The Crystal Structures of Dicyanomethylenefluorene Derivatives. IV. 9-Dicyanomethylene-2,4,5,7-tetranitrofluorene

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9-Dicyanomethylene-2,4,5,7-tetranitrofluorene, $C_{16}H_4N_6O_8$, is orthorhombic with four molecules in the unit cell: $a = 11\cdot377$ (2), $b = 12\cdot213$ (7) and $c = 11\cdot943$ (3) Å. The crystal structure consists of almost parallel pairs of crystallographically independent molecules aligned in opposite sense along the twofold axes in the non-centrosymmetric space group *Pba*2. The structure was solved by direct methods. The final R values, $R = 0\cdot0496$, $R_w = 0\cdot042$, are from a least-squares refinement of the second of two available diffractometer data sets. Overcrowding between the 4,5 nitro groups is relieved by rotations ($\sim 35°$) and bends ($\sim 10°$) of these groups about the C–N bonds as well as by propeller-like deformations in the remaining molecular framework. When the present structure is compared with the previously reported 2,4,7-trinitro and the 2,7-dinitro derivatives, a proliferation and shortening of C$\cdots$O intermolecular contacts with increased nitro-group substitution is noted. These contacts and similar ones found in other structures are compared with carbonyl–carbonyl interactions.

Introduction

9-Dicyanomethylene-2,4,5,7-tetranitrofluorene (D4F) is the fourth structure determination completed of a series of derivatives of fluorene-$\Delta^{9\alpha}$-malononitrile synthesized by T. K. Mukherjee of our laboratories (see Silverman, Krukonis & Yannoni, 1967, 1968, 1973 for parts I, II and III). These materials are electron acceptors with potentially useful photoelectronic properties. Our aim is to investigate the relationships among the electronic effects, the molecular structure and details of the intermolecular packing.

Experimental

Crystal data

$C_{16}H_4N_6O_8$, F.W. 408·3, orthorhombic, $a = 11\cdot377$ (2), $b = 12\cdot213$ (7), $c = 11\cdot943$ (3) Å, $V = 1659\cdot4$ Å³ (with Cu radiation at ambient T, $\lambda(\alpha_1) = 1\cdot54051$, $\lambda(\alpha_2) = 1\cdot54434$ Å), $d_m = 1\cdot62$ g cm^{-3} (Berman balance with toluene), $d_x = 1\cdot634$ g cm^{-3} for $Z = 4$.

Extinctions: $0kl$ when k is odd, $h0l$ when h is odd, space group is *Pbam* (No. 55) ($M = 8$) or *Pba*2 (No. 32) ($M = 4$). Structure solved in *Pba*2 with two pairs of independent molecules each at twofold sites. Absorption coefficients for X-rays: Cu $K\alpha$ 13·60, Mo $K\alpha$ 1·68 cm^{-1}.

The single specimen used for all measurements was a pinacoidal prism with edge dimensions ranging roughly from 0·2 to 0·5 mm. Data taken with Cu radiation on a Supper–Pace equi-inclination diffractometer formed the basis of the reported cell parameter values, the structure solution, and the initial refinement. The cell parameters were derived from 53 values of 2θ in the range 121–143° as determined from carefully measured counter angle positions of both the α_1 and α_2 reflections which were then input into the

least-squares lattice refinement program of Williams (1964). When a Picker diffractometer subsequently became available, the D4F specimen was used as a test crystal and yielded improved refinement results (see below) and hence is reported here. Salient details on procedure include: automatic mode, $\theta/2\theta$ scan, graphite-monochromatized molybdenum radiation ($\lambda = 0\cdot70926$ Å), take-off angle of 2°, scan speed of 1° min^{-1} with total scan widths from 2·1 to 4·1°, left/right stationary background counts of 20 s. The three check reflections showed good stability. Standard deviations estimated from the scatter in their (32) repeated measurements agree well with the theoretical values computed from counting statistics augmented by an assumed instrumental instability of 1 %. About 500 out of 2000 independent reflections had intensities less than 2σ and were classified as 'less-thans'.

Structure solution

The presence of two pairs of crystallographically independent but almost parallel molecules of twofold symmetry aligned along the c axis in space group *Pba*2, was suggested (correctly) by packing considerations. The detailed structure, however, was revealed by acentric direct methods (Karle & Karle, 1966; Karle, 1968) using the programs *FAME, MAGIA* and *TANG* (Dewar, 1970). Since this appears to be the first reported direct-method solution in space group *Pba*2 [Karle & Karle (1970) have described a solution in *Aba*2] we describe the analysis in some detail.

