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The Crystal Structures of 9-Dicyanomethylenefluorene Derivatives. III. 9-Dicyanomethylene-2,7-dibromofluorene

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Abstract. $C_{16}H_6N_2Br_2$, monoclinic, $P2_1/c$, $a=11{\cdot}61$, $b=9{\cdot}49$, $c=12{\cdot}11$ Å, $\beta=92{\cdot}3°$ (based on $\lambda=0{\cdot}7107$ Å and with e.s.d.'s of 0·3%), $Z=4$, $D_m=1{\cdot}91_5$ (Berman balance) and $D_x=1{\cdot}923$ g cm^{-3}, synthesized by Dr T. K. Mukherjee (1969) of our laboratories. In an arrangement of parallel sheets, each molecule is linked to three others roughly coplanar to it by weak donor–acceptor interactions of 3·17 and 3·23 Å between the bromine atoms and the cyano nitrogen atoms.

Introduction. Multiple-film, equi-inclination Weissenberg camera photographs (Cu $K\alpha$ radiation) of levels $hk0$–$hk9$ were taken on a rhomb of dimensions 0·2 × 0·2 × 0·7 mm and interlevel scale factors were derived by least-squares calculations from duplicate reflections measured on precession camera photographs (Mo $K\alpha$ radiation) of levels $0kl$–$2kl$ and $h0l$–$h1l$. Systematic absences were observed for $h0l$ reflections with l odd and $0k0$ reflections with k odd. 1835 reflections (about 71·0% of the accessible total) were observed and 289 recorded as unobserved. The intensities, measured by densitometry, were corrected for Lorentz and polarization factors and also in the case of the Weissenberg data for cylindrical absorption (*International Tables for X-ray Crystallography*, 1959) and spot-shape effects (Phillips, 1954).

The structure was solved by the heavy-atom method from a Patterson map and refined by full-matrix least-squares calculations (Busing, Martin & Levy, 1962). In the final cycles of anisotropic refinement, the hydrogen atoms were introduced at idealized locations with fixed anisotropic thermal parameters 1·5 times those of their attached carbon atoms. Weights were applied according to the scheme (Hughes, 1941): $F_o \leq 8{\cdot}0$, $\sigma=1{\cdot}0$ and for $F_o > 8{\cdot}0$, $\sigma=[F_o^2/64]^{1/2}$. The refinement converged at $R=9{\cdot}3$% (7·9% for observed only) and $R_w=10{\cdot}5$%. Final parameters are listed in Table 1 and distances and angles of interest given in Fig. 1.*

Discussion. The structure determination of 9-dicyanomethylene-2,7-dibromofluorene (DBF) was undertaken as part of a continuing program relating electronic properties to molecular packing arrangements within a series of photoconductive derivatives of fluorene-$\Delta^{9\alpha}$-malononitrile (for parts I and II in the series, see Silverman, Krukonis & Yannoni, 1967, 1968).

Bond lengths and angles are normal and similar to those observed in 9-dicyanomethylene-2,7-dinitrofluorene (Silverman, Krukonis & Yannoni, 1968). However, the DBF molecule is surprisingly less planar than the dinitro-derivative despite their steric similarity. Least-squares calculations (Schomaker, Waser, Marsh & Bergman, 1959) indicate that the fluorene framework consists of two asymmetric fragments, each planar to ±0·019 Å. The two planes, *i.e.* benzenoid ring C(5)–C(8), C(12), C(13) and the two-ring fragment containing atoms C(1)–C(4), C(9)–C(13), are inclined at 1·4° to each other. The bromine atoms deviate by 0·06 [Br(1)] and −0·03 Å [Br(2)] from their attached planes. The plane through the dicyanomethylene group of atoms makes a dihedral angle of 5·8° with the overall fluorene ring plane. These molecular deformations leave the bromine atoms about 0·5 Å out of the plane of the dicyanomethylene group within the same molecule but result in each bromine atom being only 0·1 Å from the plane of the dicyanomethylene group to which it is weakly linked by intermolecular donor-acceptor interactions (see below). This feature and the lack of significant inherent intramolecular crowding suggest that the unexpected molecular distortions reflect the angular requirements of these interactions in combination with other packing forces.

