

ring has an extremely distorted boat conformation as shown in Fig. 2 and Table 3. The ring consists of three parts: the two C—C double bonds [C(4)—C(5), C(6)—C(7)] connected by the single bond [C(5)—C(6)], the amide group [N(1),C(1)], and the two singly bonded C atoms [C(2),C(3)] with tetrahedral configurations. The H(1) and H(2) atoms attached to C(3) are in *gauche* positions with respect to C(8) and H(C2) respectively, and the cyano group [C(8),N(2)] is in the equatorial position of the ring.

The ring itself has some interesting and unusual features in its molecular geometry: the single bond C(5)—C(6) is fairly short (1.44 Å), indicating some conjugation with the adjacent double bonds in this part of the molecule. But the large torsion angle (49°) of C(4)—C(5)—C(6)—C(7) (Table 4), prevents the conjugation to some extent. Moreover, the bond angles in

this part are remarkably large (*ca* 130°) and also the C(6)—C(7) double bond is fairly short (1.30 Å). This unusual bonding behavior due to the large strain of the azocine ring is consistent with the fact that this compound is not subject to either Diels—Alder addition or bromination of the C(3) position by *N*-bromosuccinimide, which is characteristic of an ordinary conjugated C—C double bond (Paquette, 1964).

On the basis of the large torsion angle (51°) observed for C(6)—C(7)—N(1)—C(1) and fairly short N(1)—C(1) bond length (1.35 Å), it seems likely that the lone-pair electrons of N(1) are strongly conjugated with the carbonyl group but not with the C(6)—C(7) double bond. In other words, N(1) should be considered as a part of an amide group rather than that of an enamine group. In fact, a strong IR absorption band was observed in the region characteristic of amide groups.

Table 4. Torsion angles (°) of the ring

N(1)—C(1)—C(2)—C(3)	101
C(1)—C(2)—C(3)—C(4)	-112
C(2)—C(3)—C(4)—C(5)	13
C(3)—C(4)—C(5)—C(6)	-7
C(4)—C(5)—C(6)—C(7)	-49
C(5)—C(6)—C(7)—N(1)	7
C(6)—C(7)—N(1)—C(1)	51
C(7)—N(1)—C(1)—C(2)	5

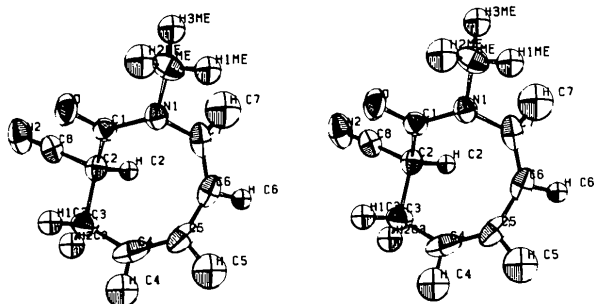


Fig. 2. A stereoview of the molecular conformation drawn with the program ORTEP (Johnson, 1965).

The authors are grateful to Assistant Professor Shigeaki Kawano of Kyushu University for the use of the crystallographic programs.

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Acta Cryst. (1979). **B35**, 780–783

Neutron Diffraction Study of Diaquaxonium 2,5-Dibromobenzenesulphonate*

BY JAN-OLOF LUNDGREN

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

(Received 11 November 1978; accepted 6 December 1978)

Abstract. [H₂O]₂[C₆H₃Br₂SO₃], monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 7.040 (2), *b* = 7.656 (1), *c* = 22.157 (2) Å, β = 96.73 (2)° [Lundgren (1972). *Acta Cryst.* **B28**, 475–

481]. Neutron wavelength 1.210 Å, μ(measured) = 0.083 mm⁻¹. Intensities were recorded at 294 K. The H₂O₂⁺ complex consists of an H₃O⁺ ion hydrogen bonded to two water molecules. The central H₃O⁺ ion is disordered, with two probable O atom positions separated by 0.68 Å. H atom positions associated with

* Hydrogen Bond Studies. CXXXVI. Part CXXXV: Nahrungsbauer, Lundgren & Andersen (1979).

one or other of the disordered H_3O^+ ions cannot be separated. The $\text{H}_3\text{O}^+\cdots\text{H}_2\text{O}$ distances are 2.43 (1)–2.53 (1) Å for the disordered model and 2.454 (5) and 2.483 (6) Å for an ordered model.