The intensity statistics lie between the centric and acentric theoretical values reflecting the approximate center of symmetry which relates the independent molecules (see *Molecular structure*). Table 1 gives the starting set for the symbolic addition process. The 320 and the 10,2,8 represent two of the three available

Table 1. *Phases in degrees for the starting set at various stages of the direct-method analysis*

Initial value is in parentheses. See text for further description.

Reflection	E	Symbolic addition*	Recycled tangent input	Recycled tangent output	Final phase
3 2 0 (0°)	4·3	0°	0°	0°	0°
10 2 8 (90°)	3·2	178	197	214	209
2 2 0 (A)	2·2	0	0	0	0
9 3 7 (W)	2·4	178	168	197	168
12 3 4 (X)	2·7	179	252	215	220
8 6 1 (Y)	2·4	360	375	343	302
7 7 2 (Z)	2·6	360	318	340	331

* One of the redundant solutions transformed by origin shift along the c axis to reveal centric character.

origin choices; the third choice had to be postponed as no E's > 1.425 were found for reflections of $gu0$ parity. The starting set yielded symbolic phases for 360/400 reflections with $E > 1.08$ to within a variance of ≤ 0.35 rad². The several E maps were identical† except for origin shifts along the polar c axis and each had mirror symmetry perpendicular to the c axis, *i.e.* represented a centric structure in the higher space group, *Pbam* (No. 55). The fluorene moiety of one molecule in mirror image across a plane roughly through the atoms C(4), C(5), C(5') and C(4') (see Fig. 2) was clearly discernible in the E maps. The ordered form in *Pba2* of this partial structure was chosen from refinement comparisons in the two space groups and used to generate a recycled input of 119 phases into the tangent formula. The input phases obeyed the criteria $E > 1.5$, $F_c/F_o > 0.30$ (input fraction of structure) (Karle, 1968) and were reasonably consistent with their initial symbolic addition value. Expansion by means of the tangent formula produced a total of 318 phases. The resulting E map contained about 85% of the structure allowing the determination to be completed by standard means.

The phases at the various stages described above are presented in Table 1 for the starting set. That the symbolic addition process led to centric solutions is believed to reflect the pseudosymmetry in the structure and the possibly related fact that the final phases of the starting reflections deviate by 0, 29, 0, 12, 40, 58, and 29° respectively from 0 or π. A random sample of 50 reflections determined during the analysis shows an average phase error of 47° for the symbolic-addition

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† Algebraic analysis had yielded 16 combinations of symbol values which incorporated an equivalent best-fit to probable relationships between the symbols arising from phases determined by multiple interactions. The corresponding 16 phase sets were seen (partly in retrospect) to be equivalent origin related sets. A twofold redundancy was removed by fixing the postponed origin choice of a $gu0$ reflection leaving an eightfold redundancy in origin along the polar c axis associated with assigning an arbitrary phase to the 10 2 8 rather than to the preferred choice of an $l = 1$ reflection. After the centric character of the E maps was manifested, it was demonstrated that each could be reduced to the same approximate set of real phases by appropriate transformations in the polar origin.

phases which improves to 39° after tangent refinement of the recycled input.

Refinement

Refinement based on the Supper–Pace diffractometer data converged at $R = 5.5$, $R_w = 5.8\%$ for ~ 1500 reflections after hydrogen atoms were located on a difference map. While the results are in agreement in important dimensional and structural features with the later refinement, the presence of systematic error in the data is suggested by differences between the independent molecules notably in the five-membered rings (see below). Hence, the subsequently available data on the Picker FACS 1 was used for a second refinement, that reported here.

This was carried out within the X-RAY 70 program system (Stewart, Kundell & Baldwin, 1970) by full-matrix least-squares calculation. All scattering factors are from Hanson, Herman, Lea & Skillman (1964) except for hydrogen atom values which were taken from Stewart, Davidson & Simpson (1965). The theoretical diffractometer weights were modified empirically in final cycles in order to minimize $F_o - F_c$ trends with F or $\sin \theta$. With 284 variables and fixed isotropic thermal parameters for hydrogen atoms, the refinement was completed at $R = 0.0496$, $R_w = [\sum w(KF_o - |F_c|)^2 / \sum wK^2 F_c^2]^{1/2} = 0.0420$ (quantity of minimization) for the 1292 observed and $R = 0.144$ for the 492 'less-thans'. While the differences in parameter standard deviations are nominal, the superiority of the second refinement to the first is clearly indicated by the following comparison.

