Organic 'Hypervalent' Bromine Compounds: the Structure of a Linear N-Bromotetramethylsuccinimide–Tetramethylsuccinimidate Complex in the Solid State

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In a study of N–Br bonding properties, the crystal structure of tetraethyl-ammonium bis(2,2,3,3-tetramethyl-2,5-pyrrolidinedionato)bromate(1−), $[N(C_2H_5)_4][Br(C_8H_{12}NO_2)_2]$, has been determined from X-ray intensity data. The crystal data are $M_r = 518.5$, orthorhombic space group $Pnma$, $a = 9.739(3)$, $b = 25.869(5)$, $c = 10.942(2)$ Å, $V = 2757(1)$ Å^3, $Z = 4$, $D_x = 1.25$, $D_m = 1.22(1)$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu = 14.93$ cm^{-1}, $T = 173(2)$ K. Final $R = 0.045$ for 1314 unique observed reflections. The almost linear complex formed between the tetramethylsuccinimidate ion and N-bromotetramethylsuccinimide is symmetric, with Br in a mirror plane, N–Br = 2.110(5) Å and N–Br–N = 177.3(3)°. A simple description of the electronic structure of Br(I) in the solid complex is $sp^3d_{z^2}$ with three lone pairs confined to the mirror plane perpendicular to the N–Br–N bond.

N-Bromoimides belong to the class of "positive bromine compounds"[1] and thus can act as electron acceptors in molecular complexes with suitable donors. The complexes formed with halogenide ions play an important role in the chemical transformations of N-bromoimides,[2–4] for example in determining the selectivity of bromine addition to or allylic bromination of alkenes by N-bromosuccinimide.[3,4]

We have determined the crystal structures of a 3:1 and a 1:1 N-bromosuccinimide–bromide complex, and found the Br⋯Br distances to be 3.038 and 2.836 Å, respectively.[5,6] Both distances are far shorter than the sum of the Br–Br van der Waals radii, which is about 3.9 Å. In both compounds a significant increase in the N–Br bond length was also noticeable as compared to that of N-bromosuccinimide.

Another type of complex is represented by N-bromo-imide–imide anion complexes.[7] Solutions of such complexes have novel and largely unexplored reactivity,[8,9] for example as reagents for carrying out base-catalysed imido substitutions of enolizable C–H bonds. The tetrabutylammonium salt of the N-bromosuccinimide–succinimidate complex (NBu$_4$+S$_2$Br$^-$, SH = succinimide) decomposes rapidly into SH and polymaleimide in solution,[8] and is thus unsuitable to use for growing crystals for an X-ray crystallographic study. However, the corresponding complex of 2,2,3,3-tetramethylsuccinimide (denoted TH) is much less reactive,[9] so that good crystals of NEt$_4$+T$_2$Br$^-$ could be prepared. In order to elucidate further the properties of the N–Br bond we have investigated the crystal structure of the tetraethylammonium salt of the 1:1 N-bromotetramethylsuccinimide–tetramethylsuccinimidate complex.

Experimental

Colourless, prismatic crystals of NEt$_4$+T$_2$Br$^-$ were prepared by repeated recrystallizations from acetonitrile. The crystals were stable in air at low temperature over several weeks. However, after a year in the cooled (ca. 0 °C) mother liquor the organic part of the anion had decomposed and the material was transformed into single crystals of NEt$_4$+Br$^-$. A cut crystal of composition NEt$_4$+T$_2$Br$^-$, bounded by (110), (01 −1) and the forms {100}, {010} and {001}, and with the size 0.200×0.125×0.300 mm^3, was used for the X-ray experiments. The measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite monochromator and MoKα radiation. The temperature at the crystal was kept at 173(2) K with a N$_2$ gas stream cooled by liquid N$_2$.[10] The long-time stability of the cryostat was about ±3 K. Lattice parameters were determined from 25 reflections with $18 < 2\theta < 44°$. Reflections $0kl$, $k+l$ odd, and $hk0$, h odd, are systematically absent, indicating orthorhombic space groups $Pnma$, or $Pn2_1a = Pna2_1$. Crystal data are $M_r = 518.5$, $a = 9.739(3)$, $b = 25.869(5)$, $c = 10.942(2)$ Å, $V = 2757(1)$ Å^3, $Z = 4$, $D_x = 1.25$, $D_m = 1.22(1)$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069(1)$ Å, $\mu = 14.93$ cm^{-1}. The density was determined by flotation in a dioxane–carbon tetrachloride mixture.

