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The Crystal Structures of 9-Dicyanomethylenefluorene Derivatives. I. 9-Dicyanomethylene-2,4,7-trinitrofluorene

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The crystal structure of 9-dicyanomethylene-2,4,7-trinitrofluorene is orthorhombic (space group *Pbcn*) with four molecules in a unit cell of dimensions $a=13\cdot12$, $b=11\cdot03$, $c=10\cdot40$ Å. Molecular centers lie on twofold special positions 4(*c*) so that the unpaired nitro group occurs randomly at one of two possible locations. 748 reflections observed on X-ray photographs were used to refine the structure by the method of least squares to an *R* index of 12·5 %. A slight twist of the fluorene framework into a propeller shape leaves outer rings out of parallelism by 3·2°. The unpaired nitro group is rotated out of the molecular plane by 19·3°. The force tending to maximize the resonance energy of this group is believed responsible for: (1) the intramolecular overcrowding of the observed configuration, (2) the slight deviation from planarity of the fluorene framework, and (3) the angular distortion in C–C–N bond angles. There is a herringbone packing arrangement with the overall molecular plane deviating by 0·5° from the intensely reflecting (302) plane. Limiting intermolecular contacts occur largely through the nitro groups.

Introduction

9-Dicyanomethylene-2,4,7-trinitrofluorene (DTF) is an electron acceptor synthesized recently by Mukherjee & Levasseur (1965). This compound forms stronger charge-transfer complexes than its precursor, 2,4,7-trinitrofluorenone. The crystallography of DTF and related nitrofluorenes form part of a program underway in our laboratories on the synthesis and structural characterization of new organic semiconductors and photoconductors (Mukherjee, 1966).

Experimental

The specimen selected for data collection was a well-developed prismatic plate with a long dimension of 0·8 mm (mounted coaxially in a glass capillary), an average width of 0·33 mm, and a thickness of 0·12 mm.

Crystal data

9-Dicyanomethylene-2,4,7-trinitrofluorene (DTF), $C_{16}H_5N_5O_6$; m.p. 266–268 °C.

Orthorhombic, $a=13\cdot12$, $b=11\cdot03$, $c=10\cdot40$ [radiation Mo $K\alpha$, $\lambda=0\cdot7017$ Å. These parameters, derived from measurements made on precession photographs (without film shrinkage corrections), are reproducible to $\pm0\cdot1\%$ but are assigned e.s.d.'s of 0·3% on the basis of previous experience (Buerger, 1964)].

Absent reflections: $0kl$ when k is odd; $h0l$ when l is odd; $hk0$ when $h+k$ is odd. Space group is *Pbcn* (no. 60).

Absorption coefficients for X-rays: Cu $K\alpha$, 12·67 cm^{-1}; Mo $K\alpha$, 1·57 cm^{-1}.

Density data: D_x $(Z=4)=1\cdot602$ g.cm^{-3}; D_m (flotation in $ZnCl_2$–H_2O solution) $=1\cdot58$ g.cm^{-3}.

Levels $hk0$–$hk8$ were taken with unfiltered copper radiation on an integrating Weissenberg camera used in the equi-inclination geometry. Levels were recorded on packets of five films, and the spots were measured photometrically with a densitometer. Faint spots were estimated visually. Levels $0kl$, $h0l$ and $h1l$ recorded with Zr-filtered Mo radiation on an integrating precession camera were used for approximate correlation of the relative scale of the several Weissenberg films as well as to measure the cell constants. 748 independent reflections, about half of those theoretically accessible, had measurable intensities. The usual Lorentz and polarization terms were the only corrections applied to the data.

Structure determination

Four molecules of DTF will satisfy the symmetry of space group *Pbcn* (no.60) if atoms C(7) and C(8) lie in special positions 4(*c*) of point symmetry 2 and if the unpaired nitro group is found randomly at C(2) or C(2′) (see Fig. 1 for the crystallographic numbering scheme). Several weak $0kl$ reflections of forbidden parity for this space group are observed, but in view of the results described below, are attributed to partial ordering in the position of this nitro group.

The strikingly intense 302 reflection and correspondingly strong 604 and 906 reflections indicated the orientation of the molecular plane, a result confirmed by the peaks assigned to intramolecular vectors in a sharpened three-dimensional Patterson map. We assumed a model in space group *Pbcn* placing the molecule in the (302) plane with C(7) and C(8) on the two-fold axis $0,y,\frac{1}{4}$. Atoms O(3) and O(4) were not included in the proposed structure, and atom N(3) was assigned a multiplicity of $\frac{1}{2}$. The position of the molecule along the b axis was determined by a trial and error procedure in which we refined each of several structures by two cycles of least squares employing the 233 strongest reflections. The various structures differed by molecular translations along the b axis spanning a total range of 13/60 in y in increments of 2/60. The density along the Harker Line $0,y,\frac{1}{2}$ had suggested the appropriate range in y for examination. The only structure in which the single overall thermal parameter remained positive also gave the lowest R value, 38·5%. The Fourier synthesis based upon the signs computed from this structure revealed the remaining oxygen atoms and provided the coordinates of the trial structure used in the refinement.