	Four-circle diffractometer	Equi-inclination diffractometer
R values	0·049	0·055
Final difference synthesis	Range from +0·205 to −0·26, 2 peaks > 0.2 e Å^{-3}	+0·32 to −0·38 23 peaks > 0.2 e Å^{-3}
C–H bond lengths	0·93–1·02 Å	0·80–1·07 Å
Bonds in central ring	1·462–1·487 Å	1·443–1·508 Å

The final reported parameters are listed in Table 2.*

Molecular structure

A stereo view (Johnson, 1965) of the crystallographically independent molecules designated† A and B is shown in Fig. 1 and bond dimensions and conformational features are shown in Fig. 2. To within experimental error there is generally good agreement be-

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* A list of structure amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30385 (13 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† An atom designation in the text without a following A or B indicates that the comment is equally applicable to either independent molecule. A numerical value along with a similar one in parentheses will refer to molecules A and B in turn.

tween the two independent molecules. A noteworthy feature is the bond length variation around the outer rings: in particular the sharp differences between the fused bond of 1·414 (1·408) Å and its opposite across the ring, 1·367 (1·357). Although thermal motion corrections have not been made, they would only mitigate these differences slightly. Similar variations are observed in D3F and D2F (see drawing) (Silverman et al., 1967, 1968) and as well in a molecule closely related to D3F, 2,4,7-trinitro-9-fluorenone (Dorset, Hybl & Ammon, 1972). Somewhat milder trends are also found in 9-fluorenone (Luss & Smith, 1972) where the fused bond is 1·390 and that opposite to it in the outer ring is the shortest at 1·376 (averages of two independent molecules). SCF–MO CI calculations of 9-fluorenone predict 1·409 and 1·396 for these two bonds – the longest and shortest in the outer ring (Kuroda & Kunii, 1967).
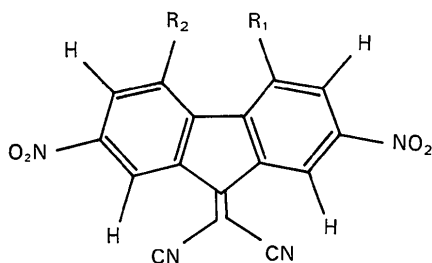
D2F: R₁ = R₂ = H
D3F: R₁ = H, R₂ = NO₂
D4F: R₁ = R₂ = NO₂ (present molecule)

The molecular conformation reflects the steric interaction between the twofold-related 4,5-nitro groups. Each independent molecule undergoes similar deformations in order to achieve 'clearance' for these groups. In addition to rotations of the nitro groups by $\sim 35°$ about the C–N bonds, further clearance is provided by: in-plane angular adjustments especially in exterior values at C(6) [134·9 (134·7)° in D4F, 130° in D2F]; out-of-plane distortions such as a bend at the C(1)–N(3) bond of 9·4 (10·2)°; and the propeller-shaped distortion in the fluorene moiety itself with a dihedral angle of 168 (169)° between twofold-related outer rings.

No part of the fluorene framework is strictly planar except possibly the group of 8 atoms C(4) C(5) C(7) C(8) C(9) C(4′) C(5′) C(9′), planar to within ± 0·020 (0·018) Å. The carbon skeleton has deviations of up to ± 0·18 Å. Each molecule has similar boat-shaped deviations from planarity in the range ± 0·03–0·04 Å in the outer rings (Table 3). However, the non-planarity in the fluorene skeleton consists largely of torsional deformations about the central ring bonds C(6)–C(6′) of 10·3 (9·8)° and about C(6)–C(5) of 9·0 (8·4)° [see Fig. 2(b)], leading to the deviations of ± 0·05 Å from the least-squares plane through the central ring and the propeller-shape of the molecule.

