operators is given for each primitive unit cell up to $N=5$.

$N=3$. $p^2p^{-1}, p^2q, p^2q^{-1}; pp^{-1}q$.
$N=4$. $p^3p^{-1}, p^3q, p^3q^{-1}; p^2q^2, p^2q^{-2};$
$p^2p^{-1}q, p^2p^{-1}q^{-1}, p^2qq^{-1};$
$pp^{-1}pq, pp^{-1}pq^{-1}, pqpq^{-1}, pqp^{-1}q, pq^{-1}p^{-1}q^{-1},$
$pp^{-1}qp^{-1}, pq^{-1}qq^{-1}, pp^{-1}q^{-1}p^{-1}\ pqq^{-1}q.$
$N=5$. $p^4p^{-1}, p^4q^{-1}; p^3p^{-2}, p^3q^2, p^3q^{-2};$
$p^3p^{-1}q, p^3p^{-1}q^{-1}, p^3qq^{-1}; p^2p^{-2}q, p^2p^{-2}q^{-1}, p^2q^2p^{-1},$
$p^2q^2q^{-1}, p^2q^{-2}p^{-1}, p^2q^{-2}q;$
$p^2p^{-1}pq, p^2p^{-1}pq^{-1}, p^2qpq^{-1}, p^2p^{-1}\ pp^{-1}, p^2qpq,$
$p^2q^{-1}pq^{-1}, p^2p^{-1}qp^{-1}, p^2qp^{-1}q, p^2q^{-1}qq^{-1},$
$p^2q^{-1}p^{-1}q^{-1}, p^2p^{-1}q^{-1}p^{-1}, p^2p^{-1}qq^{-1},$
$p^2qp^{-1}q^{-1}, p^2qq^{-1}p^{-1}, p^2qq^{-1}q;$
$pp^{-1}pp^{-1}q, pqpqp^{-1}, pq^{-1}pq^{-1}q, pp^{-1}pp^{-1}q^{-1},$
$pp^{-1}pqq^{-1}, pp^{-1}qpq^{-1}, pp^{-1}q^{-1}pq, pqpqq^{-1},$
$pq^{-1}pq^{-1}p^{-1}$.

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References

Beattie, H. J. (1967). In *Intermetallic Compounds,* edited by J. H. Westbrook, p. 152. New York: John Wiley.
Beck, P. A. (1967). *Z. Kristallogr.* **124**, 104.
Dwight, A. E. & Beck, P. A. (1959). *Trans. AIME,* **215**, 976.
Giessen, B. C. & Grant, N. J. (1965). *Acta Cryst.* **18**, 1080.
Harker, D. (1944). *J. Chem. Phys.* **12**, 315.
Laves, F. & Wallbaum, H. J. (1939). *Z. Kristallogr.* **A101**, 78.
Saito, S. (1959). *Acta Cryst.* **12**, 500.
Schubert, K. (1964). *Kristallstrukturen Zweikomponentiger Phasen.* Berlin: Springer-Verlag.

Acta Cryst. (1968). B**24**, 1481

The Crystal Structures of 9-Dicyanomethylenefluorene Derivatives. II. 9-Dicyanomethylene-2,7-dinitrofluorene

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9-Dicyanomethylene-2,7-dinitrofluorene crystallizes in the orthorhombic space group *Pnna*. There are four molecules with twofold point group symmetry in the unit cell: $a=19{\cdot}26$, $b=11{\cdot}19$, $c=6{\cdot}33$ Å. An intense reflection in conjunction with packing considerations provided sufficient information to solve the structure. A refinement by least-squares based on 613 reflections from X-ray photographs converged at an R value of 8·9%. The fluorene moiety is planar; nitro groups are rotated out-of-plane by 17·6° and the dicyanomethylene portion is rotated slightly about its formal double bond. In the herringbone packing scheme, the presence of weak self-complexing by charge transfer is suggested by the association among parallel molecules which includes π-orbital overlap between outer benzenoid rings and close approaches of 3·33 and 3·37 Å for C···C and 3·15 Å for O···C. Comparisons with the recently reported structure of the 2,4,7-trinitro derivative induce some speculations as to the connection between structural and electrical properties of the two compounds and, in particular, lead to a postulated relationship between the high photoconductivity of the present molecule and its weak self-complexing.

Introduction

9-Dicyanomethylene-2,7-dinitrofluorene (DDF) is one of a series of new electron acceptors, nitro derivatives of fluorene-$\Delta^{9\alpha}$-malononitrile, synthesized by T. K. Mukherjee of our laboratory. The relative photoconductive response of polycrystalline samples as well as the order of electron affinities among the several molecules has been determined (Mukherjee, 1966, 1968). Crystallographic results on the 2,4,7-trinitro derivative (DTF) were presented as part I of this series (Silverman, Krukonis & Yannoni, 1967). Here, we report on the structure of the 2,7-dinitro derivative, and based on a comparison with the DTF structure, offer some speculations as to the connection between the structural and electrical properties.

Experimental

Crystal data

9-Dicyanomethylene-2,7-dinitrofluorene (DDF) $C_{16}H_6N_4O_4$, $M=318{\cdot}2$; m.p. $=298-299$ °C. Orthorhombic, $a=19{\cdot}26$, $b=11{\cdot}19$, $c=6{\cdot}33$ (based on $\lambda=0{\cdot}7017$ Å and with e.s.d.'s of 0·3%).

Absent reflections: $0kl$ when $k+l$ is odd; $h0l$ when $h+l$ is odd; and $hk0$ when h is odd. Space group is *Pnna* (No. 52).
Density data: For $Z=4$, $D_x=1{\cdot}547$ g.cm^{-3}, D_m (Berman balance) $=1{\cdot}51$. Implied molecular symmetry is twofold.
Absorption coefficients for X-rays: Cu $K\alpha$, 7·74 cm^{-1}, Mo $K\alpha$, 1·57 cm^{-1}.