The intensities of 5475 reflections with $h = -11$ to 11, $k = 0$ to 30, $l = -13$ to 0 and $\sin\theta/\lambda < 0.60$ Å^{-1} were measured with $\omega/2\theta$ scans and $\Delta\omega = 1.30° + 0.60°\tan\theta$.

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The maximum counting time was 180 s, so that most reflections should have $\sigma_c(I)/I \leq 0.025$ [$\sigma_c(I)$ is based on counting statistics]. The intensities of three standard reflections (− 1 7 −3, 0 4 −4 and −2 0 −4) were measured every hour. They declined by about 20 % during the time of exposure, 192 h. The intensity data set was rescaled with fitted linear equations. The quantities I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects (numerical integration). The range of transmission factors was 0.672–0.784. The intensities were averaged to an independent data set of 2458 reflections ($R_{int} = 0.056$) of which only 1314 had $I > 3\sigma_c(I)$. It was noted that many of the weak reflections had indices h,k,l that were not all odd or all even, indicating that the lattice may be nearly centred on all faces.

Structure determination and refinement

The structure of the non-hydrogen atoms was first solved and refined in space group $P2_1/c$ [$P2_1/a$ with the present indices; the unique angle was taken as 90.14(2)° and the condition $0kl$, $k+l$ odd, was originally treated as $00l$, l odd] using the heavy-atom method. Br was located in the Harker sections of a Patterson map and the remaining N and C atoms were found in $\Delta\varrho$ maps. The subsequent least-squares refinement clearly indicated that Br and N(2) were located on mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Renewed inspection of the intensity data revealed the diffraction symmetry *mmm* and the condition $0kl$, $k+l$ odd. Consequently, the final cycles of refinement were made in the orthorhombic space group *Pnma*, with Br, N(2) and two ethyl groups in positions 4(c). Most of the hydrogen atoms,

Table 1. Atomic coordinates and the equivalent isotropic temperature factors (Å^2) with estimated standard deviations. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Atom	x	y	z	U_{eq}
Br	0.2285(1)	0.2500	0.4863(1)	0.027(1)
N(1)	0.2326(5)	0.1685(2)	0.4887(4)	0.027(2)
C(1)	0.2985(7)	0.1392(2)	0.4033(5)	0.027(2)
O(1)	0.3622(6)	0.1550(2)	0.3153(4)	0.047(2)
C(2)	0.2747(7)	0.0824(3)	0.4308(5)	0.028(2)
C(3)	0.2317(7)	0.0834(2)	0.5667(5)	0.027(2)
C(4)	0.1834(7)	0.1391(2)	0.5824(6)	0.027(2)
O(4)	0.1156(5)	0.1545(2)	0.6683(4)	0.042(2)
C(21)	0.3955(8)	0.0485(3)	0.3968(7)	0.040(3)
C(22)	0.1509(8)	0.0678(3)	0.3481(7)	0.047(3)
C(31)	0.3585(8)	0.0794(3)	0.6519(6)	0.050(3)
C(32)	0.1238(9)	0.0435(3)	0.6067(7)	0.051(3)
N(2)	0.2496(6)	0.7500	0.4933(5)	0.026(3)
C(10)	0.2578(9)	0.7500	0.3543(7)	0.032(3)
C(20)	0.1192(11)	0.7500	0.2919(9)	0.059(5)
C(30)	0.1715(8)	0.7026(3)	0.5389(6)	0.042(3)
C(40)	0.2353(9)	0.6506(3)	0.5066(7)	0.063(3)
C(50)	0.3951(10)	0.7500	0.5412(9)	0.034(3)
C(60)	0.4103(11)	0.7500	0.6780(9)	0.047(4)

Table 2. Selected interatomic distances (Å) and angles (°).

Br–N(1)	2.110(5)	C(2)–C(22)	1.555(10)
N(1)–C(1)	1.364(8)	C(3)–C(31)	1.551(10)
N(1)–C(4)	1.363(8)	C(3)–C(32)	1.506(10)
C(1)–O(1)	1.216(8)	N(2)–C(10)	1.523(10)
C(4)–O(4)	1.217(8)	N(2)–C(30)	1.527(8)
C(1)–C(2)	1.517(9)	N(2)–C(50)	1.511(11)
C(2)–C(3)	1.545(8)	C(10)–C(20)	1.513(14)
C(3)–C(4)	1.525(9)	C(30)–C(40)	1.522(12)
C(2)–C(21)	1.514(10)	C(50)–C(60)	1.504(14)

