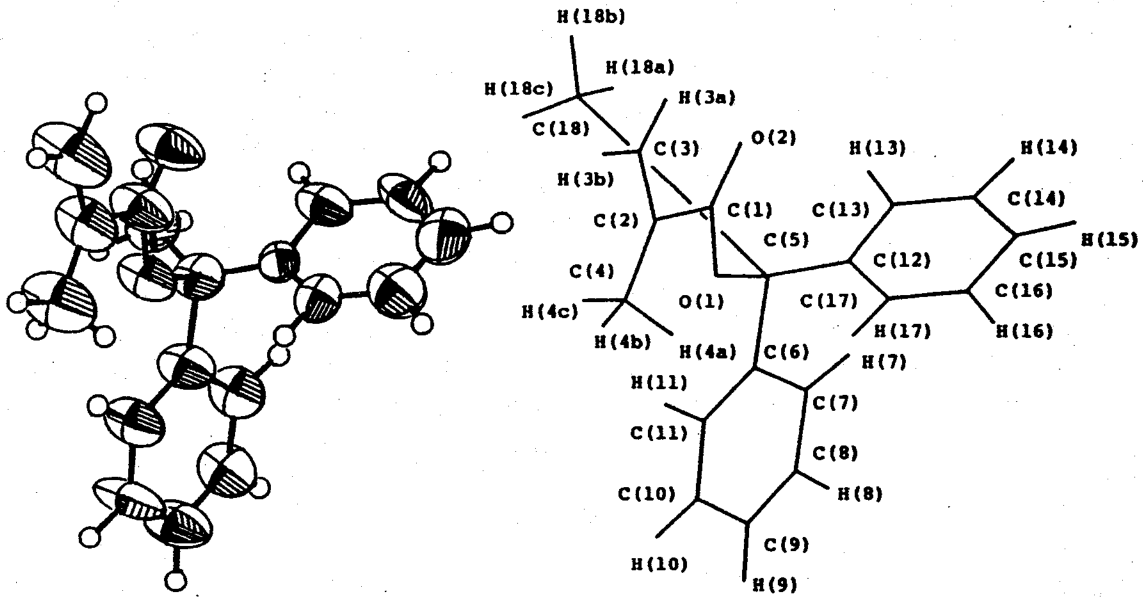


Figure 27. The molecular structure of DPEMA-1,1(*ORTEP* II)

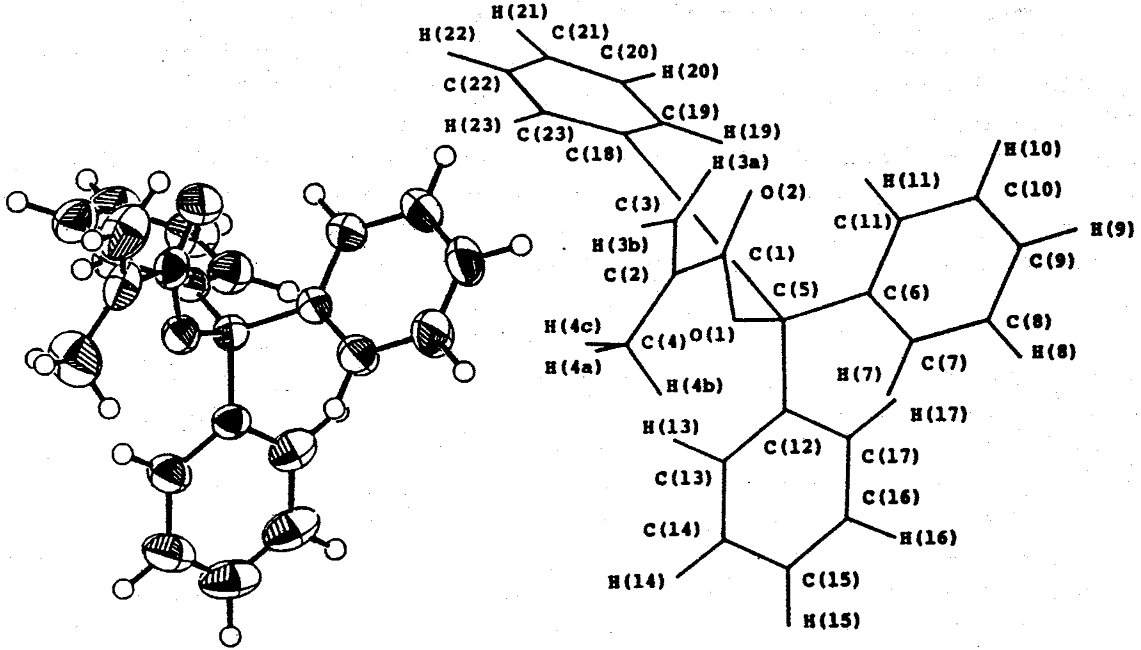


Figure 28. The molecular structure of TrMA(*ORTEP* II)

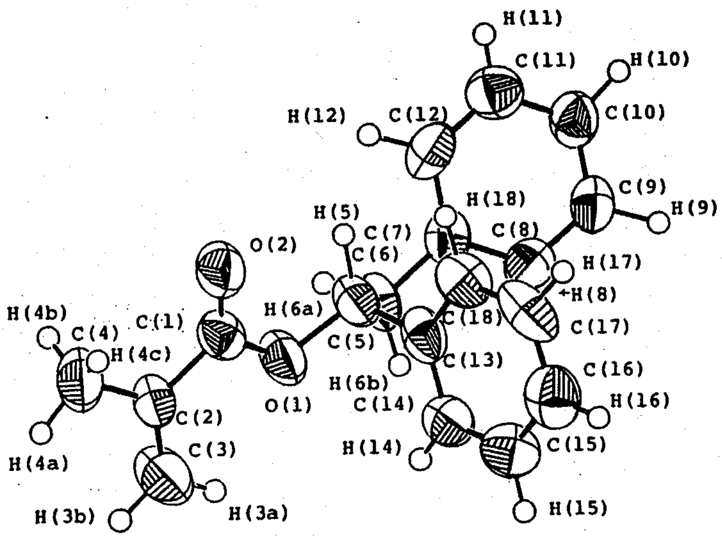
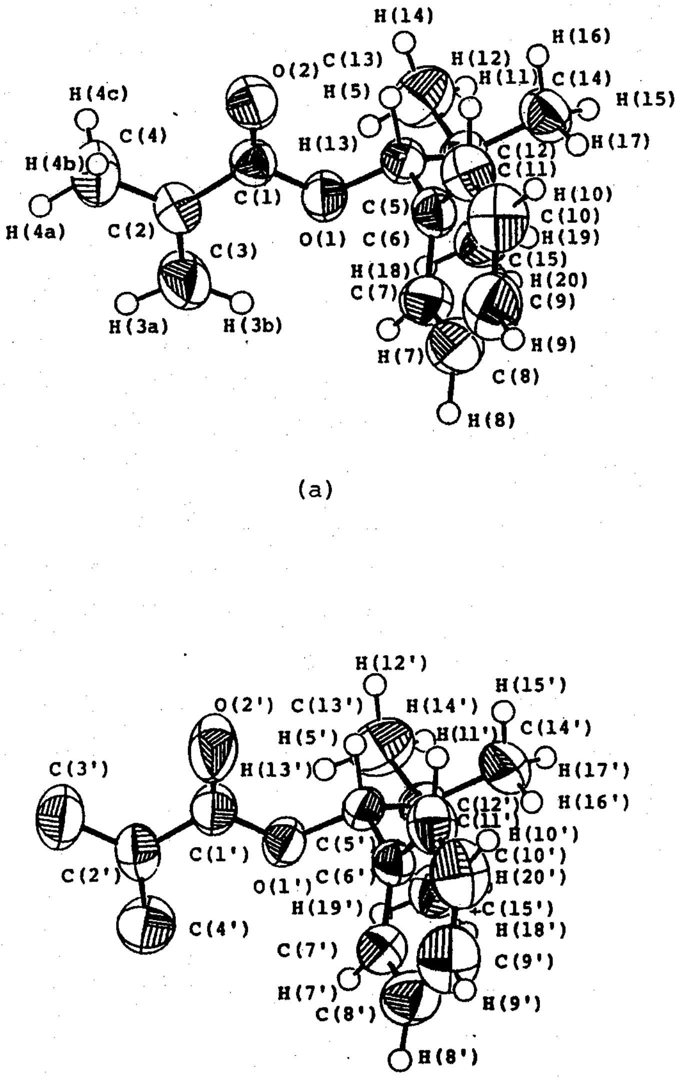


Figure 29. The molecular structure of DPEMA-1,2(*ORTEP* II)

The molecules of present study have an *antiperiplanar-synperiplanar*(*ap-sp*) or a *synperiplanar-synperiplanar*(*sp-sp*) structure. For example in DPMMA, which has an *ap-sp* structure, the conformation of the C(2)=C(3) and C(1)=O(2) double bonds about the C(1)-C(2) bond is *ap* while that of the C(1)=O(2) double and the O(1)-C(5) bonds about the C(1)-O(1) bond is *sp*. On the other hand similar achiral monomers, DPEMA-1,1, and TrMA with more bulky ester substituents than DPMMA, have the *sp-sp* structure where the conformation about the C(1)-C(2) bond is *sp*.

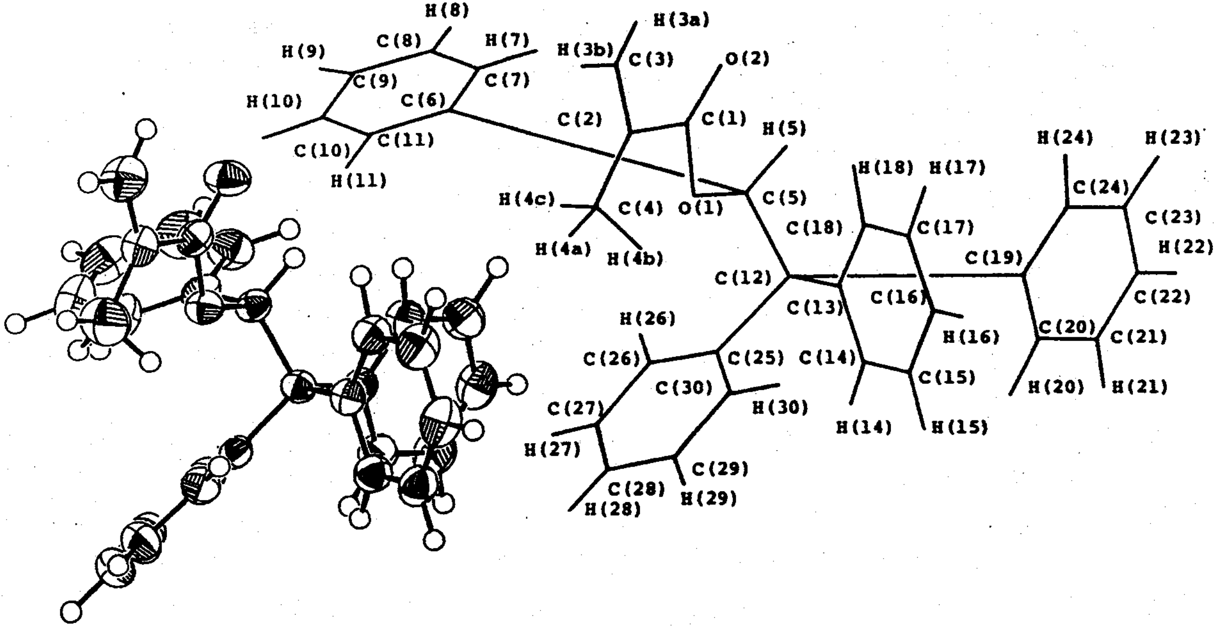
In the series of chiral monomers the DPEMA-1,2 molecule and one molecule in an asymmetric unit of *t*-BBMA have the *ap-sp* structure. But second molecule of *t*-BBMA possibly has two forms, *ap-sp* and *sp-sp* structures, disordered in a unit-cell, because bond lengths of the C(2)-C(3) [1.431(10) Å] and the



(a)