The basic data set consisted of 6 levels taken with unfiltered copper radiation about the c axis on an integrating Weissenberg camera (equi-inclination geometry). The crystal, a well-developed prism whose thickness varied from 0·14 to 0·23 mm, disintegrated shortly after Weissenberg data collection was completed. Supplementary data of levels $h0l$, $0kl$ and $1kl$ were taken with an integrating precession camera on a slightly smaller second crystal (Zr-filtered Mo radiation). These three levels were used for the cell parameter measurements and for placing the basic data set on a common scale. Spot intensities were measured with a densitometer and very faint spots estimated visually. The usual multi-exposure time and multiple film techniques enabled 613 independent reflections, 41% of those theoretically accessible, to be measured.

We estimate that neglected absorption effects could lead to errors of up to 8% in relative values of F_o in fortuitously unfavorable cases. Corrections for secondary extinction were applied as described below.

Solution of the structure was straightforward. The very intense 031 reflection suggested the approximate orientation of the molecular planes.* The remaining degree of freedom, the translational position of the molecule along the twofold axis in the a-direction, was narrowed to one of two choices by packing considerations and subsequently fixed by preliminary structure factor computations.

Refinement proceeded through cycles of full-matrix least-squares (Busing, Martin & Levy, 1962) based on F with the weighted R value,

$$R_w=\left[\frac{\Sigma\, w(F_o-|F_c|)^2}{\Sigma\, wF_o^2}\right]^{1/2}$$

minimized in the procedure. Scattering factors were taken from the tables of Hanson, Herman, Lea & Skillman (1964).

Refinement commenced at $R_w=51{\cdot}4\%$ with the conventional R value at $R=33{\cdot}9\%$ and after 12 cycles with individual isotropic thermal parameters and unit weights, R_w converged to 18·2% and R to 16·0%. Examination of root mean square values of $|F_o-|F_c||$ as a function of F_o together with previous experience in our laboratory suggested the weighting scheme: $w=[0{\cdot}64+0{\cdot}064F_o]^{-2}$ (scale is 0·25 absolute) which was employed thereafter. Two further cycles saw R_w drop from 20·2 to 19·3 and R from 16·0 to 15·0%. At this point, a difference Fourier synthesis showed 3 peaks at 0·7 to 0·9 e.Å^{-3} in expected positions for hydrogen atoms amid 10 other peaks of comparable height, most of which could be ascribed to anisotropic motion of the heavy atoms. Thereafter, hydrogen atoms were included in the refinement with isotropic thermal parameters fixed at the values of their attached carbon atoms. Three additional cycles gave $R_w=18{\cdot}7$ and $R=14{\cdot}3\%$. The introduction of anisotropic thermal parameters for the heavy atoms permitted 3 additional cycles of refinement to converge at $R_w=15{\cdot}0$, $R=11{\cdot}1\%$. Slight readjustment (by hand) of the relative scale factors of levels $hk4$ and $hk5$ and the assignment of zero weight to the 031 reflection lowered R_w to 13·7% and R to 10·5% with 2 subsequent cycles of refinement effecting little change.

As 14 of the 17 strongest reflections had $F_c>F_o$, we decided to apply an empirical secondary extinction correction based on the expression $I_c/I_o=1+g/\mu\ [I_c]$ (Pinnock, Taylor & Lipson, 1956). A plot of I_c/I_o versus I_c yielded a value for g/μ of 0·00014 (taking $I_c=[Lp]F_c^2$ with F_c on a scale of 0·25 absolute)*. After the correction, the original discrepancy index of 14% between F_o and F_c for the 17 reflections was reduced to 4%. Overall R values were lowered to $R_w=12{\cdot}2\%$ and $R=8{\cdot}9\%$. Three cycles of least-squares then completed the refinement. Final R values were $R_w=11{\cdot}7$, $R=8{\cdot}6\%$. With the inclusion of unobserved reflections in the same $\sin\theta$ range as the observed, these R values are 14·5 and 13·1% for a total of 992 reflections. Parameter changes in the final cycle were negligible for the heavy atoms and no greater than $0{\cdot}3\sigma$ for the hydrogen atoms.

The final difference synthesis had no peaks greater than ±0·5 e.Å^{-3} and a typical 'noise' level of 0·15 e.Å^{-3}. Final parameters are listed in Table 1; structure factor comparisons are given in Table 2.

Discussion

In our discussion of the present results, frequent comparisons with the structure of DTF (Silverman, Krukonis & Yannoni, 1967) will be found useful.

Molecular conformation

Fig. 1 compares the dimensions of the two molecules. Representative standard deviations in the present structure are ±0·01 Å and 0·7° for heavy atom bond lengths and angles and ±0·1 Å for C–H bonds. The

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* In the final structure, the overall molecular planes deviate by about 2° from the (031) planes and parallel molecular pairs are offset from coplanarity by 0·33 Å. This suffices to produce an 031 reflection which is about 40% of a total in-phase scattering of electrons and whose structure factor is twice as large as that of any other reflection.

* We thank Professor D. P. Shoemaker who points out that this expression for extinction is in error for our upper level reflections in that the correction really depends on $Q\propto 1+\cos^2 2\theta/\sin 2\theta$ which is $\propto$ [Lp] for equatorial reflections only. However, recomputation on this basis leads to corrected F_o values too little changed from those given in the F-table to make further refinement meaningful.

