on the basis of energy calculations for the non-protonated molecule (Chachaty, Pappalardo & Scarlata, 1976). On the other hand, theoretical calculations (Galasso, De Alti & Bigotto, 1971) and molar Kerr constant studies (Aroney, Le Fevre & Saxby, 1963; Le Fevre & Saxby, 1966) predict for the diphenyl sulphide molecule a non-planar structure with angles of *ca* 42–48° between the phenyl ring planes because of the steric contact between *ortho* H atoms. It is therefore reasonable that in this case the presence of a single H atom in the *ortho* position has too little steric influence to alter significantly the planar structure of the molecule. In addition, the contact distance of 2·63 Å between the two N atoms strongly suggests the existence of an intramolecular N—H···N hydrogen bond. The C—S—C angle of 108 (1)° shows that the S atoms are sp^3-hybridized. The mean value of the two C—S bond lengths is 1·755 Å, which is appreciably shorter than the paraffinic distance of 1·81 Å, but is in agreement with the $C(sp^2)$—S bond with two atoms bonded to the S atoms, *e.g.* 1·77 Å in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968), and 1·765 Å in methixene (Chu, 1972). The relative shortness of the S—C bonds could indicate involvement of the sulphur *d* orbitals with the pyridine π systems and *via* hyperconjugation they also contribute to the cation's planarity. Bond distances and angles in the pyridine rings have normal values. As shown in the [001] projection of the unit cell (Fig. 2) the entire structure comprises alternate cationic and anionic units developing along [100]. The thickness of the $[UO_2Cl_4]^{2-}$ groups and of the protonated ligands is roughly 3·3 and 5 Å, respectively, in the **b** direction.

We thank Professor G. Pappalardo for supplying the crystals and Mrs M. Magnabosco for technical assistance.

References

Aroney, M., Le Fevre, R. J. W. & Saxby, J. D. (1963). *J. Chem. Soc. B*, pp. 1167–1173.

Bell, J. D., Blount, J. F., Briscoe, O. V. & Freeman, H. C. (1968). *J. Chem. Soc. D*, pp. 1656–1657.

Chachaty, C., Pappalardo, G. C. & Scarlata, G. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1234–1238.

Chu, S. S. C. (1972). *Acta Cryst.* B**28**, 3625–3632.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–18.

Cromer, D. T. & Mann, J. B. (1968). A**24**, 321–324.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Galasso, V., De Alti, G. & Bigotto, A. (1971). *Tetrahedron*, **27**, 6151–6158.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Le Fevre, R. J. W. & Saxby, J. D. (1966). *J. Chem. Soc. B*, pp. 1064–1066.

Pappalardo, G. C. & Seminara, A. (1976). *J. Inorg. Nucl. Chem.* **38**, 1993–1995.

Shannon, R. D. & Prewitt, C. T. (1970). *Acta Cryst.* B**26**, 1046–1048.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). XRAY system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). B**34**, 2624–2626

(2-Oxopropyl)mercury Bromide

By J. A. Potenza, L. Zyontz and J. San Filippo Jr

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903, *USA*

and R. A. Lalancette

Department of Chemistry, Rutgers University, Newark, New Jersey 07102, *USA*

(*Received* 14 *February* 1978; *accepted* 12 *April* 1978)

Abstract. C_3H_5OHgBr, triclinic, $P\bar{1}$, $a = 6{\cdot}752$ (1), $b = 5{\cdot}733$ (1), $c = 7{\cdot}979$ (1) Å, $\alpha = 83{\cdot}14$ (1), $\beta = 95{\cdot}53$ (1), $\gamma = 101{\cdot}47$ (1)°, $Z = 2$, $D_o = 3{\cdot}70$ (5), $D_c = 3{\cdot}741$ g cm^{-3}. The structure contains two short intermolecular Hg···O(CO) contacts [2·81 (2), 2·82 (2) Å] which are consistent with the relatively low carbonyl stretching frequency observed (1645 cm^{-1}), assuming that formation of weak intermolecular Hg···O bonds also weakens the carbonyl bond. The Hg—Br and Hg—C distances are 2·441 (5) and 2·08 (4) Å, respectively, while the C—Hg—Br angle is 176 (1)°.

Introduction. Milky-white, irregularly shaped crystals of (2-oxopropyl)mercury bromide, obtained from acetone–petroleum ether, were provided by Mr John Feeney (1976). A large crystal was air blown around a

Carborundum ring to yield a sphere of diameter 0·16 mm which was glued to the end of a glass rod and centered on a Syntex $P2_1$ computer-controlled diffractometer. Diffractometer examination of the reciprocal lattice revealed no systematic absences. Using a θ–2θ scan and graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å), intensity data were collected in the range $4 < 2\theta < 60°$. Three standard reflections, measured at 47-reflection intervals, remained constant to ±5% throughout the data collection period. Of the 1746 unique reflections measured, 771 with $F^2 \geq 3\sigma(F^2)$ (counting statistics) were used in the structure solution and refinement. Spherical absorption corrections (*International Tables for X-ray Crystallography*, 1972) were applied to all data with μ for Mo $K\alpha$ = 331 cm^{-1}.

