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2,4-Dibromo-o-cresyl 3′,5′-dinitrosalicylate*

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Abstract. $C_{14}N_2O_7H_8Br_2$, orthorhombic, *Pbca*, $a = 9{\cdot}69$ (1), $b = 26{\cdot}32$ (2), $c = 12{\cdot}73$ (1) Å, $V = 3246{\cdot}7$ Å^3, F.W. 476, $Z = 8$, $D_c = 1{\cdot}947$, $D_o = 1{\cdot}935$ g cm^{-3}, λ (Cu $K\alpha$) = 1·5418 Å. The compound was supplied by Professor S. Swaminathan, University of Madras. The structure is stabilized by van der Waals contacts.

Introduction. The crystals in the form of thin needles were obtained by evaporation of an aqueous solution. The unit-cell data were obtained from precession photographs with Cu $K\alpha$ radiation. The space group is *Pbca* as deduced from systematic absences ($0kl$ absent with k odd, $h0l$ absent with l odd and $hk0$ absent with h odd) on Weissenberg photographs. Intensities were collected with Cu $K\alpha$ radiation by the equi-inclination multiple-film Weissenberg technique for layers hkl, $h = 0$ to 8 and $k = 0$ and 1. The intensities were visually estimated and corrected for Lorentz and polarization factors. Long exposures ranging from 100 to 200 h were necessary and reflexions with $\sin\theta > 0{\cdot}75$ could not be recorded. 985 reflexions had measurable intensity. No absorption correction was applied ($\mu t < 1$). The two sets of data were cross-correlated with 165 common reflexions (Rollett & Sparks, 1960).

The structure was determined by the heavy-atom method. Refinement was by block-diagonal and full-matrix least-squares calculations with anisotropic temperature factors for non-carbon and isotropic for C atoms. H atoms were ignored. Cruickshank, Bujosa, Lovell & Truter's (1961) weighting scheme of the type $w = (50 + |F_o| + 0{\cdot}0057|F_o|^2)^{-1}$ was used. The quantity minimized was $\sum w(|F_o| - k|F_c|)^2$. Several cycles of refinement were calculated on an IBM 360/44 with a block-diagonal program (Shiono, 1968), and the last cycle on an IBM 370 with a full-matrix program (Gantzel, Sparks & Trueblood, 1961). The final R was 0·104. The maximum parameter shifts in the last cycle were less than one tenth of their estimated standard deviations. The final goodness of fit, $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m is the number of observations and n the number of parameters refined, was 0·90. Scattering factors were from *International Tables for X-ray Crystallography* (1962). The corrections due to the anomalous dispersion ($\Delta f' = -1{\cdot}0$ and $\Delta f'' = 1{\cdot}4$ for Br, *International Tables for X-ray Crystallography*, 1962) were included. The final positional and thermal parameters are given in Table 1.*

Discussion. The bond distances and angles are shown in Fig. 1. The average standard deviation in C–C bonds is 0·04 Å and in the rest 0·037 Å; that in bond angles is 3°. The average C–C length within the phenyl rings is 1·37 Å. The dimensions of the two nitro groups are in agreement with those observed in other nitro compounds (Sutherland & Hogg, 1974). The average C–N and C–Br lengths are 1·49 and 1·88 Å respectively, in agreement with the standard values. The dimensions of the carboxyl moiety also conform with those observed in other structures (Kanters, Kroon, Peerdeman & Schoone, 1967). The C(1)–C(7) length of 1·66 Å is too long, but no significance can be attached to this in view of the limited accuracy of the structure determination.

Table 1. *Positional* (*fractional*) *parameters of non-hydrogen atoms with their standard deviations*

	x	y	z
Br(1)	−0·0611 (5)	0·0320 (2)	0·2322 (4)
Br(2)	0·2675 (4)	−0·1179 (1)	0·0437 (3)
N(1)	−0·0937 (22)	0·2656 (8)	−0·0444 (18)
N(2)	0·1118 (30)	0·3090 (9)	0·2901 (23)
O(1)	0·0909 (24)	0·0998 (7)	0·0826 (15)
O(2)	0·0484 (29)	0·3481 (8)	0·2864 (19)
O(3)	−0·1063 (25)	0·3098 (8)	−0·0584 (24)
O(4)	−0·1387 (22)	0·2326 (8)	−0·0987 (19)
O(5)	0·1952 (30)	0·3002 (9)	0·3596 (23)
O(6)	0·1928 (26)	0·2035 (8)	0·3136 (17)
O(7)	0·2050 (23)	0·1156 (8)	0·2319 (20)
C(1)	0·2450 (32)	0·0359 (10)	0·0058 (23)
C(2)	0·2829 (33)	−0·0143 (11)	0·0014 (24)
C(3)	0·2138 (33)	−0·0492 (11)	0·0646 (26)
C(4)	0·1165 (33)	−0·0383 (10)	0·1333 (25)
C(5)	0·0773 (35)	0·0145 (10)	0·1391 (25)
C(6)	0·1382 (35)	0·0489 (11)	0·0795 (25)
C(7)	0·3158 (21)	0·0806 (6)	−0·0694 (16)
C(8)	0·1329 (35)	0·1325 (10)	0·1610 (25)
C(9)	0·0838 (28)	0·1838 (9)	0·1491 (21)
C(10)	0·1201 (35)	0·2182 (11)	0·2307 (28)
C(11)	0·0753 (30)	0·2677 (9)	0·2164 (22)
C(12)	0·0123 (31)	0·2836 (11)	0·1291 (25)
C(13)	−0·0184 (28)	0·2499 (9)	0·0529 (22)
C(14)	0·0190 (32)	0·1986 (10)	0·0651 (25)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30941 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

