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First X-Ray Structure Determination of a Bismuthio Ylide: 4,4-Dimethyl-2,6-dioxo-1-triphenylbismuthiocyclohexanide

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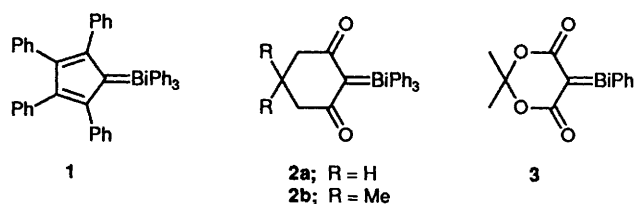
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The first X-ray structure analysis of a bismuthio ylide has been made for 4,4-dimethyl-2,6-dioxo-1-triphenylbismuthiocyclohexanide. The Bi-C_{ylide} bond is 2.16 Å, only 0.05–0.06 Å shorter than the Bi-C_{ph} single bond, revealing that the Bi-C_{ylide} bond is polarized as C[−]-Bi⁺ or O[−]-C=Bi⁺ with little double bond character between the Bi and the ylidic carbon.

Bismuthio ylides are the heaviest and least understood of all the carbon-hetero atom ylides. Although several papers^{1–6} have appeared on them since 1967 when the first was reported,⁷ no definite structural proofs for their identity has hitherto been described. Bismuthio ylides react with numerous compounds in a variety of different ways depending on the substrates involved and the reaction conditions employed.^{8–10} This behaviour stands in marked contrast to that of the ylides derived from lighter elements (P, As, and Sb) of the same group.

The bismuthio ylide **1** described by Lloyd⁷ was a deep blue, high-melting solid (m.p. 195 °C; decomp.) which readily decomposed in solution, while the ylide **2b** obtained by Barton² was a gummy substance. Recently, the ylides **2b** and **3** were obtained pure as pale yellow crystals,⁶ the former crystallizing from benzene-hexane as single crystals suitable for X-ray structural elucidation.

As shown in Fig. 1,¹¹ three phenyl groups of the bismuthio ylide have regular bond angles and distances. The dioxo-cyclohexane ring, which has pseudo mirror symmetry and lies through two methine groups, C(19) and C(22), is almost planar (root-mean-square deviation of 0.021 Å), except for the two methyl groups on C(22). The bismuth atom lies on this plane with a deviation of 0.036 Å. The most interesting features of

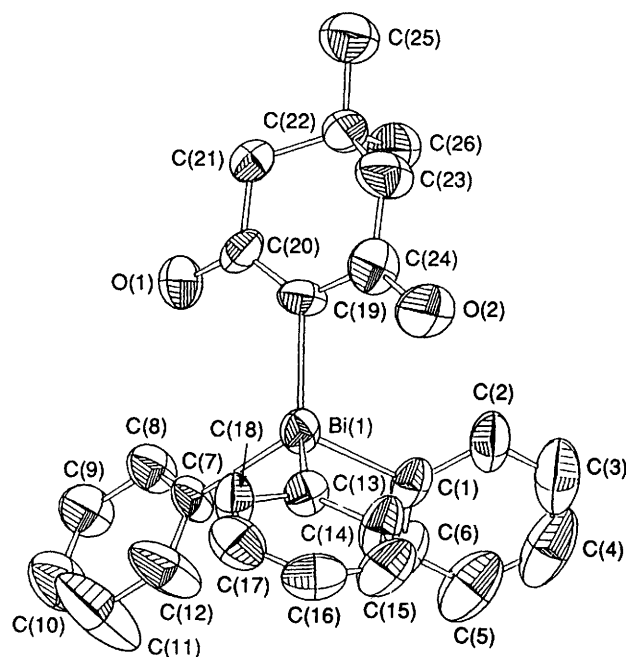


this compound are the carbon-bismuth bonds. The bismuth atom has a distorted tetragonal configuration with bond angles C_{ph}-Bi-C_{ph} = 101.6(4)–103.1(4)° and C(19)-Bi-C_{ph} = 111.8(4)–119.6(4)°. The bond length of Bi-C(19), 2.16 Å, is slightly shorter than the single bond length of Bi-C_{ph}, 2.21(1)–2.22(1) Å. The lengths of the Bi-C_{ph} bond obtained here are comparable with those of triphenylbismuth, 2.21–2.25 Å.¹² These facts suggest that the ylide bond has a large degree of ionic character as Bi⁺-C[−] or Bi⁺-C=C-O[−], in accordance with expectation that the vacant 6d orbitals of bismuth would not effectively overlap the 2p-orbitals of the carbanionic moiety.