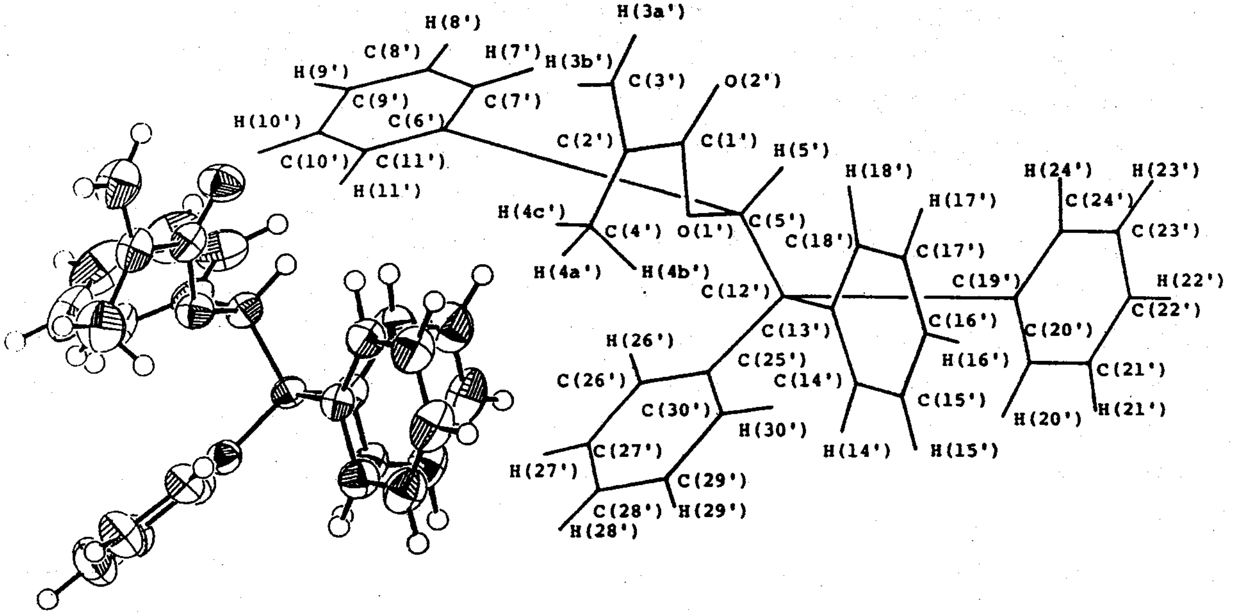
(b)

Figure 30. The molecular structures of *t*-BBMA molecules, (a) molecule 1, (b) molecule 2(*ORTEP* II)



(a)

Figure 31. The molecular structures of TrBzMA molecules(*ORTEP* II), (a) molecule 1, (b) molecule 2



(b)

Figure 31. (continued)

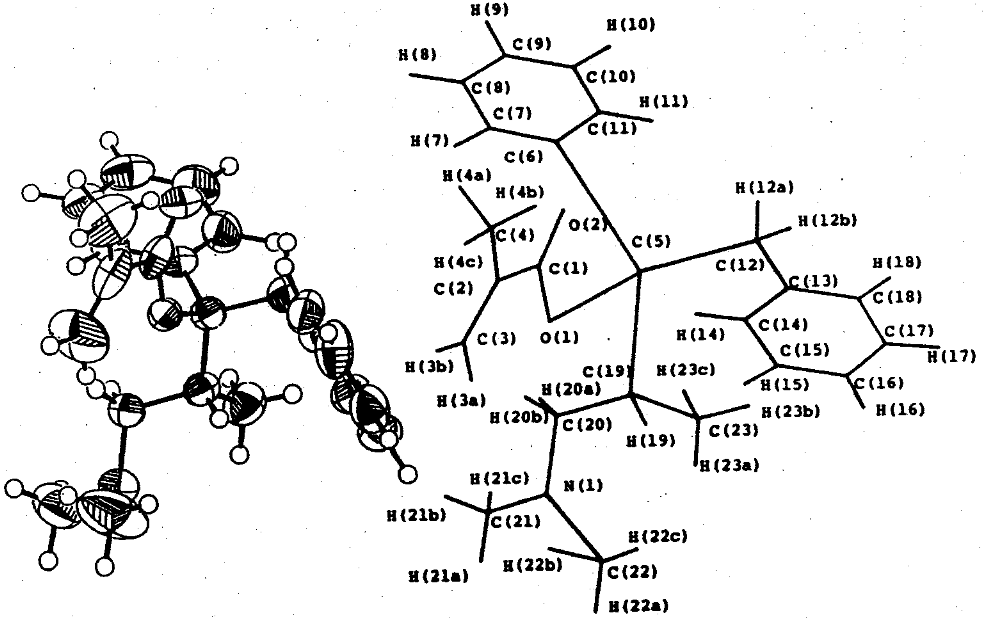


Figure 32. The molecular structure of ChMA(*ORTEP* II)

Table 24. Bond lengths[Å] and bond angles[°] of DPMMA with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.340(4)	O(1)-C(5)	1.456(4)
O(2)-C(1)	1.194(4)	C(1)-C(2)	1.492(5)
C(2)-C(3)	1.332(5)	C(2)-C(4)	1.466(5)
C(5)-C(6)	1.507(4)	C(5)-C(12)	1.512(4)
C(6)-C(7)	1.371(5)	C(6)-C(11)	1.399(5)
C(7)-C(8)	1.398(5)	C(8)-C(9)	1.388(5)
C(9)-C(10)	1.362(6)	C(10)-C(11)	1.387(6)
C(12)-C(13)	1.385(5)	C(12)-C(17)	1.373(5)
C(13)-C(14)	1.394(6)	C(14)-C(15)	1.361(7)
C(15)-C(16)	1.364(7)	C(16)-C(17)	1.397(6)

b) Bond angles

C(1)-O(1)-C(5)	117.3(3)	O(1)-C(1)-C(2)	123.1(3)
O(1)-C(1)-C(2)	112.3(3)	O(2)-C(1)-C(2)	124.6(3)
C(1)-C(2)-C(3)	121.0(3)	C(1)-C(2)-C(4)	115.4(3)
C(3)-C(2)-C(4)	123.6(4)	O(1)-C(5)-C(6)	107.5(3)
O(1)-C(5)-C(12)	108.4(3)	C(6)-C(5)-C(12)	113.8(3)
C(5)-C(6)-C(7)	123.3(3)	C(5)-C(6)-C(11)	117.8(3)
C(7)-C(6)-C(11)	118.9(3)	C(6)-C(7)-C(8)	121.0(3)
C(7)-C(8)-C(9)	119.4(4)	C(8)-C(9)-C(10)	119.7(4)
C(9)-C(10)-C(11)	121.2(4)	C(6)-C(11)-C(10)	119.8(4)
C(5)-C(12)-C(13)	119.9(3)	C(5)-C(12)-C(17)	120.6(3)
C(13)-C(12)-C(17)	119.5(3)	C(12)-C(13)-C(14)	119.3(4)
C(13)-C(14)-C(15)	120.9(5)	C(14)-C(15)-C(16)	119.9(5)
C(15)-C(16)-C(17)	120.1(4)	C(12)-C(17)-C(16)	120.2(4)

Table 25. Bond lengths[Å] and bond angles[°] of DPEMA-1,1 with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.35(3)	O(1)-C(5)	1.52(3)
O(2)-C(1)	1.16(3)	C(1)-C(2)	1.58(4)
C(2)-C(3)	1.38(5)	C(2)-C(4)	1.43(4)
C(5)-C(6)	1.59(3)	C(5)-C(12)	1.42(3)
C(5)-C(18)	1.55(3)	C(6)-C(7)	1.42(3)
C(6)-C(11)	1.39(3)	C(7)-C(8)	1.39(3)
C(8)-C(9)	1.35(4)	C(9)-C(10)	1.38(4)
C(10)-C(11)	1.37(4)	C(12)-C(13)	1.45(3)
C(12)-C(17)	1.37(3)	C(13)-C(14)	1.42(3)
C(14)-C(15)	1.40(4)	C(15)-C(16)	1.40(4)
C(16)-C(17)	1.38(3)		

b) Bond angles

C(1)-O(1)-C(5)	116(2)	O(1)-C(1)-O(2)	128(3)
O(1)-C(1)-C(2)	107(2)	O(2)-C(1)-C(2)	125(3)
C(1)-C(2)-C(3)	113(3)	C(1)-C(2)-C(4)	120(3)
C(3)-C(2)-C(4)	127(3)	O(1)-C(5)-C(6)	99(2)
O(1)-C(5)-C(12)	111(2)	O(1)-C(5)-C(18)	105(2)
C(6)-C(5)-C(12)	111(2)	C(6)-C(5)-C(18)	106(2)
C(12)-C(5)-C(18)	123(2)	C(5)-C(6)-C(7)	115(2)
C(5)-C(6)-C(11)	127(2)	C(7)-C(6)-C(11)	118(2)
C(6)-C(7)-C(8)	117(2)	C(7)-C(8)-C(9)	124(3)
C(8)-C(9)-C(10)	118(3)	C(9)-C(10)-C(11)	121(3)
C(6)-C(11)-C(10)	122(3)	C(5)-C(12)-C(13)	119(2)
C(5)-C(12)-C(17)	124(2)	C(13)-C(12)-C(17)	117(2)
C(12)-C(13)-C(14)	114(2)	C(13)-C(14)-C(15)	128(3)
C(14)-C(15)-C(16)	116(2)	C(15)-C(16)-C(17)	117(2)
C(12)-C(17)-C(16)	128(2)		

Table 26. Bond lengths[Å] and bond angles[°] of TrMA with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.353(4)	O(1)-C(5)	1.464(3)
O(2)-C(1)	1.198(4)	C(1)-C(2)	1.500(4)
C(2)-C(3)	1.351(5)	C(2)-C(4)	1.450(5)
C(5)-C(6)	1.533(4)	C(5)-C(12)	1.539(4)
C(5)-C(18)	1.530(4)	C(6)-C(7)	1.386(4)
C(6)-C(11)	1.383(4)	C(7)-C(8)	1.384(5)
C(8)-C(9)	1.374(5)	C(9)-C(10)	1.376(5)
C(10)-C(11)	1.391(5)	C(12)-C(13)	1.384(4)
C(12)-C(17)	1.396(4)	C(13)-C(14)	1.393(5)
C(14)-C(15)	1.373(5)	C(15)-C(16)	1.370(6)
C(16)-C(17)	1.396(5)	C(18)-C(19)	1.394(4)
C(18)-C(23)	1.389(4)	C(19)-C(20)	1.395(5)
C(20)-C(21)	1.384(5)	C(21)-C(22)	1.365(5)
C(22)-C(23)	1.388(5)		

b) Bond angles

C(1)-O(1)-C(5)	120.7(2)	O(1)-C(1)-O(2)	124.8(3)
O(1)-C(1)-C(2)	110.3(3)	O(2)-C(1)-C(2)	125.0(3)
C(1)-C(2)-C(3)	116.5(3)	C(1)-C(2)-C(4)	119.2(3)
C(3)-C(2)-C(4)	124.3(3)	O(1)-C(5)-C(6)	108.0(2)
O(1)-C(5)-C(12)	103.5(2)	O(1)-C(5)-C(18)	110.2(2)
C(6)-C(5)-C(12)	110.9(2)	C(6)-C(5)-C(18)	116.1(2)
C(12)-C(5)-C(18)	107.4(2)	C(5)-C(6)-C(7)	117.8(3)
C(5)-C(6)-C(11)	123.8(3)	C(7)-C(6)-C(11)	118.3(3)
C(6)-C(7)-C(8)	120.9(3)	C(7)-C(8)-C(9)	120.4(4)
C(8)-C(9)-C(10)	119.4(4)	C(9)-C(10)-C(11)	120.2(3)
C(6)-C(11)-C(10)	120.7(3)	C(5)-C(12)-C(13)	121.5(3)
C(5)-C(12)-C(17)	120.0(3)	C(13)-C(12)-C(17)	118.4(3)
C(12)-C(13)-C(14)	120.9(3)	C(13)-C(14)-C(15)	120.0(4)
C(14)-C(15)-C(16)	119.9(4)	C(15)-C(16)-C(17)	120.5(4)
C(12)-C(17)-C(16)	120.1(3)	C(5)-C(18)-C(19)	119.7(3)
C(5)-C(18)-C(23)	121.6(3)	C(19)-C(18)-C(23)	118.4(3)
C(18)-C(19)-C(20)	120.7(3)	C(19)-C(20)-C(21)	119.8(3)
C(20)-C(21)-C(22)	119.6(4)	C(21)-C(22)-C(23)	121.2(3)
C(18)-C(23)-C(22)	120.3(3)		

Table 27. Bond lengths[Å] and bond angles[°] of DPEMA-1,2 with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.33(3)	O(1)-C(5)	1.48(2)
O(2)-C(1)	1.19(2)	C(1)-C(2)	1.49(2)
C(2)-C(3)	1.33(3)	C(2)-C(4)	1.46(2)
C(5)-C(6)	1.57(2)	C(5)-C(13)	1.51(2)
C(6)-C(7)	1.52(2)	C(7)-C(8)	1.38(2)
C(7)-C(12)	1.40(2)	C(8)-C(9)	1.41(2)
C(9)-C(10)	1.38(2)	C(10)-C(11)	1.36(2)
C(11)-C(12)	1.41(2)	C(13)-C(14)	1.41(2)
C(13)-C(18)	1.36(2)	C(14)-C(15)	1.39(2)
C(15)-C(16)	1.37(2)	C(16)-C(17)	1.41(3)
C(17)-C(18)	1.40(2)		

b) Bond angles

C(1)-O(1)-C(5)	116.7(10)	O(1)-C(1)-O(2)	123.6(12)
O(1)-C(1)-C(2)	111.7(11)	O(2)-C(1)-C(2)	124.6(12)
C(1)-C(2)-C(3)	120.3(13)	C(1)-C(2)-C(4)	116.2(11)
C(3)-C(2)-C(4)	123.4(13)	O(1)-C(5)-C(6)	103.1(10)
O(1)-C(5)-C(13)	108.8(10)	C(6)-C(5)-C(13)	114.3(10)
C(5)-C(6)-C(7)	109.6(10)	C(6)-C(7)-C(8)	119.9(11)
C(6)-C(7)-C(12)	121.3(11)	C(8)-C(7)-C(12)	118.8(12)
C(7)-C(8)-C(9)	119.8(12)	C(8)-C(9)-C(10)	120.9(13)
C(9)-C(10)-C(11)	119.6(13)	C(10)-C(11)-C(12)	120.5(13)
C(7)-C(12)-C(11)	120.4(12)	C(5)-C(13)-C(14)	121.9(11)
C(5)-C(13)-C(18)	118.4(11)	C(14)-C(13)-C(18)	119.7(12)
C(13)-C(14)-C(15)	120.2(12)	C(14)-C(15)-C(16)	121.7(13)
C(15)-C(16)-C(17)	116.6(14)	C(16)-C(17)-C(18)	122.9(14)
C(13)-C(18)-C(17)	118.8(12)		

