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## Structure of a 'Hypervalent' Linear Bis(phthalimidato)bromate(I) Complex

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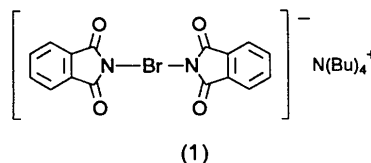
### Abstract

In tetrabutylammonium bis(phthalimidato)bromate(I) the anion is symmetric about Br, which is on a twofold axis. The Br atom is almost linearly coordinated by the two phthalimidato groups with N—Br—N = 176.0 (6)° and Br—N = 2.105 (8) Å. The dihedral angle between the least-squares plane of the two phthalimidato ligands is 87.0 (2)°. The elec-

tronic structure of Br can be described as an  $sp^3d_{z^2}$  hybridization with three lone pairs in a plane perpendicular to the N—Br—N bond. The formal oxidation state of Br is +1.

### Comment

The title compound (1) was investigated as part of a study of N—Br—N bonding properties. The complex was prepared as described by Barry, Finkelstein, Moore, Ross & Ebersson (1984) and then recrystallized from an acetonitrile solution by the addition of diethyl ether and pentane. This yielded colourless needles which had the expected NMR spectra.



The bis(phthalimidato)bromate(I) ion (Fig. 1) is symmetric having equal Br—N distances as the Br atom is on a twofold axis (Table 1, Fig. 2). The coordination around Br is almost linear (Table 2), implying that the electrons around the Br atom are equally distributed between the two phthalimidato ligands. The Br—N distance is large compared to 1.817 (7) Å in *N*-bromosuccinimide (Jabay, Pritzkow & Jander, 1977), showing an increased electron density in the N—Br—N region of the title compound. There are ten electrons equally distributed around the Br atom, just as for Xe in XeF<sub>2</sub>, I in IBr<sub>2</sub><sup>-</sup> and the central Br in symmetric Br<sub>3</sub><sup>-</sup>. In a simple electronic model the hybridization of Br can be described as  $sp^3d_{z^2}$  with three lone pairs in the plane perpendicular to the N—Br—N bond. The electron-withdrawing phthalimidato ligands thus cause the formal oxidation state of Br to be +1. The least-squares planes of the two phthalimidato ligands are inclined at 87.0 (2)° with respect to each other. The O atoms are located within the planes, while the Br atom is 0.272 (2) Å out of both planes.

A short review of some structural parameters for compounds with linear N—Br—N bonding is given in Table 3. This shows that the average Br—N distance within a molecule is nearly constant, ranging from 2.102 to 2.142 Å. One short bond consequently results in the elongation of the other. This was also found for compounds with a linear N—I—N bond (Brock, Fu, Blair, Chen & Lowell, 1988). Table 3 also shows that the dihedral angle between the least-squares planes varies from 0 to 90°, indicating that the distance between the ligands is too long for them to interact. In *N,N'*-biphthalimide (Apreada, Foces-Foces, Cano & Garcia-Blanco, 1978) the distance between the two ring systems is shorter,

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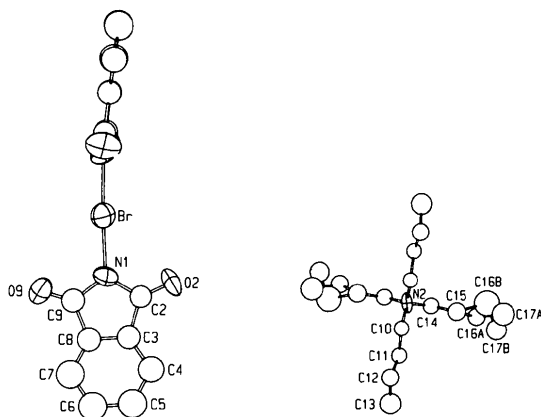


Fig. 1. Perspective drawing of the two ions in the structure; H atoms are excluded for clarity. The displacement ellipsoids in the bis(phthalimidato)bromate(I) ion (left) are scaled to include 50% probability; in the tetrabutylammonium ion (right) they include 30% probability.

