A Novel Hydrogen-bonded Complex formed by Reaction between Bromine and 1,4-Diazabicyclo[2.2.2]octane in Dichloromethane Solution

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The reaction between bromine and 1,4-diazabicyclo[2.2.2]octane (DABCO) in dichloromethane solution produces a novel complex consisting of a linear chain of three hydrogen-bonded DABCO units terminated at each end by a $Br_3{\cdot}Br_3{\cdot}Br$ counterion apparently bearing a total formal charge of 3−; these chains are cross-linked by hydrogen bonds to a fourth diprotonated DABCO unit, and the whole structure is characterised by a number of unusually close interatomic contacts.

Although complexes between amines and either halogens (Cl_2 or Br_2)[1] or *N*-halogenosuccinimides[2] have been known for some time, and are found to be very useful oxidation reagents,[1—3] few structural studies of these species have been carried out.[4] We recently reported the *X*-ray structure of a complex formed between *N*-bromosuccinimide (NBS) and the tertiary base 1,4-diazabicyclo[2.2.2]octane (DABCO) which contained the longest N–Br bond yet observed.[5] Much interest has been shown in the related complex that forms between this base and bromine itself,[4a] owing to the possibility of forming a cationic polymer consisting of alternating DABCO and Br^+ units with Br_3^- counterions.

When dilute dichloromethane solutions of Br_2 and DABCO are mixed and allowed to evaporate at room temperature, orange crystals of a high-melting and diamagnetic (e.s.r.) complex (**1**) are obtained. The *X*-ray structure† and micro-analysis‡ of (**1**) indicate that partial protonation of the base has occurred, the protons presumably resulting from radical oxidation of the solvent by bromine or oxygen. The *X*-ray analysis (Figure 1) reveals an essentially linear chain *ca.* 53 Å in length consisting of three central DABCO units. These are terminated at each end by seven bromine atoms (comprising approximately a co-linear arrangement of two Br_3 and one Br units) and the chains are cross-linked by a fourth DABCO molecule.§

A number of unusual features are associated with this array. (a) The linear DABCO–DABCO–DABCO unit has two very short N–N contacts (2.66 and 2.68 Å) indicating the probable presence of two symmetrical N–H–N hydrogen bonds.[6] (b) The two single bromines (presumed to be Br^- ions) immediately adjacent to the ends of the DABCO chain have different environments. One of these ions is involved in three hydrogen-bonding interactions with the central and the cross-linking DABCO molecules,[7] and the other is involved only with the central DABCO. (c) The two co-linear Br_3 units which terminate the chain have very short Br_3–Br_3 contacts of 3.25 and 3.23 Å. (d) The two Br_3–Br^- distances of 3.60 and 3.66 Å are both significantly less than the corresponding van

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† *Crystal data:* $C_{24}H_{54}Br_{14}N_8$ monoclinic, $a = 13.230(4)$, $b = 16.166(3)$, $c = 21.373(6)$ Å, $\beta = 100.95(2)°$, $U = 4488$ Å^3; space group $P2_1/a$, $Z = 4$, $M_r = 1573.42$, $D_c = 1.40$ g cm^{-3}, $\mu = (\text{Cu-}K_\alpha) = 153$ cm^{-1}; 3298 independent observed reflections [$|F_0| > 3\sigma(F_0)$, $\theta < 50°$] were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) and using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption-corrected data to give $R = 0.073$, $R_w = 0.081$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

‡ Satisfactory for C, H, and N; for Br, found: 68.2; calc.: 71.1%.

§ The anisotropic thermal parameters of the methylene carbons of the cross-chain linking DABCO unit indicate disorder to be present. However, this is confined to the carbon atoms and does not affect the nitrogen atoms of this unit, which have normal values. This disorder therefore does not affect any discussions of the proposed bonding.