The structure was solved by the heavy-atom method and refined using full-matrix least-squares techniques; the computer programs used have been described previously (Potenza, Giordano, Mastropaolo & Efraty, 1974). Approximate coordinates for the Hg and Br atoms were determined readily from a normal sharpened Patterson map. The distribution of peaks in this map arising from vectors between the heavy atoms suggested that the structure was centrosymmetric. Oxygen and C atom coordinates were determined from an electron-density map based on phases from the heavy atoms. No attempt was made to locate H atoms. Neutral-atom scattering factors were obtained from Cromer & Waber (1965); both real and imaginary components of the anomalous dispersion factors (*International Tables for X-ray Crystallography*, 1962) were applied to Hg and Br.

Refinement was based on F and the function minimized was $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ where $w = 1/\sigma^2$. For the final refinement cycles, weights were determined by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This led to the following assignments: $\sigma(F_o) = -0{\cdot}058|F_o| + 11{\cdot}60$ for $|F_o| < 84{\cdot}7$, $\sigma(F_o) = 0{\cdot}038|F_o| + 3{\cdot}07$ for $84{\cdot}7 < |F_o| < 131{\cdot}7$ and $\sigma(F_o) = 0{\cdot}138|F_o| - 11{\cdot}02$ for $|F_o| > 131{\cdot}7$. Utilizing anisotropic thermal parameters for all atoms, the structure converged with $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}090$ and $R_{wF} = 0{\cdot}101$.* For the final refinement cycle, all parameter changes were less than $0{\cdot}55\sigma$, where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed no extraneous peaks. Atomic parameters are shown in Table 1 while a view of the molecule, showing bond distances and angles, is given in Fig. 1. A stereoview of the molecular packing is given in Fig. 2.

Excluding atom C(2), r.m.s. thermal displacements along the principal axes of the ellipsoids are reasonable and vary from 0·17 to 0·36 Å. C(2) shows an unusually small value of 0·06 Å along one axis. The reasons for this are not entirely clear and may be related to the relatively large value of the linear absorption coefficient of the compound (uncompensated absorption). We do note, however, that the ellipsoid for C(2) does 'point' in a reasonable direction, *i.e.* approximately normal to the various bond axes.

Discussion. A number of α-substituted ketone and aldehyde mercurials have been synthesized and characterized by IR spectroscopy (Allmann, Flatau & Musso, 1972; Feeney, 1976). In each case, the carbonyl stretching frequency was significantly lower than that found for the free aldehyde or ketone. Examination of the IR spectrum of (2-oxopropyl)mercury bromide revealed a band centered at 1645 cm^{-1} (KBr) which, although low in frequency, was assigned as a carbonyl stretching mode. The present structural study was undertaken to characterize the nature of the interaction leading to this low frequency.

Structural parameters of the molecule are in general agreement with accepted values. All C and O atoms are planar to within ±0·02 Å while the bond angles with C(2) as vertex range from 118 (3) to 121 (3)°,

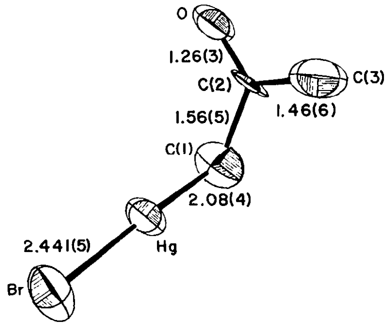

Fig. 1. (2-oxopropyl)mercury bromide showing the atom numbering scheme and bond distances. Bond angles are as follows: Br–Hg–C(1), 176 (1); Hg–C(1)–C(2), 108 (2); O–C(2)–C(1), 118 (3); O–C(2)–C(3), 121 (3); C(1)–C(2)–C(3), 120 (3)°.

Table 1. *Final atomic parameters*

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses. Coordinate values are × 10^3.

	x	*y*	*z*
Hg	43·4 (2)	861·2 (2)	−218·1 (2)
Br	−223·7 (6)	1056·2 (8)	−365·3 (5)
O	194 (4)	283 (4)	−60 (3)
C(1)	279 (6)	717 (8)	−83 (5)
C(2)	278 (4)	469 (4)	−146 (4)
C(3)	364 (8)	456 (7)	−306 (6)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33542 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