An important proposal made by Lloyd in 1988 concerning the structure and reactivity of carbonyl or sulphonyl substituted arsonium and stibonium ylides,⁴ was that interaction between

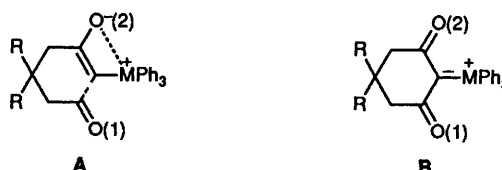
Table 1. Selected bond lengths and atomic distances of the bismuthio ylide

| | Length (Å) |
|--------------------|------------|
| Bi—C ⁻ | 2.156(11) |
| Bi—C ^{Ph} | 2.210 |
| Bi...O(1) | 3.352(2) |
| Bi...O(2) | 3.019(4) |
| C—C[=O(1)] | 1.412(16) |
| C—C[=O(2)] | 1.401(18) |
| C=O(1) | 1.261(15) |
| C=O(2) | 1.236(19) |

**Fig. 1.** An ORTEP¹¹ drawing of **2b** with atomic numbering. Non-hydrogen atoms are depicted as 50% probability ellipsoids.

the heteroatom and substituent oxygen atoms would favour the canonical form **A** with a non-symmetrical crystallographic structure; such compounds would be characterized by low reactivity. Such a non-symmetrical structure was found for the bismuthio ylide described here; thus one Bi—O distance is significantly less than the other (Table 1). Although the observed lowfield ¹³C NMR signal of the ylidic carbon (δ 113) is consistent with the canonical form **A**, some doubt remains about its contribution to the structure of the bismuthio ylide; if the canonical form **A** is substantial, the length of C=O(1) bond, being more remote from the metallic atom, should be shorter than that of another C=O(2) group. This applies well to the arsonium and stibonium ylides, but the opposite result was observed for the bismuthio ylide; the C=O(1) bond is longer than the C=O(2). Probably, the non-symmetrical structures of these ylides are the consequence of both electrostatic and steric factors, and do not always reflect the electron density distributions directly.¹³

Lloyd and his co-workers reported the isolation of 1-triphenylbismuthio-2,6-dioxocyclohexanide (**2a**) from the copper-catalysed reaction of a diazo compound with triphenyl-



bismuthine.⁴ It was claimed to be insoluble in common solvents and to lack reactivity toward 2,4-dinitrobenzaldehyde even under prolonged heating in benzene. However, in our hands, both bismuthio ylides **2a**¹⁰ and **2b**, the identity of the latter now being confirmed unambiguously by X-ray analysis, are quite soluble in most organic solvents and react smoothly with a variety of compounds including the less reactive 4-methoxybenzaldehyde.⁸⁻¹⁰ Thus, the khaki product described by Lloyd as the ylide **2a** is highly likely to be some polymeric substances derived from decomposition of the initially formed ylide.

References

- 1 B. H. Freeman, D. Lloyd and M. I. C. Singer, *Tetrahedron*, 1972, **28**, 343.
- 2 D. H. R. Barton, J. Blazejewski, B. Charpiot, J. Finet, W. B. Motherwell, M. T. B. Papoula and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2667.
- 3 D. Lloyd, I. Gosney and R. A. Ormiston, *Chem. Soc. Rev.*, 1987, **16**, 45.
- 4 G. Ferguson, C. Glidewell, I. Gosney, D. Lloyd, S. Metcalfe and H. Lumbroso, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1829.
- 5 C. Glidewell, D. Lloyd and S. Metcalfe, *Synthesis*, 1988, 319.
- 6 H. Suzuki, T. Murafuji and T. Ogawa, *Chem. Lett.*, 1988, 847.
- 7 D. Lloyd and M. I. Singer, *J. Chem. Soc., Chem. Commun.*, 1967, 1042.
- 8 T. Ogawa, T. Murafuji and Suzuki, *Chem. Lett.*, 1988, 849.
- 9 T. Ogawa, T. Murafuji, K. Iwata and H. Suzuki, *Chem. Lett.*, 1989, 325.
- 10 T. Ogawa, T. Murafuji and H. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1989, 1749.
- 11 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976). Crystal structure data of **2b**: monoclinic, space group $P2_1/n$, $a = 15.564(2)$, $b = 14.520(2)$, $c = 10.160(1)$ Å, $\beta = 90.16(2)^\circ$, $V = 2296.0(5)$ Å³, $T = 297$ K, $Z = 4$, $D_x = 1.674$ Mg m⁻³, $D_m = 1.67$ Mg m⁻³ (floatation), $\mu(\text{Mo-K}\alpha) = 0.710$ 69 Å⁻¹, $F(000) = 1120$. Intensity data were collected on a Rigaku AFC4 four-circle diffractometer in the range $2 < 2\theta < 55^\circ$. Data were corrected for Lorentz-polarization and absorption effects. The structure was solved from conventional heavy-atom method using SHELXS86¹⁴ program and refined by block-diagonal least-squares using UNICSIII¹⁵ to $R = 0.056$, $wR = 0.050$ for 3647 reflections. Neutral atomic scattering factors from International Tables for X-ray Crystallography.¹⁶ Atomic coordinates, bond lengths and bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.* They have also been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG).
- 12 D. M. Hawley and G. Ferguson, *J. Chem. Soc. A*, 1968, 2059.
- 13 As a possibility, the non-symmetrical structure may be a result of orbital symmetry demand: M. V. Veidis, G. H. Schreiber, T. E. Gough and G. J. Palenik, *J. Am. Chem. Soc.*, 1969, **91**, 1859.
- 14 G. M. Sheldrick, *SHELXS86, Program for crystal structure determination*, University of Göttingen, Federal Republic of Germany, 1986.
- 15 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, **55**, 69.
- 16 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974, vol. 4 (present distributor, D. Reidel, Dordrecht).

* For details see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.