The only significant conformational difference between molecules A and B is found in the magnitude and opposite sense of the nitro group rotations about C(3)–N(2) of +9 and −16° [Fig. 2(b)]. The pseudo-center of symmetry which relates the two molecules is broken by this feature as well as by the relative sense
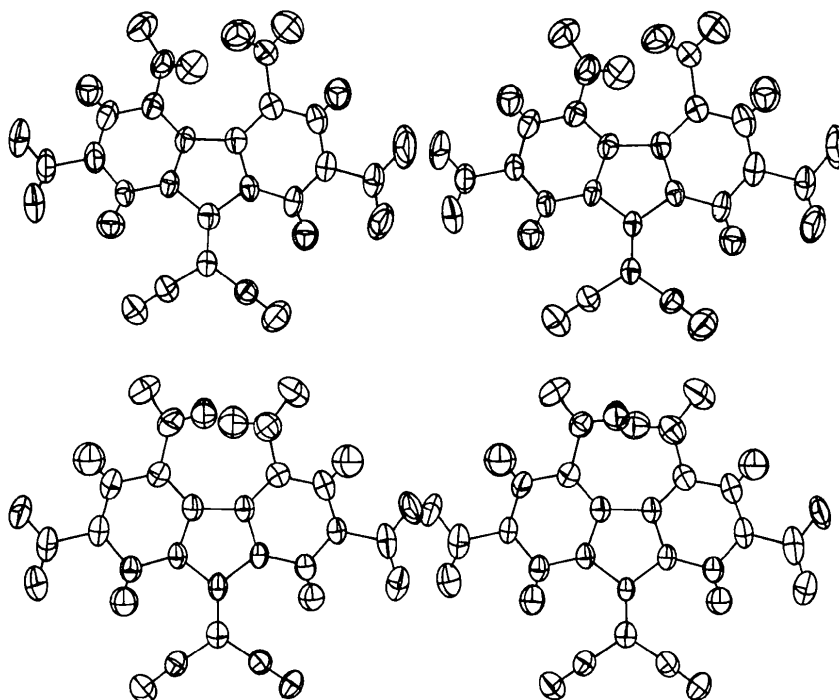

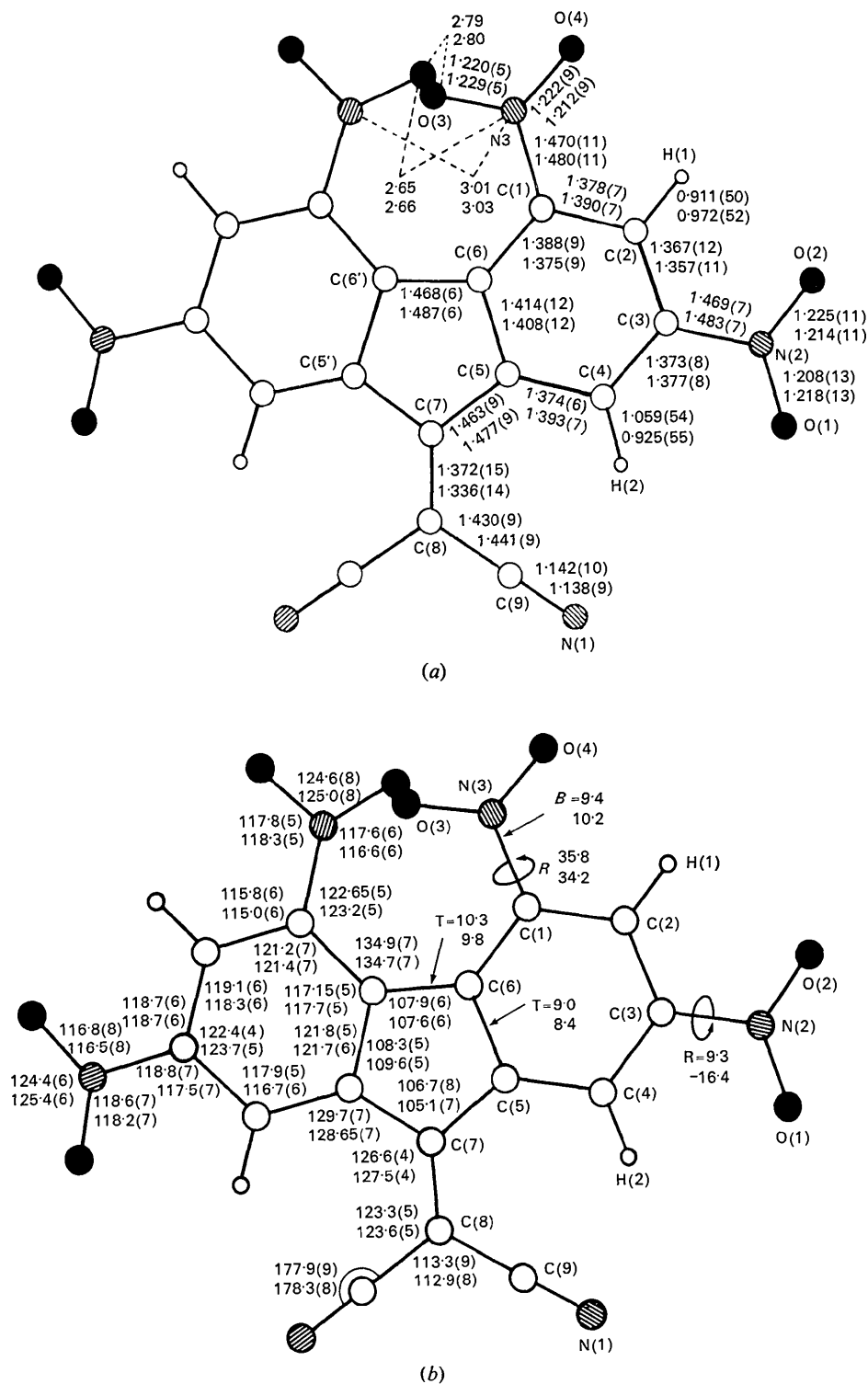Fig. 1. Juxtaposition of stereoscopic drawings of the independent molecules A (top) and B (bottom).