The intermolecular packing scheme consists not of the herringbone arrangements found in the other 9-dicyanomethylene structures (parts I and II and unpublished results) but in networks of unidirectional parallel sheets, each coplanar to within ±0·5 Å. Those parallel molecules in neighboring sheets, which are related by the c-glide plane, overlap in projection in much the same way as do pairs in the corresponding 2,7-dinitro-derivative [Silverman *et al.* (1968); see Fig. 4(*a*)] with the bromine atoms 'replacing' the nitro groups. However the short C···C approaches between such pairs in the latter structure have no counterpart in the present one. Sheets are formed by weak donor–acceptor intermolecular Br···N linkages in which each molecule is coordinated to three others (Fig. 1). The close ap-

* The structure-factor list has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30127. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

proaches of 3·17, 3·23 Å, which are 0·2–0·3 Å shorter than the sum of the non-bonded radii, as well as the almost linear intermolecular C–Br···N angles, 167 and 172°, indicate a weak, self-complexing. The intermolecular 'bonding' is weaker than but presumably analogous to that found in the prototype chain-

Table 1. *Final fractional positional coordinates and thermal parameters with estimated standard deviations in parentheses*

The anisotropic temperature factor is of the form: $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.

(*a*) Non-hydrogen atoms ($\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	10054 (1)	3137 (1)	7329 (1)	73 (1)	137 (1)	63 (1)	−4 (1)	−9 (1)	−11 (1)
Br(2)	4717 (1)	2257 (1)	63 (1)	76 (1)	105 (1)	63 (1)	7 (1)	−12 (1)	2 (1)
N(1)	8617 (9)	−1544 (9)	5348 (8)	109 (9)	81 (10)	94 (9)	5 (8)	−35 (7)	8 (7)
N(2)	6770 (9)	−1782 (9)	2223 (8)	98 (8)	77 (9)	93 (9)	12 (7)	−6 (6)	−6 (7)
C(1)	8685 (9)	2109 (10)	5489 (9)	61 (8)	80 (10)	67 (9)	16 (7)	−4 (6)	6 (7)
C(2)	9075 (8)	3339 (10)	6031 (8)	65 (8)	102 (11)	44 (7)	−10 (7)	0 (5)	−12 (7)
C(3)	8806 (9)	4689 (10)	5667 (9)	63 (8)	77 (11)	77 (9)	−17 (7)	−7 (6)	−16 (7)
C(4)	8114 (8)	4849 (10)	4723 (9)	55 (7)	60 (10)	95 (10)	0 (6)	2 (6)	−10 (7)
C(5)	6530 (9)	4609 (9)	2437 (8)	76 (8)	60 (9)	63 (8)	2 (7)	−8 (6)	1 (6)
C(6)	5851 (9)	4201 (10)	1526 (9)	74 (8)	72 (11)	81 (10)	16 (7)	−5 (7)	16 (7)
C(7)	5669 (8)	2778 (10)	1331 (8)	57 (7)	94 (10)	47 (7)	8 (7)	−1 (5)	−3 (7)
C(8)	6157 (8)	1706 (9)	1963 (8)	57 (7)	70 (9)	58 (8)	−1 (6)	−3 (5)	9 (6)
C(9)	7472 (7)	1288 (9)	3743 (7)	52 (7)	67 (9)	42 (7)	−3 (6)	−6 (5)	8 (5)
C(10)	7989 (8)	2298 (9)	4532 (8)	59 (7)	53 (8)	66 (8)	−5 (6)	11 (5)	−2 (6)
C(11)	7709 (8)	3678 (9)	4157 (8)	56 (7)	60 (9)	67 (8)	3 (6)	1 (5)	6 (6)
C(12)	7003 (8)	3568 (9)	3134 (8)	56 (7)	65 (9)	53 (7)	−4 (6)	−2 (5)	0 (6)
C(13)	6832 (8)	2123 (9)	2879 (8)	45 (6)	60 (9)	70 (8)	0 (6)	11 (5)	−2 (6)
C(14)	7573 (8)	−158 (9)	3793 (8)	62 (8)	63 (10)	62 (8)	2 (6)	6 (6)	7 (6)
C(15)	8165 (8)	−905 (9)	4653 (8)	66 (8)	73 (10)	61 (8)	4 (7)	−7 (6)	−1 (7)
C(16)	7104 (8)	−1045 (9)	2923 (8)	57 (7)	58 (9)	67 (8)	6 (6)	−5 (5)	7 (7)