Refinement was accomplished by the method of full-matrix least squares (Busing, Martin & Levy, 1962) based on F_o with the weighted R value $R_w = \left[\frac{\Sigma w(F_o-|F_c|)^2}{\Sigma w_0^2F}\right]^{\frac{1}{2}}$ minimized in the procedure. Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The nitro group involved in the disorder was placed with a multiplicity of $\frac{1}{2}$ at C(2)

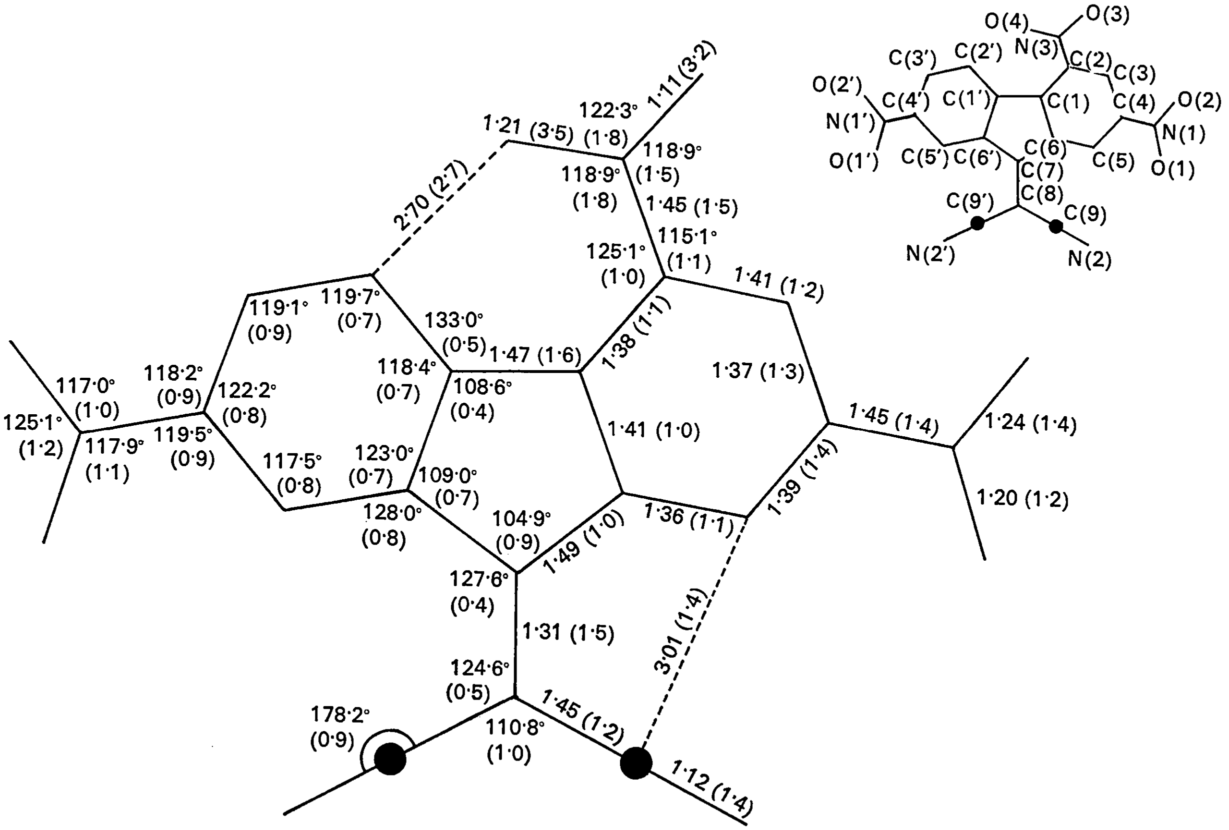

Fig. 1. The dimensions of the molecule: standard deviations, enclosed by parentheses, in units of 0·01 Å for bond lengths and in degrees for bond angles. The crystallographic numbering is shown in the smaller figure.

and C(2′). The first stage of refinement employed unit weights for all reflections and gave $R_w=30\%$ and a standard R value of 22·6% after 5 cycles. Individual isotropic thermal parameters as well as separate scale factors for levels $hk0$ to $hk8$ were varied. The scatter in values of $(F_o-|F_c|)$ as a function of F_o for the last cycle suggested the following standard deviations from which new weights were derived: $\sigma=3{\cdot}0$ for $F_o\le 20$, $\sigma=4{\cdot}5$ for $20<F_o\le 40$, $\sigma=5{\cdot}5$ for $40<F_o\le 60$, $\sigma=7{\cdot}5$ for $60<F_o\le 100$, $\sigma=0{\cdot}1F_o$ for $100<F_o\le 200$, $\sigma=0{\cdot}2F_o$ for $F_o>200$. (F_o as given, is roughly 3·25 absolute). The reflections 200, 400, 600 and 002 were assigned zero weights. Refinement was continued for four additional cycles with R_w dropping to 26·6% and R to 18·4%. Four more cycles with thermal parameters allowed to vary anisotropically completed the refinement. Parameter changes during the last cycle were typically well below $0{\cdot}1\sigma$ [except for changes of $0{\cdot}2\sigma$ in the parameters of O(1) and $0{\cdot}4\sigma$ in the β_{12} parameters of O(4)]. Final R values are: $R_w=17{\cdot}2\%$ and $R=12{\cdot}5\%$ for the 748 observed reflections; $R_w=20{\cdot}2\%$ and $R=17{\cdot}1\%$ when 218 unobserved reflections in the same θ range as the observations are included. There were about 5 observations per parameter and the final goodness of fit $[\Sigma w(F_o-|F_c|)^2/(N_0-N_v)]^{\frac{1}{2}}$ was 1·5.*

As scale factors for individual levels were allowed to vary during the anisotropic portion of the refinement, we fixed arbitrarily the parameter β_{33} of atom C(2) at its isotropic value in order to remove the indeterminacy produced by this mode of refinement (Lingafelter & Donohue, 1966). The expected strong interactions (values from 0·5 to 0·7 in the correlation matrix) occurred between the scale parameters and β_{33} parameters of the other atoms. An overall scale factor of 3·0 refined to individual values ranging from 3·0 to 3·5 for the 9 Weissenberg levels. They had been placed on a common scale previously by the supplementary precession camera data.