Table 28. Bond lengths[Å] and bond angles[°] of t-BBMA with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.342(7)	O(1)-C(5)	1.451(7)
O(1')-C(1')	1.318(7)	O(1')-C(5')	1.449(7)
O(2)-C(1)	1.193(7)	C(1)-C(2)	1.481(8)
O(2')-C(1')	1.205(9)	C(1')-C(2')	1.469(9)
C(2)-C(3)	1.359(10)	C(2)-C(4)	1.475(10)
C(2')-C(3')	1.431(10)	C(2')-C(4')	1.416(10)
C(5)-C(6)	1.506(8)	C(5)-C(12)	1.546(8)
C(5')-C(6')	1.525(8)	C(5')-C(12')	1.542(8)
C(6)-C(7)	1.407(9)	C(6)-C(11)	1.379(9)
C(6')-C(7')	1.391(8)	C(6')-C(11')	1.384(9)
C(7)-C(8)	1.390(10)	C(8)-C(9)	1.369(11)
C(7')-C(8')	1.386(10)	C(8')-C(9')	1.376(11)
C(9)-C(10)	1.398(11)	C(10)-C(11)	1.373(10)
C(9')-C(10')	1.367(12)	C(10')-C(11')	1.402(11)
C(12)-C(13)	1.550(10)	C(12)-C(14)	1.530(9)
C(12')-C(13')	1.541(9)	C(12')-C(14')	1.501(9)
C(12)-C(15)	1.528(9)		
C(12')-C(15')	1.523(9)		

Table 28. (continued)

b) Bond angles

C(1)-O(1)-C(5)	116.9(5)	O(1)-C(1)-O(2)	123.2(6)
C(1')-O(1')-C(5')	119.3(5)	O(1')-C(1')-O(2')	122.1(6)
O(1)-C(1)-C(2)	113.0(5)	O(2)-C(1)-C(2)	123.8(6)
O(1')-C(1')-C(2')	114.1(5)	O(2')-C(1')-C(2')	123.8(6)
C(1)-C(2)-C(3)	120.3(6)	C(1)-C(2)-C(4)	117.3(6)
C(1')-C(2')-C(3')	116.6(6)	C(1')-C(2')-C(4')	119.1(6)
C(3)-C(2)-C(4)	122.3(6)	O(1)-C(5)-C(6)	108.7(5)
C(3')-C(2')-C(4')	124.3(7)	O(1')-C(5')-C(6')	107.7(5)
O(1)-C(5)-C(12)	107.5(5)	C(6)-C(5)-C(12)	115.7(5)
O(1')-C(5')-C(12')	107.5(5)	C(6')-C(5')-C(12')	115.8(5)
C(5)-C(6)-C(7)	121.1(5)	C(5)-C(6)-C(11)	119.7(6)
C(5')-C(6')-C(7')	121.5(5)	C(5')-C(6')-C(11')	118.7(5)
C(7)-C(6)-C(11)	119.2(6)	C(6)-C(7)-C(8)	119.1(6)
C(7')-C(6')-C(11')	119.8(6)	C(6')-C(7')-C(8')	120.6(6)
C(7)-C(8)-C(9)	120.8(7)	C(8)-C(9)-C(10)	120.1(8)
C(7')-C(8')-C(9')	119.0(7)	C(8')-C(9')-C(10')	121.2(8)
C(9)-C(10)-C(11)	119.3(7)	C(6)-C(11)-C(10)	121.4(7)
C(9')-C(10')-C(11')	120.2(7)	C(6')-C(11')-C(10')	119.1(6)
C(5)-C(12)-C(13)	108.2(5)	C(5)-C(12)-C(14)	108.7(5)
C(5')-C(12')-C(13')	107.8(5)	C(5')-C(12')-C(14')	109.1(5)
C(5)-C(12)-C(15)	112.5(5)	C(13)-C(12)-C(14)	108.4(5)
C(5')-C(12')-C(15')	112.4(5)	C(13')-C(12')-C(14')	109.2(5)
C(13)-C(12)-C(15)	109.8(5)	C(14)-C(12)-C(15)	109.2(5)
C(13')-C(12')-C(15')	108.6(5)	C(14')-C(12')-C(15')	109.7(5)

Table 29. Bond lengths[Å] and bond angles[°] of TrBzMA with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.354(4)	O(1)-C(5)	1.456(4)
O(1')-C(1')	1.354(4)	O(1')-C(5')	1.453(4)
O(2)-C(1)	1.201(4)	O(1)-C(2)	1.484(5)
O(2')-C(1')	1.205(4)	C(1')-C(2')	1.480(5)
C(2)-C(3)	1.382(5)	C(2)-C(4)	1.427(6)
C(2')-C(3')	1.368(5)	C(2')-C(4')	1.440(5)
C(5)-C(6)	1.525(4)	C(5)-C(12)	1.573(4)
C(5')-C(6')	1.514(5)	C(5')-C(12')	1.584(4)
C(6)-C(7)	1.391(5)	C(6)-C(11)	1.385(5)
C(6')-C(7')	1.392(5)	C(6')-C(11')	1.387(5)
C(7)-C(8)	1.379(6)	C(8)-C(9)	1.371(6)
C(7')-C(8')	1.389(6)	C(8')-C(9')	1.383(7)
C(9)-C(10)	1.371(6)	C(10)-C(11)	1.396(5)
C(9')-C(10')	1.379(7)	C(10')-C(11')	1.395(6)
C(12)-C(13)	1.551(4)	C(12)-C(19)	1.549(4)
C(12')-C(13')	1.551(4)	C(12')-C(19')	1.549(4)
C(12)-C(25)	1.541(4)	C(13)-C(14)	1.386(5)
C(12')-C(25')	1.535(4)	C(13')-C(14')	1.394(5)
C(13)-C(18)	1.395(5)	C(14)-C(15)	1.389(5)
C(13')-C(18')	1.388(5)	C(14')-C(15')	1.391(5)
C(15)-C(16)	1.369(5)	C(16)-C(17)	1.374(5)
C(15')-C(16')	1.377(6)	C(16')-C(17')	1.376(6)
C(17)-C(18)	1.399(5)	C(19)-C(20)	1.400(5)
C(17')-C(18')	1.395(5)	C(19')-C(20')	1.393(5)
C(19)-C(24)	1.390(5)	C(20)-C(21)	1.393(5)
C(19')-C(24')	1.387(5)	C(20')-C(21')	1.392(5)
C(21)-C(22)	1.383(5)	C(22)-C(23)	1.373(5)
C(21')-C(22')	1.378(5)	C(22')-C(23')	1.388(6)

Table 29. (continued)

C(23)-C(24)	1.392(5)	C(25)-C(26)	1.401(5)
C(23')-C(24')	1.401(5)	C(25')-C(26')	1.397(5)
C(25)-C(30)	1.393(5)	C(26)-C(27)	1.395(5)
C(25')-C(30')	1.392(5)	C(26')-C(27')	1.385(5)
C(27)-C(28)	1.376(6)	C(28)-C(29)	1.374(6)
C(27')-C(28')	1.380(6)	C(28')-C(29')	1.378(6)
C(29)-C(30)	1.384(5)		
C(29')-C(30')	1.384(5)		
C(31)-C(32)	1.350(8)	C(32)-C(33)	1.368(8)
C(33)-C(31')	1.359(8)	C(34)-C(35)	1.357(7)
C(35)-C(36)	1.380(7)	C(36)-C(34')	1.352(7)

b) Bond angles

C(1)-O(1)-C(5)	116.9(3)	O(1)-C(1)-O(2)	123.1(3)
C(1')-O(1')-C(5')	117.5(3)	O(1')-C(1')-O(2')	122.7(3)
O(1)-C(1)-C(2)	111.8(3)	O(2)-C(1)-C(2)	125.0(3)
O(1')-C(1')-C(2')	112.0(3)	O(2')-C(1')-C(2')	125.3(3)
C(1)-C(2)-C(3)	117.4(3)	C(1)-C(2)-C(4)	119.2(3)
C(1')-C(2')-C(3')	117.7(3)	C(1')-C(2')-C(4')	119.2(3)
C(3)-C(2)-C(4)	123.4(4)	O(1)-C(5)-C(6)	108.4(3)
C(3')-C(2')-C(4')	123.1(4)	O(1')-C(5')-C(6')	108.8(3)
O(1)-C(5)-C(12)	105.5(2)	C(6)-C(5)-C(12)	115.2(3)
O(1')-C(5')-C(12')	105.2(3)	C(6')-C(5')-C(12')	115.2(3)
C(5)-C(6)-C(7)	120.1(3)	C(5)-C(6)-C(11)	121.3(3)
C(5')-C(6')-C(7')	119.7(3)	C(5')-C(6')-C(11')	121.5(3)
C(7)-C(6)-C(11)	118.6(3)	C(6)-C(7)-C(8)	120.3(4)
C(7')-C(6')-C(11')	118.8(4)	C(6')-C(7')-C(8')	120.6(4)
C(7)-C(8)-C(9)	120.7(4)	C(8)-C(9)-C(10)	120.0(4)
C(7')-C(8')-C(9')	120.1(5)	C(8')-C(9')-C(10')	119.9(5)
C(9)-C(10)-C(11)	119.9(4)	C(6)-C(11)-C(11)	120.5(3)
C(9')-C(10')-C(11')	120.1(4)	C(6')-C(11')-C(10')	120.5(4)

Table 29. (continued)

C(5)-C(12)-C(13)	108.9(3)	C(5)-C(12)-C(19)	111.0(3)
C(5')-C(12')-C(13')	108.8(3)	C(5')-C(12')-C(19')	110.9(3)
C(5)-C(12)-C(25)	107.5(3)	C(13)-C(12)-C(19)	104.3(3)
C(5')-C(12')-C(25')	106.5(3)	C(13')-C(12')-C(19')	104.8(3)
C(13)-C(12)-C(25)	114.1(3)	C(19)-C(12)-C(25)	111.1(3)
C(13')-C(12')-C(25')	114.5(3)	C(19')-C(12')-C(25')	111.3(3)
C(12)-C(13)-C(14)	121.8(3)	C(12)-C(13)-C(18)	121.0(3)
C(12')-C(13')-C(14')	120.8(3)	C(12')-C(13')-C(18')	122.0(3)
C(14)-C(13)-C(18)	116.9(3)	C(13)-C(14)-C(15)	121.4(3)
C(14')-C(13')-C(18')	117.0(3)	C(13')-C(14')-C(15')	121.2(4)
C(14)-C(15)-C(16)	121.0(4)	C(15)-C(16)-C(17)	119.1(4)
C(14')-C(15')-C(16')	120.6(4)	C(15')-C(16')-C(17')	119.2(4)
C(16)-C(17)-C(18)	120.2(4)	C(13)-C(18)-C(17)	121.3(3)
C(16')-C(17')-C(18')	120.0(4)	C(13')-C(18')-C(17')	121.8(3)
C(12)-C(19)-C(20)	118.9(3)	C(12)-C(19)-C(24)	123.2(3)
C(12')-C(19')-C(20')	119.4(3)	C(12')-C(19')-C(24')	122.7(3)
C(20)-C(21)-C(22)	120.4(3)	C(21)-C(22)-C(23)	119.4(4)
C(20')-C(21')-C(22')	120.2(4)	C(21')-C(22')-C(23')	119.2(4)
C(22)-C(23)-C(24)	120.6(4)	C(19)-C(24)-C(23)	121.0(3)
C(22')-C(23')-C(24')	120.4(4)	C(19')-C(24')-C(23')	120.8(3)
C(12)-C(25)-C(26)	121.9(3)	C(12)-C(25)-C(30)	120.5(3)
C(12')-C(25')-C(26')	122.4(3)	C(12')-C(25')-C(30')	120.0(3)
C(26)-C(25)-C(30)	117.4(3)	C(25)-C(26)-C(27)	120.4(3)
C(26')-C(25')-C(30')	117.1(3)	C(25')-C(26')-C(27')	120.9(3)
C(26)-C(27)-C(28)	120.9(4)	C(27)-C(28)-C(29)	119.4(4)
C(26')-C(27')-C(28')	120.8(4)	C(27')-C(28')-C(29')	119.0(4)
C(28)-C(29)-C(30)	120.3(4)	C(25)-C(30)-C(29)	121.7(3)
C(28')-C(29')-C(30')	120.2(4)	C(25')-C(30')-C(29')	121.8(3)
C(31)-C(32)-C(33)	119.5(5)	C(32)-C(33)-C(31')	119.8(6)
C(33')-C(31)-C(32)	120.7(5)	C(34)-C(35)-C(36)	119.9(5)
C(35)-C(36)-C(34')	119.6(5)	C(36')-C(34)-C(35)	120.5(5)