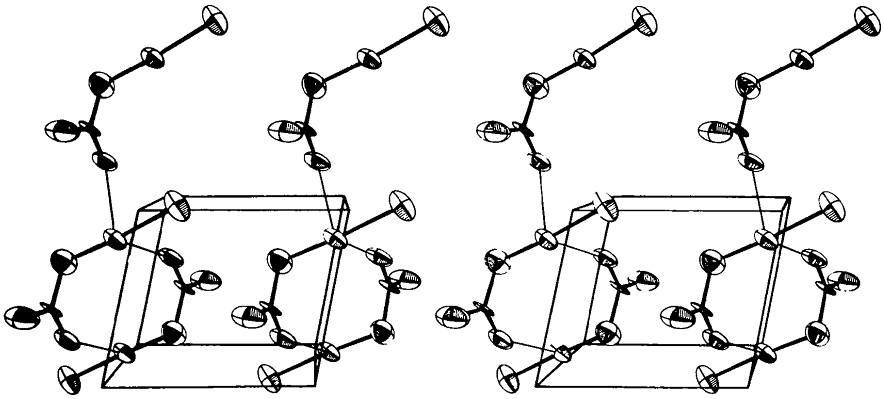

Fig. 2. Stereoscopic packing diagram of (2-oxopropyl)mercury bromide showing the coordination geometry of Hg. Weak intermolecular Hg···O bonds are indicated by light lines.

suggesting sp^2 hybridization at that atom. The Br—Hg—C(1) angle [176 (1)°] is equivalent to the C—Hg—C angle [175·3 (3)°] found for $C(HgOCOCF_3)_4$ (Grdenić, Kamenar, Korpar-Colig, Sikirica & Jovanovski, 1974) and approximates the 180° angle expected for free organo-mercurials. The Hg—Br distance [2·441 (5) Å] lies between those of 2·433 (5) and 2·473 (12) Å reported for $HgBr_2.2C_4H_8O_2$ and $HgBr.C_4H_8O$, respectively (Frey & Monier, 1971), while the Hg—C(1) distance lies at the short end of the range (2·08–2·15 Å) found with several organomercury compounds (Grdenić, Kamenar & Nagl, 1977).

The tendency of Hg to coordinate additional atoms weakly in the solid state has been noted by Grdenić (1965). In the present structure, molecules are oriented such that the shortest intermolecular contacts involving Hg occur with O atoms on molecules related by a cell translation along *b* [Hg···O′, 2·82 (2) Å] and by molecules related by inversion followed by a cell translation along *b* [Hg···O″, 2·81 (2) Å]. These distances are slightly shorter than the sum of the van der Waals radius of O and the metallic radius of divalent Hg (2·90 Å). They are approximately the same as that separating different Hg—O chains in the hexagonal form of HgO [2·79 (2) Å, Aurivillius & Carlsson (1958)] and significantly longer than the Hg···O distances of 2·70 (2) and 2·56 (3) Å reported, respectively, for bis-(dipivaloylmethyl)mercury (Allmann *et al.*, 1972) and $C_7H_7OHg.C_7H_6O_2N$ (Kobayashi, Iitaka & Kido, 1970). With HgO, this short distance is thought to imply a weak bonding interaction (Cotton & Wilkinson, 1972). The short Hg···O contacts in the title complex are consistent with the low carbonyl stretching frequency observed if it is assumed that they imply weak Hg···O bonding which also weakens the carbonyl bond. No other contacts involving Hg are short enough to imply electronic interaction stronger than that arising from van der Waals forces. Assuming O′ and O″ to be weakly coordinated to Hg, the coordination geometry of Hg is that of an octahedron with two *cis* sites vacant. The angles between *cis* ligands with Hg as vertex range from 85 to 90°.

We thank the Center for Computer and Information Services, Rutgers University, for providing computer time.

References

Allmann, R., Flatau, K. & Musso, H. (1972). *Chem. Ber.* **105**, 3067–3077.

Aurivillius, K. & Carlsson, I.-B. (1958). *Acta Chem. Scand.* **12**, 1297–1304.

Cotton, F. A. & Wilkinson, G. (1972). *Advanced Inorganic Chemistry*, pp. 516–517. New York: Interscience.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Feeney, J. E. (1976). Masters Dissertation, Rutgers Univ., New Brunswick, NJ, USA.

Frey, M. & Monier, J.-C. (1971). *Acta Cryst.* B**27**, 2487–2490.

Grdenić, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.

Grdenić, D., Kamenar, B., Korpar-Colig, B., Sikirica, M. & Jovanovski, G. (1974). *J. Chem. Soc. Chem. Commun.* pp. 646–647.

Grdenić, D., Kamenar, B. & Nagl, A. (1977). *Acta Cryst.* B**33**, 587–589.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1972). Vol. II, 3rd ed. Birmingham: Kynoch Press.

Kobayashi, Y., Iitaka, Y. & Kido, Y. (1970). *Bull. Chem. Soc. Jpn*, **43**, 3070–3078.

Potenza, J., Giordano, P., Mastropaolo, D. & Efraty, A. (1974). *Inorg. Chem.* **13**, 2540–2544.