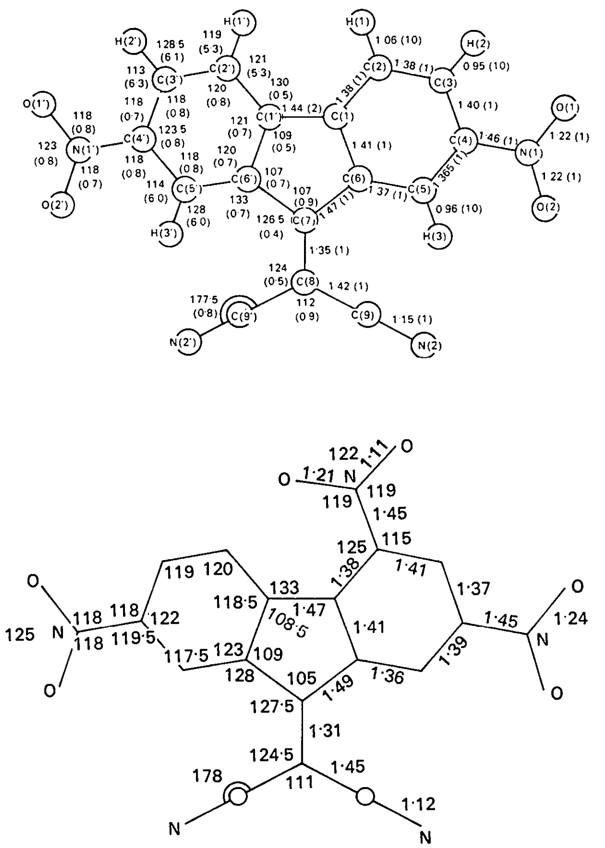

Fig. 1. Comparison of the dimensions of the present molecule DDF (top) with those of 9-dicyanomethylene-2,4,7-trinitrofluorene DTF (bottom). The crystallographic numbering is shown for the former; standard deviations, in units of 0·01 Å for bond lengths and in degrees for bond angles, are enclosed in parentheses. In the DTF crystal, the molecular symmetry is twofold in a statistical sense since the third nitro group occurs randomly on either half of the molecule.

DDF molecule as a whole appears to be a more fully aromatic system than is the case for the trinitro derivative as can be seen by the consistent (but only possibly significant) differences in bond lengths in the central ring and dicyanomethylene groups. The values for DDF of 1·35, 1·42 and 1·15 for the formally double, single and triple bonds respectively of the dicyanomethylene group agree well with the corresponding values of 1·36, 1·40, 1·15 in 10-dicyanomethyleneanthrone (Silverman & Yannoni, 1967*b*) as well as with values found for neutral species in 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its various ion radical salts (Fritchie & Arthur, 1966: see their Table 4 for further comparisons and earlier references). The range in C–H bond lengths, 0·95 – 1·06 Å, is typical for X-ray results.

Bond angles in the benzene rings of DDF follow closely the trend found in *o*-nitrobenzoic acid and various other nitro derivatives as pointed out by Sakore, Tavale & Pant (1967) in that the ring angle at the nitro group site is somewhat greater than 120°, angles at the *ortho* ring positions are less than 120°, and the other three angles remain close to 120°. The pattern is perturbed in the DTF molecule by intramolecular overcrowding induced by the unpaired nitro group (Silverman & Yannoni, 1967*a*).

Least-squares planes were computed for several parts of the molecule (Schomaker, Waser, Marsh & Bergman, 1959). The carbon framework of DDF is planar to within experimental error except for atom C(9) which is 0·037 Å or 4·1 e.s.d. away from the appropriate plane, $9{\cdot}470y+3{\cdot}376z=3{\cdot}2115$ Å. Deviations from least-squares planes defined by the atoms of the fluorene group are compared for the two molecules in Fig. 2. For DDF, plane defining atoms are within 1·8 e.s.d. of the plane $9{\cdot}461y+3{\cdot}384z=3{\cdot}211$ Å. In DTF, a slight distortion into a propeller shape is found which

Table 1. *Final positions of the atoms of the asymmetric unit in fractional coordinates* (x,y,z) *and the final anisotropic thermal parameters* (β_{ij}) *from the expression*

$$T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$$

Numbers in parentheses are standard deviations which refer to the last significant figure(s) listed.

	x	y	z	$\beta_{11}10^4$	$\beta_{22}10^4$	$\beta_{33}10^4$	$\beta_{12}10^4$	$\beta_{13}10^4$	$\beta_{23}10^4$
C(1)	0·0787 (4)	0·2166 (7)	0·3470 (14)	15 (2)	38 (7)	152 (25)	−2 (3)	0 (6)	−16 (10)
C(2)	0·0238 (4)	0·1739 (7)	0·4641 (14)	16 (2)	41 (6)	167 (30)	0 (3)	6 (7)	−18 (13)
C(3)	0·0364 (5)	0·1077 (7)	0·6433 (16)	19 (2)	44 (7)	181 (30)	−2 (3)	24 (7)	−21 (13)
C(4)	0·1054 (4)	0·0884 (7)	0·7019 (13)	25 (3)	37 (7)	82 (28)	−2 (3)	23 (7)	−8 (11)
C(5)	0·1609 (4)	0·1297 (7)	0·5895 (15)	18 (2)	33 (6)	124 (29)	6 (3)	10 (7)	2 (11)
C(6)	0·1480 (4)	0·1936 (6)	0·4084 (14)	14 (2)	32 (6)	127 (27)	−7 (3)	4 (6)	11 (11)
C(7)	0·1935 (6)	0·2500	0·2500	19 (3)	19 (8)	127 (36)	0	0	−4 (15)
C(8)	0·2637 (5)	0·2500	0·2500	13 (3)	40 (9)	136 (36)	0	0	42 (16)
C(9)	0·3050 (4)	0·1967 (7)	0·4108 (16)	17 (2)	42 (6)	187 (31)	−7 (3)	−1 (8)	48 (13)
N(1)	0·1193 (4)	0·0145 (6)	0·8868 (12)	28 (2)	31 (5)	157 (24)	2 (3)	23 (8)	−17 (10)
N(2)	0·3390 (5)	0·1568 (8)	0·5415 (17)	30 (3)	93 (9)	365 (36)	−4 (4)	−28 (9)	113 (16)
O(1)	0·0721 (4)	−0·0463 (7)	0·9573 (13)	36 (3)	100 (8)	316 (27)	6 (4)	59 (7)	90 (12)
O(2)	0·1768 (4)	0·0201 (6)	0·9675 (12)	38 (3)	78 (7)	232 (25)	−4 (4)	−23 (7)	48 (10)
H(1)*	−0·028 (5)	0·199 (8)	0·427 (16)	13	38	119	0	0	0
H(2)*	0·004 (5)	0·080 (9)	0·746 (17)	14	42	130	0	0	0
H(3)*	0·205 (5)	0·113 (9)	0·654 (17)	14	41	128	0	0	0

* Thermal parameters fixed at isotropic values 1·9, 2·1, 2·0 Å² for H(1), H(2), H(3) respectively. See text.

