Acta Cryst. (1975). **B31**, 2727

2-Bromo-4,6-dinitrophenol

By R. J. Neustadt and F. W. Cagle Jr

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, *U.S.A.*

(*Received* 13 *May* 1975; *accepted* 18 *June* 1975)

Abstract. $C_6H_3N_2O_5Br$, monoclinic, space group $P2_1/c$, $a=5{\cdot}9319$ (6), $b=9{\cdot}6849$ (9), $c=14{\cdot}9813$ (15) Å, $\beta=98{\cdot}668$ (8)° (23 ± 1 °C), $D_m=2{\cdot}025$ g cm^{-3}, $D_x=2{\cdot}0532$ (3) g cm^{-3} ($Z=4$). This compound was prepared by nitration and rearrangement from 4-bromophenol using the procedure of Van Erp (*Rec. Trav. chim. Pays-Bas* (1910). **29**, 187–237). Orange yellow crystals, m.p. 116–118 °C, were grown from methanol.

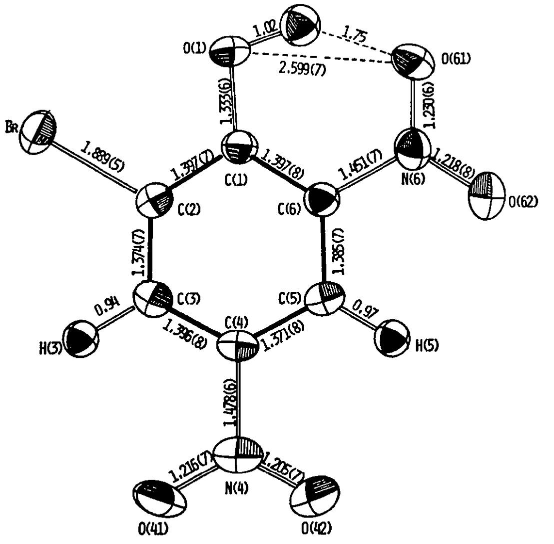

Fig. 1. 2-Bromo-4,6-dinitrophenol (33 % probability ellipsoids) viewed normal to the benzene ring. Bond lengths (Å) with e.s.d.'s. The estimated error for bonds to H atoms is ± 0·05 Å.

Introduction. Cell parameter and intensity data were obtained on a Syntex $P\bar{1}$ autodiffractometer. Mo $K\alpha$ radiation (0·710688 Å) was used, with a graphite monochromator. A scintillation counter was used to record the data. Coincidence corrections were made. The unit-cell parameters were determined by least-squares refinement from 15 reflections $16° < 2\theta < 43°$. The crystal used for intensity measurements was carefully shaped to the form of a sphere 0·12 mm in radius. Intensity data were measured with a θ–2θ scan of 2°. Absorption corrections [μ(Mo) = 52·1 cm^{-1}] were applied for the spherical shape. Check reflections showed no appreciable loss of intensity during data collection. There were 1965 unique reflections ($2\theta < 55°$) in one quadrant of the Ewald sphere. Of these, 118 were systematically extinct, $0k0$ with $k=2n+1$, and $h0l$ with $l=2n+1$. The preliminary crystallographic examination and space group choice were made using film data (Cu $K\alpha$ radiation) from the Weissenberg goniometer. This structure was determined by the heavy-atom method. Block-diagonal least-squares refinement gave a final residual index ($R=\sum||F_o|-|F_c||/\sum|F_o|$) of 0·050 (all unique reflections which were not systematically extinct). The residual index calculated for the 1287 reflections with $I>3\sigma(I)$ was 0·037. The quantity minimized was $\sum w(F_o-F_c)^2$ where $w=(14{\cdot}0+|F_o|+0{\cdot}005|F_o|^2)^{-1}$ (Cruickshank, 1970). Values of the atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962). The scattering factor for Br was corrected for anomalous dispersion. Bond lengths are shown in Fig. 1 and bond angles in Fig. 2. Data reduction and refinement were made with X-RAY

Table 1. *Atomic parameters in fractional coordinates and thermal parameters with e.s.d.'s* (× 10^4)