(*b*) Hydrogen atoms ($\times 10^3$)

H(1)	883 (11)	151 (14)	577 (11)	9	13	9	2	−1	0
H(3)	906 (11)	525 (15)	604 (11)	9	12	11	−2	−1	−2
H(4)	791 (10)	590 (12)	433 (11)	9	9	13	0	0	−1
H(5)	661 (11)	582 (12)	261 (10)	12	9	9	0	−1	1
H(6)	552 (11)	477 (15)	116 (11)	11	11	11	2	−1	2
H(8)	608 (10)	70 (13)	181 (9)	8	12	7	0	0	1

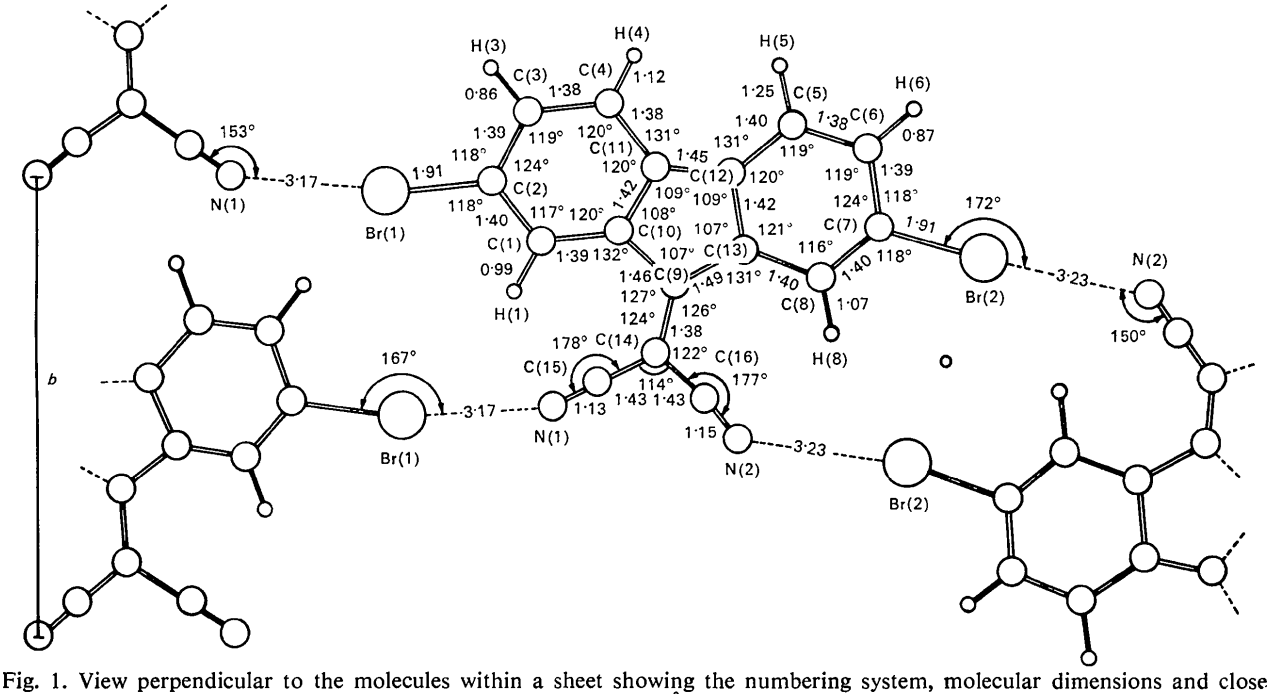

Fig. 1. View perpendicular to the molecules within a sheet showing the numbering system, molecular dimensions and close C–Br···N contacts. Typical standard deviations are ±0·013 Å and ±0·8° for bond lengths and angles respectively.

like structures of Br–C≡N (Geller & Schawlow, 1955) with Br···N = 2·87 Å and Br–C≡C–C≡N (Bjorvatten, 1968) with Br···N = 2·96 Å. Other examples of such weak Br···N interactions are found in: 2,4-dibromodiazoaminobenzene (Omel'Chanko & Kondrashev, 1966), Br···N = 3·22 Å, C–Br···N = 163°; bromotricyanomethane (Witt, Britton & Mahon, 1972) Br···N = 3·03 Å, C–Br···N = 163°; and 2,4,6-tribromobenzonitrile (Carter & Britton, 1972), Br···N = 3·06 Å, C–Br···N = 170° (angles computed from published coordinates).