Table 2. *Structure Factors*

The columns from left to right are h, k, F_o and $10F_c$. Values corrected for extinction are tagged with an asterisk. A value of $38=10\langle\bar{F}_c\rangle$ was assigned to F_o for identification of the unobserved reflections. This value is somewhat greater than the half-threshold value for observed each level. Among these are the unmeasured reflections (1 11 2), (12 1 3), (3 9 3) and (1 10 4) which are found as faint streaks on the films.

l = 0			
0	0		6480
4	0	1134*	-1104
6	0	736*	759
8	0	621*	-613
10	0	144	-113
12	0	326	320
14	0	173	-156
16	0	154	-140
18	0	162	-152
20	0	102	-48
22	0	188	-181
24	0	60	-35
2	1	1062*	-917
4	1	647*	-649
6	1	115	108
8	1	371	-363
10	1	152	-143
12	1	120	-129
14	1	178	-192
16	1	150	-160
18	1	120	96
22	1	86	72
0	2	121	-100
2	2	441	427
4	2	643*	-575
6	2	334	-313
10	2	162	136
12	2	89	-91
14	2	231	-214
16	2	153	161
18	2	304	279
20	2	122	-107
2	3	236	-216
4	3	433	438
8	3	170	-158
10	3	451	-448
12	3	315	-327
16	3	380	380
18	3	119	92
0	4	393	382
2	4	428	-420
4	4	191	-195
6	4	460	-459
8	4	183	-150
10	4	335	322
14	4	137	106
16	4	395	374
18	4	105	-127
22	4	83	63
2	5	267	-250
4	5	530	527
6	5	338	286
8	5	113	76
10	5	132	149
12	5	225	-201
14	5	193	157
0	6	353	374
2	6	180	-173
4	6	276	-305
6	6	560*	657
10	6	121	-122
22	6	61	-80
2	7	189	175
4	7	135	150
6	7	282	246
8	7	141	-128
10	7	273	-247
12	7	107	57
14	7	152	-113
18	7	144	-114
2	8	272	-198
4	8	140	-41
14	8	192	-170
18	8	127	118
4	9	358	339
6	9	161	-107
10	9	152	115
12	9	148	-183
14	9	199	205
18	9	72	-53
0	10	219	225
2	10	120	93
4	10	153	-139
12	10	143	-152
2	11	288	-267
6	11	114	126
8	11	130	-137
12	11	178	149
14	11	106	-110
4	12	116	130
10	12	91	91
12	12	78	-80
2	13	91	-108
10	13	97	-126
4	14	103	-128
20	1	38	9
8	2	38	51
6	3	38	-17
12	4	38	5
20	4	38	-82
8	6	38	31
12	6	38	52
14	6	38	-12
16	6	38	-36
18	6	38	17
20	6	38	-56
16	7	38	8
0	8	38	67
6	8	38	39
8	8	38	55
10	8	38	-45
12	8	38	-21
16	8	38	31
2	9	38	-25
8	9	38	-15
16	9	38	34
6	10	38	35
8	10	38	78
10	10	38	70
4	11	38	-16
10	11	38	-20
2	12	38	-12
4	12	38	48
6	12	38	-21
4	13	38	-33
6	13	38	-32
8	13	38	-15
2	14	38	-18
l = 1			
3	0	734*	445
5	0	253	-233
9	0	254	257
11	0	196	186
13	0	134	108
15	0	202	-210
17	0	300	-309
19	0	151	138
23	0	64	-62
0	1	170	142
1	1	124	-113
2	1	65	-46
4	1	355	-378
5	1	183	189
6	1	453	-503
8	1	252	-240
9	1	243	244
10	1	212	212
11	1	137	-116
13	1	205	-194
15	1	164	-190
16	1	299	323
17	1	122	128
20	1	124	-120
22	1	73	54
1	2	1138*	1162
2	2	381	393
3	2	400	446
4	2	723*	808
5	2	109	99
6	2	200	184
7	2	113	-123
8	2	154	171
9	2	201	-172
10	2	143	145
11	2	115	99
12	2	103	-63
14	2	201	199
16	2	108	99
17	2	144	138
0	3	2513*	2600
1	3	789*	830
2	3	88	-89
3	3	209	-178
4	3	590*	-611
5	3	194	-189
6	3	704*	768
8	3	322	-329
10	3	174	-169
11	3	149	128
12	3	220	212
13	3	142	-135
16	3	133	-102
17	3	122	-129
22	3	130	-131
1	4	526	-471
4	4	89	97
5	4	241	-239
6	4	233	229
7	4	161	-171
8	4	300	-300
10	4	252	-244
11	4	94	93
13	4	115	-105
14	4	155	-153
15	4	76	-70
19	4	100	98
0	5	140	116
1	5	50	-65
2	5	62	-55
4	5	216	-227
5	5	89	-93
7	5	210	184
9	5	249	227
11	5	122	-108
14	5	239	-232
15	5	122	-125
17	5	92	76
19	5	205	183
1	6	162	158
3	6	280	-225
4	6	501	480
5	6	87	-95
6	6	118	-106
8	6	134	-134
10	6	101	-95
11	6	116	-95
12	6	283	-274
14	6	134	128
16	6	176	183
19	6	100	65
0	7	231	210
1	7	278	-231
3	7	112	-120
4	7	114	-130
6	7	108	-84
7	7	99	-96
10	7	197	192
11	7	174	161
12	7	133	-121
13	7	144	-121
15	7	218	201
16	7	124	110
18	7	109	-98
1	8	99	95
2	8	315	-297
3	8	112	132
4	8	163	143
5	8	183	-107
6	8	196	160
7	8	154	149
8	8	75	-83
9	8	94	116
11	8	76	41
16	8	91	71
2	9	92	-88
6	9	205	190
7	9	122	137
8	9	184	139
11	9	107	-122
13	9	183	175
14	9	96	-91
15	9	64	-52
1	10	77	69
5	10	109	82
10	10	145	-138
11	10	141	137
12	10	95	-105
15	10	111	-118
0	11	107	-74
2	11	119	-82
5	11	127	86
13	11	180	-159
3	12	193	139
7	12	88	-96
8	12	135	115
10	12	83	75
1	13	134	107
5	13	155	-133
8	13	62	32
2	14	151	-125
7	0	38	-34
21	0	38	19
3	1	38	18
12	1	38	48
14	1	38	31
18	1	38	52
19	1	38	56
21	1	38	45
13	2	38	8
15	2	38	-39
7	3	38	87
9	3	38	13
14	3	38	-55
15	3	38	-66
18	3	38	-73
19	3	38	39
20	3	38	-63
21	3	38	-24
2	4	38	42
3	4	38	-33
9	4	38	43
12	4	38	-31
15	4	38	-42
17	4	38	35
19	4	38	-28
3	5	38	-30
6	5	38	-32
8	5	38	46
10	5	38	-4
12	5	38	-36
13	5	38	3
16	5	38	38
2	6	38	-42
7	6	38	-37
9	6	38	-60
13	6	38	-7
15	6	38	-52
17	6	38	87
18	6	38	25
2	7	38	-67
5	7	38	28
8	7	38	27
9	7	38	53
14	7	38	1
17	7	38	35
10	8	38	37
11	8	38	41
13	8	38	-1
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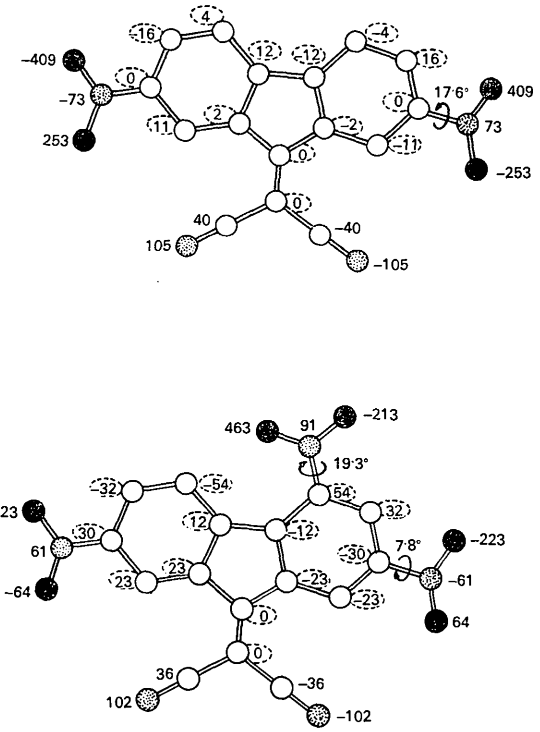