The final Fourier maps show no features inconsistent with the disordered structure in *Pbcn*, but location of the hydrogen atoms was not possible. The agreement of observed and calculated structure factors as well as the final stereochemistry leaves little doubt as to the correctness of the structure. However, the several weak $0kl$ reflections with k odd observed on our films could mean that the structure is an ordered one in space group $Pna2_1$ (no.33). This possibility was tested by least-squares refinement (not carried to convergence) and rejected on the basis of unreasonable results. Seeking an alternative explanation, we computed structure factors using the final parameters but allowed a partial ordering by varying the relative weights used in the

Table 1. *Final positional parameters x,y,z in fractional coordinates, anisotropic thermal parameters β_{ij}, and r.m.s. displacements $\mu(R_i)$ in Å along the three principal axes of the thermal ellipsoids*

The standard deviations given in parentheses refer to the last significant figure listed.
Anisotropic thermal parameters are based on the expression $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.

	x	y	z	$\beta_{11}10^4$	$\beta_{22}10^4$	$\beta_{33}10^4$	$\beta_{12}10^4$	$\beta_{13}10^4$	$\beta_{23}10^4$	$\mu(R_1)$	$\mu(R_2)$	$\mu(R_3)$
C(1)	0·4640 (5)	0·3819 (6)	0·1958 (7)	36 (4)	58 (7)	61 (15)	−3 (4)	8 (4)	1 (6)	0·16 (1)	0·19 (1)	0·20 (1)
C(2)	0·4143 (6)	0·4734 (7)	0·1299 (8)	50 (5)	76 (8)	70*	−2 (5)	−7 (5)	9 (7)	0·19 (1)	0·21 (1)	0·23 (1)
C(3)	0·3480 (7)	0·4440 (9)	0·0275 (10)	59 (6)	99 (10)	107 (15)	−5 (6)	8 (7)	31 (8)	0·20 (2)	0·23 (1)	0·28 (2)
C(4)	0·3332 (6)	0·3243 (9)	−0·0039 (8)	51 (5)	123 (11)	71 (14)	−17 (6)	−23 (6)	25 (8)	0·16 (2)	0·21 (1)	0·30 (1)
C(5)	0·3785 (7)	0·2303 (9)	0·0649 (8)	54 (5)	105 (9)	66 (15)	−6 (5)	−4 (6)	31 (7)	0·17 (2)	0·21 (1)	0·27 (1)
C(6)	0·4432 (6)	0·2610 (7)	0·1616 (8)	43 (4)	60 (7)	59 (14)	1 (4)	−5 (5)	13 (6)	0·16 (2)	0·19 (1)	0·21 (1)
C(7)	0·5	0·1785 (10)	0·25	40 (6)	69 (10)	53 (16)	0	−1 (7)	0	0·17 (2)	0·19 (1)	0·21 (2)
C(8)	0·5	0·0595 (9)	0·25	48 (7)	53 (10)	90 (18)	0	−7 (7)	0	0·18 (2)	0·20 (2)	0·23 (2)
C(9)	0·4436 (7)	−0·0149 (9)	0·1603 (10)	70 (6)	85 (9)	122 (15)	−17 (6)	−11 (8)	−14 (9)	0·20 (2)	0·26 (1)	0·27 (1)
N(1)	0·2654 (7)	0·2962 (10)	−0·1099 (10)	86 (7)	138 (11)	156 (15)	−27 (7)	−54 (8)	40 (10)	0·21 (2)	0·26 (1)	0·37 (1)
N(2)	0·4019 (8)	−0·0709 (8)	0·0881 (11)	129 (9)	96 (9)	178 (17)	−31 (8)	−46 (9)	−25 (9)	0·20 (2)	0·30 (1)	0·37 (1)
N(3)	0·4268 (14)	0·6023 (12)	0·1541 (18)	107 (13)	53 (13)	60 (22)	33 (10)	13 (13)	12 (13)	0·16 (3)	0·18 (3)	0·32 (2)
O(1)	0·2421 (8)	0·1923 (8)	−0·1261 (11)	154 (10)	143 (11)	262 (18)	−71 (8)	−131 (11)	62 (11)	0·20 (3)	0·27 (1)	0·50 (1)
O(2)	0·2366 (6)	0·3821 (8)	−0·1771 (8)	103 (7)	156 (10)	151 (15)	0 (6)	−61 (6)	40 (8)	0·20 (2)	0·31 (1)	0·37 (1)
O(3)	0·4057 (24)	0·6678 (22)	0·0772 (24)	280 (35)	181 (27)	225 (39)	73 (26)	−65 (29)	67 (27)	0·23 (4)	0·40 (3)	0·52 (3)
O(4)	0·4590 (16)	0·6348 (14)	0·2577 (34)	194 (30)	77 (13)	260 (38)	48 (13)	13 (35)	−32 (24)	0·19 (2)	0·38 (2)	0·42 (3)

* See refinement section of text.