Table 30. Bond lengths[Å] and bond angles[°] of ChMA with estimated standard deviations in parentheses

a) Bond lengths

O(1)-C(1)	1.345(5)	O(1)-C(5)	1.466(5)
O(2)-C(1)	1.202(6)	C(1)-C(2)	1.503(7)
C(2)-C(3)	1.387(10)	C(2)-C(4)	1.417(9)
C(5)-C(6)	1.528(6)	C(5)-C(12)	1.562(6)
C(5)-C(19)	1.563(6)	C(6)-C(7)	1.375(7)
C(6)-C(11)	1.388(7)	C(7)-C(8)	1.406(7)
C(8)-C(9)	1.399(8)	C(9)-C(10)	1.341(9)
C(10)-C(11)	1.383(9)	C(12)-C(13)	1.502(7)
C(13)-C(14)	1.386(7)	C(13)-C(18)	1.384(7)
C(14)-C(15)	1.395(8)	C(15)-C(16)	1.368(9)
C(16)-C(17)	1.378(9)	C(17)-C(18)	1.393(9)
C(19)-C(20)	1.518(7)	C(19)-C(23)	1.537(7)
N(1)-C(20)	1.464(8)	N(1)-C(21)	1.448(9)
N(1)-C(22)	1.501(14)		

b) Bond angles

C(1)-O(1)-C(5)	120.8(4)	O(1)-C(1)-O(2)	125.4(4)
O(1)-C(1)-C(2)	110.7(4)	O(2)-C(1)-C(2)	123.9(4)
C(1)-C(2)-C(3)	119.9(6)	C(1)-C(2)-C(4)	116.5(5)
C(3)-C(2)-C(4)	123.5(6)	O(1)-C(5)-C(6)	110.2(4)
O(1)-C(5)-C(12)	108.9(4)	O(1)-C(5)-C(19)	101.4(3)
C(6)-C(5)-C(12)	111.7(4)	C(6)-C(5)-C(19)	112.6(4)
C(12)-C(5)-C(19)	111.5(4)	C(5)-C(6)-C(7)	121.0(4)
C(5)-C(6)-C(11)	121.1(5)	C(7)-C(6)-C(11)	117.8(5)
C(6)-C(7)-C(8)	121.8(5)	C(7)-C(8)-C(9)	117.4(5)
C(8)-C(9)-C(10)	121.5(6)	C(9)-C(10)-C(11)	120.0(6)
C(6)-C(11)-C(10)	121.4(5)	C(5)-C(12)-C(13)	116.3(4)
C(12)-C(13)-C(14)	121.1(5)	C(12)-C(13)-C(18)	121.4(5)
C(14)-C(13)-C(18)	117.4(5)	C(13)-C(14)-C(15)	120.8(5)
C(14)-C(15)-C(16)	120.2(6)	C(15)-C(16)-C(17)	120.6(6)
C(16)-C(17)-C(18)	118.4(6)	C(13)-C(18)-C(17)	122.5(5)
C(5)-C(19)-C(20)	112.7(4)	C(5)-C(19)-C(23)	113.6(4)
C(20)-C(19)-C(23)	108.7(4)	C(20)-N(1)-C(21)	112.4(5)
C(20)-N(1)-C(22)	109.5(7)	C(21)-N(1)-C(22)	108.4(7)
N(1)-C(20)-C(19)	112.5(5)		

Table 31. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of DPMMA.
(The planes are defined in terms of Cartesian coordinates[Å] by $AX+BY+CZ=D$, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.5865, 0.0322, 0.8093, and 13.4026

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.095(2)	0.083(2)	0.009(3)	0.007(3)	0.079(2)	-0.082(2)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.5656, -0.0279, 0.8242, and 13.0044

C(1)	C(2)	C(3)	C(4)
-0.000(2)	0.001(3)	-0.000(1)	-0.000(1)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = 0.6077, 0.1062, 0.7871, and 13.8169

O(1)	O(2)	C(1)	C(2)
-0.001(1)	-0.001(1)	0.003(3)	-0.001(1)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = 0.5403, 0.1808, 0.8218, and 13.0976

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = 0.8139, 0.4328, 0.3877, and 17.1756

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
-0.005(3)	0.007(3)	-0.001(3)	-0.007(3)	0.008(3)	-0.002(3)

Plane 6: C(12), C(13), C(14), C(15), C(16), and C(17)
A, B, C, D[Å] = -0.5423, -0.3830, 0.7478, and -8.1566

C(12)	C(13)	C(14)	C(15)	C(16)	C(17)
0.003(3)	0.004(3)	-0.007(4)	0.007(4)	0.000(3)	-0.003(3)

Dihedral angles:
between planes 2 and 3: 8.3(2)
between planes 3 and 4: 6.1(3)
between planes 1 and 5: 36.4(2)
between planes 1 and 6: 74.0(2)

Table 32. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of DPEMA-1,1.
(The planes are defined in terms of Cartesian coordinates[Å] by $AX+BY+CZ=D$, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.1092, -0.1554, 0.9818, and -2.9914

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.017(5)	0.020(8)	0.02(3)	-0.01(2)	-0.08(3)	0.07(2)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.1357, -0.2110, 0.9680, and -3.2068

C(1)	C(2)	C(3)	C(4)
0.002(6)	-0.01(2)	0.00(2)	0.00(1)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = 0.1106, -0.1382, 0.9842, and -2.8629

O(1)	O(2)	C(1)	C(2)
-0.002(3)	-0.003(5)	0.01(3)	-0.004(6)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = -0.1296, 0.1124, -0.9852, and 2.5675

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = -0.2590, 0.0895, -0.9617, and 1.9637

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
0.01(2)	-0.02(2)	0.02(2)	-0.02(2)	0.00(2)	-0.00(2)

Plane 6: C(12), C(13), C(14), C(15), C(16), and C(17)
A, B, C, D[Å] = 0.7050, -0.6688, -0.2362, and -2.8907

C(12)	C(13)	C(14)	C(15)	C(16)	C(17)
-0.01(1)	0.01(2)	-0.01(2)	0.01(2)	-0.01(2)	0.01(2)

Dihedral angles:
between planes 2 and 3: 5(2)
between planes 3 and 4: 2(2)
between planes 1 and 5: 9.5(7)
between planes 1 and 6: 87.1(7)

Table 33. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of TrMA.
(The planes are defined in terms of Cartesian coordinates[Å] by $AX+BY+CZ=D$, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = -0.6815, 0.4926, -0.5412, and 0.7186

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
0.184(2)	-0.168(2)	-0.011(3)	-0.002(3)	0.158(2)	-0.162(2)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = -0.7688, 0.4103, -0.4905, and -0.0055

C(1)	C(2)	C(3)	C(4)
-0.000(2)	0.000(3)	-0.000(1)	-0.000(1)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = -0.5640, 0.5879, -0.5800, and 1.5168

O(1)	O(2)	C(1)	C(2)
0.000(1)	0.000(1)	-0.000(3)	0.000(1)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = -0.5697, 0.5415, -0.6181, and 1.5405

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = -0.6428, 0.1699, 0.7469, and -2.4500

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
0.007(2)	-0.000(3)	-0.007(3)	0.008(3)	-0.001(3)	-0.007(3)

Plane 6: C(12), C(13), C(14), C(15), C(16), and C(17)
A, B, C, D[Å] = -0.4154, 0.2757, -0.8669, and 1.7411

C(12)	C(13)	C(14)	C(15)	C(16)	C(17)
0.007(2)	-0.007(3)	0.001(3)	0.005(3)	-0.004(3)	-0.002(3)

Plane 7: C(18), C(19), C(20), C(21), C(22), and C(23)
A, B, C, D[Å] = -0.6298, -0.7182, 0.2960, and -3.9691

C(18)	C(19)	C(20)	C(21)	C(22)	C(23)
-0.009(2)	0.006(3)	-0.002(3)	0.001(3)	-0.004(3)	0.008(3)

Dihedral angles:
between planes 2 and 3: 16.4(2)
between planes 3 and 4: 3.5(2)
between planes 1 and 5: 83.2(1)
between planes 1 and 6: 27.4(1)

Table 34. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of DPEMA-1,2.
(The planes are defined in terms of Cartesian coordinates[Å] by AX+BY+CZ=D, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c*)

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.1758, 0.1355, 0.9751, and 7.5628

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.032(5)	0.025(5)	0.009(12)	0.002(10)	0.095(14)	-0.058(10)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = -0.1898, -0.0765, -0.9788, and -7.9960

C(1)	C(2)	C(3)	C(4)
-0.004(4)	0.011(10)	-0.010(9)	-0.005(5)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = 0.1664, 0.1596, 0.9731, and 7.2775

O(1)	O(2)	C(1)	C(2)
-0.001(3)	-0.002(3)	0.008(11)	-0.002(3)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = -0.2293, -0.2205, -0.9481, and -9.1629

Plane 5: C(7), C(8), C(9), C(10), C(11), and C(12)
A, B, C, D[Å] = 0.1838, -0.4373, 0.8803, and 5.7070

C(7)	C(8)	C(9)	C(10)	C(11)	C(12)
-0.003(9)	-0.005(9)	0.015(11)	-0.014(10)	0.005(10)	0.003(10)

Plane 6: C(13), C(14), C(15), C(16), C(17), and C(18)
A, B, C, D[Å] = -0.8806, 0.4161, -0.2268, and -25.1637

C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
-0.005(9)	0.015(9)	-0.016(10)	0.008(11)	0.006(11)	-0.004(9)

Dihedral angles:
between planes 2 and 3: 5.0(7)
between planes 3 and 4: 5.2(10)
between planes 1 and 5: 33.8(5)
between planes 1 and 6: 71.4(4)

Table 35. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of t-BBMA.
(The planes are defined in terms of Cartesian coordinates[Å] by $AX+BY+CZ=D$, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

a) MOLECULE 1

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.2327, -0.8739, 0.4269, and -9.1660

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.020(2)	0.020(2)	0.003(6)	-0.001(5)	0.067(6)	-0.052(5)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.1879, -0.8885, 0.4187, and -9.2575

C(1)	C(2)	C(3)	C(4)
0.002(2)	-0.006(5)	0.004(4)	0.003(3)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = -0.2495, 0.8680, -0.4293, and 9.1268

O(1)	O(2)	C(1)	C(2)
0.000(1)	0.000(2)	-0.001(5)	0.001(2)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = -0.3145, 0.8801, -0.3558, and 9.4912

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = 0.4549, 0.6947, 0.5572, and 9.7654

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
0.011(4)	-0.002(5)	-0.012(6)	0.016(6)	0.002(6)	-0.013(5)

Dihedral angles:
between planes 2 and 3: 3.8(3)
between planes 3 and 4: 5.7(5)
between planes 1 and 5: 74.7(3)

Table 35. (continued)

b) MOLECULE 2

Plane 1': O(1'), O(2'), C(1'), C(2'), C(3'), and C(4')
A, B, C, D[Å] = 0.3330, 0.8727, 0.3571, and 4.7533

O(1')	O(2')	C(1')	C(2')	C(3')	C(4')
-0.011(2)	0.018(4)	0.016(6)	0.001(6)	-0.035(5)	0.032(6)

Plane 2': C(1'), C(2'), C(3'), and C(4')
A, B, C, D[Å] = 0.3124, 0.8726, 0.3756, and 4.8205

C(1')	C(2')	C(3')	C(4')
0.000(2)	-0.002(6)	0.001(3)	0.001(3)

Plane 3': O(1'), O(2'),C(1'), and C(2')
A, B, C, D[Å] = -0.3462, -0.8698, -0.3517, and 4.7511

O(1')	O(2')	C(1')	C(2')
0.001(1)	0.004(3)	-0.010(6)	0.003(2)

Plane 4': C(1'), O(1'), and C(5')
A, B, C, D[Å] = -0.4063, -0.8256, -0.3916, and -4.9612

Plane 5': C(6'), C(7'), C(8'), C(9'), C(10'), and C(11')
A, B, C, D[Å] = -0.4321, 0.1026, 0.8960, and 1.7976

C(6')	C(7')	C(8')	C(9')	C(10')	C(11')
-0.002(4)	0.005(5)	-0.005(5)	0.001(7)	0.003(6)	-0.000(5)

Dihedral angles:
between planes 2' and 3': 2.4(3)
between planes 3' and 4': 4.9(5)
between planes 1' and 5': 74.6(2)

Table 36. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of TrBzMA (The planes are defined in terms of Cartesian coordinates[Å] by AX+BY+CZ=D, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

a) MOLECULE 1

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.2058, 0.6653, -0.7176 and 8.7612

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.006(1)	0.007(2)	0.002(3)	0.007(3)	-0.023(3)	0.021(4)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = -0.2013, -0.6787, 0.7063, and -8.9560

C(1)	C(2)	C(3)	C(4)
0.001(1)	-0.005(3)	0.002(2)	0.004(2)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = -0.2047, -0.6607, 0.7222, and -8.6821

