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Molecular Structure of the *s*-Triazine – Br_2 Complex

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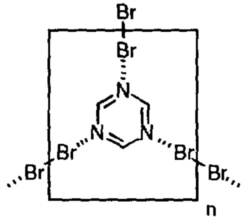
Abstract: *s*-Triazine forms a unique 1:2 molecular complex with dibromine assembled via a combination of N···Br interactions and C-H···N hydrogen bonds. Copyright © 1996 Elsevier Science Ltd

The intense current interest in self-organizing molecular systems has brought about something of a renaissance in the study of the weaker and more subtle intermolecular forces, such as halogen···O/N interactions and C-H···O/N hydrogen bonds, due to an awareness that these may serve as supramolecular design principles.[1] An acknowledged challenge in this area has been to engineer systems which assemble hexagonal arrays,[2] influenced by such well known examples as the hydrogen-bonded trimesic acid,[3] melamine-cyanuric acid,[4] and guanine[5] hexamers.

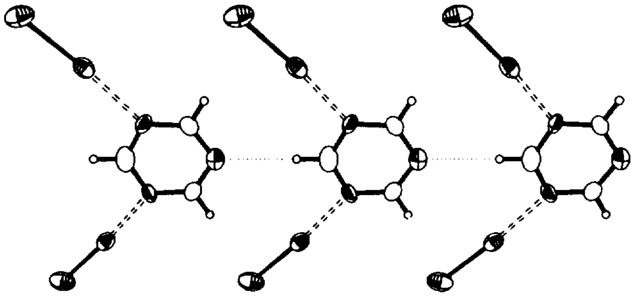
It was for these reasons that we were intrigued by a very early report[6] on a complex between *s*-triazine and molecular bromine which reportedly analyzed as $C_3H_3N_3Br_3$. This molecular formula could be interpreted in terms of the secondary structure shown in Figure 1. Although N-donors do not usually interact with both halogen atoms of an X_2 molecule due to the polarisation of the X-X bond, the weakly basic triazine molecule can be compared to phenazine and pyrazine, whose I_2 complexes do show N···I-I···N bridging in the solid state.[7,8] This phenomenon is also observed in the 1:2 complex between Br_2 and the weak acetonitrile donor.[9]

Figure 1



We therefore undertook a crystallographic investigation of this complex. Following the published procedure,[6] a solution of bromine in CCl_4 was added to a solution of *s*-triazine in the same solvent at 0 °C. In the course of the addition the deposition of orange-brown platelets was observed. X-ray analysis[10] of this volatile solid revealed not the structure shown in Figure 1, but a 2:1 complex (i.e. $C_3H_3N_3Br_4$), assembled via a novel combination of N···Br and C-H···N interactions (Figure 2). The N···Br distance is 2.515 Å, which is a violation of the van der Waals radii of nearly 1 Å. There are only two other examples of complexes which involve the bonding of a nitrogen lone pair to molecular bromine, one with a longer N···Br distance (acetonitrile-Br_2; 2.84 Å)[9] and one shorter (hexamethylenetetramine-Br_2; 2.26 Å).[11] The linear strand of triazine molecules is characterized by short C-H···N contacts of 2.42 Å, which can be regarded as hydrogen bonds.[12] These are not observed in the crystal structure of *s*-triazine alone.[13] There is also a close approach of the two remaining hydrogens to the bromine molecules associated with the neighbouring ring, and the fact that Br_2 is displaced towards these protons (C-N···Br angle 115° vs. 130° on the other side) may indicate a cohesive interaction. The extended structure consists of essentially flat, infinite strips of $(Br_2)_2$-triazine units in parallel sheets separated by van der Waals contact (3.45 Å).

Figure 2



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10. Crystal data: $C_3H_3Br_4N_3$, M=400.7, monoclinic, a=14.399(12), b=6.035(5), c=10.966(4) Å, β= 102.18(5)°, U=931.5(8)$Å^3$, space group *C2/c*, Z=4, D_{calc}=2.857 g cm^{-3}, $F(000)$=728, μ(Mo-K_α)=17.22 mm^{-1}. A total of 1046 data ($2\theta_{max}$=50°) were collected at 150 K on a Stoe Stadi-4 four-circle diffractometer equipped with graphite-monochromated (Mo-K_α) radiation (λ=0.71073 Å). Merging gave 814 unique reflections (R_{int}=0.051), of which 556 had $F \geq 4\sigma(F)$. Absorption corrections were applied to the data using ψ-scans (min. and max. transmission factors 0.031 and 0.137, respectively). The structure was solved by direct methods[14] and refined[15] on F^2 with the non-H atoms allowed anisotropic thermal motion. Hydrogen atoms were initially placed in geometrically calculated positions and thereafter allowed to ride on their parent C atoms with $U_{iso}(H)=1.2U_{eq}(C)$. At final convergence $R(F)$=0.0483 and $wR(F^2)$=0.1249 for 47 refined parameters, g.o.f. on F^2=1.09, max. Δ/σ<0.003, max. Δ_ρ=0.98 e $Å^{-3}$.
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