Fig. 2. Atomic deviations in units of 0·001 Å from planes fit by least-squares to the fluorene moieties of the present molecule (top) and of DTF (bottom). Out of plane rotations of the several nitro groups are indicated schematically. Circled deviations are those of plane-defining atoms.

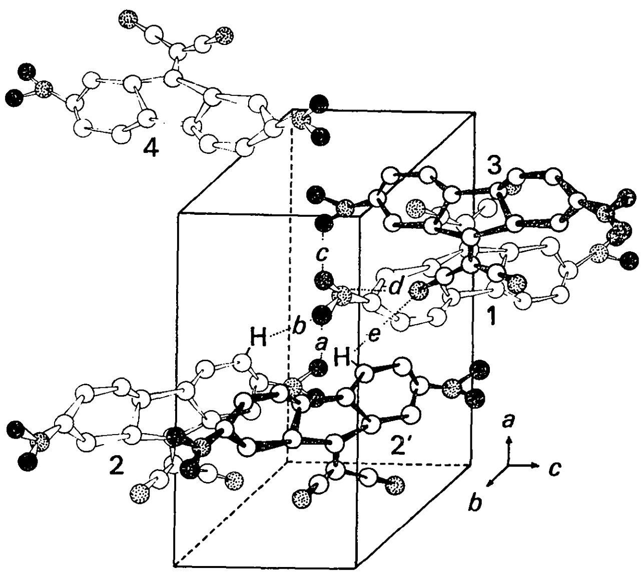

Fig. 3. Packing arrangement in the DDF structure showing four molecules of a unit cell and a c-axis translated fifth molecule (2′). A few close approaches are indicated. a, [O···O] = 3·01 Å; b, [O···H] = 2·41 Å; c, [O···O] = 2·85 Å; d, [N···N] = 3·00 Å; e, [N···H] = 2·61 Å.

helps to accommodate the overcrowded nitro group (Silverman & Yannoni, 1967*a*). Nitro group nitrogens of both molecules are displaced from the benzene ring planes by similar amounts, 0·06 – 0·09 Å. An interesting feature is the almost identical configuration of the planar dicyanomethylene group which rotates by about 2·3° about the C(7)–C(8) bond in each molecule.

The rotation out of plane of the nitro groups in DDF by 17·6° is greater than typical values ($<10°$) found for such relatively uncrowded substituents. However, some comparable examples are found in *s*-trinitrobenzene–skatole complex (Hanson, 1964), in *p*-nitrobenzoic acid (Sakore & Pant, 1966), in *m*-dinitrobenzene (Trotter & Williston, 1966), and finally in *s*-trinitrobenzene–anthracene complex (Brown, Wallwork & Wilson, 1964) where there are nitro groups from 13°–18° out of plane. As pointed out by Dashevskii, Struchkov & Akopyan (1966), losses of 'conjugation energy' from nitro group rotations of up to 18° ($\sim$0·6 kcal.mole^{-1}) are still comparable to the energy of intermolecular interactions or to that of thermal motion and hence such rotations are effected relatively easily.

