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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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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.

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