O(1)	O(2)	C(1)	C(2)
-0.000(1)	-0.000(1)	0.001(3)	-0.000(1)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = -0.1491, -0.6715, 0.7259, and -8.5408

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = -0.1185, -0.5819, -0.8046, and -8.5719

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
-0.002(2)	-0.003(3)	0.008(3)	-0.003(3)	-0.004(3)	0.005(3)

Plane 6: C(13), C(14), C(15), C(16), C(17), and C(18)
A, B, C, D[Å] = -0.3280, -0.6240, 0.7092, and -9.4863

C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
0.022(2)	-0.017(3)	-0.006(3)	0.020(3)	-0.008(3)	-0.017(3)

Plane 7: C(19), C(20), C(21), C(22), C(23), and C(24)
A, B, C, D[Å] = -0.8624, 0.1761, -0.4746, and -0.8409

C(19)	C(20)	C(21)	C(22)	C(23)	C(24)
-0.010(2)	0.011(3)	-0.001(3)	-0.010(3)	0.010(3)	0.004(3)

Plane 8: C(25), C(26), C(27), C(28), C(29), and C(30)
A, B, C, D[Å] = 0.0430, 0.0372, 0.9984, and -0.0854

C(25)	C(26)	C(27)	C(28)	C(29)	C(30)
-0.014(2)	0.013(3)	0.003(3)	-0.017(3)	0.007(3)	0.009(3)

Dihedral angles:
between planes 2 and 3: 1.4(2)
between planes 3 and 4: 3.3(2)
between planes 1 and 5: 80.5(2)
between planes 1 and 6: 7.4(1)
between planes 1 and 7: 73.7(1)
between planes 1 and 8: 46.9(1)
between planes 6 and 7: 80.6(2)
between planes 6 and 8: 47.9(2)
between planes 7 and 8: 59.7(2)

Table 36. (continued)

b) MOLECULE 2

Plane 1': O(1'), O(2'), C(1'), C(2'), C(3'), and C(4')
A, B, C, D[Å] = 0.5167, -0.6768, -0.5244, and -2.1313

O(1')	O(2')	C(1')	C(2')	C(3')	C(4')
-0.015(1)	0.017(2)	0.002(3)	0.011(3)	-0.061(3)	-0.050(3)

Plane 2': C(1'), C(2'), C(3'), and C(4')
A, B, C, D[Å] = -0.4974, 0.7091, 0.4998, and 2.1928

C(1')	C(2')	C(3')	C(4')
0.003(1)	-0.010(3)	0.005(2)	0.005(2)

Plane 3': O(1'), O(2'),C(1'), and C(2')
A, B, C, D[Å] = -0.5246, 0.6659, 0.5364, and 2.0856

O(1')	O(2')	C(1')	C(2')
-0.000(1)	-0.001(1)	0.002(3)	-0.001(1)

Plane 4': C(1'), O(1'), and C(5')
A, B, C, D[Å] = 0.5393, -0.6720, -0.5076, and -1.9103

Plane 5': C(6'), C(7'), C(8'), C(9'), C(10'), and C(11')
A, B, C, D[Å] = -0.8104, -0.5034, 0.2990, and -6.2071

C(6')	C(7')	C(8')	C(9')	C(10')	C(11')
-0.002(2)	0.002(3)	0.001(1)	-0.003(4)	0.001(4)	0.002(3)

Plane 6': C(13'), C(14'), C(15'), C(16'), C(17'), and C(18')
A, B, C, D[Å] = 0.4044, -0.7080, -0.5790, and -2.6126

C(13')	C(14')	C(15')	C(16')	C(17')	C(18')
-0.022(2)	0.018(3)	0.008(3)	-0.023(3)	0.006(3)	0.018(3)

Plane 7': C(19'), C(20'), C(21'), C(22'), C(23'), and C(24')
A, B, C, D[Å] = -0.8856, 0.1216, -0.4482, and -0.0888

C(19')	C(20')	C(21')	C(22')	C(23')	C(24')
0.010(2)	-0.013(3)	0.002(3)	0.010(3)	-0.009(3)	-0.005(3)

Plane 8': C(25'), C(26'), C(27'), C(28'), C(29'), and C(30')
A, B, C, D[Å] = -0.8105, -0.0304, -0.5849, and -4.2908

C(25')	C(26')	C(27')	C(28')	C(29')	C(30')
-0.002(2)	0.005(3)	-0.003(3)	-0.007(3)	0.009(3)	-0.004(3)

Dihedral angles:
between planes 2' and 3': 3.4(2)
between planes 3' and 4': 1.6(3)
between planes 1' and 5': 76.4(2)
between planes 1' and 6': 7.4(1)
between planes 1' and 7': 72.3(1)
between planes 1' and 8': 45.2(2)
between planes 6' and 7': 79.4(2)
between planes 6' and 8': 49.8(2)
between planes 7' and 8': 63.1(2)

Table 36. (continued)

c) Benzene molecule

Plane A: C(31), C(32), C(33), C(31'), C(32'), and C(33')
A, B, C, D[Å] = -0.1236, -0.8780, 0.4624, and -0.5728

C(31)	C(32)	C(33)	C(31')	C(32')	C(33')
-0.001(5)	0.001(4)	-0.001(4)	0.001(5)	-0.001(4)	0.001(4)

Plane B: C(34), C(35), C(36), C(34'), C(35'), and C(36')
A, B, C, D[Å] = -0.2910, 0.8982, 0.3296, and 15.0765

C(34)	C(35)	C(36)	C(34')	C(35')	C(36')
-0.003(4)	0.004(4)	-0.003(3)	0.003(3)	-0.004(4)	0.003(4)

Table 37. Least-squares planes, deviations of atoms from the planes[Å] and dihedral angles between the planes[°] of ChMA.
(The planes are defined in terms of Cartesian coordinates[Å] by $AX+BY+CZ=D$, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis is parallel to c^*)

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = -0.4032, -0.4187, -0.8137, and -7.3820

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
-0.025(2)	0.034(2)	-0.002(4)	-0.013(5)	0.191(8)	-0.144(6)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, D[Å] = 0.3069, 0.3536, 0.8836, and 7.2628

C(1)	C(2)	C(3)	C(4)
-0.001(1)	0.004(5)	-0.003(4)	-0.002(3)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, D[Å] = -0.4178, -0.4330, -0.7987, and -7.3866

O(1)	O(2)	C(1)	C(2)
0.001(1)	0.003(2)	-0.009(4)	0.004(2)

Plane 4: C(1), O(1), and C(5)
A, B, C, D[Å] = 0.3707, 0.4536, 0.8104, and 7.4186

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, D[Å] = -0.5192, -0.7807, 0.3478, and -0.7302

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
-0.001(3)	-0.003(4)	0.004(4)	-0.003(4)	-0.001(5)	0.003(4)

Plane 6: C(13), C(14), C(15), C(16), C(17), and C(18)
A, B, C, D[Å] = -0.9922, -0.0427, -0.1171, and -5.2647

C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
0.009(3)	-0.008(4)	-0.003(4)	0.015(5)	-0.010(5)	-0.004(4)

Dihedral angles:

between planes 2 and 3:	9.2(2)
between planes 3 and 4:	3.0(4)
between planes 1 and 5:	75.3(2)
between planes 1 and 6:	59.1(2)

C(2)-C(4)[1.416(10) Å] are equal within the range of error. Two molecules of TrBzMA with more bulky ester substituents have the *sp-sp* structure but the molecule of ChMA with rather bulky ester substituents has the *ap-sp* structure. Generally the conformation about the C(1)-O(1) bond is *sp* but there is no rule to define the conformation about the C(1)-C(2) bond. Bulky ester substituents have much influence on the former conformation by steric repulsion between the methacryl group and the substituents while probably they are not effective for the control of the latter conformation. The results of electron diffraction studies[21-23)] and the molecular polarizability measurement[24)] of methyl methacrylate suggested the *ap-sp* structure but NMR studies[25,26)] of molecular complexes between methyl methacrylate and Lewis acids supported the *sp-sp* structure. The conformational analysis by lanthanide induced shifts of methacrylates[27,28)] led to a conclusion that both *ap-sp* and *sp-sp* structures probably exist in solution.

The molecules of present study have the planar methacryl residues. The methacryl residues(plane 1 or 1'), have comparatively poor planarity(especially in TrMA), can be divided into two highly planar portions, planes 2(or 2') and 3(or 3').

The structural parameters of these methacrylate molecules are summarized in Table 31.

The C-C and C-O bond lengths of the corresponding bonds have similar values and the corresponding bond angles have also similar values except for the disordered molecule of *t*-BBMA. The C-C, C-O, and C-H bond lengths not listed in Table 31 are respectively equal to the sums of the covalent radii within the expeimental errors. The dihedral angles between

Table 31.

Structure of methacryl moieties of various methacrylates

Compound	DPMMA	DPEMA-1,1	TrMA	DPEMA-1,2	*t*-BBMA		TrBzMA		ChMA
					Mol. 1	Mol. 2	Mol. 1	Mol. 2	
Bond lengths[Å]									
C(1)-C(2)	1.492(5)	1.58(4)	1.500(4)	1.49(2)	1.481(8)	1.469(9)	1.484(5)	1.480(5)	1.503(7)
C(2)=C(3)	1.332(5)	1.38(5)	1.351(5)	1.33(3)	1.359(10)	1.431(10)	1.368(5)	1.382(5)	1.387(7)
C(2)-C(4)	1.466(5)	1.43(4)	1.450(5)	1.46(2)	1.475(10)	1.416(10)	1.427(6)	1.440(5)	1.417(9)
C(1)-O(1)	1.340(4)	1.35(3)	1.353(4)	1.33(2)	1.342(7)	1.318(7)	1.354(4)	1.354(5)	1.345(5)
C(1)=O(2)	1.194(4)	1.16(3)	1.198(4)	1.19(2)	1.193(7)	1.205(9)	1.205(4)	1.201(4)	1.202(6)
O(1)-C(5)	1.456(5)	1.52(3)	1.464(3)	1.48(2)	1.451(7)	1.449(7)	1.456(4)	1.453(4)	1.466(5)
Bond angles[°]									
C(1)-C(2)-C(3)	121.0(3)	113(3)	116.5(3)	120.3(13)	120.4(6)	116.6(6)	117.4(3)	117.7(3)	119.9(6)
C(1)-C(2)-C(4)	115.4(3)	120(3)	119.2(3)	116.2(10)	117.3(6)	119.1(6)	119.2(3)	119.2(3)	116.5(5)
C(3)-C(2)-C(4)	123.6(4)	127(3)	124.3(3)	123.4(13)	122.3(6)	124.3(7)	123.4(4)	123.1(4)	123.5(6)
C(2)-C(1)-O(1)	112.3(3)	107(2)	110.3(3)	111.7(11)	113.0(5)	114.1(5)	111.8(3)	112.0(3)	110.7(4)
C(2)-C(1)-O(2)	124.6(3)	125(3)	125.0(3)	124.6(12)	123.8(6)	123.8(6)	125.0(3)	125.3(3)	123.9(4)
O(1)-C(1)-O(2)	123.1(3)	128(3)	124.8(3)	123.6(12)	123.2(6)	122.1(6)	123.1(3)	122.7(3)	125.4(4)
C(1)-O(1)-C(5)	117.3(3)	116(2)	120.7(2)	116.7(10)	116.9(5)	119.3(5)	116.9(3)	117.5(3)	120.8(4)
Dihedral angles[°] between planes a)									
II and III	8.3(2)	5(2)	16.4(2)	5.0(7)	3.8(3)	2.4(3)	1.4(2)	3.4(2)	9.2(3)
III and IV	6.1(3)	2(2)	3.5(2)	6.0(10)	5.7(5)	4.8(5)	3.3(2)	1.6(2)	3.0(4)
I and V	74.6(2)	87.1(7)	83.2(1)	71.4(4)	74.7(3)	74.6(2)	80.5(2)	76.4(2)	75.3(2)
Conformation	*ap-sp*	*sp-sp*	*sp-sp*	*ap-sp*	*ap-sp*	*ap-sp* b)	*sp-sp*	*sp-sp*	*ap-sp*

a) Plane I: O(2), O(1), C(1), C(2), C(3) and C(4); Plane II: C(1), C(2), C(3) and C(4); Plane III: O(1), O(2), C(1) and C(2); Plane IV: O(1), C(1) and C(5); Plane V: Planes of the phenyl groups on the C(5) atoms which have the smallest torsion angle referred to the C(1) atom about the O(1)-C(5) bond(As for mol. 2 of *t*-BBMA and TrBzMA the atom numbering scheme O(1'), O(2'), C(1'), C(2'), C(3'),..... is used instead).

b) There is the possibility of the disorder about the conformation of two double bonds.

the methacryl planes and the planes of benzene rings nearest to them have similar values.

The Molecular Conformation about the O(1)-C(5) Bond

As mentioned above, the methacryl group has the planar structure. The possible conformations of a methacrylate molecule, therefore, are four types as illustrated in Figure 33, considering rotation around the O(1)-C(5) bond. This figure shows the molecular model viewed from the C(5) (or C(5')) atom down to the O(1) (or O(1')), where the most bulky substituents is R_1, the second R_2, and the smallest R_3. Among these conformations the most probable one was considered to be (a) according to the Prelog rule$^{29)}$.