Molecular packing and thermal motion

Fig. 3 is a drawing of the herringbone packing arrangement. Four molecules of a unit cell are grouped in maypole fashion about a zigzag line of nitro group atoms along the direction $x, \frac{1}{2}, \frac{1}{2}$. Some of the 'limiting' contacts are shown in the Figure with the closest approaches of each type: 2·85 Å for O···O, 3·00 Å for N···N, 2·41 Å for O···H, and 2·61 Å for N···H.

While the above intermolecular distances are all normal, the most interesting aspect of the present structure is found in the association of parallel molecular pairs such as 1 and 2 in Fig. 3 (which deviate from coplanarity by 0·33 Å) with one of the c-axis translated molecules such as 2′. This arrangement is shown in projection perpendicular to the planes (Fig. 4*a*). Molecules related by c-axis translation are 3·38 Å apart and have appreciable overlap between the π-electron clouds of their outer rings. In addition to the O(2)···C(7) contact of 3·15 Å, there are short C···C distances of 3·37 and 3·33 Å. C···C distances in this range and the overlap feature are found in certain weak charge-transfer complexes such as anthracene-*s*-trinitrobenzene (Brown, Wallwork & Wilson, 1964) with a molecular plane separation of 3·28 Å and a closest C···C distance of 3·30 Å (low temperature structure) or the complex of 2,4,6-tri(dimethylamino)-1,3,5-triazine with *s*-trinitrobenzene (Williams & Wallwork, 1966) with a 3·28 Å separation of parallel molecular planes. This apparent self-complexing by charge-transfer is found in chloranil (Chu, Jeffrey & Sakurai, 1962) and in closer analogy to the present structure occurs in tetrahydroxy-*p*-benzoquinone (Klug, 1965) where overlap between C=O bonds of parallel molecules leads to C···O and C···C distances of 3·09 and 3·31 Å respectively.

These features are absent in the DTF crystal structure (Fig. 4(*b*)) except for a still shorter C···O approach of 3·01 Å. It is difficult to assess the significance of the C···O contacts in the present molecule in relation to the other features which point to the self-complexing. While generally accepted radii suggest 3·1 Å as the appropriate van der Waals radius for C···O, it is Klug's contention (1965) that the 'normal' C···O distance is 3·3–3·4 Å. A survey of the literature (not exhaustive) has discovered only three structures with NO_2···C approaches in the range found in DDF and DTF: *viz.* values of 3·01 and 3·12 Å in cyclotetramethylene tetranitramine (Eiland & Pepinsky, 1955), a value of 3·19 in 2,4,6-tri(dimethylamino)-1,3,5-triazine/*s*-trinitrobenzene complex (Williams & Wallwork, 1966), and values of 3·06 and 3·14 Å in 2,3,4,6-tetranitroaniline (Dickinson, Steward & Holden, 1966). Possibly, these are polar interactions similar to, but weaker than, the C···O interactions found in various carbonyl structures (Bolton, 1965 and references therein). The presence of competing electron withdrawing groups would enhance the tendency of a given nitro group to partake in such interactions and that the three examples cited above as well as the two present molecules all involve multi-nitro group substituents is probably not a coincidence. We feel, intuitively, that it is unlikely that the energy gain from these NO_2···C interactions has 'forced' the DDF molecules into a configuration best viewed as involving C···C repulsions, but rather that there is weak charge-transfer bonding between outer rings of the molecules not found in the DTF structure.

The nature of the thermal motion is consistent with the proposed self-complexing. The r.m.s. components of the anisotropic motion along the principal axes, the directions of these axes and the values of the diagonal terms of the U_{ij} tensor (in Å^2) transformed to molecular axes are all listed in Table 3 (Busing, Martin & Levy, 1964). The rigid body approximation (Cruickshank, 1956) turns out to be an inadequate model in the present case. For the fluorene framework the motion out of plane is damped relative to that within the plane, a pattern found in other weak complexes such as those of *s*-trinitrobenzene with indole (Hanson, 1964) or with acepleiadylene (Hanson, 1966). In contradistinction, planar molecules making face-to-face contact usually tend to vibrate against each other (Hirshfeld & Rabinovich, 1965; examples are cited on p. 238). The reduced motion of O(2) perpendicular to the plane [r.m.s. displacement of about 0·25 Å as compared with 0·30 Å for O(1)], a possible consequence of the specific interaction of O(2) and C(7) discussed above, represents a perturbation from the type of torsional oscillation frequently found (Trueblood, Goldish & Donohue, 1961). As no coherent model for viewing the thermal motion has been found, we have not incorporated any corrections for thermal motion into our reported values.

A comparison among a series of $\Delta^{9\alpha}$-malononitrile nitro derivatives and in particular between the two molecules treated here suggests a correlation between structure and electrical properties. The present compound has the lowest electron affinity of the series, 1·1eV, together with the highest photoconductive response (a ratio of light to dark conductivity of about 2·10^4). DTF, with the highest electron affinity (except for the 2,4,5,7-tetranitro derivative), 1·3eV, shows only slight photoconductivity (Mukherjee, 1966, 1968). It is presumably the planarity and/or the lower electron affinity of the DDF molecule which leads to donor-acceptor behavior in the DDF crystal but not in that of DTF. We suspect that the high photoconductivity