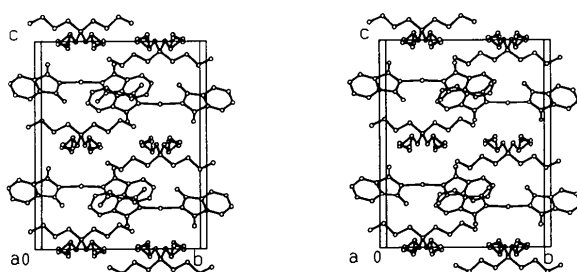


Fig. 2. Stereoscopic view of the unit-cell content. All atoms are drawn with the same small arbitrary radius.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Br	0.75	0.25	0.3047 (1)	0.073 (1)
N1	0.6858 (8)	0.1187 (6)	0.3007 (6)	0.068 (6)
C2	0.6034 (8)	0.0936 (6)	0.2516 (6)	0.060 (7)
C3	0.5939 (8)	-0.0046 (6)	0.2612 (6)	0.068 (6)
C4	0.5295 (8)	-0.0652 (6)	0.2242 (6)	0.082 (7)
C5	0.5385 (8)	-0.1545 (6)	0.2431 (6)	0.104 (9)
C6	0.6086 (8)	-0.1827 (6)	0.2975 (6)	0.102 (8)
C7	0.6731 (8)	-0.1218 (6)	0.3342 (6)	0.097 (8)
C8	0.6656 (8)	-0.0327 (6)	0.3145 (6)	0.070 (6)
C9	0.7268 (8)	0.0459 (6)	0.3415 (6)	0.067 (7)
O2	0.5586 (11)	0.1430 (8)	0.2116 (7)	0.100 (7)
O9	0.7932 (10)	0.0495 (8)	0.3882 (7)	0.092 (7)
N2	0.75	0.25	0.0486 (13)	0.096 (10)
C10	0.7172 (20)	0.3268 (12)	0.0989 (10)	0.087 (7)
C11	0.6718 (18)	0.4124 (13)	0.0639 (1)	0.096 (7)
C12	0.6576 (21)	0.4844 (17)	0.1174 (12)	0.122 (9)
C13	0.6049 (24)	0.5629 (18)	0.0875 (15)	0.183 (13)
C14	0.6597 (17)	0.2234 (15)	-0.0012 (12)	0.106 (8)
C15	0.5581 (20)	0.1930 (18)	0.0357 (14)	0.135 (10)
C16A	0.4787 (57)	0.1825 (42)	-0.0326 (34)	0.123 (22)
C16B	0.4703 (91)	0.1234 (76)	-0.0122 (61)	0.266 (51)
C17A	0.3914 (81)	0.1261 (60)	0.0026 (42)	0.211 (36)
C17B	0.3844 (66)	0.1849 (42)	-0.0156 (36)	0.162 (26)

Table 2. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Br—N1	2.105 (8)	N1—Br—N1 <sup>i</sup>	176.0 (6)
C2—O2	1.178 (16)	N1—C2—O2	125.1 (10)
C9—O9	1.191 (16)	N1—C9—O9	126.7 (10)

Symmetry code: (i)  $\frac{3}{2} - x, \frac{1}{2} - y, z$ .

Table 3. Some structural parameters of compounds with linear N—Br—N' units

Complex	N—Br—N' ( $^\circ$ )	Br—N ( $\text{\AA}$ )	Br—N' ( $\text{\AA}$ )	Dihedral angle ( $^\circ$ )	Reference
Bis(phthalimidato)-bromate(I)	176.0 (6)	2.105 (8)	2.105 (8) <sup>a</sup>	87.0 (2)	This paper
Bis(tetramethylsuccinimidato)-bromate(I)	177.3 (3)	2.110 (5)	2.110 (5) <sup>b</sup>	0	Elding, Albertsson, Svensson & Ebersson (1990)
Bis(quinuclidine)-bromine(I)	180	2.120 (2)	2.156 (2)	— <sup>c</sup>	Blair, Parris, Hii & Brock (1983)
Bis(quinoline)-bromine(I) <sup>d</sup>	176.6 (4)	2.100 (6)	2.185 (7)	11.4	Alcock & Robertson (1975)
Quinuclidine- <i>N</i> -bromosuccinimide	177.5 (3)	2.099 (7)	2.145 (7)	4.2	Robertson (1975)
Quinuclidine- <i>N</i> -bromosuccinimide	178.3 (2)	2.025 (5) <sup>e</sup>	2.179 (5)	— <sup>c</sup>	Brock (1991)
1,4-Diazabicyclo[2.2.2]octanebis-( <i>N</i> -bromosuccinimide)	175.1 (2)	2.332 (4) <sup>e</sup>	1.945 (4)	— <sup>c</sup>	Crowston, Lobo, Sundaresan, Rzepa & Williams (1984)

Notes: (a) N' is related to N by a twofold axis. (b) N' is related to N by a mirror plane. (c) Non-planar ligand. (d) Two independent molecules. (e) N refers to the quinuclidine or the 1,4-diazabicyclo[2.2.2]octane ligand and N' to the succinimide ligand.

and consequently the dihedral angle ( $78^\circ$ ) is closer to  $90^\circ$ .