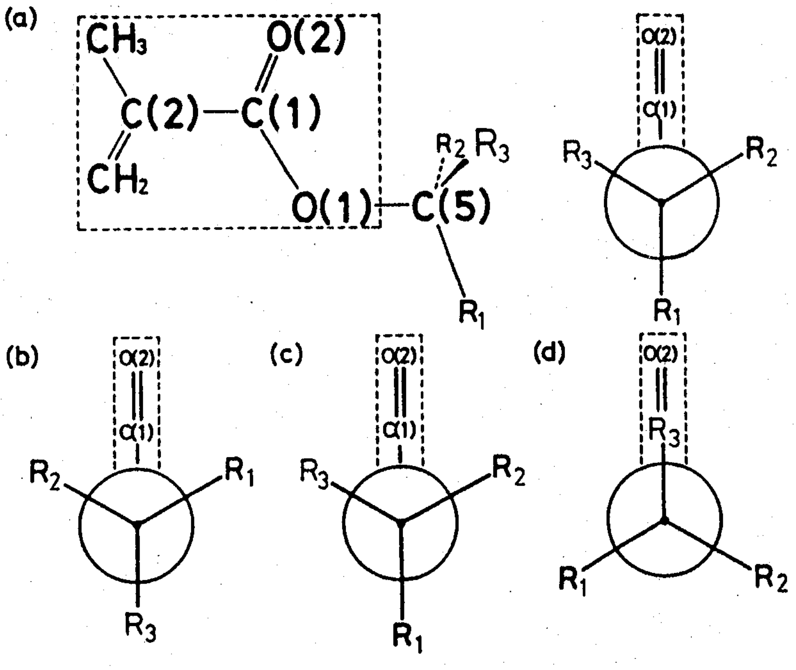


Figure 33. The possible conformations of the methacrylate molecules

Figures 34 and 35 show the actual molecule viewed from the C(5) (or C(5')) atom down to the O(1) (or O(1')) with torsion angles of ester substituents about the O(1)-C(5) bond referred to the O(1)-C(1) bond. The molecules depicted in Figure 34

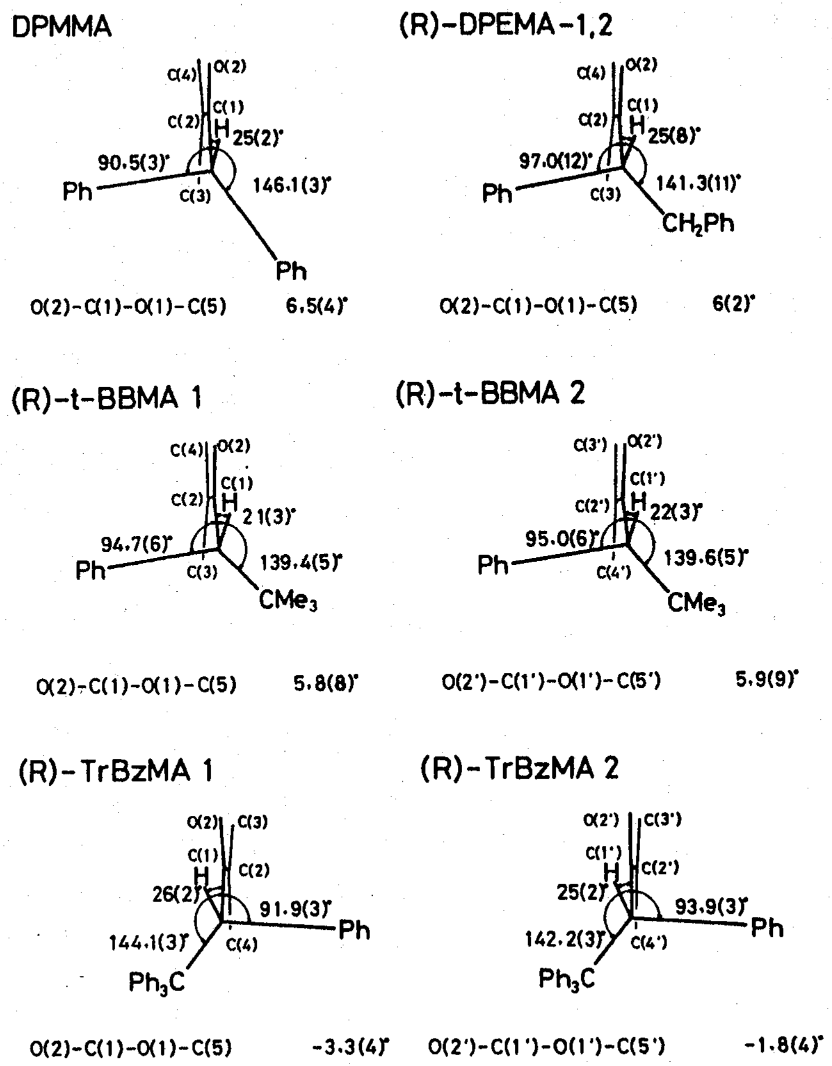


Figure 34. The actual conformation of methacrylate molecules about the O(1)-C(5) bond which have the hydrogen atom on the C(5) atom

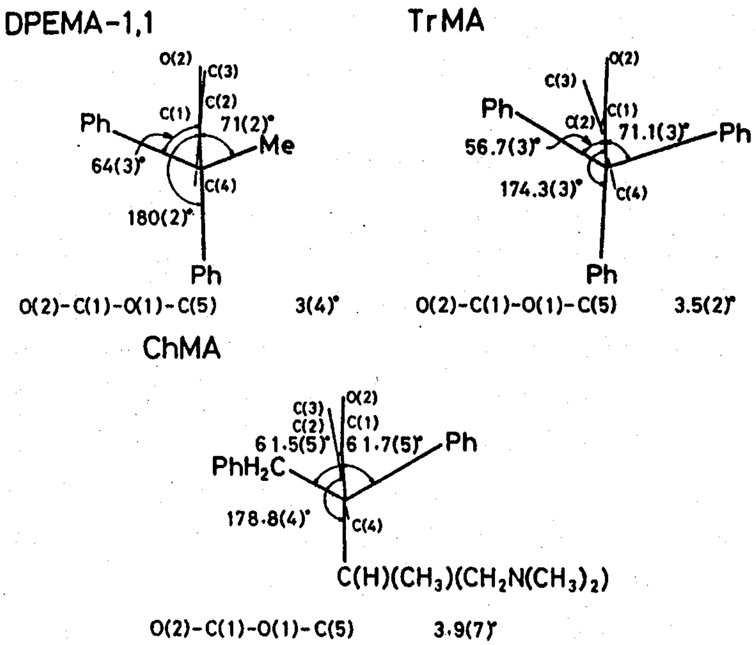


Figure 35. The actual conformation of methacrylate molecules about the O(1)-C(5) bond which have no hydrogen atom on the C(5) atom

which have the hydrogen atom on the C(5) atom, have conformations like (d). On the other hand the molecules drawn in Figure 35, which have no hydrogen on the C(5) atom, have conformations like (a). The lanthanide induced shift study of methacrylates with the hydrogen atom on the C(5) atom(see Figure 34)$^{28)}$ indicated that the conformation with the hydrogen atom closest to the carbonyl oxygen(O(2) or O(2')) is also the most probable one in solution(in toluene-d_8).

Crystal Packings

The packings of methacrylate molecules in crystal are shown in Figures 36, 37, 38, 39, 40, 41 and 42, respectively. In general, the packing of the molecules seems to be determined by van der Waals forces between the methacryl group and the vicinal one. The packing of the molecules of *t*-BBMA is fairly loose. It may cause the disorder discussed before. In the crystal of TrBzMA the benzene molecules, which lie on a symmetry center, work as the adhesion that combines layers of TrBzMA molecules.

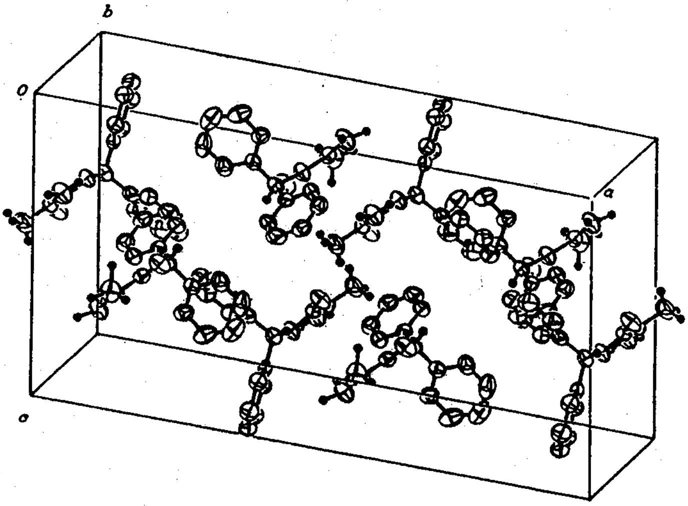


Figure 36. The crystal structure of DPMMA(*ORTEP* II)

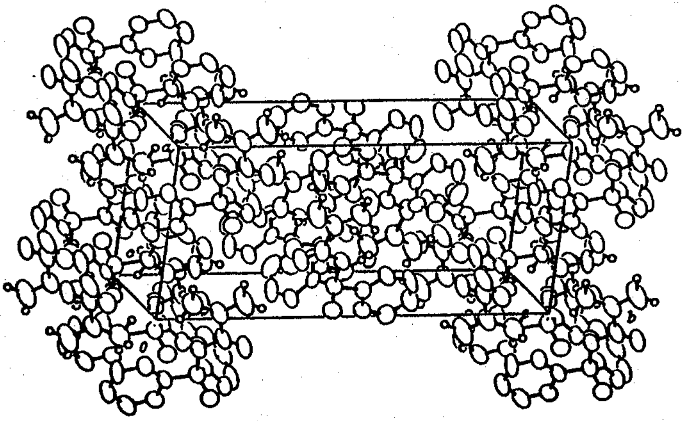


Figure 37. The crystal structure of DPEMA-1,1(*ORTEP* II)

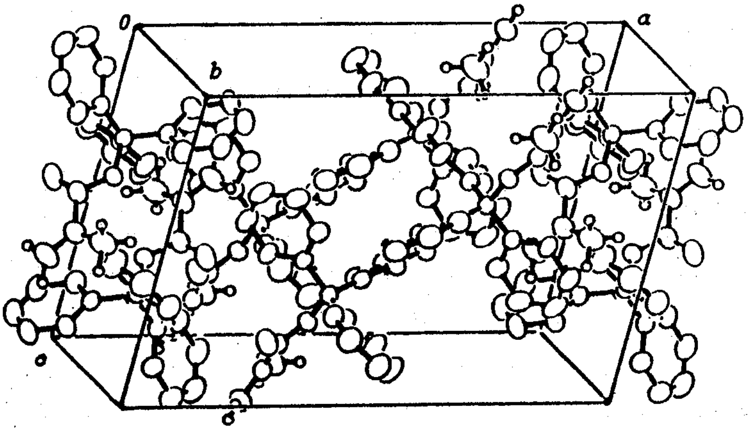


Figure 38. The crystal structure of TrMA(*ORTEP* II)

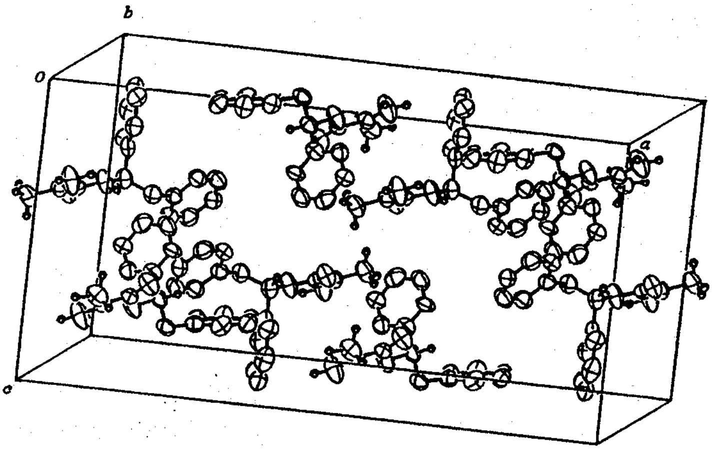


Figure 39. The crystal structure of DPEMA-1,2(*ORTEP* II)

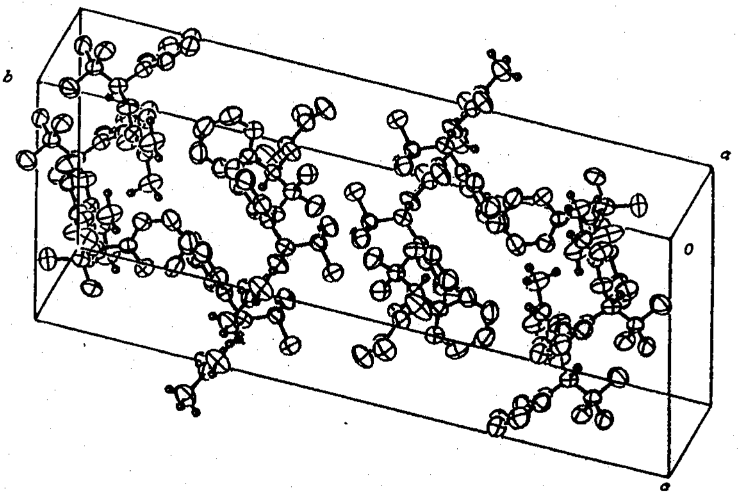


Figure 40. The crystal structure of *t*-BBMA(*ORTEP* II)

