

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

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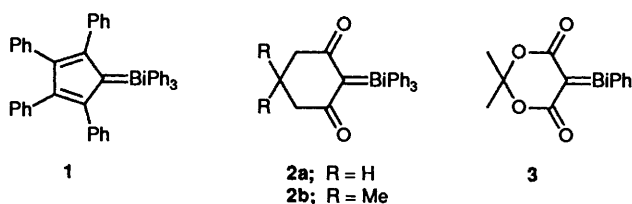
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The first X-ray structure analysis of a bismuthio ylide has been made for 4,4-dimethyl-2,6-dioxo-1-triphenylbismuthiocyclohexanide. The Bi-C_{ylide} bond is 2.16 Å, only 0.05–0.06 Å shorter than the Bi-C_{ph} single bond, revealing that the Bi-C_{ylide}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

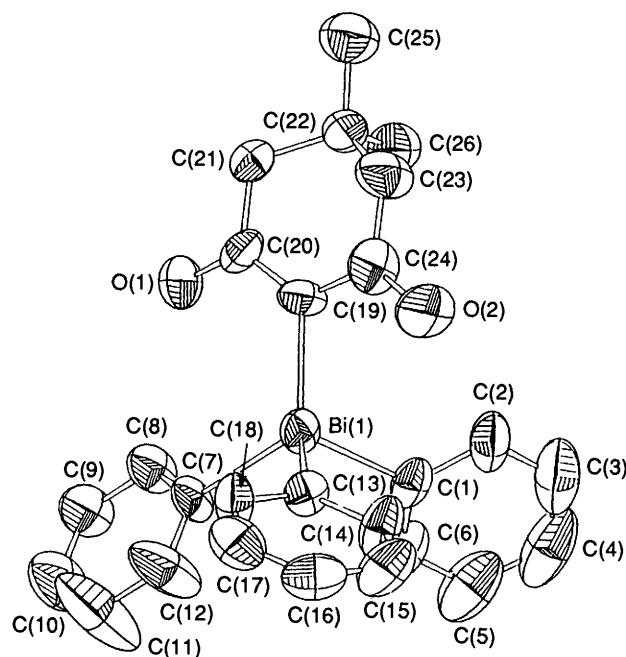


this compound are the carbon-bismuth bonds. The bismuth atom has a distorted tetragonal configuration with bond angles C_{ph}-Bi-C_{ph} = 101.6(4)–103.1(4)° and C(19)-Bi-C_{ph} = 111.8(4)–119.6(4)°. The bond length of Bi-C(19), 2.16 Å, is slightly shorter than the single bond length of Bi-C_{ph} 2.21(1)–2.22(1) 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

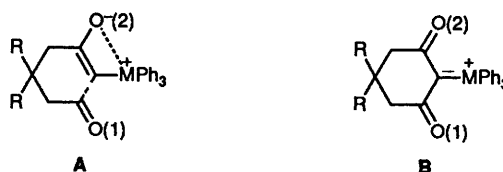
Table 1. Selected bond lengths and atomic distances of the bismuthio ylide

	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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