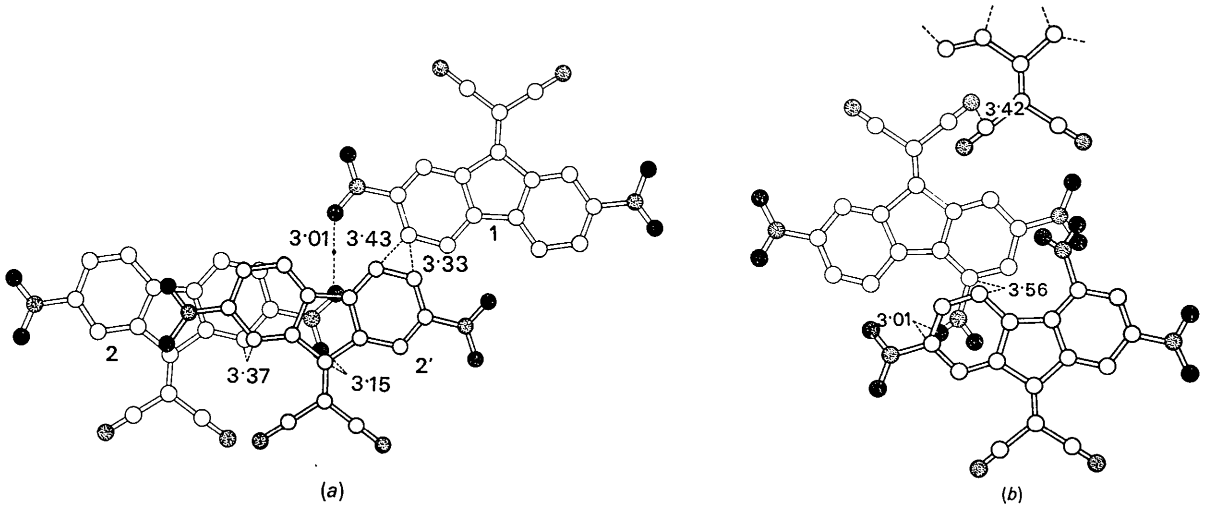

Fig. 4. (*a*) Overlap of parallel molecules viewed in projection perpendicular to the molecular planes. The arrangement corresponds to a grouping such as molecules 1, 2 and 2' of Fig. 3. (*b*) The degree of overlap in the crystal structure of DTF viewed in the same fashion.

of the former is related to the excitation by light of this self-complex. By further crystallographic studies on members of the series which are intermediate in electron affinity and photoconductivity to this pair, we hope to establish the validity of these speculations and to fill in the picture of electrical property-structure relationships for this interesting group of molecules.

References

Bolton, W. (1965). *Acta Cryst.* **18**, 5.

Brown, D. S., Wallork, S. C. & Wilson, A. (1964). *Acta Cryst.* **17**, 168.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program.* USAEC report ORNL-TM-305.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program.* USAEC Report ORNL-TM-306.

Chu, S. C. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* **15**, 661.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Dashevskii, V. G., Struchkov, Yu. T. & Akopyan, Z. A. (1966). *J. Struct. Chem.* (*USSR*), **7**, 555.

Dickinson, C., Stewart, J. M. & Holden, J. R. (1966). *Acta Cryst.* **21**, 663.

Eiland, P. F. & Pepinsky, R. (1955). *Z. Kristallogr.* **106**, 273.

Fritchie, C. J., Jr & Arthur, P., Jr (1966). *Acta Cryst.* **21**, 139.

Hanson, A. W. (1964). *Acta Cryst.* **17**, 559.

Hanson, A. W. (1966). *Acta Cryst.* **23**, 476.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Hirshfeld, F. L. & Rabinovich, D. (1965). *Acta Cryst.* **19**, 235.

Klug, H. P. (1965). *Acta Cryst.* **19**, 983.

Mukherjee, T. K. (1966). *J. Phys. Chem.* **70**, 3848.

Mukherjee, T. K. (1968). *Tetrahedron*, **24**, 721.

Pinnock, P. R., Taylor, C. A. & Lipson, H. (1956). *Acta Cryst.* **9**, 173.

Sakore, T. D. & Pant, L. M. (1966). *Acta Cryst.* **21**, 715.

Table 3. *Thermal motion data for the heavy atoms*

R.m.s. displacements in Å (D) along the principal axes (P_i) of the thermal elipsoid and the angle in degrees of each axis with respect to the c, b and $-a$ axes (φ_c, φ_b, φ_{-a} respectively). Standard deviations in parentheses are in units of 0·01 Å and degrees respectively. Also given are mean-square displacements in Å^2 (S) along the molecular axes (M_i). M_1 is parallel to the molecule and along a; M_2 is perpendicular to the molecular plane and M_3, also parallel, completes the cartesian system.