Fig. 2. Molecular numbering scheme, dimensions and other conformational features. Upper numbers refer to molecule A, lower to molecule B; e.s.d. in parentheses. (a) Bond lengths and selected intramolecular contacts in Å with e.s.d.'s in units of 0·001 Å. (b) Bond angles and conformational features in degrees with e.s.d's in units of 0·1°. R = rotations of nitro groups with respect to least-squares planes through outer benzenoid rings, T = bond torsional angles defined as interplanar angles between three-atom planes on each side of bond, B = 'bend' angle between the C(1)–N(3) bond and the plane defined by atoms C(6), C(1) and C(2).

Table 2. *Results of refinement based on Picker FACS* 1 *data. Final positional parameters as fractional coordinates, anisotropic thermal parameters* β_{ij} *from the expression* exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ *and r.m.s. displacements* u_i *in* Å *along the principal axes of the thermal elipsoid*

SP and PA refer to special position and polar axis respectively. u_i values are $\times 10^2$, the others are $\times 10^4$.

|	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	u_1	u_2	u_3
C(1)A	4031 (4)	3922 (4)	12042 (7)	65 (4)	57 (3)	73 (4)	3 (3)	4 (3)	5 (3)	20	21	23
C(2)A	3415 (4)	2985 (4)	11778 (7)	66 (4)	57 (3)	94 (6)	−5 (3)	4 (4)	24 (4)	18	21	28
C(3)A	3377 (4)	2643 (4)	10689 (7)	62 (4)	47 (4)	97 (6)	−10 (3)	−17 (4)	7 (4)	17	20	28
C(4)A	3856 (4)	3243 (4)	9830 (PA)	59 (4)	39 (3)	84 (5)	−4 (3)	−11 (4)	1 (3)	17	19	25
C(5)A	4472 (4)	4174 (4)	10101 (7)	50 (5)	35 (3)	65 (5)	−2 (3)	3 (3)	4 (3)	16	18	22
C(6)A	4621 (3)	4514 (3)	11224 (7)	50 (3)	40 (3)	68 (5)	4 (3)	−2 (3)	6 (3)	17	19	22
C(7)A	5000 (SP)	5000 (SP)	9370 (9)	45 (5)	44 (5)	69 (7)	3 (4)	0 (SP)	0 (SP)	17	18	22
C(8)A	5000 (SP)	5000 (SP)	8222 (9)	55 (5)	48 (5)	77 (7)	−3 (4)	0 (SP)	0 (SP)	18	20	24
C(9)A	4475 (4)	4153 (5)	7564 (8)	70 (4)	70 (4)	70 (5)	−6 (4)	−1 (4)	−10 (4)	20	22	24
N(1)A	4074 (4)	3489 (4)	7009 (8)	109 (5)	101 (5)	104 (6)	−12 (4)	−13 (4)	−24 (4)	23	28	31
N(2)A	2742 (4)	1630 (4)	10420 (8)	92 (5)	61 (5)	122 (7)	−30 (4)	−24 (5)	17 (5)	18	24	32
N(3)A	3899 (4)	4316 (3)	13198 (7)	102 (4)	83 (3)	81 (4)	−17 (3)	20 (3)	4 (4)	21	25	28