Introduction. The present investigation was undertaken to study the hydrated-proton complex in the trihydrate of 2,5-dibromobenzenesulphonic acid. The structure has been determined from X-ray data (Lundgren, 1972). The H atoms were not located in the X-ray study and the formulation H_7O_3^+ for the proton-water complex was inferred from bond distances and angles involving only non-hydrogen atoms. Neutron diffraction studies of structures where the proton-water complex H_7O_3^+ is described in terms of a diaqua-oxonium ion, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$, and an aquadiaqua-hydrogen ion, $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})$, respectively, were reported for 2,5-dichlorobenzenesulphonic acid trihydrate by Rozière & Williams (1978) and *o*-sulphobenzoic acid trihydrate by Attig & Williams (1976).

Well-shaped large crystals of the trihydrate of $\text{C}_6\text{H}_3\text{Br}_2\text{SO}_3\text{H}$ were grown from water. A parallelepiped with volume 33.2 mm³ was chosen for the data collection. The intensities for 2519 independent reflexions up to $\sin \theta/\lambda = 0.67 \text{ \AA}^{-1}$ were recorded at 294 K with an ω - 2θ step-scan technique on a Hilger & Watts computer-controlled four-circle diffractometer at the Swedish Atomic Energy R2 Reactor at Studsvik. Three test reflexions were monitored regularly, but no systematic changes in their intensities were observed. The data were corrected for Lorentz and absorption effects. The absorption correction was made by the Gaussian quadrature method with a $6 \times 4 \times 4$ grid. The transmission factors were in the range 0.779–0.831. Variances assigned to the intensities were $\sigma^2(I) = \sigma_c^2(I) + 0.0004I^2$, where σ_c^2 is based on Poisson counting statistics.

The H atoms were located from a difference synthesis based on non-hydrogen parameters from the X-ray study. Least-squares refinement minimizing $\sum w(F_o^2 - F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$, included 227 parameters: one scale factor, an isotropic extinction parameter, positional and anisotropic thermal parameters for the 25 independent atoms.

Nine strong low-order reflexions, for each of which the intensity loss due to extinction was more than 50%, were given zero weight. Refinement including 2188 reflexions with $F_o^2 > 0$ gave $R(F^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2 = 0.087$ and $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2} = 0.087$. An anisotropic extinction model, mosaic-spread dominated, type I (Coppens & Hamilton, 1970), gave $R = 0.084$ and $R_w = 0.084$. This model appreciably improved the fit for the extinction-affected reflexions as was shown in a δR plot (Abrahams & Keve, 1971) of the 280 data with extinction intensity losses >15%. Very large anisotropy of the thermal motion of the O atom of H_3O^+ indicated some type of disorder. Refine-

ment including two half O atoms with anisotropic thermal parameters was therefore carried out. Other parameters were not varied. The R values were $R = 0.079$ and $R_w = 0.079$. The standard deviation of an observation of unit weight, S , was 1.08. The coherent scattering amplitudes were those given by Bacon (1972). Final positional and thermal parameters are given in Table 1.* The programs used for all calculations on IBM 370/155 and IBM 1800 computers have been described by Lundgren (1976).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34138 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$)

O($w2'$) and O($w2''$) are the atoms in the disordered model.