Temperature factor: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4494 (8)	7016 (6)	5307 (3)	203 (13)	92 (6)	34 (2)	−6 (7)	6 (4)	−3 (3)
C(2)	4611 (9)	6217 (5)	6089 (3)	229 (15)	83 (5)	30 (2)	−14 (7)	17 (4)	−5 (3)
C(3)	6352 (9)	6354 (6)	6801 (4)	237 (14)	86 (6)	37 (2)	22 (8)	20 (5)	−3 (3)
C(4)	8043 (9)	7328 (6)	6717 (3)	214 (14)	98 (6)	31 (2)	5 (8)	−1 (5)	−10 (3)
C(5)	8011 (8)	8158 (6)	5974 (4)	178 (13)	98 (6)	39 (2)	−14 (7)	10 (5)	−7 (3)
C(6)	6226 (9)	7983 (6)	5273 (4)	224 (14)	93 (6)	32 (2)	−4 (7)	10 (5)	−1 (3)
O(1)	2720 (8)	6814 (5)	4660 (3)	282 (14)	159 (7)	38 (2)	−69 (8)	−34 (4)	10 (3)
Br	2294 (1)	4902 (1)	6162 (1)	275 (2)	103 (1)	53 (1)	−43 (1)	29 (1)	0 (1)
N(4)	9916 (8)	7499 (5)	7479 (3)	249 (14)	143 (7)	40 (2)	11 (8)	−11 (4)	−13 (3)
O(41)	9823 (9)	6829 (6)	8160 (3)	406 (19)	222 (9)	35 (2)	−20 (10)	−25 (5)	9 (3)
O(42)	11453 (9)	8276 (6)	7388 (4)	341 (16)	174 (7)	71 (3)	−76 (9)	−53 (6)	6 (4)
N(6)	6201 (9)	8877 (6)	4495 (3)	276 (16)	125 (6)	38 (2)	−12 (8)	21 (5)	7 (3)
O(61)	4786 (8)	8662 (6)	3820 (3)	378 (16)	203 (8)	32 (2)	−63 (10)	−16 (4)	28 (3)
O(62)	7547 (10)	9833 (5)	4539 (4)	382 (18)	140 (7)	61 (3)	−54 (8)	30 (6)	18 (3)

Table 2. *Hydrogen positions in fractional coordinates* $(\times 10^3)$ *and isotropic temperature factors*

Temperature factor: $\exp[-B(\sin\theta/\lambda)^2]$.

The hydrogen atom positions were determined from a ΔF map and were not refined. The temperature factors were refined.

	x	y	z	B
H(1)	283	758	418	4·1
H(3)	642	570	740	3·0
H(5)	937	891	594	3·1

70 (Stewart, Kundell & Baldwin, 1970). Final parameters are given in Tables 1 and 2.*

Discussion. Andersen & Andersen (1975) have recently published the crystal and molecular structure of 2-chloro-4,6-dinitrophenol. Their compound crystallizes in the noncentrosymmetric space group $P2_12_12_1$. However, the molecular structures of the chloro compound and that reported in this paper are quite similar. In considering the structure reported here, it is instructive to examine the resonance hybrid shown in Fig. 3. This is the *ortho* analogue of a hybrid suggested by Hayes & Branch (1943) to account for the enhanced acidity of 4-nitrophenol. It should be noted that the C(1)–O(1) distance 1·333 (6) Å is shorter than the 1·37–1·38 Å values reported by Maartmann-Moe (1965) for the C–O distances in phloroglucinol. The C(6)–N(6) distance of 1·451 (7) Å is shorter than the C–N distances of 1·484 (8) and 1·487 (9) Å reported by Trotter & Williston (1966) for 1,3-dinitrobenzene. The C(4)–N(4) distance of 1·478 (6) Å is quite similar to the distances reported for 1,3-dinitrobenzene. The O(1)–O(61) distance of 2·599 (7) Å is within the usual range for hydrogen-bonded O atoms (Stout & Jensen, 1968). No C atom deviates significantly from the least-squares plane of the ring. The angle between the plane of O(41)–N(4) O(42) and the plane of the ring is 5·0°, while the angle between the plane of O(61)–N(6)–O(62) and the plane of the ring is 9·4°. The C(2)–C(3) bond is 1·9 σ shorter and the C(4)–C(5) bond is 2·0σ shorter than the average (1·387 Å) of the bond lengths in the phenol ring. Pearce & Simkins (1968) have reported the pK_a of 2·35 for 2-bromo-4,6-dinitrophenol. Figs. 1, 2 and 4 were drawn with *ORTEP* (Johnson, 1970).

The equipment used in this research was provided by the University of Utah Research Fund and by the National Science Foundation Science Development Grant GU 3866. Support was also received from PHS Grant No. RR07092. In addition we wish to thank Professor W. J. Horton for a discussion of the organic chemistry of this compound.

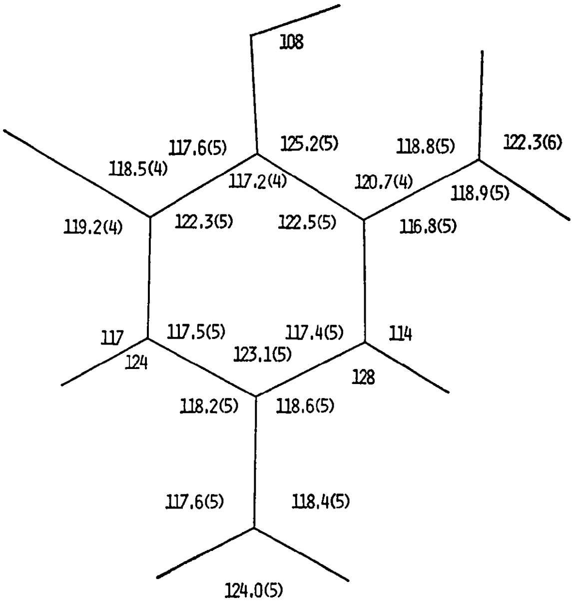

Fig. 2. Bond angles (°) with e.s.d.'s in 2-bromo-4,6-dinitrophenol. The estimated error for bonds to H atoms is ±5°.