N(1)–Br–N(1)	177.3(3)	C(2)–C(3)–C(32)	117.2(6)
C(1)–N(1)–C(4)	111.8(5)	C(4)–C(3)–C(31)	104.0(5)
N(1)–C(1)–C(2)	109.2(5)	C(4)–C(3)–C(32)	111.7(6)
N(1)–C(1)–O(1)	126.5(6)	C(31)–C(3)–C(32)	109.7(6)
O(1)–C(1)–C(2)	124.2(6)	C(3)–C(4)–N(1)	109.5(5)
C(1)–C(2)–C(3)	102.2(6)	C(3)–C(4)–O(4)	124.4(6)
C(1)–C(2)–C(21)	113.2(6)	N(1)–C(4)–O(4)	126.1(6)
C(1)–C(2)–C(22)	103.8(5)	C(10)–N(2)–C(30)	110.6(4)
C(3)–C(2)–C(21)	117.2(6)	C(10)–N(2)–C(50)	107.3(6)
C(3)–C(2)–C(22)	110.8(6)	C(30)–N(2)–C(30)	106.9(7)
C(21)–C(2)–C(22)	108.5(6)	C(30)–N(2)–C(50)	110.7(4)
C(2)–C(3)–C(4)	102.0(5)	N(2)–C(10)–C(20)	113.8(7)
C(2)–C(3)–C(31)	111.2(6)	N(2)–C(30)–C(40)	115.4(6)
		N(2)–C(50)–C(60)	115.9(8)

from three CH_2 and seven CH_3 groups, were found in $\Delta\varrho$ maps, the rest were placed in calculated positions before the final cycles (tetrahedral carbon atoms, C–H = 0.95 Å). The number of observed intensity data was too small to allow a refinement of the H-atom parameters.

The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma_c^2(F_o) + (0.045F_o)^2]$. All non-H atoms were assigned anisotropic thermal parameters ($U_{iso} = 0.076$ Å^2 for the H atoms). 1314 reflections with $I > 3\sigma_c(I)$ were used in the refinement of 154 parameters (2181 reflections and 289 parameters in space group $P2_1/c$). Refinement converged to $R = 0.045$, $R_w = 0.069$, $S = 1.262$ and $\Delta/\sigma \leq 0.091$ ($R = 0.063$, $R_w = 0.089$ in $P2_1/c$ without H atoms). The final $\Delta\varrho$ map was featureless with maximum and minimum values 0.61 and −0.39 e Å^{-3}. Atomic scattering factors were taken from Ref. 11. The computer programs used are described in Ref. 12.

Discussion

Atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2.* The structure contains almost linear [T_2Br]$^-$ complexes with Br on mirror planes, and tetraethylammonium ions with N(2) and two ethyl groups on mirror planes. The complex anion is shown in Fig. 1 and the cation in Fig. 2, with the atomic numbering.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, selected torsion angles, least-squares plane data and distances and angles involving H atoms are available on request from one of the authors (M.E.).
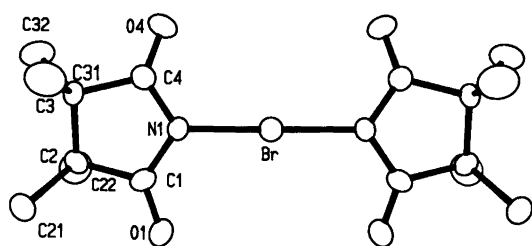
Fig. 1. A perspective drawing of the T$_2$Br$^-$ complex (stripped of its H atoms) with the atomic numbering. The thermal ellipsoids are scaled to include 50 % probability.
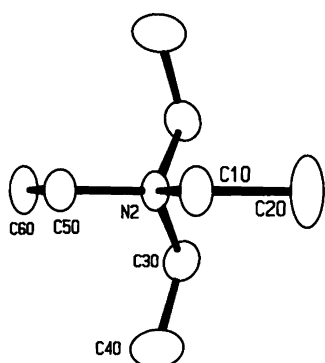

Fig. 2. A perspective drawing of the non-H atoms of the tetraethylammonium ion with the atomic numbering. The thermal ellipsoids are as in Fig. 1.

A stereoscopic view of the molecular packing is shown in Fig. 3.