O(1)A	2789 (4)	1282 (4)	9474 (8)	155 (5)	77 (4)	145 (7)	−52 (4)	−17 (5)	−14 (5)	18	33	35
O(2)A	2153 (4)	1222 (5)	11171 (8)	155 (5)	117 (5)	174 (7)	−84 (5)	−7 (5)	31 (5)	18	34	41
O(3)A	3819 (3)	5302 (3)	13341 (6)	129 (4)	85 (3)	98 (3)	11 (3)	22 (3)	−12 (3)	23	27	31
O(4)A	3841 (4)	3633 (4)	13943 (7)	188 (5)	118 (4)	86 (4)	−41 (4)	16 (4)	26 (3)	21	30	37
H(1)A	3092 (44)	2616 (38)	12365 (42)	Fixed $\beta = 5\cdot25$						26	26	26
H(2)A	3784 (45)	2894 (44)	9022 (45)	Fixed $\beta = 5\cdot1$						25	25	25
C(1)B	4389 (4)	−1283 (4)	4442 (7)	58 (3)	57 (3)	66 (4)	3 (3)	0 (3)	−7 (3)	19	20	23
C(2)B	3734 (4)	−2212 (4)	4696 (7)	62 (4)	53 (4)	88 (5)	−6 (3)	−4 (4)	−18 (3)	18	21	26
C(3)B	3447 (4)	−2398 (4)	5782 (7)	56 (3)	46 (3)	88 (5)	−9 (3)	−5 (4)	−4 (4)	17	21	25
C(4)B	3815 (4)	−1748 (4)	6656 (4)	59 (4)	59 (4)	68 (5)	−4 (3)	1 (4)	0 (4)	19	21	22
C(5)B	4444 (4)	−809 (3)	6376 (7)	48 (3)	36 (3)	69 (5)	4 (3)	4 (3)	−2 (3)	16	18	22
C(6)B	4697 (4)	−540 (3)	5255 (7)	46 (3)	37 (3)	74 (5)	5 (3)	−3 (3)	0 (3)	16	18	23
C(7)B	5000 (SP)	0 (SP)	7129 (8)	53 (5)	40 (5)	59 (6)	2 (4)	0 (SP)	0 (SP)	17	19	21
C(8)B	5000 (SP)	0 (SP)	8247 (9)	67 (5)	52 (5)	65 (6)	−5 (4)	0 (SP)	0 (SP)	19	21	22
C(9)B	4420 (5)	−822 (5)	8914 (8)	82 (5)	78 (5)	68 (5)	−14 (4)	−3 (4)	−6 (4)	21	23	26
N(1)B	3984 (4)	−1469 (4)	9460 (7)	121 (5)	105 (5)	82 (5)	−37 (5)	14 (4)	18 (4)	20	27	32
N(2)B	2743 (4)	−3389 (4)	6061 (9)	77 (4)	55 (5)	138 (7)	−21 (3)	9 (5)	−17 (5)	17	24	32
N(3)B	4831 (4)	−1230 (3)	3278 (6)	103 (4)	69 (3)	79 (3)	1 (3)	3 (4)	−11 (3)	21	25	26
O(1)B	2730 (4)	−3693 (4)	7030 (7)	153 (5)	78 (4)	117 (6)	−41 (3)	10 (4)	12 (5)	20	30	34
O(2)B	2232 (4)	−3821 (5)	5290 (7)	134 (4)	117 (4)	127 (5)	−76 (4)	5 (4)	−40 (4)	17	30	39
O(3)B	5820 (3)	−845 (3)	3147 (6)	103 (3)	83 (3)	97 (3)	−4 (3)	29 (3)	−14 (3)	22	25	30
O(4)B	4226 (4)	−1608 (3)	2538 (6)	160 (5)	132 (4)	74 (4)	−30 (4)	−18 (4)	−30 (30)	20	31	35
H(1)B	3509 (47)	−2719 (40)	4108 (44)	Fixed $\beta = 6\cdot3$						28	28	28
H(2)B	3689 (42)	−1851 (42)	7414 (46)	Fixed $\beta = 4\cdot8$						25	25	25
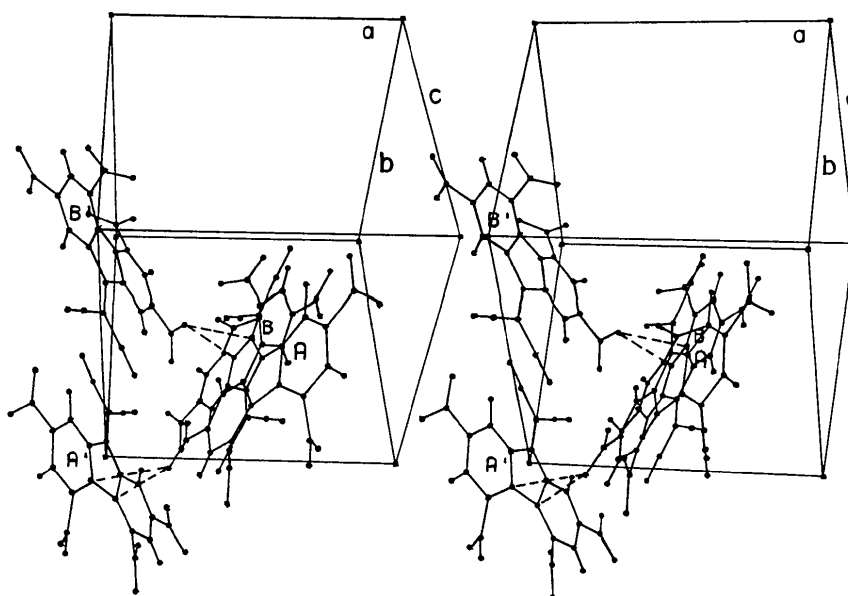
Fig. 3. Stereoscopic view of the structure with closest C···O approaches indicated by dotted lines.