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* As a referee has pointed out, the strong reflections (about 5% of the data) show pronounced extinction effects. However, the usual type of empirical plot does not show a systematic linear effect with I_c and in view of this as well as the structural disorder, no extinction correction was made. In any case, these reflections are heavily discriminated against in the refinement.

placement of the nitro group at C(2) and C(2′). The ordering was assumed to follow the equivalent positions of *Pna*2₁. The structure factors used in the refinement in space group *Pbcn* are rather insensitive to these weights, *e.g.* $R=12{\cdot}5\%$ for weights 0·65, 0·35 and $R=12{\cdot}7\%$ for weights 0·8, 0·2. However, the 0*kl* reflections for *k* odd are quite sensitive and one notes (Table 4) that three of the four largest computed values correspond to three of the four strongest observed extinction violations. For these reflections weights of 0·65,

Table 2. *Observed and calculated structure factors*

The columns from left to right are *h*, *k*, F_o and $4F_c$.

h	k	F_o	$4F_c$
	$l=0$		
0	0		2944
2	0	117	142
4	0	179	216
6	0	259	-341
8	0	83	75
10	0	123	-128
12	0	54	53
1	1	154	159
3	1	159	-162
5	1	45	-46
7	1	17	14
9	1	129	-113
15	1	39	-41
0	2	144	-181
2	2	292	365
4	2	193	-227
8	2	99	-92
10	2	46	47
12	2	41	38
16	2	32	-31
1	3	220	-294
3	3	104	-78
5	3	92	-74
7	3	71	69
9	3	117	106
11	3	49	57
13	3	56	29
15	3	22	25
0	4	25	-27
2	4	61	53
4	4	161	-196
6	4	70	-54
8	4	50	-43
14	4	34	39
1	5	75	-81
3	5	196	-192
5	5	39	30
7	5	86	-80
9	5	69	58
11	5	41	24
13	5	65	55
0	6	35	-19
2	6	84	-71
4	6	91	98
6	6	33	26
12	6	57	51
1	7	85	91
3	7	71	66
5	7	63	-65
7	7	70	67
9	7	44	38
11	7	48	54
13	7	33	-34
2	8	116	119
6	8	71	-67
8	8	86	-98
10	8	44	-44
12	8	65	-71
3	9	111	109
5	9	41	35
7	9	33	-37
9	9	27	23
2	10	41	-40
4	10	67	45
6	10	57	-58
1	11	37	-40
3	11	55	-39
7	11	28	23
4	12	28	-27
	$l=1$		
1	1	197	204
2	1	232	231
3	1	131	127
4	1	85	-88
5	1	96	88
6	1	42	-35
7	1	39	35
8	1	110	104
11	1	24	-21
12	1	27	-16
15	1	16	12
16	1	17	-21
0	2	171	-184
1	2	224	275
2	2	88	82
3	2	15	12
4	2	161	-164
5	2	21	-28
7	2	55	54
8	2	84	-84
9	2	33	29
10	2	30	-31
11	2	42	-38
12	2	53	-53
13	2	31	24
14	2	43	-37
16	2	19	-30
1	3	122	-130
2	3	154	-180
4	3	122	-122
5	3	155	174
7	3	68	52
8	3	92	81
9	3	71	56
10	3	20	-26
14	3	21	26
15	3	31	-28
0	4	151	139
1	4	151	163
2	4	95	116
3	4	174	182
4	4	100	-102
5	4	25	10
7	4	94	-90
8	4	15	-1
11	4	17	18
1	5	97	114
2	5	101	101
3	5	34	20
4	5	32	26
5	5	32	-35
6	5	55	-42
12	5	35	-34
13	5	21	19
0	6	125	146
1	6	60	54
2	6	66	-58
3	6	96	95
4	6	26	-19
5	6	36	-32
6	6	118	-130
8	6	49	-41
10	6	27	-31
11	6	51	-48
1	7	28	-18
2	7	27	31
4	7	78	-73
5	7	38	-20
7	7	39	32
9	7	43	40
10	7	45	-45
11	7	73	79
13	7	35	43
14	7	30	41
1	8	29	32
2	8	40	-43
3	8	43	48
4	8	41	-33
5	8	42	-39
6	8	57	-54
1	9	23	30
2	9	67	49
3	9	42	-30
4	9	51	54
5	9	55	-53
7	9	39	-39
8	9	33	-31
0	10	53	43
2	10	84	90
5	10	72	68
8	10	28	-22
4	11	28	19
6	11	23	-16
8	11	24	-21
9	11	21	16
	$l=2$		
0	0	70	-113
1	0	74	57
2	0	402	-416
3	0	910	-1159
4	0	476	-550
5	0	83	60
6	0	98	96
7	0	131	-142
9	0	92	110
12	0	22	18
13	0	31	36
16	0	17	-20