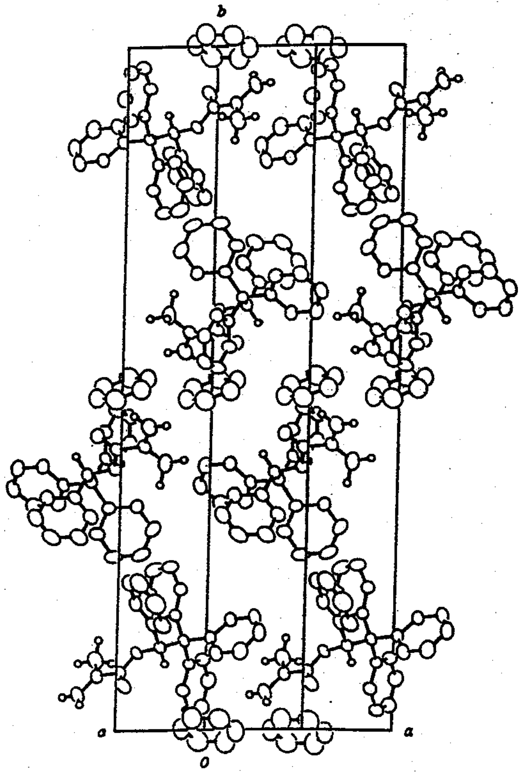


Figure 41.
The crystal structure of TrBzMA(*ORTEP* II)

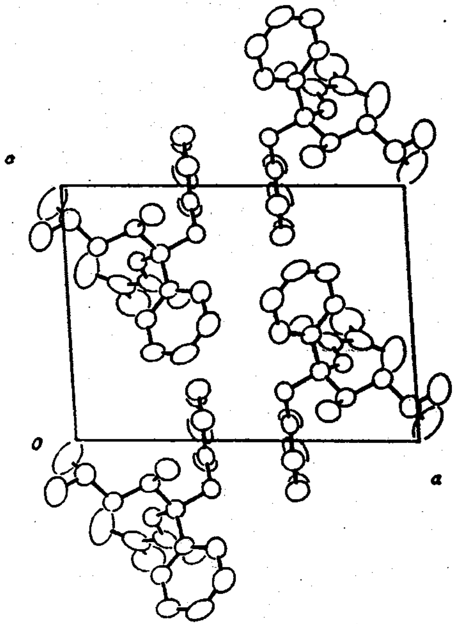
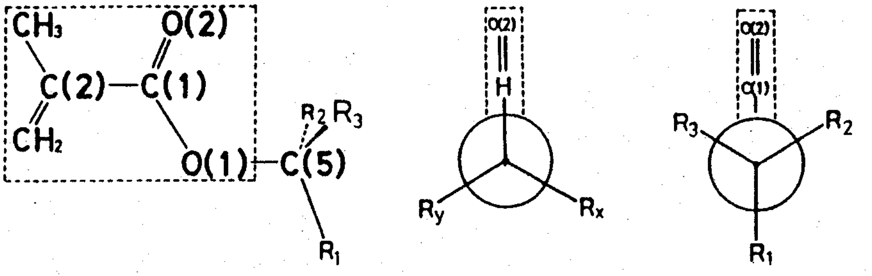


Figure 42.
The crystal structure of ChMA(*ORTEP* II)

Table 32.

Summary of the conformation of methacrylates



(d) (a)

Compound	C(1)-C(2)	C(1)-O(1)	O(1)-C(5)
DPMMA	*ap*	*sp*	(d)
DPEMA-1,1	*sp*	*sp*	(a)
TrMA	*sp*	*sp*	(a)
DPEMA-1,2	*ap*	*sp*	(d)
t-BBMA(1,2)	*ap*, *ap**	*sp*	(d)
TrBzMA(1,2)	*sp*, *sp*	*sp*	(d)
ChMA	*ap*	*sp*	(a)

2.3. Conclusion

The structural features of methacrylate molecules are summarized in Table 32.

The methacryl groups have a planar structure: some molecules have the *ap*-*sp* structure and others have the *sp*-*sp* structure. As to the conformation about the O(1)-C(5) bond the methacrylate molecules which bear no hydrogen atom on the C(5) atom have conformation like (a), while the methacrylates with one hydrogen atom on the C(5), which were used in the study of the asymmetric selective polymerization with Grignard reagent-(−)-sparteine complexes, have conformation like (d).

CHAPTER III

The Asymmetric Selective Polymerization of Racemic Methacrylates with Active Grignard Reagent-(–)-Sparteine Derivative Complexes.

Introduction

In this chapter the whole behavior about the asymmetric selective polymerization of racemic methacrylates with catalytically active Grignard reagent-(–)-sparteine derivative complexes, especially the enantiomer selection mechanism is discussed on the basis of the molecular structures of the initiators discussed in Chapter I and that of the monomers mentioned in Chapter II.

In Chapter I, the molecular structures of the initiators are described and discussed. In catalytically active EtMgBr-(–)-sparteine(4a), the Et group coordinates to the Mg atom at the spatially less opened side(C(7)-side) of the cavity of a sparteine skeleton, and this type of structure is classified as "type A". On the other hand, in less active EtMgBr-(+)-6-benzylsparteine(7), the Et group coordinates to the Mg atom at the spatially more opened side(C(9)-side) of the cavity of the sparteine skeleton, and this is named as "type B". This polymerization is considered to proceed in a coordination mechanism. In the initiation the Mg atom needs a sufficient room to accommodate the methacrylate monomer in its neighborhood in order to reveal the initiation activity. However, *t*-BuMgCl-(–)-sparteine(4g), with a bulky *t*-Bu group and EtMgBr-(−)-α-isosparteine(5) which has a ligand skeleton with less opened cavity than (−)-sparteine, do not have a sufficient space in neighborhood of the Mg atom. Actually they do not have initiation activity.

In Chapter II, the molecular structure of α-substituted benzyl methacrylates is described and discussed. The methacryl group in each monomer has planar structure. The conformation about the bond between this methacryl group and the α-carbon atom of the benzyl group(the O(1)-C(5) or O(1')-C(5') bond) is examined. The methacrylates with no hydrogen atom on the α-carbon(C(5) or C(5')) atom have conformations in which the largest substituents lies on the farthest position from a carbonyl oxygen(O(2) or O(2')) as expected by the Prelog rule, whereas the methacrylates with one hydrogen on the α-carbon atom have conformations in which the smallest substituents, the hydrogen atom lies closest to the carbonyl oxygen. For example, Figure 43 shows space-filling models(*PLUTO*) of such methacrylates(DPEMA-1,2 and *t*-BBMA), where two large substituents situate on either sides of the methacrylate plane apart from the carbonyl oxygen(O(2)).

3.1. The Mechanism of the Asymmetric Selective Polymerization

The Mechanism of the Asymmetric Selective Polymerization

As mentioned above, it is considered that the present asymmetric selective polymerization proceeds in a coordinated, anionic polymerization mechanism: the monomer always coordinates to an active center of the initiator before being attacked and incorporated into a polymer chain end since the

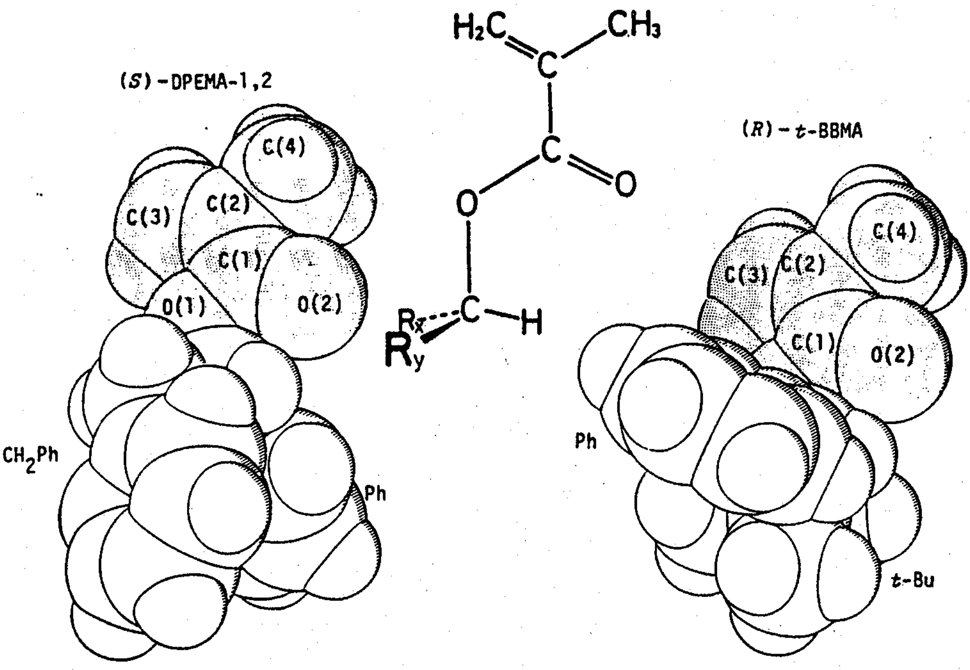
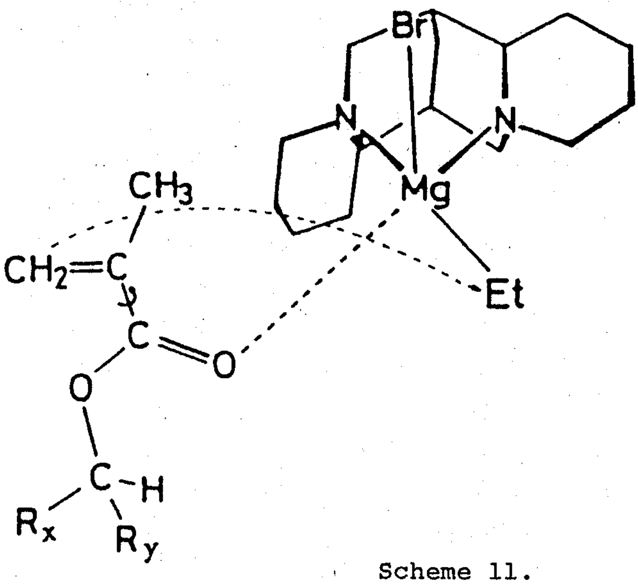


Figure 43. The space-filling models of DPEMA-1,2(left) and *t*-BBMA(right)(*PLUTO*)

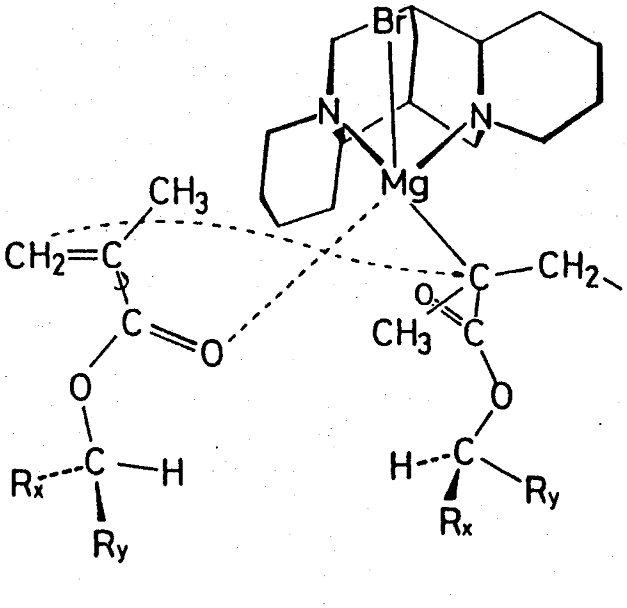


Scheme 11.

rate of the polymerization is independent of the monomer concentration(Scheme 11).

According to this mechanism, in the initial stage of the polymerization the monomer coordinates through its carbonyl oxygen to the Mg atom in the complexes, and then its C=C double bond is attacked by a carbanion of the complex. In this stage the most favorable direction of monomer access is the one as drawn in Scheme 11 for active complex 4a of type A, where the bulky alcohol part is placed at the remote position from the Br atom and the steric repulsion between the substituents of this part and sparteine skeleton seems to be minimized. On the other hand, for complex 7 of type B which has a reversed spatial arrangement between Grignard reagent and sparteine skeleton, the most favorable direction is the one from right-top to the central Mg atom in Scheme 11. However in this case the steric repulsion between the substituents and sparteine skeleton seems to be larger. As for the structure of monomer, the monomer can coordinate to the Mg atom easily because the smallest hydrogen atom of the substituents of α-carbon is situated at the closest position to the carbonyl oxygen. From the information obtained in Chapter II, α,α-dimethylbenzyl methacrylate has two methyl groups on both sides of the carbonyl oxygen. Actually this monomer showed no reactivity in the copolymerization with (*RS*)-MBMA by active Grignard reagent-(–)-sparteine. This means that the spatial room around the carbonyl oxygens of monomers have much influence on their reactivity.