Thermal parameters (× 10^4) are given by $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	175 (6)	31 (1)	126 (4)	9 (4)	49 (10)	−8 (3)
Br(2)	160 (5)	10 (0)	134 (4)	12 (3)	−48 (9)	−6 (2)
N(1)	104 (32)	12 (4)	41 (19)	4 (18)	−1 (48)	−1 (16)
N(2)	116 (39)	11 (4)	83 (24)	5 (22)	−30 (56)	−4 (16)
O(1)	174 (35)	13 (3)	60 (16)	15 (17)	−86 (43)	−25 (11)
O(2)	179 (38)	13 (3)	123 (26)	5 (21)	33 (6)	−2 (15)
O(3)	152 (34)	13 (3)	174 (31)	7 (18)	−25 (60)	20 (17)
O(4)	109 (30)	17 (4)	98 (22)	9 (18)	−90 (43)	7 (16)
O(5)	207 (43)	23 (5)	109 (27)	2 (24)	−100 (64)	−18 (18)
O(6)	204 (37)	16 (4)	58 (17)	18 (20)	−76 (44)	−20 (13)
O(7)	141 (30)	16 (3)	119 (23)	23 (18)	−158 (47)	−33 (16)

	B		*B*		*B*
C(1)	3·8 (6)	C(6)	4·3 (7)	C(11)	3·1 (5)
C(2)	4·2 (7)	C(7)	0·8 (4)	C(12)	3·7 (6)
C(3)	4·2 (7)	C(8)	3·7 (6)	C(13)	3·1 (5)
C(4)	4·2 (6)	C(9)	2·7 (5)	C(14)	3·6 (6)
C(5)	4·3 (7)	C(10)	4·4 (7)		

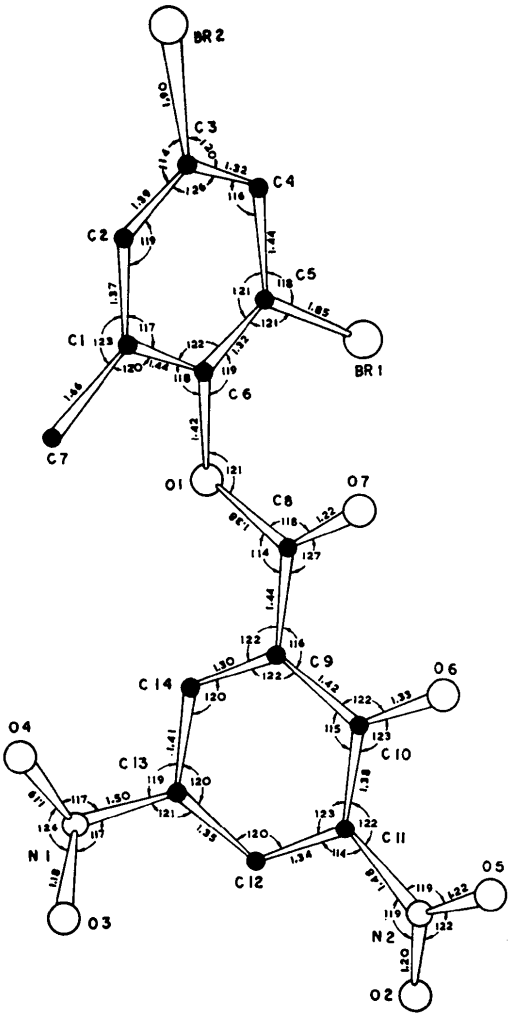

Fig. 1. Bond lengths (Å) and angles (°).