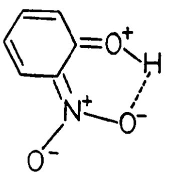

Fig. 3. A resonance hybrid of 2-nitrophenol.

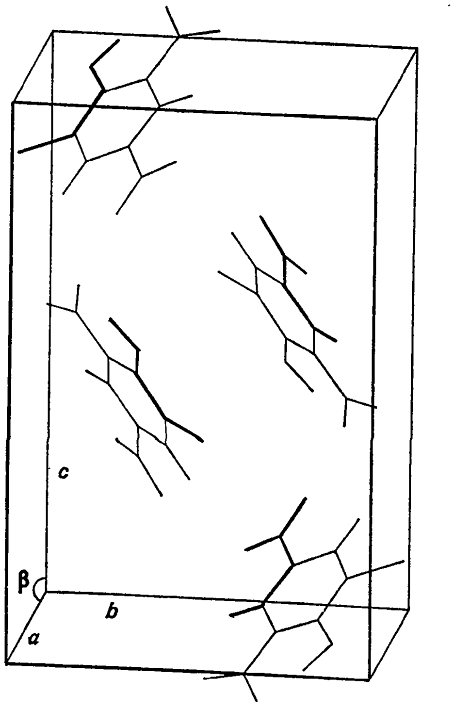

Fig. 4. Arrangement of molecules in the unit cell of 2-bromo-4,6-dinitrophenol.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31222 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Acta Cryst. (1975). B31, 2729

1-Benzothiepin 1,1-Dioxide

BY NORITAKE YASUOKA, YASUSHI KAI AND NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, 565, Japan

(*Received* 28 *May* 1975; *accepted* 27 *June* 1975)

Abstract. $C_{10}H_8O_2S$, monoclinic, $P2_1/n$ (No. 14), $a=7{\cdot}597$ (2), $b=17{\cdot}897$ (4), $c=6{\cdot}855$ (2) Å, $\beta=108{\cdot}84$ (1)° [λ(Mo $K\alpha_1$) $=0{\cdot}70926$ Å], $Z=4$, $D_c=1{\cdot}45$ g cm^{-3}, F.W. 192·3, μ(Mo $K\alpha$) $=3{\cdot}2$ cm^{-1}. The thiepin ring takes a boat form and shows bond alternation, while the benzo ring maintains a conjugated structure.

Introduction. Crystals were supplied by Professor I. Murata and his co-workers at Osaka University. A crystal of approximate dimensions 0·2 × 0·2 × 0·3 mm was mounted on a Rigaku automated, four-circle, single-crystal diffractometer. The Rigaku soft-ware system for a FACOM-R-controlled diffractometer was used to find low-order reflexions and to calculate unit-cell parameters. The orientation and the unit-cell dimensions of the crystal were confirmed by a θ–2θ scan along several reciprocal lattice axes and a preliminary intensity data collection within a full sphere of a small radius in the reciprocal lattice. Systematic absences were: $h0l$, $h+l=2n+1$ and $0k0$, $k=2n+1$. The good quality of the crystal was established by an ω-scan of several reflexions. (These procedures show that intensity data can be collected without preliminary photographic investigation.)

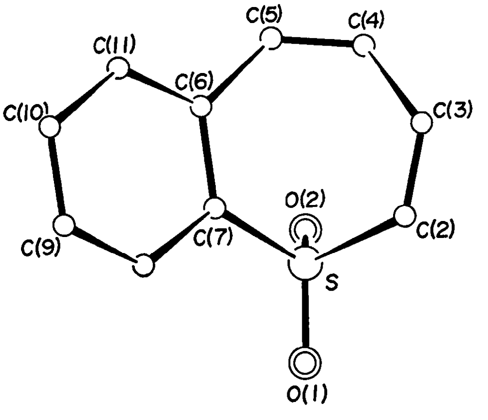

Fig. 1. The molecular structure of 1-benzothiepin 1,1-dioxide projected onto the plane passing through the atoms C(2), C(3), C(6) and C(7).

The θ–2θ scan technique was employed for data collection. The integrated intensity was determined by scanning over the peak at a rate of 4° min^{-1}, and subtracting the background obtained by averaging the two values measured for 5 s at both ends of a scan. The scan range in 2θ was from $-0{\cdot}9$° from the $K\alpha_1$ peak to 0·9° from the $K\alpha_2$ peak. 1548 unique reflexions were measured out to a 2θ (Mo $K\alpha_1$) value of 50°, and of these, 215 reflexions were less than $\sigma(F)$ and recorded as zero. Five standard reflexions were measured after every 59 reflexions; their intensities remained constant throughout the data collection. Graphite-monochromatized Mo $K\alpha$ radiation was used.

The heavy-atom method was used for the structure solution. The most plausible location of the sulphur atom was chosen by interpreting a three-dimensional Patterson map. Subsequent Fourier syntheses revealed all the non-hydrogen atoms. All the H atoms were located on a difference Fourier synthesis after anisotropic refinement of the model. The least-squares refinement was carried out with the *FMLS* program (Ashida, 1973). Atomic scattering factors for C, O and