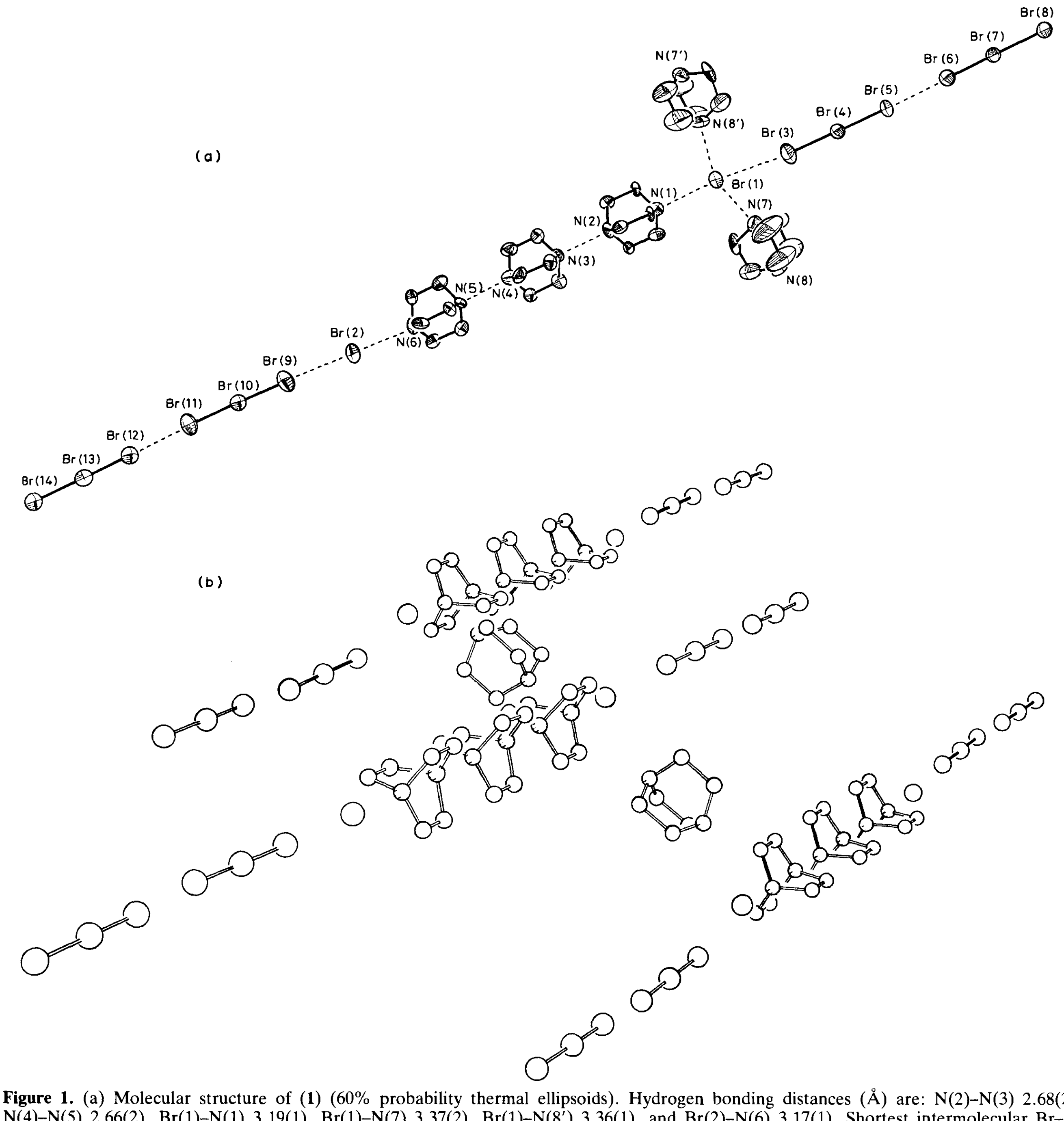

Figure 1. (a) Molecular structure of (**1**) (60% probability thermal ellipsoids). Hydrogen bonding distances (Å) are: N(2)–N(3) 2.68(2), N(4)–N(5) 2.66(2), Br(1)–N(1) 3.19(1), Br(1)–N(7) 3.37(2), Br(1)–N(8′) 3.36(1), and Br(2)–N(6) 3.17(1). Shortest intermolecular Br–Br contacts (Å): Br(1)–Br(3) 3.663(3), Br(5)–Br(6) 3.227(3), Br(2)–Br(9) 3.597(3), and Br(11)–Br(12) 3.246(3). Bond lengths within the Br$_3$ units: Br(3)–Br(4) 2.537(3), Br(4)–Br(5) 2.547(2), Br(6)–Br(7) 2.439(3), Br(7)–Br(8) 2.710(3), Br(9)–Br(10) 2.507(3), Br(10)–Br(11) 2.586(3), Br(12)–Br(13) 2.447(3), and Br(13)–Br(14) 2.695(3). Selected N–Br–Br and Br–Br–Br angles along chain (°); N(1)–Br(1)–Br(3) 160.6(2), N(6)–Br(2)–Br(9) 174.2(2), Br(4)–Br(5)–Br(6) 176.8(1), and Br(10)–Br(11)–Br(12) 176.0(1). (b) The packing of Br$_7$·DABCO$_3$·Br$_7$ chains showing the interchain linking *via* the isolated DABCO molecules.

der Waals distance (3.9 Å).[8] (e) The two terminal Br$_3$ units display internal asymmetry whereas the inner pair do not (Figure 1).

Since the *X*-ray analysis did not reveal the hydrogen atom positions, it was not possible to determine exactly the number of protons present in (**1**). Nevertheless the Br(1)–N(1), N(2)–N(3), N(4)–N(5), N(6)–Br(2), Br(1)–N(7), and Br(1)–N(8′) distances are all consistent with hydrogen-bonding interactions[6,7] and this and the microanalytical data suggest the presence of six protons. The most probable arrangement is that the cross-linking DABCO unit is the only one to be doubly protonated, the six basic sites of the central three DABCO units sharing the remaining four protons. If this is correct, the two terminal Br$_7$ chains must therefore each carry a formal charge of 3$-$. The close linear approaches