	P_i	D	φ_c	φ_b	φ_{-a}	M_i	10^2S
C(1)	1	0·14 (2)	62 (15)	31 (15)	104 (22)	1	2·78
	2	0·17 (1)	74 (31)	84 (31)	20 (1)	2	2·07
	3	0·19 (1)	148 (24)	60 (21)	80 (34)	3	3·42
C(2)	1	0·15 (2)	59 (16)	34 (23)	77 (27)	1	2·93
	2	0·17 (1)	78 (27)	112 (29)	25 (28)	2	2·28
	3	0·20 (1)	33 (19)	115 (16)	110 (29)	3	3·74
C(3)	1	0·14 (2)	133 (7)	118 (22)	124 (16)	1	3·51
	2	0·17 (1)	81 (15)	147 (23)	59 (20)	2	2·36
	3	0·23 (1)	44 (6)	106 (10)	130 (7)	3	4·10
C(4)	1	0·10 (3)	157 (30)	99 (17)	111 (6)	1	4·68
	2	0·15 (1)	84 (16)	170 (1)	81 (10)	2	1·90
	3	0·23 (1)	68 (5)	96 (7)	157 (5)	3	2·12
C(5)	1	0·13 (2)	73 (37)	33 (30)	63 (12)	1	3·46
	2	0·15 (2)	151 (27)	65 (37)	104 (21)	2	2·25
	3	0·20 (1)	67 (14)	71 (10)	149 (10)	3	2·34
C(6)	1	0·11 (2)	111 (15)	39 (10)	121 (9)	1	2·56
	2	0·17 (2)	160 (1)	104 (34)	74 (46)	2	2·55
	3	0·18 (1)	95 (50)	126 (16)	144 (24)	3	2·05
C(7)	1	0·11 (2)	85 (21)	5 (21)	90	1	3·63
	2	0·16 (1)	174 (21)	84 (21)	90	2	1·48
	3	0·19 (2)	90	90	180	3	2·31
C(8)	1	0·11 (3)	133 (10)	43 (10)	90	1	2·42
	2	0·16 (1)	90	90	0	2	3·95
	3	0·20 (2)	43 (10)	47 (10)	90	3	1·32
C(9)	1	0·11 (5)	122 (10)	37 (11)	107 (11)	1	3·29
	2	0·18 (7)	112 (11)	85 (23)	23 (13)	2	4·55
	3	0·23 (3)	41 (23)	53 (20)	75 (12)	3	1·92
N(1)	1	0·12 (2)	59 (11)	34 (12)	76 (7)	1	5·20
	2	0·17 (1)	43 (11)	124 (12)	67 (7)	2	1·76
	3	0·24 (1)	63 (6)	91 (5)	153 (6)	3	3·40
N(2)	1	0·15 (2)	131 (3)	44 (5)	76 (8)	1	5·54
	2	0·23 (1)	93 (6)	112 (8)	20 (1)	2	10·02
	3	0·34 (1)	41 (3)	54 (3)	74 (5)	3	3·33
O(1)	1	0·14 (1)	137 (3)	62 (6)	119 (6)	1	6·75
	2	0·24 (1)	89 (7)	42 (5)	48 (5)	2	9·29
	3	0·34 (1)	47 (2)	62 (4)	124 (4)	3	3·49
O(2)	1	0·17 (1)	140 (7)	51 (8)	80 (6)	1	7·05
	2	0·24 (1)	115 (11)	133 (9)	53 (14)	2	6·44
	3	0·29 (1)	120 (5)	113 (6)	141 (8)	3	3·19

SAKORE, T. D., TAVALE, S. S. & PANT, L. M. (1967). *Acta Cryst.* **22**, 720.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SILVERMAN, J. & YANNONI, N. F. (1967*a*). *J. Phys. Chem.* **71**, 1381.
SILVERMAN, J. & YANNONI, N. F. (1967*b*). *J. Chem. Soc.* (B) p. 194.
SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1967). *Acta Cryst.* **23**, 1057.
TROTTER, J. & WILLISTON, C. S. (1966). *Acta Cryst.* **21**, 285.
TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.
WILLIAMS, R. M. & WALLWORK, S. C. (1966). *Acta Cryst.* **21**, 406.

Acta Cryst. (1968). B**24**, 1488

The Crystal Structures of DL-α-Amino-n-butyric Acid

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The structures of the *A* and *B* crystalline modifications of DL-α-amino-n-butyric acid have been determined. *A* is monoclinic, space group $P2_1/a$, with $a=9·85$, $b=4·77$, $c=11·94$ Å, $\beta=101·0°$. *B* is tetragonal, space group $P4_2/n$, with $a=13·40$, $c=5·82$ Å. Full-matrix least-squares refinement with anisotropic temperature factors yielded final *R* indices 0·13 and 0·12 for *A* and *B* respectively. In *A* the γ-C atom is distributed mainly among three positions corresponding to *trans*, *gauche* I and *gauche* II with respect to the nitrogen atom. In *B* γ-C is located only at the *trans* position to the nitrogen atom. Within the *A* crystals the molecules form a double layer parallel to the 001 plane through N–H· · ·O hydrogen bonds so that single layers are formed by two of the three kinds of hydrogen bond and they are joined together by the third kind to form a double layer. In *B*, one of the three kinds of hydrogen bond links the molecules head to tail along the *c* axis. The second kind links the molecules to form a column and the columns are joined together through lateral hydrogen bonds of the third kind.

Introduction

In the course of a study on the infrared absorption spectra of amino acids, Tsuboi, Iitaka, Suzuki & Mizushima (1959) found two crystalline modifications of DL-α-amino-n-butyric acid ($CH_3CH_2CH(NH_2)COOH$). These two modifications were named *A* and *B*. On the basis of infrared absorption studies they suggested that the *A* and *B* modifications are composed of the molecules of different conformational isomers. To confirm this suggestion and to determine the accurate molecular conformations of the isomers, an X-ray analysis of the crystal structures of both *A* and *B* modifications has been carried out. A preliminary report of the present work has been published (Ichikawa, Iitaka & Tsuboi, 1968).

Experimental

The crystals of the *A* modification (monoclinic) were grown from warm saturated aqueous solutions by slow cooling. They are colorless plates elongated along the *b* axis with cleavages on (001) and bounded by {001} dominating and smaller {100} faces. Crystals of the *B* modification (tetragonal) were obtained by slow recrystallization from aqueous solutions with excess of ethanol. These crystals are fine needles often fibrous but sometimes square pyramids, elongated along the *c* axis and usually mixed with the tabular *A* form crystals. The lattice dimensions were measured on precession photographs taken with Cu *K* radiation. X-ray photographs of the crystal of the *A* modification generally showed weak diffuse scattering extending in the **c*** direction along the row lines in reciprocal space. Relative intensities of these diffuse lines to the Bragg reflexions were found to vary to some extent from specimen to specimen.

Crystal data

DL-α-Amino-n-butyric acid,
$C_4H_9NO_2$ ($CH_3CH_2CH(NH_2)COOH$)

Crystal system	*A* Monoclinic	*B* Tetragonal
a	9·85 ± 0·01 Å	13·40 ± 0·01 Å
b	4·77 ± 0·005	
c	11·94 ± 0·01	5·82 ± 0·005
β	101·0° ± 0·2°	
U	551·3 Å³	1045·3 Å³
Z	4	8
Volume/molecule	137·83 Å³	130·66 Å³
Systematic absences	*h*0*l* when $h\neq 2n$ 0*k*0 when $k\neq 2n$	*hk*0 when $h+k\neq 2n$ 00*l* when $l\neq 2n$
Space group	$P2_1/a$	$P4_2/n$