1	1	54	50
2	1	84	-79
3	1	157	-156
4	1	18	-3
5	1	134	125
6	1	38	-31
7	1	106	94
8	1	15	18
13	1	57	60
14	1	29	-31
16	1	22	-12
0	2	85	-100
1	2	265	-325
2	2	27	29
3	2	80	85
4	2	26	12
5	2	180	-173
7	2	98	94
8	2	18	-18
9	2	34	20
11	2	45	40
13	2	45	-36
14	2	19	18
15	2	25	-32
1	3	106	84
2	3	48	40
3	3	113	147
4	3	95	121
5	3	48	-53
6	3	91	82
8	3	63	61
9	3	40	-35
11	3	57	-49
13	3	29	-34
14	3	30	-34
0	4	187	198
1	4	109	-127
3	4	93	-92
4	4	96	94
5	4	75	-67
7	4	36	40
8	4	76	76
11	4	32	39
12	4	30	-26
13	4	30	25
14	4	20	-20
1	5	148	147
2	5	48	43
3	5	59	60
4	5	47	-50
5	5	61	46
6	5	123	112
7	5	22	-23
9	5	43	-43
10	5	63	66
12	5	29	-35
1	6	85	82
2	6	33	-28
3	6	20	31
5	6	33	27
7	6	38	-32
8	6	51	-43
9	6	39	32
10	6	22	-21
1	7	27	-24
2	7	73	-70
3	7	39	-45
4	7	45	39
5	7	75	-74
7	7	56	-51
8	7	58	62
10	7	39	-46
0	8	172	-147
1	8	51	-49
3	8	24	-23
4	8	24	22
5	8	104	-101
6	8	33	34
7	8	31	-28
8	8	54	54
9	8	21	-27
10	8	66	71
11	8	26	23
1	9	110	-106
2	9	21	-3
4	9	40	-47
5	9	33	-32
6	9	31	-21
7	9	48	-41
0	10	25	-17
1	10	51	51
2	10	25	13
3	10	34	-37
4	10	45	36
7	10	26	-24
9	10	22	23
1	11	47	38
4	11	28	23
6	11	21	23
0	12	19	18
1	12	28	-22
2	13	28	23
	$l=3$		
1	1	55	-66
2	1	99	81
3	1	150	-131
4	1	216	-204
5	1	49	-45
6	1	153	-135
9	1	10	-7
10	1	31	-21
11	1	39	-33
13	1	32	-30
14	1	28	30
0	2	158	179
1	2	40	-21
2	2	72	68
4	2	63	56
5	2	198	-214
6	2	8	6
7	2	45	33
8	2	44	40
9	2	48	-43
10	2	46	35
11	2	56	-54
12	2	48	50
14	2	21	26
1	3	139	-162
2	3	114	117
3	3	13	-9
5	3	76	66
6	3	73	65
7	3	25	-26
8	3	30	-18
9	3	45	-52
10	3	22	-18
12	3	63	-64
13	3	40	35
0	4	198	229
1	4	78	-76
2	4	29	27
3	4	59	57
4	4	144	-149
5	4	42	-53
6	4	68	-63
7	4	10	5
8	4	41	29
13	4	36	-32
1	5	38	35
2	5	26	-16
3	5	69	-70
5	5	54	-40
6	5	45	-44
7	5	18	18
8	5	42	47
10	5	53	53
11	5	11	-19
0	6	65	64
1	6	69	70
2	6	59	68
3	6	100	-114
6	6	41	39
7	6	19	13
9	6	75	74
10	6	32	27
1	7	33	-27
2	7	49	43
6	7	50	48
7	7	45	-42
8	7	87	114
9	7	32	-38
0	8	74	81
1	8	36	35
2	8	24	24
3	8	52	-51
5	8	19	-20
7	8	16	18
8	8	39	23
9	8	32	31
1	9	75	79
2	9	51	-57
4	9	35	-40
5	9	33	-29
10	9	18	17
0	10	28	-37
1	10	82	-78
3	10	35	-43
5	10	43	-50
6	10	30	-23
7	10	30	-22
8	10	27	-34
11	10	8	14
5	11	22	-17
6	11	16	18
10	11	6	-8
	$l=4$		
0	0	257	-283
1	0	187	-194
2	0	171	153
3	0	107	113
4	0	72	-52
5	0	205	189
6	0	392	429
7	0	210	204
8	0	50	30
9	0	16	-18
10	0	24	21
11	0	22	-25
12	0	30	33
13	0	26	-22
1	1	35	18
2	1	63	52
3	1	131	-126
4	1	48	50
5	1	47	37
6	1	52	49
7	1	24	32
8	1	65	-51
9	1	64	-70
10	1	42	42
11	1	59	-60
12	1	17	21
13	1	20	-25
0	2	41	34
1	2	28	-31
2	2	169	-182
3	2	65	69
4	2	143	153
5	2	29	-21
6	2	23	-14
7	2	38	-29
8	2	66	63
10	2	50	-53
11	2	35	42
12	2	24	-27
1	3	37	-21
2	3	104	-99
3	3	37	38
4	3	23	-13
5	3	20	19
6	3	81	-94
8	3	44	-30
9	3	29	35
10	3	43	-37
11	3	48	-48
12	3	32	37
15	3	17	21
0	4	183	-205
1	4	93	87
2	4	94	-93
3	4	76	-80
4	4	33	-34
5	4	118	116
6	4	31	36
8	4	44	42
9	4	45	-39
10	4	38	24
11	4	56	-61
1	5	71	-65
2	5	38	-35
3	5	14	10
4	5	101	-97
5	5	21	-13
6	5	64	-75
7	5	39	47
9	5	79	-80
0	6	45	46
1	6	46	40
2	6	30	32
4	6	19	-19
5	6	49	-39
6	6	37	36
7	6	40	-48
8	6	30	-23
9	6	12	13
1	7	50	47
2	7	70	-73
3	7	58	57
4	7	60	-48
5	7	73	68
7	7	51	-39
8	7	38	33
9	7	12	13
0	8	53	-53
2	8	63	-66