	<i>x</i>	<i>y</i>	<i>z</i>
Br(1)	3074 (4)	2558 (3)	948 (1)
Br(2)	1979 (4)	558 (3)	4200 (1)
S	3354 (7)	3355 (6)	6511 (2)
O(1)	3470 (5)	1470 (3)	6575 (1)
O(2)	5181 (4)	4208 (4)	6707 (1)
O(3)	1790 (4)	4107 (3)	6789 (1)
C(1)	2884 (3)	3728 (2)	5719 (1)
C(2)	2753 (3)	5403 (2)	5470 (1)
C(3)	2378 (4)	5627 (3)	4844 (1)
C(4)	2134 (4)	4175 (3)	4461 (1)
C(5)	2277 (3)	2522 (3)	4716 (1)
C(6)	2645 (3)	2278 (3)	5336 (1)
O($w1$)	1594 (6)	-2202 (4)	3208 (1)
O($w2$)	2206 (9)	122 (5)	2473 (2)
O($w3$)	2512 (7)	3271 (4)	2667 (2)
H(3)	2271 (10)	6945 (4)	4659 (3)
H(4)	1815 (10)	4344 (8)	3978 (2)
H(6)	2764 (8)	981 (5)	5529 (2)
H(11)	2661 (9)	7017 (7)	3253 (2)
H(12)	440 (8)	7131 (7)	3178 (2)
H(21)	2778 (10)	9593 (7)	2130 (3)
H(22)	1919 (9)	9233 (7)	2791 (3)
H(23)	2408 (9)	1403 (8)	2563 (3)
H(31)	3548 (11)	3808 (9)	2913 (3)
H(32)	2205 (10)	4038 (8)	2340 (3)
O($w2'$)	2718 (13)	128 (12)	2554 (4)
O($w2''$)	1808 (11)	127 (12)	2411 (4)

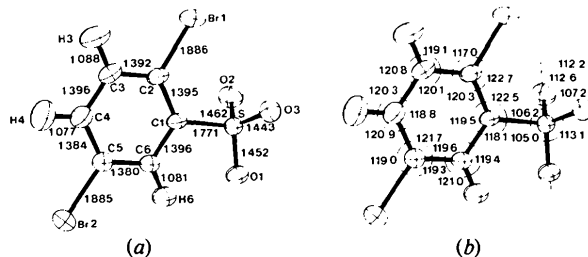


Fig. 1. (a) Bond distances (Å) and (b) angles (°) in the 2,5-dibromobenzenesulphonate ion. E.s.d.'s of C-C and C-Br bonds are 0.003 Å and for other bonds 0.005 Å. E.s.d.'s of angles involving H or O are 0.3–0.4° and of other angles 0.2°. Thermal ellipsoids are scaled to enclose 50% probability.

Discussion. No significant differences in atomic positions for the non-hydrogen atoms from the present and the X-ray study were found. The thermal parameters were also the same except the U_{11} components which were all 1.5 times larger in the X-ray case where the crystal was mounted about **a**. This type of systematic error in two-circle diffractometer data is often observed when no experimental interlayer scaling has been made. Interatomic distances and angles in the 2,5-dibromobenzenesulphonate ion are shown in Fig. 1. The geometry of the anion and the molecular packing were discussed by Lundgren (1972).

A proton-water complex with the empirical formula $H_7O_3^+$ may be described as the dihydrate of an oxonium ion, $H_3O^+(H_2O)_2$, or as the monohydrate of a diaqua-hydrogen ion, $H_5O_2^+(H_2O)$ (e.g. Lundgren & Olovsson, 1976). In the present case the complex is clearly an

oxonium dihydrate (Fig. 2) because the central H_3O^+ ion is hydrogen bonded to two water molecules by two equally short 2.45–2.50 Å bonds. The third hydrogen bond involving H_3O^+ is a 2.58 Å bond to a sulphonate O atom. The water molecules are also hydrogen bonded to sulphonate O atoms. No hydrogen bond exists between different $H_7O_3^+$ complexes. Bond distances and angles involving the H atoms in the $H_7O_3^+$ complex as obtained from the ordered model are listed in Table 2.