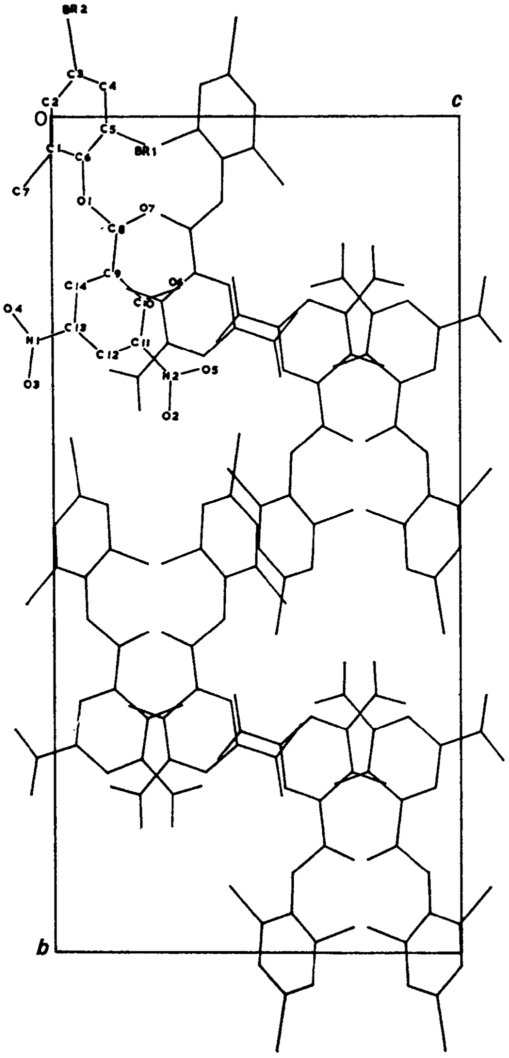

Fig. 2. Projection of the structure along the *a* axis.

Table 2. *Least-squares planes and atomic deviations* (Å)

Equation to the plane $AX+BY+CZ=D$ with respect to the crystallographic axes *a*, *b* and *c* where, X, Y, Z and D are in Å.

Carboxyl group

$0{\cdot}8194X+0{\cdot}2270Y-0{\cdot}5263Z=0{\cdot}7653$

C(9)	−0·0008
C(8)	0·0027
O(1)	−0·0008
O(7)	−0·0010

Benzene ring I

$0{\cdot}6873X+0{\cdot}1472Y+0{\cdot}7113Z=1{\cdot}8293$

C(1)	−0·0063
C(2)	0·0117
C(3)	−0·0114
C(4)	0·0050
C(5)	0·0005
C(6)	0·0003
Br(1)*	−0·0096
Br(2)*	−0·1093
C(7)*	−0·0425

Benzene ring II

$0{\cdot}8761X+0{\cdot}1965Y-0{\cdot}4403Z=0{\cdot}8338$

C(9)	−0·0077
C(10)	0·0209
C(11)	−0·0226
C(12)	0·0123
C(13)	0·0059
C(14)	−0·0103
N(1)*	−0·0066
N(2)*	0·0871
O(6)*	0·0978

* Atoms not included in the plane.

The equations for the best planes through the benzene rings and the carboxyl group are given in Table 2, with the deviations of individual atoms from these planes: All three are planar within experimental error. Br(1) is almost in the plane of ring I while Br(2) is 0·11 Å out of the plane. The angles between the carboxyl group and rings I and II are 77° and 6° respectively. The distance between O(7) and O(6) is 2·54 Å, less than the sum of their van der Waals radii, owing to the fact that the angle of rotation about C(8)–C(9) is small. The angles between the two nitro groups and ring II are 12° [N(1)] and 24° [N(2)].

The packing projected down **a** is depicted in Fig. 2. The molecule runs along the longest axis. There are two short intermolecular contacts: $Br(2)\cdots O(4^{ii})$, 3·34, and $Br(1^{iii})\cdots O(7^{iv})$, 3·19 Å.

Symmetry code: (i) $x,1+y,z$; (ii) $\bar{x},1-y,\bar{z}$; (iii) $1+x,y,z$; (iv) $\frac{1}{2}+x,y,\frac{1}{2}-z$].

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Die Kristallstruktur von Dizirkondiorthophosphat

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(*Eingegangen am 7. Januar 1975; angenommen am 18. Februar 1975*)

Abstract. Dizirconium diorthophosphate, $Zr_2O(PO_4)_2$, orthorhombic, *Cmca*, $a=6{\cdot}624$ (1), $b=8{\cdot}637$ (2), $c=11{\cdot}872$ (2) Å, $V=679{\cdot}2$ (4) Å^3, $Z=4$, $D_x=3{\cdot}80$ g cm^{-3}. The ZrO_7 coordination polyhedron is a slightly distorted pentagonal bipyramid with a mean Zr–O distance of 2·143 Å. ZrO_7 polyhedra and PO_4 tetrahedra share edges to form infinite chains of composition $[ZrO_3PO_4]^{5-}$ along [100]. Individual chains form a three-dimensional array *via* common corners.

Einleitung. Die Verbindung Dizirkondiorthophosphat ist zuerst von Harrison, McKinstry & Hummel (1954) mit der Formel $(ZrO)_2P_2O_7$ beschrieben worden und nicht erst von Gebert & Flörke (1972). Einkristalle dieser Verbindung wurden von Gebert & Flörke (1972) beim Abkühlen einer Schmelze der Zusammensetzung ZrP_2O_7: $TiP_2O_7=50$: 50 Mol% erhalten, nachdem das Material sieben Tage lang in einem Platin-Tiegel bei 1580°C getempert worden war.

Für die Messung der Intensitätsdaten wurde ein quaderförmiger Einkristall mit den ungefähren Abmessungen 0,1 × 0,3 × 0,15 mm benutzt. Die Gitter-

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