Table 3. *Deviations in* $10^3 \times Å$ *from least-squares planes through the outer benzenoid ring (plane* 1) *and the central five-membered ring (plane* 2) *for independent molecules A and B*

Plane-defining atoms are indicated by asterisks.

	A 1	B 1	A 2	B 2
C(1)	22*	31*	231	216
C(2)	16*	5*	213	167
C(3)	−37*	−32*	27	4
C(4)	18*	21*	−43	−49
C(5)	19*	14*	−30*	−29*
C(6)	−38*	−39*	48*	47*
C(7)	162	135	0 (SP)*	0 (SP)*
C(8)	309	266	0 (SP)	0 (SP)
C(9)	327	293	−46	−47
C(1')	−379	−384	−231	−216
C(2')	−306	−300	−213	−167
C(3')	25	−10	−27	−4
C(4')	189	140	43	49
C(5')	119	83	30*	29*
C(6')	−110	−125	−48*	−47*
C(9')	458	394	46	46
N(1)	335	338	−93	−60
N(1')	592	476	93	60
N(2)	−74	−68	−21	−58
N(2')	131	91	21	58
N(3)	262	292	614	613
N(3')	−914	−916	−614	−613
O(1)	−230	225		
O(2)	116	−380		
O(1')	528	23		
O(2')	−250	224		
O(3)	975	996		
O(4)	−233	−145		
O(3')	−1664	−1652		
O(4')	−609	−651		

Equations of planes in the form $lX + mY + nZ + p = 0$ where X, Y, Z are coordinates in Å along the a, b, c orthorhombic axes.

Mol.	Plane	l	m	n	p
A	1	−0·8320	0·5440	−0·1068	2·7661
B	1	0·8538	−0·5115	0·0974	−5·5502
A	2	−0·8460	0·5333	0	1·5559
B	2	0·8556	−0·5176	0	−4·8671

of the bend out-of-plane of nitrogen atom N(3)A versus that of N(3)B. The presence of the pseudosymmetry is readily apparent from Table 2 where the A atoms are closely related to the corresponding B atoms by $x_A \doteq x_B$, $y_A \doteq y_B + 0·5$, $z_A + z_B \doteq C$ for the atoms C(1)–C(9), N(1), N(2).

No extensive analysis of the thermal motion has been undertaken. The r.m.s. displacements are given in Table 2 and the general character of the thermal motion can be gleaned from Fig. 1.

The crystal structure

Fig. 3 is a stereoscopic view of the crystal structure. In its herring-bone packing arrangement it has features in common with both D3F and D2F (Silverman et al. 1967, 1968). A comparison of the closest contacts between non-hydrogen atoms in the three structures reveals that with an increase in nitro-group substitution, unlike 'polar' type contacts become increasingly dominant in the structures. The trend shows up most clearly in the proliferation and shortening in the C···O contacts below 3·3 Å with one such contact at 3·15 Å in D2F, four down to 3·01 Å in D3F and twelve down to 2·90 Å in the present structure. The last value is 0·2 Å shorter than the sum of the usually quoted van der Waals radii, a value still more anomalous if one accepts Klug's (1965) contention that a C···O contact less than 3·3 Å is abnormally short. The narrow range of N–O···C intermolecular angles in all three structures also suggests a specific interaction. The results of a search for similar contacts involving nitro-group oxygen to carbon contacts in single-component molecular crystals, summarized in Table 4, offer further support for this hypothesis. The values of the inter-molecular angle at the oxygen atom computed from the published positional parameters range from 90–165° but 17 out of the 23 values in the table lie between 95 and 145°, suggesting approximate alignment along the oxygen lone pair.