3	8	112	112
4	8	17	22
5	8	44	47
6	8	56	-68
7	8	47	56
8	8	34	27
2	9	65	53
3	9	69	68
8	9	19	26
9	9	21	25
10	9	16	19
0	10	60	-57
1	10	21	31
2	10	21	15
3	10	21	22
2	11	16	-15
4	11	24	-23
7	11	16	-15
2	12	10	-24
	$l=5$		
2	1	117	131
3	1	76	-59
4	1	28	11
5	1	43	23
6	1	64	56
7	1	109	89
8	1	80	65
9	1	85	65
10	1	28	-28
11	1	34	26
0	2	66	-63
1	2	117	139
2	2	118	-125
3	2	39	-34
4	2	56	-50
5	2	38	33
6	2	26	-31
7	2	87	81
8	2	46	-43
9	2	82	78
11	2	28	-17
1	3	52	41
2	3	84	66
3	3	74	78
4	3	15	12
5	3	25	17
6	3	37	-36
7	3	21	23
8	3	29	35
9	3	103	-87
10	3	47	44
13	3	13	15
0	4	148	160
1	4	70	-58
2	4	46	-35
3	4	77	-86
4	4	23	-15
5	4	28	29
6	4	34	-21
7	4	10	14
8	4	48	45
9	4	51	45
10	4	35	-37
13	4	12	-14
1	5	22	24
2	5	34	-27
3	5	47	-50
4	5	23	-14
5	5	27	31
6	5	20	-20
7	5	58	72
9	5	24	24
11	5	28	-21
12	5	22	-18
0	6	103	-110
1	6	40	-36
2	6	30	-34
3	6	9	12
4	6	40	-38
5	6	86	-82
6	6	55	48
7	6	26	24
8	6	19	-16
9	6	30	-27
13	6	12	-21
1	7	26	33
2	7	14	11
3	7	43	42
4	7	81	-92
5	7	81	83
6	7	50	-56
7	7	19	6
9	7	14	-14
11	7	17	-29
0	8	58	-57
2	8	30	-26
3	8	30	-22
4	8	49	-38
6	8	34	35
8	8	14	16
11	8	10	-9
1	9	45	-50
2	9	49	-46
3	9	31	-25
6	9	23	20
7	9	26	24
8	9	24	23
0	10	31	-34
2	10	35	-35
4	10	45	49
5	10	43	44
6	10	38	38
8	10	21	31
9	10	13	18
2	11	23	-22
3	11	16	14
5	11	12	-11
6	11	8	18
7	11	18	-24
	$l=6$		
0	0	123	113
1	0	37	-93
2	0	55	-55
4	0	24	26
6	0	44	-35
7	0	22	-20
8	0	153	-151
9	0	106	-82
10	0	120	-121
1	1	95	97
4	1	40	43
5	1	23	-20
7	1	81	72
8	1	80	-79
0	2	51	59
1	2	104	98
2	2	31	-21
5	2	88	82
6	2	36	-29
7	2	92	-87
8	2	48	49
9	2	23	-16
1	3	63	-64
2	3	19	14
3	3	40	-34
4	3	55	47
6	3	54	61
7	3	47	-33
8	3	50	-50
9	3	74	76
0	4	34	-30
1	4	36	-38
2	4	117	120
3	4	75	87
5	4	40	43
7	4	67	66
8	4	81	-64
1	5	38	-38
2	5	47	49
3	5	33	-34
4	5	55	48
5	5	29	33
6	5	34	-43
7	5	58	49
8	5	40	33
2	6	30	-26
3	6	29	28
4	6	57	-56
5	6	22	-20
1	7	87	-90
4	7	48	-31
5	7	42	28
0	8	88	91
1	8	46	37
2	8	69	69
4	8	66	67
6	8	51	-47
7	8	29	-27
5	9	43	-37
6	9	46	-38
7	9	32	-30
2	10	26	19
3	10	25	21
5	10	29	-28
	$l=7$		
1	1	54	51
2	1	28	27
3	1	25	-18
4	1	38	-31
5	1	31	-31
6	1	41	40
7	1	51	-42
9	1	38	-25
0	2	29	30
1	2	19	20
2	2	87	99
4	2	42	39
5	2	99	-101
6	2	89	86
7	2	20	22
9	2	30	-32
1	3	14	-14
2	3	22	14
3	3	52	-54
4	3	23	-25
5	3	24	25
6	3	100	-114
7	3	33	35
8	3	34	-23
0	4	18	-18
3	4	72	-64
4	4	37	-30
5	4	43	37
6	4	52	58
7	4	38	-30
9	4	25	19
3	5	42	-41
4	5	52	58
5	5	21	-20
6	5	43	47
7	5	19	22
1	6	39	40
2	6	30	-28
3	6	69	68
4	6	41	42
5	6	33	27
7	6	31	29
8	6	21	16
1	7	75	-74
2	7	68	73
3	7	54	-56
5	7	21	-18
7	7	18	25
3	8	40	39
4	9	23	24
5	9	31	34
3	10	14	21
7	10	27	-33
3	11	16	15
	$l=8$		
1	0	43	-37
2	0	43	-22
3	0	65	-58
4	0	39	23
5	0	48	-58
6	0	53	54
7	0	43	-30
10	0	37	40
11	0	46	47
12	0	57	76
13	0	14	20
2	1	59	-56
3	1	68	-74
4	1	40	30
5	1	57	-54
6	1	18	19
7	1	45	-50
8	1	33	36
0	2	20	22
1	2	12	-5
2	2	66	59
3	2	31	-27
4	2	74	-72
5	2	51	51
6	2	35	-27
7	2	19	-8
10	2	24	24
1	3	41	42
2	3	15	-8
3	3	79	82
5	3	37	-39
6	3	62	61
7	3	23	-18
8	3	32	-27
0	4	26	33
1	4	39	-39
3	4	30	-29
4	4	66	66
5	4	65	-59
6	4	46	-41
7	4	23	-26
1	5	43	46
2	5	35	42
3	5	26	-30
4	5	21	18
0	6	62	69
7	6	22	22
2	7	39	35
0	8	73	-84
3	8	45	-42
4	8	34	-32
5	8	32	-31
6	8	23	-25
9	8	18	21

