2-(2,4-Dibromophenyl)-4-oxo-1,2,3-benzotriazin-2-ium-3-ide

By M. A. Hamid* and A. Hargreaves

Department of Pure and Applied Physics, University of Manchester Institute of Science and Technology, Manchester, M 60 1QD, England

Abstract. $C_{13}H_7Br_2N_3O$, M.W. 381·1, crystallizes in two forms: a triclinic one, space group $P\bar{1}$, with $a = 20·243$ (13), $b = 8·110$ (6), $c = 4·041$ (3) Å, $\alpha = 78·41$ (3), $\beta = 87·14$ (3), $\gamma = 78·71$ (2)°, $Z = 2$ [$U = 637$ Å³, $D_m = 2·0$, $D_x = 1·99$ g cm⁻³, μ(Mo $K\alpha$) = 68 cm⁻¹, crystal dimensions $0·03 \times 0·05 \times 0·8$ mm]; and an orthorhombic one, space group $Pca2_1$, with $a = 41·01$ (5), $b = 15·40$ (4), $c = 4·00$ (4) Å, $Z = 8$. The triclinic structure is described. Fourier syntheses showed up the positions of all light atoms and it was possible, therefore, to determine the structure without using chemical information about the sterochemistry of the molecule and to distinguish between conflicting structures suggested by different chemical studies; the existence of a six-membered ring containing three nitrogen atoms is established. The structural parameters were refined by the minimum residual method to an R value of 0·095.

Introduction. This compound was first reported by Chattaway & Walker (1925, 1927). On the basis of degradative results they proposed the molecular configuration of Fig. 1(*a*). Gibson (1962), whilst examining some 1,3-dipolar addition reactions (Huisgen, 1961), suggested the linear arrangement for the three N atoms shown in Fig. 1(*c*) and presented supporting evidence from IR and UV spectral data. Re-examination and extension of data led Kerber (1972) and later McKillop & Kobylecki (1974) to urge adoption of the structure given in Fig. 1(*b*), which incorporates a six-membered ring containing three N atoms. The purpose of the present X-ray study, commenced before the last two papers appeared, was to establish the correct molecular configuration.

The compound was supplied by Professor M. S. Gibson, formerly of the Chemistry Department, UMIST. It proved to be difficult to grow undistorted crystals suitable for X-ray analysis. The triclinic form was grown from a solution in chlorobenzene as fairly long, platy, needle-shaped crystals, which deteriorated in light. As only one of a very large number of crystals examined by X-rays was found to be substantially free from distortion, all the crystallographic and X-ray data were collected from a single mounting of this specimen, with rotation about the needle (*c*) axis.

* Present address: Physics Department, P.O. Box 656, Tripoli University, Libya.

Cell dimensions and space group were obtained from oscillation, Weissenberg and precession photographs. Intensity measurements were made on a Hilger and Watts computer-controlled four-circle diffractometer with a scintillation counter, pulse height discrimination and the $\omega/2\theta$ scan technique. The intensities of 1458 non-equivalent reflexions with $\theta \le 30°$ were measured using Mo $K\alpha$ radiation. Cell parameters were refined by least-squares fitting to the measured angles of 14 independent reflexions which were evenly spaced throughout the reciprocal-lattice sphere. Two standard reflexions were monitored throughout the data collection and later used to check these data for any instabilities in the system and to check that no appreciable decomposition of the crystal had occurred. Intensities were corrected for Lorentz–polarization but not for absorption. Intensity statistics (Foster & Hargreaves, 1963) were applied to determine the space group unequivocally.

The positional coordinates of the two Br atoms in each molecule were determined from a three-dimensional Patterson synthesis and refined by the method of minimum residual refinement (Bhuiya & Stanley, 1963). Structure factor calculations with Br contributions gave $R = \sum||F_o| - |F_c||/\sum|F_o| = 0·31$. A three-dimensional Fourier synthesis, with phases based only on the Br positions, revealed the positions of all the light atoms other than H. Inclusion of these 17 light atoms with a single isotropic factor reduced R to 0·16. Further minimum residual refinement until final shifts were less than 0·2 e.s.d.'s, with individual isotropic temperature factors for the light atoms and anisotropic temperature factors for the Br atoms, gave a final R value of 0·095 for the 1458 measured reflexions; H
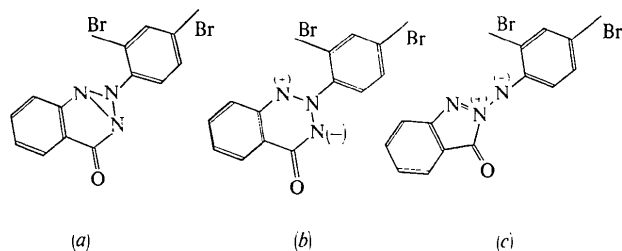
Fig. 1. Possible molecular configurations of $C_{13}H_7Br_2N_3O$.