In the second stage, the growing end is formed. The growing end has a tertiary carbon atom as *t*-BuMgCl-(–)-sparteine(4g). The complex 4g that has the four-coordinate Mg atom indicates no reactivity. The monomer, according to the mechanism mentioned above, always coordinates to the active center. Therefore, the active center has the Mg atom which is coordinated by at least five ligands(or six ligands): in five-coordinate structure, ligands are two N atoms of (–)-sparteine, halogen atom, the growing end, and the carbonyl oxygen of a monomer(in six-coordinate structure, the growing end works as bidentate where the carbonyl oxygen of the first monomer unit also coordinates to the Mg atom). The most probable five-coordinate structure is depicted in Scheme 12.



Scheme 12.

In the active center produced from the type A complex, the Br atom that coordinates at the more opened side of sparteine skeleton is probably able to shift in order to offer the growing end and the monomer a sufficient space to coordinate.

On the contrary, in the active center formed from the type B complex, it is diffcult for the Br atom at less opened side of sparteine skeleton to move, and thus the active center is forced to have a four-coordinate structure. This probably makes the type B complex poorly reactive.

Enantiomer Selection of Methacrylates

The models to explain the mechanism of (*S*)- and (*R*)-enantiomer selection postulated from the results described above are illustrated in Figures 44 and 45, respectively.

The first example is a (*S*)-selected monomer, DPEMA-1,2(Figure 44). This monomer has a hydrogen atom, a phenyl group and a benzyl group on a carbon of chiral center.

(1). The initiator molecule before reaction is drawn.

(2). The initiation of the polymerization is drawn. The monomer, which coordinates to the initiator, is then attacked by the anion to form an active center. In this case favorable direction of the monomer to be accessed, as drawn in the Figure is examined and postulated by using the space-filling models.

(3). The first propagation step of the polymerization is given. This space-filling model of the active center is built up on the basis of the information from the molecular structure determined; the structure of the monomer is assumed the same structure as determined by the X-ray analysis. In the growing end, the ester part is cut from the methacrylate and the sp^3 hybridization is postulated for the anionic carbon. All the ligands are drawn to be coordinated to the Mg atom in the manner to minimize the steric repulsion between the ligands.

The steric hindrance of the Br atom, the growing end, and

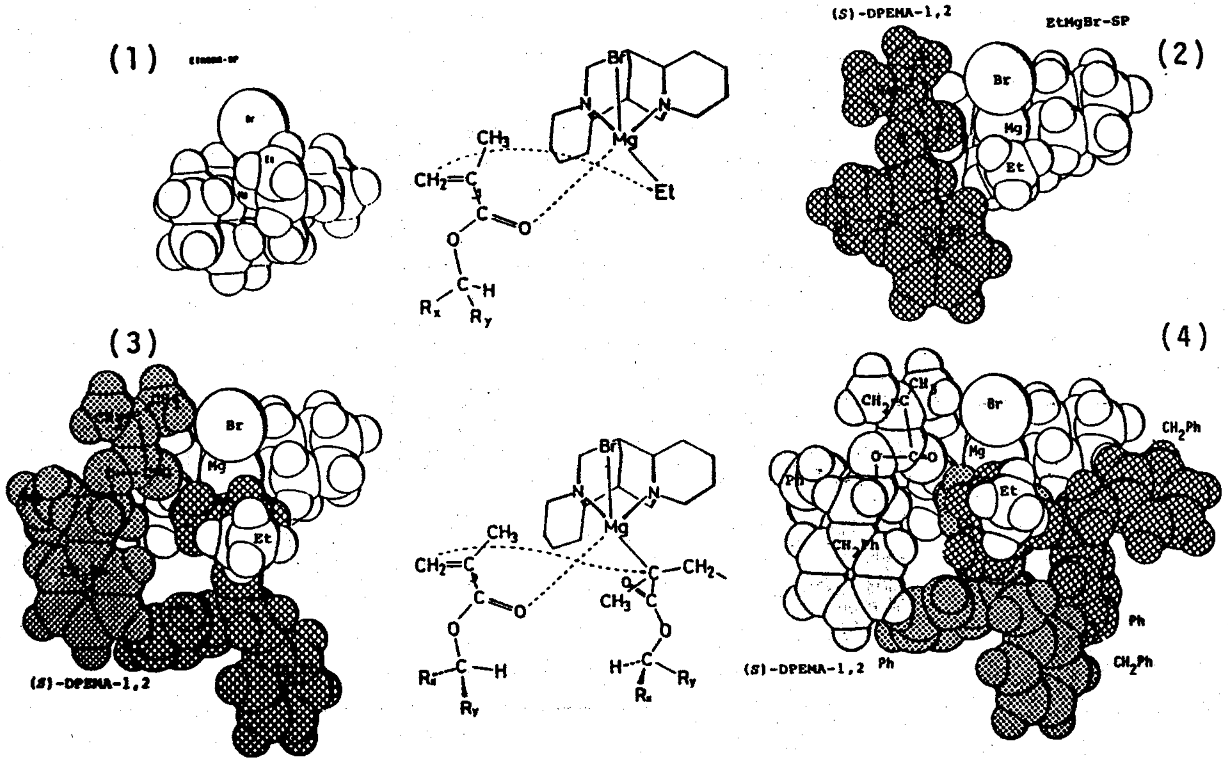


Figure 44. The postulated mechanism of enantiomer selection for DPEMA-1,2

the sparteine are avoided effectively when the monomer approaches to the active center in such direction as shown in the Figure. As for the monomer it is favorable to bear the substituents on the chiral carbon which are repulsed more weakly by the bulky growing end; thus (*S*)-monomer is more favorable to coordinate the active center in DPEMA-1,2.

(4). The second propagation step of the polymerization is showed. In this Figure, the first and the second monomers are incorporated into the polymer chain and the third monomer coordinates to the active center. The polymerization probably proceeds in the same manner at the beginning of the reaction. The elongating polymer chain needs a space to accommodate itself. The active center produced from the type A complex has a sufficient space to accommodate the polymer chain around the sparteine skeleton. This polymer chain serves as the block to limit the direction of the monomer to be accessed.

The second example is a (*R*)-selected monomer, *t*-BBMA(Figure 45). This monomer has a hydrogen atom, a phenyl group and a *t*-Bu group on the chiral carbon.

(1). The initiator before reaction.

(2). The initiation step of the polymerization.

(3). The first propagation step of the polymerization.

(4). The second propagation step of the polymerization.

In the steps (2), (3), and (4), the *t*-BBMA monomer is considered able to coordinate the active center favorably when the *t*-Bu group is placed at the most remote position from the growing end, because the steric repulsion between the reactive center and the *t*-Bu group is larger than that between the reactive center and the phenyl group. Therefore, in this catalyst system (*R*)-monomers of *t*-BBMA are polymerized

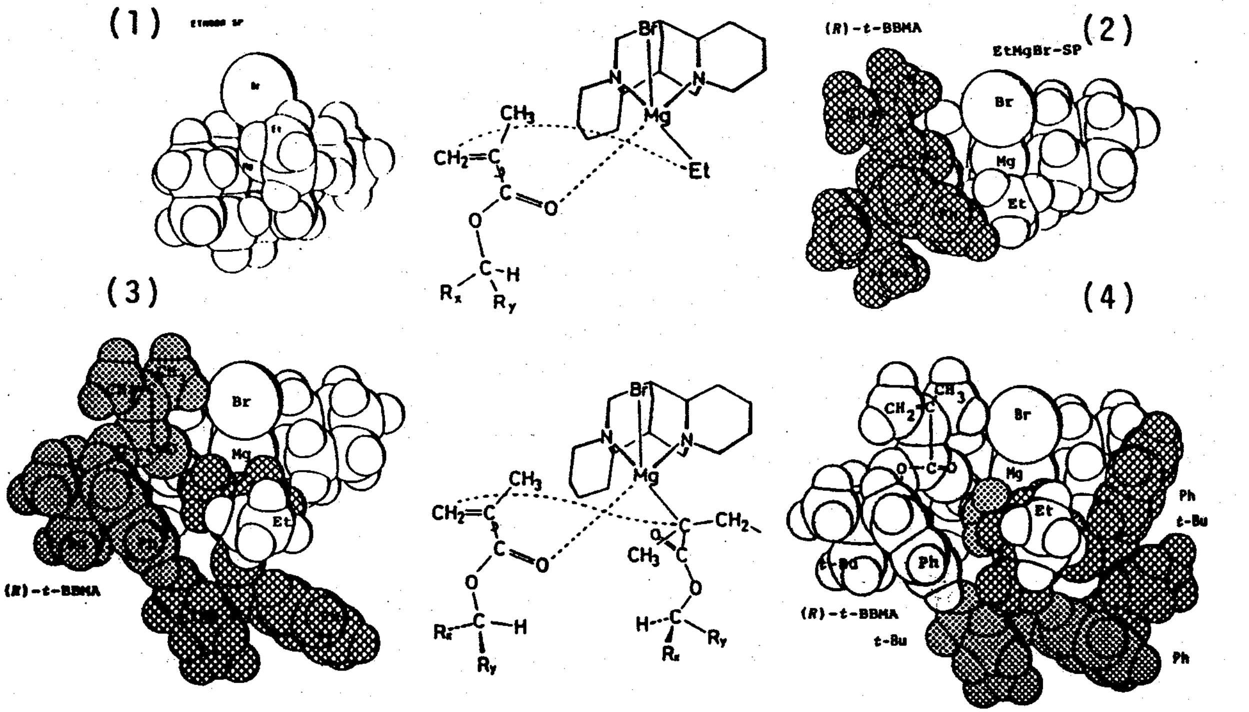


Figure 45. The postulated mechanism of enantiomer selection for *t*-BBMA

preferentially. Thus the direction of enantiomer selection of the methacrylates is considered to be judged from the difference of the bulkiness to the reaction center of two substituents which locate on either sides of the methacryl plane.

The third example is TrBzMA which has a hydrogen atom, a phenyl group and a triphenylmethyl group(Figure 46). Judging from the selection rule mentioned above (*S*)-enantiomers may be polymerized preferentially because in the (*S*)-monomer the bulky triphenylmethyl group can be placed at the remote position from the reactive center. Actually the (*S*)-enantiomers are polymerized preferentially over the (*R*)-antipodes.

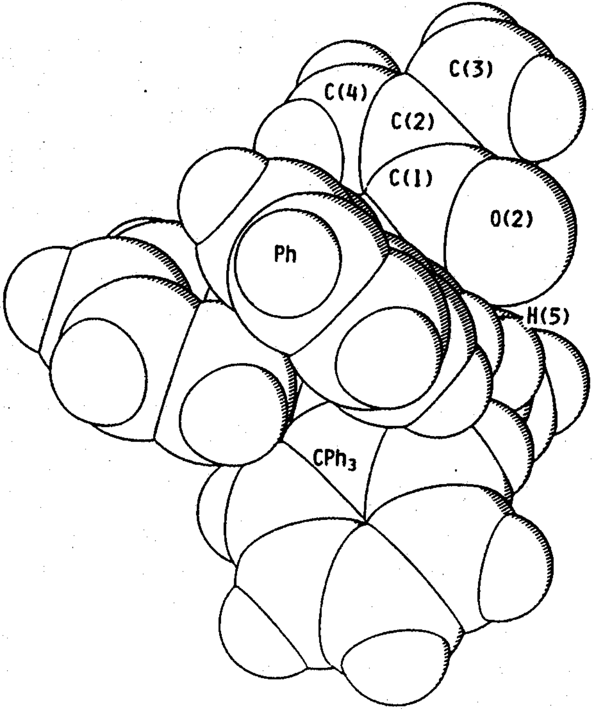


Figure 46. The space-filling model of (*S*)-TrBzMA(*PLUTO*)

3.2. Conclusion

From the kinetic studies on this asymmetric selective polymerization the coordinated anionic polymerization mechanism is adopted as the most probable one. According to this mechanism the polymerization reaction proceeds as follows:

1) The initiation. A methacrylate, that coordinates to the initiator, is then attacked by a carbon atom of the initiator to form the growing end.

2) The enantiomer selection in the propagation. In coordination of the monomer to the active center produced in 1), one enantiomer is selected by the difference in the steric repulsion between the monomer and the active center.

3) The propagation. The second monomer, that coordinated to active center in 2), is then attacked by the growing end. Immediately the third monomer coordinates to the active center and the structure of the active center is always maintained in the same manner in subsequent propagation steps.

The active center derived from the complex of type A is considered able to have a five-coordinate Mg atom, while the active center from the complex of type B has probably four-coordinate structure. This may cause large difference in catalytic activity between two type complexes.

The molecular structure of α-monosubstituted benzyl methacrylate is considered to be favorable to coordinate to the Mg atom in the initiator or the active center because the smallest hydrogen atom is placed at the closest position to a carbonyl oxygen. The enantiomer selected is considered to be the one of which the largest ester substituent is placed at the most remote position from the growing end.

This successful design of reaction system is attained by the modification of Grignard reagent environment with (−)-sparteine ligand which effectively controls the direction of the substrate access. It is also one of the important factors of this success to select α-monosubstituted benzyl methacrylate as the monomer.

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(2) The Molecular Structure of
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