References

BJORVATTEN, T. (1968). *Acta Chem. Scand.* **22**, 410–420.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CARTER, V. B. & BRITTON, D. (1972). *Acta Cryst.* B**28**, 945–950.

GELLER, S. & SCHAWLOW, A. C. (1955). *J. Chem. Phys.* **23**, 779–783.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.

International Tables for X-ray Crystallography (1959). Vol. II. p. 295. Birmingham: Kynoch Press.

MUKHERJEE, T. K. (1969). *J. Phys. Chem.* **73**, 4381–4382.

OMEL'CHANKO, YU. A. & KONDRASHEV, YU. D. (1966). *Sov. Phys. Crystallogr.* **10**, 690–693.

PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746–751.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1967). *Acta Cryst.* **23**, 1057–1063.

SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1968). *Acta Cryst.* B**24**, 1481–1488.

WITT, J. R., BRITTON, D. & MAHON, C. (1972). *Acta Cryst.* B**28**, 950–955.

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The Crystal Structure of Meionite

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Abstract. Meionite with cell formula $(Ca_{7\cdot32}Na_{0\cdot39}K_{0\cdot19}Fe_{0\cdot038}Mg_{0\cdot004}Sr_{0\cdot015})(Si_{12\cdot41}Al_{11\cdot33})O_{48\cdot51}[Cl_{0\cdot053}(SO_4)_{0\cdot053}(CO_3)_{1\cdot895}]$ is tetragonal, $P4_2/n$ rather than $I4/m$, $a = 12\cdot194$ (4), $c = 7\cdot557$ (4) Å, $D_x = 2\cdot78$ g cm^{-3}. This mineral is from Monte Somma, Italy. The structure is similar to that of marialite but with significant differences in atomic coordinates and Al site occupancies. The CO_3 groups are essentially disordered on the (001) plane and displaced from the site 0,0,0. The Ca ion is 8-coordinated rather than 6-coordinated.

Introduction. The intensities and cell dimensions were measured from a transparent, colourless crystal about 0·4 mm wide, using the integrating precession camera (Zr-filtered Mo $K\alpha$ radiation). 688 reflexions were collected, of which 166 had an intensity less than the minimum observable value and were assigned a value of $I_{min}/3$ (Hamilton, 1955). Lorentz and polarization corrections were applied. The systematic absences were hkl with $h+k+l$ odd, $hk0$ with $h+k$ odd and $00l$ with l odd. The apparent space groups is $I4/m$ but the most probable space group of this impure meionite should be $P4_2/n$ (Lin, 1971; Lin & Burley, 1971, 1973*b*). The trial-structure atomic parameters correspond to those of marialite (Lin & Burley, 1973*a*). Full-matrix least-square refinement with isotropic temperature factors and Cruickshank's weighting scheme gave a residual $[R = \sum(|F_o| - |F_c|)/\sum|F_o|]$ of 0·079 first based on $I4/m$ and 0·072 subsequently based on $P4_2/n$. Those unobserved reflexions consistent with $P4_2/n$ were given a much smaller weight inferred from the relationship between the intensity of $h+k+l$ odd reflexions and composition of scapolites (Lin & Burley 1971, 1973*b*). The refined parameters are listed in Table 1. A table of F_{cal} and F_{obs} values is obtainable.* The bond lengths and angles are in Tables 2 and 3.

Discussion. The structure is similar to that of marialite (Lin & Burley, 1973*a*) but some significant differences mainly arising from the chemical difference are observed. Ignoring the difference in z coordinates, the structure can be considered as being derived from the marialite structure by rotating (type 1) tetrahedra rings counter-clockwise while rotating (type 2) tetrahedra rings clockwise. Thus the oval-shaped cation channels relatively increase their long diameter and decrease the short one. This meionite is the most Ca, CO_3-rich scapolite found in nature. The role of the CO_3 group in this meionite is similar to that described in mizzonite (Papike & Stephenson, 1966). The CO_3 group is positionally disordered maily on the xy plane, though it could tilt slightly from this plane, as indicated by the very high thermal factor and z coordinates of O(7).

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30133 (11pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.