of both the Br$_3$ units and the Br$^-$ ion seems incompatible with such an overall charge. Polyhalide chains containing more than three atoms and carrying a single negative charge are always non-linear,[9] with intra-chain angles in the region of 100°. The linearity of (**1**) therefore tends to argue against significant charge transfer from the Br_7^{3-} chain to the central positively charged DABCO units. It is possible that the bromine chains may be held together by hydrogen bonds. We discount this for two reasons. In the first instance the Br_3–Br_3 distances of *ca.* 3.24 Å [between Br(5) and Br(6) or Br(11) and Br(12)] are too short for the linear insertion of a proton.[10] Secondly, although the distance of *ca.* 3.65 Å between Br(2) and Br(9) or between Br(1) and Br(3) could be associated with a Br–H–Br interaction (*cf.* 3.09 Å for a symmetrical Cl–H–Cl bond[10]) the addition of an extra proton into the Br chain would require an additional negative charge to be accommodated.

Asymmetry in trihalide anions is fairly common. However in all reported examples (with only one exception[11]) this symmetry is associated with a close approach to one of the terminal halide atoms by a positive counter ion or dipole.[12] There are in (**1**) however no other close approaches to the terminal asymmetric Br_3 units; the closest contact is 4.1 Å, consistent with normal van der Waals interactions. Although we also observe several short C–Br contacts of less than 3.5 Å, the absence of corresponding H–Br contacts of less than 2.94 Å eliminates the possibility of C–H–Br_3 hydrogen bond interactions. We currently have no satisfactory theoretical explanation for the unusual structural features of (**1**).

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