The most striking feature of the $H_7O_3^+$ complex obtained from the ordered model is the very large anisotropy of the O atom in the H_3O^+ ion. The r.m.s. components of thermal vibration along the ellipsoid axes are 0.192 (1), 0.222 (1) and 0.481 (1) Å. The largest component is along a perpendicular to the H_3O^+ ion. This large anisotropy and the flatness of the H_3O^+ ion – the distance from O(w2) to the plane through H(21), H(22) and H(23) is 0.1 Å, compared to the value 0.3 Å observed for H_3O^+ in oxonium *p*-toluenesulphonate (Lundgren & Williams, 1973) and oxonium trifluoromethanesulphonate (Lundgren, Tellgren & Olovsson, 1978) – suggest some type of inversional disorder for the H_3O^+ ion. A refinement including two half O atoms converged to give a 0.680 (12) Å separation between the half O positions. The hypothesis that this disordered model is not significantly better than the ordered model can be rejected at the 0.001 significance level (Hamilton, 1965). There is no reason to believe that the positions of the H atoms belonging to these half-oxonium ions are the same and equal to the positions obtained for the ordered model. However, the resolution of the neutron data does not allow the refinement of separate H positions. The water molecules may also have slightly different positions in the two cases. The geometries of the water molecules obtained in the ordered model are quite normal, however (Table 2). The $H_3O^+ \cdots O$ distances for the disordered H_3O^+ ions are 2.599 (9), 2.484 (9), 2.426 (10) and 2.609 (9), 2.525 (9), 2.509 (10) Å for O = O(1), O(w1) and O(w3), respectively. Whether the disorder is dynamic, involving the inversion of the H_3O^+ ion, or static, corresponding to random stacking of two different $H_7O_3^+$ units, cannot be determined from the present data.

The same type of disorder is probably present in $[H_7O_3]^+[C_6H_3Cl_2SO_3]^-$ (Rozière & Williams, 1978). These two compounds are, however, not isostructural.

This work has been supported by grants from the Swedish Natural Science Research Council, which are gratefully acknowledged.

Table 2. Hydrogen-bond distances (Å) and angles (°)

Distances and angles refer to the ordered model (see text). The distances and angles involving $H_3O^+(w2)$ give only approximate values for the distances and angles for the disordered H_3O^+ ions. The formal e.s.d.'s of the values in the table are the same as for $H_2O(w1)$ and $H_2O(w3)$.

X	H	Y	X–H	H...Y	X...Y	X–H...Y
O(w1)	H(11)...	O(2)	0.956 (7)	1.779 (7)	2.730 (5)	172.3 (6)
O(w1)	H(12)...	O(3)	0.955 (7)	1.842 (6)	2.794 (5)	173.7 (5)
O(w2)	H(21)...	O(1)	0.99	1.60	2.58	172
O(w2)	H(22)...	O(w1)	1.02	1.47	2.48	174
O(w2)	H(23)...	O(w3)	1.01	1.45	2.45	175
O(w3)	H(31)...	O(2)	0.939 (7)	1.908 (7)	2.785 (5)	152.3 (7)
O(w3)	H(32)...	O(3)	0.951 (8)	1.872 (7)	2.800 (5)	169.1 (6)
H(11)–O(w1)–H(12)			108.9 (6)	H(21)–O(w2)–H(22)		113
H(31)–O(w3)–H(32)			105.3 (7)	H(21)–O(w2)–H(23)		119
				H(22)–O(w2)–H(23)		123

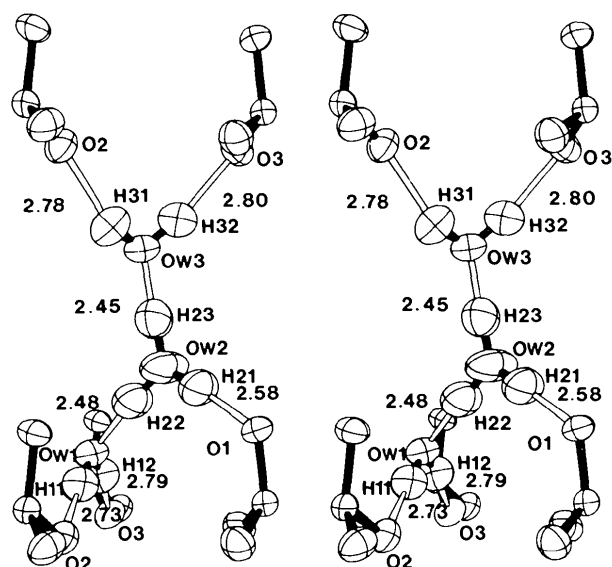


Fig. 2. Stereoscopic ORTEP drawing (Johnson, 1965) of the $H_7O_3^+$ complex. Thermal ellipsoids are scaled to enclose 50% probability. The position of the O(w2) atom obtained from the ordered model is shown in the figure.