0·35 produce effects of about the correct order of magnitude. The significance of this imperfect correlation is difficult to assess, especially as there is no reason to expect that any partial ordering in the nitro group position at C(2) would tend to follow the symmetry of space group $Pna2_1$. However, it does lend some support to the view that the presence of these weak reflections, which are inconsistent with space group *Pbcn*, is a consequence of a degree of order in the nitro group positions at C(2) rather than a result of deviations of the other atoms from the symmetry of this space group.

Table 1 presents the final positional and thermal parameters along with the e.s.d.'s computed from the least-squares equations. In Table 2, the observed and calculated structure factors are compared. Table 3 lists computed values for unobserved reflections (not used in the refinement) and Table 4 the results of the computations on the forbidden 0*kl* reflections.

Discussion

Fig. 1 shows the molecular dimensions. Standard deviations in the bond distances are typically ±0·01 Å with larger values (±0·03 Å) for N(3)–O distances. Bond lengths in the ring system are close to those in fluorene itself (Burns & Iball, 1955). We attach no particular significance to the short value of N(3)–O(3) in view of the disorder and the absence of correction for thermal motion. Bond lengths in the dicyanomethylene group are close to expected values for an ethylenic double bond such as C(7)–C(8) and a single bond between sp^2- and sp-hybridized carbon atoms such as C(8)–C(9). This is in contrast to the dimensions of this group in several of the TCNQ salts (Fritchie & Arthur, 1966, Table 4) or in 10-dicyanomethyleneanthrone (Silverman & Yannoni, 1967*a*) where values from 1·36–1·40 Å for bonds corresponding to C(7)–C(8) and values from 1·40–1·43 Å corresponding to C(8)–C(9) are found. Apparently, in these systems greater conjugation with the ring system and/or the presence of a negative charge on a TCNQ ion-radical is responsible for a degree of double bond character in C(8)–C(9) and single bond character in C(7)–C(8) not seen in the present compound.

Standard deviations in bond angles range from 0·4 to 1·0° in general with larger values of 1·5–1·8° for angles involving O(3) and O(4). The overcrowding between O(4) and the hydrogen atom on C(2′) is reflected in the difference of 10° between the two C–C–N angles at C(2). A closely similar configuration for a substituent is found in 9-anthraldehyde (Trotter, 1959*c*) and in both cases an attempt to maximize resonance energy is involved (see below). A second intramolecular interaction, that between C(5) and C(9), causes exterior angles at C(7) and C(8) to increase by a few degrees to 127·6° and 124·6° respectively with concomitant decreases in the ring angle at C(7) to 104·9° and in the angle C(9′)–C(8)–C(9) to 110·9°. These in-plane or angular adjustments increase the intramolecular contact C(5)···C(9) to 3·01 Å close to the typical value of 3·0 Å for interacting carbon atoms in overcrowded aromatic systems (Ferguson & Robertson, 1963).

Table 3. *Structure factor comparisons for unobserved reflections*

Format is as in Table 2.

		$l=0$	
11	1	0	-5
13	1	0	5
6	2	0	19
14	2	0	19
10	4	0	7
12	4	0	-11
8	6	0	0
10	6	0	1
4	8	0	20
5	11	0	-17
2	12	0	10
		$l=1$	
10	1	0	5
13	1	0	-9
14	1	0	-5
6	2	0	11
15	2	0	9
3	3	0	12
6	3	0	14
11	3	0	4
12	3	0	5
13	3	0	14
6	4	0	-1
9	4	0	7
10	4	0	16
7	5	0	-11
8	5	0	-5
9	5	0	-18
10	5	0	13
11	5	0	10
7	6	0	14
9	6	0	-19
3	7	0	1
6	7	0	-12
8	7	0	-8
12	7	0	-5
1	10	0	-10
3	10	0	-3
6	10	0	21
7	10	0	7
1	11	0	-9
2	11	0	-0
3	11	0	-17
5	11	0	-6
7	11	0	-0
		$l=2$	
8	0	0	-1
10	0	0	-6
11	0	0	-11
14	0	0	-10
15	0	0	14
9	1	0	-2
10	1	0	9
11	1	0	16
12	1	0	-2
15	1	0	15
6	2	0	11
10	2	0	-13
12	2	0	5
10	3	0	4
12	3	0	-6
6	4	0	-8
9	4	0	9
10	4	0	-14
8	5	0	3
11	5	0	3
4	6	0	21
6	6	0	5
6	7	0	12
9	7	0	5
2	8	0	6
3	9	0	-9
5	10	0	4
6	10	0	6
8	10	0	6
2	11	0	9
3	11	0	14
5	11	0	4
1	13	0	0
		$l=3$	
8	1	0	4
12	1	0	11
3	2	0	21
13	2	0	11
4	3	0	-8
11	3	0	-0
9	4	0	-3
10	4	0	4
11	4	0	13
12	4	0	14
4	5	0	-23
9	5	0	-11
4	6	0	-8
5	6	0	-11
8	6	0	-7
3	7	0	-10
4	7	0	16
5	7	0	-15
4	8	0	6
6	8	0	3
3	9	0	10
6	9	0	2
7	9	0	-5
8	9	0	1
9	9	0	8
2	10	0	-24
4	10	0	-8
9	10	0	-15
10	10	0	-13
1	11	0	17
2	11	0	-5
3	11	0	-3
4	11	0	19
8	11	0	-12
9	11	0	21
		$l=4$	
9	2	0	-2
7	3	0	-2
13	3	0	-0
14	3	0	3
7	4	0	-31
8	5	0	-16
3	6	0	6
6	7	0	18
1	8	0	6
1	9	0	2
4	9	0	23
5	9	0	17
6	9	0	20
7	9	0	14
1	11	0	1
3	11	0	-9
5	11	0	-3
6	11	0	-8
7	11	0	-15
1	12	0	4
		$l=5$	
1	1	0	-2
10	2	0	-9
11	3	0	-3
12	3	0	20
11	4	0	-0
12	4	0	13
8	5	0	-18
10	5	0	-3
10	6	0	-7
11	6	0	-17
12	6	0	-15
8	7	0	-2
10	7	0	-3
1	8	0	6
5	8	0	-20
7	8	0	0
9	8	0	-2
10	8	0	-17
4	9	0	-4
5	9	0	9
1	10	0	5
3	10	0	19
7	10	0	7
1	11	0	10
4	11	0	5
		$l=6$	
5	0	0	1
3	1	0	-7
6	1	0	-25
3	2	0	5
4	2	0	-4
5	3	0	-9
4	4	0	-10
6	4	0	-14
0	6	0	1
1	6	0	10
6	6	0	16
2	7	0	-3
3	7	0	-4
3	8	0	-27
5	8	0	21
1	9	0	-2
2	9	0	20
3	9	0	16
4	9	0	-17
1	10	0	-2
4	10	0	-7
		$l=7$	
8	1	0	8
3	2	0	-7
8	2	0	-8
1	4	0	-21
2	4	0	-8
8	4	0	-0
1	5	0	3
2	5	0	9
6	6	0	-3
4	7	0	-0
6	7	0	-7
1	8	0	4
2	8	0	-4
1	9	0	11
2	9	0	0
3	9	0	15
1	10	0	13
2	10	0	16
4	10	0	-3
5	10	0	15
6	10	0	-11
1	11	0	-7
2	11	0	-22
		$l=8$	
8	0	0	-0
9	0	0	10
1	1	0	10
8	2	0	3
9	2	0	-4
4	3	0	15
2	4	0	-4
1	6	0	-3
2	6	0	10
3	6	0	16
4	6	0	-7
5	6	0	-2
6	6	0	0
1	7	0	-6
1	8	0	0
7	8	0	-5
8	8	0	-26