Table 1. *Fractional positional coordinates with estimated standard deviations, $\sigma(x,y,z)$, in Å and isotropic thermal parameters, B (Å^2), with estimated standard deviations in parentheses*

	x	y	z	$\sigma(x,y,z)$	B*
N(1)	0·2788	0·5809	0·3257	0·010	3·0 (1)
N(2)	0·2789	0·7321	0·3830	0·009	2·3 (1)
N(3)	0·3225	0·7928	0·5418	0·010	2·8 (1)
C(4)	0·3798	0·6751	0·6692	0·012	2·9 (2)
C(5)	0·4428	0·3738	0·7261	0·013	3·5 (2)
C(6)	0·4444	0·2078	0·6797	0·015	4·1 (2)
C(7)	0·3914	0·1666	0·5351	0·014	3·6 (2)
C(8)	0·3349	0·2900	0·4179	0·014	3·9 (2)
C(9)	0·3335	0·4587	0·4479	0·012	3·0 (2)
C(10)	0·3864	0·5040	0·6143	0·012	2·8 (2)
C(1')	0·2212	0·8632	0·2452	0·013	3·2 (2)
C(2')	0·1558	0·8420	0·3337	0·012	2·9 (2)
C(3')	0·1024	0·9730	0·1989	0·012	3·1 (2)
C(4')	0·1162	0·1185	0·9971	0·013	3·3 (2)
C(5')	0·1814	0·1406	0·9046	0·013	3·5 (2)
C(6')	0·2354	0·0113	0·0485	0·012	3·1 (2)
O(1)	0·4193	0·7269	0·8180	0·010	4·2 (1)
Br(1)	0·0430	0·2919	0·8203	0·0017	5·26 (2)
Br(2)	0·1343	0·6491	0·6267	0·0014	4·30 (2)

* For Br(1) and Br(2) the anisotropic thermal parameters are given by T_1 and T_2, where $T_1(hkl) = \exp[-(0.0021h^2 + 0.0153k^2 + 0.1215l^2 + 0.0023hk + 0.0049hl - 0.0054kl)]$, $T_2(hkl) = \exp[-(0.0022h^2 + 0.0130k^2 + 0.0902l^2 - 0.0021hk + 0.0076hl + 0.0035kl)]$.

atoms were not included. The atomic scattering factors used were those of Cromer & Mann (1968). The final positional and thermal parameters are given in Table 1.*

Discussion. The atom numbering is shown in Fig. 2. Table 2 gives the least-squares planes. Planes I and III are individually planar within the accuracy of the structure but plane II departs significantly from planarity. The angle between planes I and II is 130° 9' and that between planes II and III is 2° 54'. Bond lengths are given in Table 3 and bond angles in Table 4.

Fig. 2 shows the packing of the molecules viewed along c and gives the shorter intermolecular distances; there are no strong intermolecular forces. Molecules

Table 2. *Equations of the least-squares planes through various groups of atoms and the displacements of atoms from these planes*

(a) Parameters of the plane equations in the form $AX + BY + CZ = 1$; X, Y and Z are orthogonal coordinates in Å related to the triclinic cell by the transformations $X = xa \sin \beta \sin \gamma^*$, $Y = -xa \sin \beta \cos \gamma^* + yb \sin \alpha$, $Z = xa \cos \beta + yb \cos \alpha + zc$.

Plane I through C(1'), C(2'), C(3'), C(4'), C(5') and C(6')
$$-0.1890X + 0.6683Y + 0.9368Z = 1$$
Plane II through N(1), N(2), N(3), C(4), C(9) and C(10)
$$0.5288X + 0.0962Y - 0.6217Z = 1$$
Plane III through C(5), C(6), C(7), C(8), C(9) and C(10)
$$0.6038X + 0.0884Y - 0.7757Z = 1$$

(b) Displacements (Å) from the planes. Atoms not included in derivation of the planes are italicized.