The mirror plane implies that the negative charge from the tetramethylsuccinimidate anion is equally distributed

between the two imidato ligands. The bonding in the succinimide groups uses 120 of 130 valence-shell electrons in the [T$_2$Br]$^-$ ion, leaving 10 for the linear N–Br–N bond. The electronic configuration of Br may thus be compared to that about the central atoms in XeF$_2$, IBr$_2^-$ or symmetric Br$_3^-$. It should be described as an $sp^3d_{z^2}$ hybrid (**1**) with three lone pairs confined to the Br mirror plane[13] (the N atoms have planar surroundings). With electron-withdrawing ligands the formal oxidation state of Br in T$_2$Br$^-$ is thus +I.

(1)
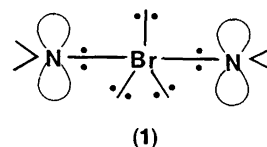
The [T$_2$Br]$^-$ complex is similar to the 'hypervalent 10–I–2 sytem' in the [(C$_6$F$_5$)$_2$I]$^-$ complex investigated by Farnham and Calabrese,[14] although in the latter complex the ligands are approximately perpendicular to each other about the >C–I–C< bond. Reich *et al.*[15] recently found evidence of a [(C$_6$H$_5$)$_2$I]$^-$ complex in THF–HMPA solution. In these complexes the organic anions serve as apical ligands stabilizing a linear configuration about a central halogen atom.

As could be expected from the shape and presumed electron configuration of the complex, the N–Br bond length is quite long, 2.110(5) Å compared with 1.817(7) Å in pure SBr,[16] 1.869(5) Å in the 1:3 complex [Br(SBr)$_3$]$^-$,[5] and 1.896(6) Å in the 1:1 complex [Br(SBr)]$^-$.[6] The N–Br–N angle is 177.3(3)°.

The relevant part of the molecular geometry of the tetramethylsuccinimide ligand is within the limits of error the same as in SH,[17] SBr,[16] NEt$_4^+$[BrSBr]$^-$[6] and Cs$^+$[Br (SBr)$_3$].[5] All C–C single-bond distances are near 1.53(2) Å,
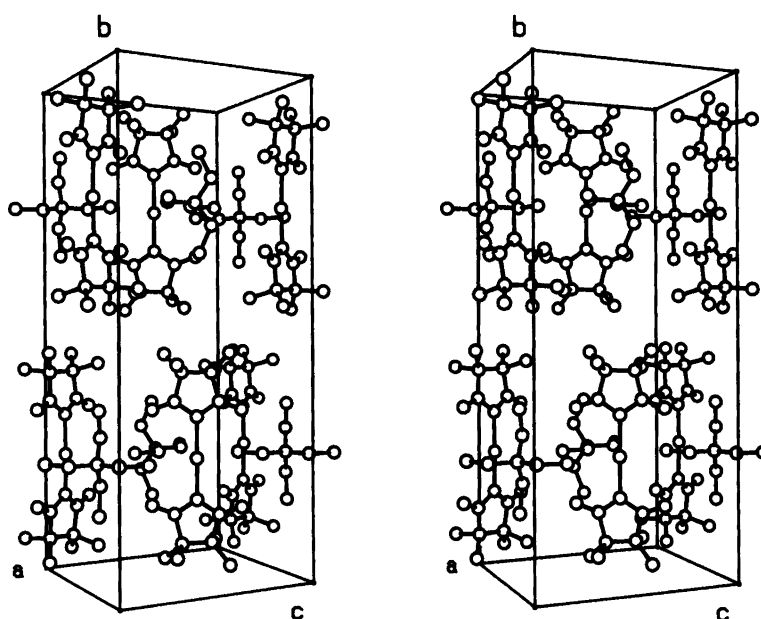

Fig. 3. A stereoscopic view of the unit cell content of NEt$_4^+$T$_2$Br$^-$.

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and the C–N and C–O bond lengths are 1.364(6) and 1.217(6) Å, respectively. The endocyclic torsion angles show that the succinimide ring is twisted, with an r.m.s. deviation of 0.094 Å from the least-squares plane through the ring atoms. The bond distances and angles of the tetraethylammonium ion in the present compound are comparable to those in the salt $NEt_4^+[BrSBr]^-$.[6]

The molecular packing depicted in Fig. 3 shows that the compound crystallizes in electrically neutral layers perpendicular to the *b* axis. Adjacent layers are predominantly held together by van der Waals forces between the C(21), C(22), C(31) and C(32) methyl groups, with the carbon atoms 3.7–3.9 Å apart. The positions of Br form an almost F-centred lattice, in agreement with the approximate condition found for weak or missing reflections.

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