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Acta Cryst. (1979). **B35**, 783–785

1-(4-Chlorophenyl)-2-morpholino-2-thioethanone

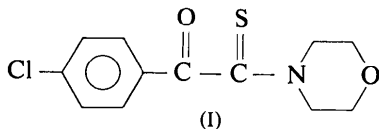
BY K. ANN KERR* AND J. H. G. VAN ROODE†

Departments of Chemistry and Physics, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

(Received 28 July 1978; accepted 5 December 1978)

Abstract. $C_{12}H_{12}ClNO_2S$, orthorhombic, $Pn2_1a$, $a = 7.3211$ (9), $b = 11.315$ (2), $c = 15.336$ (2) Å, $Z = 4$, $D_c = 1.410$ Mg m $^{-3}$. The molecule consists of two independent π systems with an O–C(2)–C(1)–S torsion angle of 92°. This lack of conjugation across the C(1)–C(2) bond is consistent with the high barrier to rotation about the C–N bond reported in NMR studies.

Introduction. The high barrier to rotation about the C–N bond in thioamides is generally attributed to participation of the N lone pair in the π system of the thiono group. Groups capable of conjugation with the thiono group can reduce this barrier (Sandström, 1967; Brown & Katekar, 1969). For example, the activation energy for rotation in *N,N*-dimethylthioacetamide is 183 kJ mol $^{-1}$ (Neuman & Young, 1965) compared with 64.4 kJ mol $^{-1}$ in *N,N*-dimethylthiobenzamide ($T_c = 356$ K) (Schwenker & Rosswag, 1967). The coalescence temperature for the title compound (I) is above 443 K (Krueger & Fulea, 1975), implying that the rotational barrier in this compound is among the highest so far observed. The X-ray study was undertaken to explain this apparent anomaly.



* To whom correspondence should be addressed.

† Present address: Department of Chemistry, Memorial University of Newfoundland, Cornerbrook, Newfoundland.

The title compound was obtained from benzene as yellow crystals. The specimen used for analysis was approximately 0.22 mm on each side and was cut from a larger crystal. Intensity data were collected on a Picker FACS I diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), the θ – 2θ scan mode, a scan range of $\Delta 2\theta = (1.7 + 0.285 \tan \theta)^\circ$ and a scan of 1° min^{-1} . Background was measured for 40 s at either end of the scan. Both hkl and $hk\bar{l}$ reflections were measured to a maximum 2θ value of 100° . These were averaged to give 698 independent reflections of which 535 had intensities greater than $3\sigma(I)$, where $\sigma^2(I) = T + B + (0.02I)^2$. T is the total peak count and B is the background count normalized to the time interval of the scan. Reflections $0kl$, $k + l \neq 2n$ and $hk0$, $h \neq 2n$ were systematically absent, indicating space group $Pnma$ or $Pn2_1a$. The latter was chosen on the basis of intensity statistics. No absorption correction was made [$\mu(\text{Cu } K\alpha) = 4.06 \text{ mm}^{-1}$].

The structure was solved by direct methods and refined by least squares with the y coordinate of C(1) fixed. Owing to the small number of observed reflections, the refinement was performed in two large blocks, with parameters of the 4-chlorobenzoyl group in one block and those of the thiono group and the morpholine ring in the other block. The scale factor and the parameters of C(1) and C(2) were included in both blocks. Extinction was not included and unit weights were used throughout. H atoms were located in difference maps and included in the model but were not refined. The final conventional R value was 0.0387 for the 535 observed reflections and 0.0632 for the full