Plane I		Plane II		Plane III	
C(1')	−0·021	N(1)	−0·008	C(4)	−0·187
C(2')	0·002	N(2)	0·000	C(5)	0·000
C(3')	−0·021	N(3)	−0·004	C(6)	0·017
C(4')	0·004	C(4)	−0·048	C(7)	−0·006
C(5')	0·002	C(9)	−0·030	C(8)	0·023
C(6')	0·007	C(10)	0·081	C(9)	−0·015
		O(1)	−0·034	C(10)	−0·020
				N(1)	0·002
				N(2)	−0·031
				N(3)	−0·106
				O(1)	−0·250

Table 3. *Bond lengths (Å) (e.s.d.'s in parentheses)*

C(1')−C(2')	1·388 (17)	C(10)−C(5)	1·418 (17)
C(2')−C(3')	1·404 (17)	C(5)−C(6)	1·390 (20)
C(3')−C(4')	1·362 (17)	C(6)−C(7)	1·373 (20)
C(4')−C(5')	1·389 (18)	C(7)−C(8)	1·396 (19)
C(5')−C(6')	1·415 (18)	C(8)−C(9)	1·392 (19)
C(6')−C(1')	1·374 (17)	C(9)−C(10)	1·435 (16)
C(1')−N(2)	1·465 (15)	C(9)−N(1)	1·371 (15)
N(1)−N(2)	1·293 (13)	C(4)−O(1)	1·209 (16)
N(2)−N(3)	1·337 (13)	C(2')−Br(2)	1·874 (12)
N(3)−C(4)	1·397 (15)	C(4')−Br(1)	1·890 (13)
C(4)−C(10)	1·429 (16)		

Table 4. *Bond angles (°) (e.s.d.'s in parentheses)*

C(1')−C(2')−C(3')	118·4 (1·1)	C(5)−C(6)−C(7)	121·1 (1·3)
C(2')−C(3')−C(4')	119·4 (1·1)	C(6)−C(7)−C(8)	121·7 (1·3)
C(3')−C(4')−C(5')	112·7 (1·2)	C(7)−C(8)−C(9)	118·3 (1·2)
C(4')−C(5')−C(6')	118·0 (1·2)	C(8)−C(9)−C(10)	121·3 (1·1)
C(5')−C(6')−C(1')	118·9 (1·1)	C(9)−C(10)−C(5)	117·9 (1·0)
C(6')−C(1')−C(2')	122·4 (1·1)	C(9)−C(10)−C(4)	119·5 (1·0)
C(6')−C(1')−N(2)	114·8 (1·1)	C(10)−C(9)−N(1)	118·1 (1·0)
C(1')−N(2)−N(3)	116·2 (0·9)	C(9)−N(1)−N(2)	118·0 (1·0)
N(1)−N(2)−N(3)	132·0 (0·9)	N(3)−C(4)−O(1)	115·7 (1·1)
N(2)−N(3)−C(4)	113·5 (1·0)	C(1')−C(2')−Br(2)	124·8 (1·0)
N(3)−C(4)−C(10)	120·9 (1·0)	C(3')−C(4')−Br(1)	116·6 (1·0)
C(10)−C(5)−C(6)	119·6 (1·2)		

are stacked on top of one another along **c** in parallel orientations so that every atom is separated in this direction from identical atoms at distances of 4·04 Å.

It is clear from the well-resolved atoms in the Fourier maps, from the final value of the R index and from the unexceptionable bond lengths, bond angles and intermolecular contacts, that the structure has been correctly determined and that it is consistent with Fig. 1(*b*), which includes a six-membered dipolar ring containing three N atoms. The unlikely structure of Fig. 1(*a*) (Chattaway & Walker, 1925, 1927) is ruled out by the observed N(1)–N(3) distance of 2·4318 (14) Å and the structure of Fig. 1(*c*) is quite different from the observed stereochemistry of the molecule.

A Fourier projection down the short axis of the orthorhombic form of the crystals shows two non-equivalent molecules with similar structures to that found for the triclinic crystals and confirms that the N atoms are incorporated in a six-membered ring.

Fig. 2. Structure of 2-(2,4-dibromophenyl)-4-oxo-1,2,3-benzo-triazin-2-ium-3-ide viewed along **c**.

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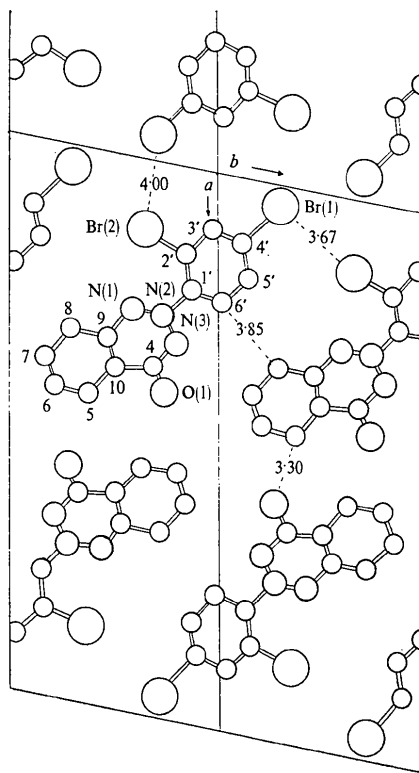McKILLOP, A. & KOBYLECKI, R. J. (1974). *J. Org. Chem.* **39**, 2710–2714.