Table 4. *Close nitro-group oxygen to carbon approaches in various single-component molecular crystals*

Compound	Intermolecular C···O distances (Å)	Intermolecular N–O···C angles (°)	References
9-Dicyanomethylene-2,4,5,7-tetranitrofluorene	2·90, 2·99, 3·02, 3·04, 3·18, 3·20	133, 126, 131, 131, 144, 90	Present work
9-Dicyanomethylene-2,4,7-trinitrofluorene	3·01	126	Silverman, Krukonis & Yannoni (1967)
9-Dicyanomethylene-2,7-dinitrofluorene	3·15	112	Silverman, Krukonis & Yannoni (1968)
2,4,7-Trinitro-9-fluorenone	3·08	143	Dorset, Hybl & Ammon (1972)
Cyclotetramethylene tetranitramine	3·01, 3·12	111, 157	Eiland & Pepinsky (1955)
Anhydrous dilituric acid	2·99	112	Bolton (1963)
2,3,4,6-Tetranitroaniline	3·06, 3·14	99, 125	Dickinson, Stewart & Holden (1966)
2,4,6-Trinitrophenetole	2·96	123	Gramaccioli, Destro & Simonetta (1968)
3,5-Dinitro-4-methylbenzoic acid	3·05	124	Grant & Richards (1969)
1,3,5-Trinitrobenzene	2·94, 3·05, 3·07	164, 115, 166	Choi & Abel (1972)
4,5-Dinitronaphthalic anhydride	2·97, 3·00, 3·03, 3·10	140, 140, 152, 152	Bordner & Jones (1972)

Other well-known intermolecular interactions involving oxygen atoms in one-component systems include: hydrogen bonding for which a scatter similar to that in Table 4 is found for donor oxygen intermolecular angles in alcohols, carbonyl bases, and amides (Pimentel & McClellan, 1960); so-called 'charge-transfer' bonding between oxygen and halogen atoms in benzo-, naphtho-, and anthraquinones with ring halogen substituents (Gaultier, Hauw & Schvoerer, 1971); and intermolecular C···O contacts sometimes as short as 2·8 Å which occur between a carbonyl oxygen and the carbon atom of a second carbonyl group in small multicarbonyl ring structures such as chloranil, barbituric acid, etc. (Bolton, 1964).

Bolton ascribes the latter interactions to dipole–dipole forces and interprets the fact that the intermolecular angles at oxygen atoms fall in the range 150–163° by noting that such forces marginally favor a linear angle (180°) over a direction along the p orbitals of the sp^2 hybridized oxygen atom (120°). While the nitro-group oxygen contacts in Table 4 are slightly longer than and have a distinctly different intermolecular specificity from the carbonyl interactions, there are several instances which point to a connection between them. For example, the short contact of 2·77 Å with C–O···C intermolecular angle 154·7° found in parabanic acid (Bolton, 1964) 'changes' to one of 2·84 Å, 132° in the complex of parabanic acid with urea (Colman & Medlin, 1970) and is now found between a carbonyl oxygen and the same carbonyl group carbon in another molecule of parabanic acid. A second case is found in anhydrous alloxan (Bolton, 1964) where there is a short C···O contact of 2·79 Å, 154·7°. In a hydrated form of the molecule (Singh, 1965), the shortest contacts are 2·95, 2·98 and 3·04 Å with corresponding angles of 121, 118 and 109° and are found between hydroxyl oxygens and ring carbons.

A certain dual character in the intermolecular angles at the oxygen atom suggested by the above cases is occasionally also found in hydrogen bonding. For example, in 5-hydroxy-5-ethylbarbituric acid (Gatehouse & Craven, 1971), two carbonyl oxygen donors have sharply different intermolecular angles of 123 and 170°.

The viewpoint employed by Kollman (1972) in a *Theory of Hydrogen-Bond Directionality* is felt to be relevant to these results. Based on the fact that individual terms in the bonding energy are far more sensitive to angular orientation than is the overall energy, Kollman rationalizes many observed intermolecular configurations as compromises between dipole–dipole favored directions (180°) and directions favored by charge-transfer forces (much smaller angles often roughly along lone-pair directions). Similar effects operative in the weaker forms of intermolecular 'bonding' encountered here may explain the differences between the intermolecular geometry observed for the

carbonyl interactions and those highlighted in Table 4. Charge-transfer forces apparently play a larger role for the latter interactions.

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