In the tetrabutylammonium ion, one of the crystallographically independent butyl groups is disordered with the ethyl group adopting two alternative positions (Fig. 1). The conformation can be described as *ap* and *ac*; the torsion angles C14—C15—C16(A,B)—C17(A,B) are  $164(4)$  and  $-115(6)^\circ$  respectively. In the other butyl group the ethyl group adopts the *ap* conformation, C10—C11—C12—C13 =  $-174(2)^\circ$ . The ions are arranged in layers in the *ab* plane (Fig. 2). The crystal is stabilized by van der Waals interactions only; the shortest contact, C6—O2( $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ), is  $3.311(16) \text{\AA}$ .

## Experimental

### Crystal data

$\text{C}_{16}\text{H}_{36}\text{N}^+ \cdot \text{C}_{16}\text{H}_8\text{BrN}_2\text{O}_4^-$   
 $M_r = 614.60$

Orthorhombic

*Pccn*

$a = 12.288(14) \text{\AA}$

$b = 14.863(11) \text{\AA}$

$c = 18.479(16) \text{\AA}$

$V = 3375(3) \text{\AA}^3$

$Z = 4$

$D_x = 1.21 \text{ Mg m}^{-3}$

$D_m = 1.20 \text{ Mg m}^{-3}$

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

by integration from crystal shape

$T_{\min} = 0.75, T_{\max} = 0.87$

3813 measured reflections

1575 independent reflections

517 observed reflections

$[I > 3\sigma(I)]$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{\AA}$

Cell parameters from 23 reflections

$\theta = 7.3-13.7^\circ$

$\mu = 1.239 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Needle

$0.262 \times 0.125 \times 0.125 \text{ mm}$

Colourless

$R_{\text{int}} = 0.051$

$\theta_{\text{max}} = 20^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = -17 \rightarrow 17$

3 standard reflections

frequency: 120 min

intensity variation: linear decay by 45%

## Refinement

Refinement on $F$	$(\Delta/\sigma)_{\max} = 0.60$
Final $R = 0.063$	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
$wR = 0.069$	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
517 reflections	Atomic scattering factors
89 parameters	from <i>International Tables</i>
H-atom parameters not refined	for <i>X-ray Crystallography</i>
	(1974, Vol. IV)
$w = [\sigma^2(F) + 0.001F^2]^{-1}$	

The density was determined by flotation in a dioxane/ $\text{CCl}_4$  solution. A linear correction was made for the decay in intensity of the three standard reflections. The structure was solved by direct methods using *MULTAN80* (Main *et al.*, 1980). As a result of the large decay in intensity (few observed reflections) and disorder in the tetrabutylammonium ion (large displacement parameters), rigid-body least-squares refinement was used for the ring system in the phthalimidato group with structural parameters taken from *N, N'*-biphthalimide (Apreada, Foces-Foces, Cano & Garcia-Blanco, 1978). All H atoms were placed in calculated positions and assigned an isotropic displacement parameter identical to that of the corresponding C atom. Br, N and O atoms were refined with anisotropic displacement parameters. The disorder in one of the butyl groups was interpreted as statistical with the occupancy factors fixed at 0.5. The *SHELX76* program system (Sheldrick, 1976) was used in the refinement.

We would like to thank Professor C. P. Brock for a useful discussion and for providing us with the results of her work prior to publication.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55227 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1007]

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## Structure of an Intermediate in the Synthesis of Corymbolone

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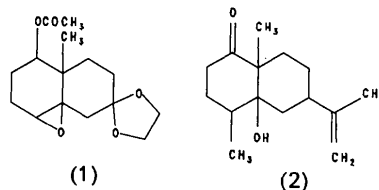
(Received 15 April 1992; accepted 8 July 1992)

## Abstract

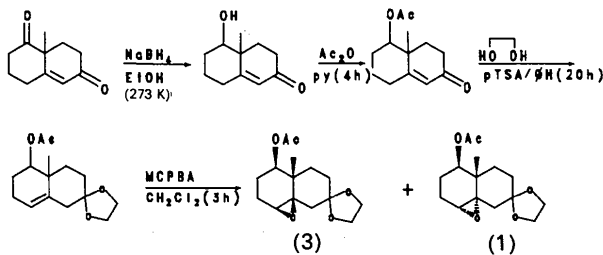
In the title compound, 7,7-ethylenedioxy-4 $\alpha$ , $\beta$ -methyl-1 $\alpha$ , $\beta$ ,2,4 $\alpha$ ,4 $\alpha$ ,5,6,7,8-octahydro-3*H*-naphth-[1,8*a-b*]oxiren-4-yl acetate, the epoxide ring is *trans* to the axial methyl group of the ring junction, which is *cis* to the equatorial acetate group. The six-membered rings are *trans*-fused, one in a chair and the other in a sofa conformation.

## Comment

The title compound (1) is a key intermediate in the synthesis of sesquiterpenoid natural products such as corymbolone (2) (Gambarino, Gambaro & Chamy, 1985).



It was prepared in four stages as shown in the scheme below.



Compound (1) was obtained together with a minor amount of its isomer (3). The isomeric mixture was