Table 4. *Observed and calculated structure factors for symmetry forbidden 0kl reflections*

Weights of 0·65, 0·35 are assumed for the nitro group occupancy of C(2), C(2′). Reflections not observed on the films are indicated by zeros in the F_o column. See text for further explanation.

k	l	F_o	$4F_c$
1	1	43	38
3	1	0	12
5	1	0	12
7	1	0	0
9	1	0	2
1	2	14	33
3	2	43	27
5	2	0	7
1	3	21	10
3	3	24	14
5	3	43	3
1	4	0	1
3	4	0	11
5	4	0	10
7	4	0	5
1	5	0	9
3	5	0	1
5	5	0	4
7	5	0	3
1	7	16	2
3	7	14	9
5	7	0	2
1	8	0	7
3	8	0	1
5	8	0	9

The least-squares method of Schomaker, Waser, Marsh & Bergman (1959) was used to fit a plane to the positions of the 13 atoms of the fluorene moiety (equation: $10{\cdot}030x-6{\cdot}707z=3{\cdot}338$) and a second plane to the atomic positions in an outer benzene ring ($10{\cdot}047x+0{\cdot}316y-6{\cdot}684z=3{\cdot}457$). Deviations are shown in Fig. 2.

The carbon framework shows highly significant deviations from planarity of up to ±0·054 Å. The benzene ring plane which passes within ±0·019 Å or 2·4 e.s.d. of the defining atoms is out of parallelism with the *b* axis by 1·6°. Hence, the fluorene moiety consists of essentially planar outer benzene rings twisted by 3·2° with respect to each other into a propeller shape. The atoms of the five membered ring lie within ±0·009 Å or 1·3 e.s.d. of their least-squares plane ($10{\cdot}157x-6{\cdot}587z=3{\cdot}432$). The dicyanomethylene group is planar to within ±0·016 Å or 1·6 e.s.d. and appears to follow the twist of the fluorene moiety by rotating about the C(7)–C(8) direction by 2·3°. Thus, atoms C(5), C(6), C(7), C(8) and C(9) are left planar to within ±0·011 Å or 1·4 e.s.d.

The paired nitro groups and the unpaired nitro group are rotated out of plane by 7·8 and 19·3° respectively. Overcrowded environments similar to that experienced by the nitro group at C(2) are found in 9, 10-dinitroanthracene (Trotter, 1959*a*), 9-nitroanthracene (Trotter, 1959*b*), and 1,5-dinitronaphthalene (Trotter, 1960), where the nitro groups are 64, 85 and 49° out-of-plane respectively. In the first and third molecules, mild overcrowding is produced by nitro groups attempting to move as close to planarity as possible. Of the three, 1,5-dinitronaphthalene is most closely related to the present compound in having substantial overcrowding on one side of the nitro group only. Here, the final intramolecular approaches of interacting atoms are 2·94 Å for C···O and 2·31 Å for H···O as compared with van der Waals radii of 3·1 and 2·6 Å for O···C and O···H respectively. More severe overcrowding is found in the configuration of the present molecule where these approaches shorten to 2·70 Å for O(4)···C(2′) and 1·94 Å between O(4) and the hydrogen atom on C(2′) (hypothetical position).

For a nitro group substituent in the 9,10-position of anthracene, Trotter (1959*d*) has computed that the point of balance between the force of resonance energy acting toward the plane and the forces resisting the planar configuration should occur at an angle of 65° out-of-plane, agreeing well with the value found in 9,10-dinitroanthracene. Potential function calculations described in detail elsewhere (Silverman & Yannoni, 1967*b*) predict that the corresponding minimum for the present nitro group at C(2) is within ±10° (depending on the 'hardness' of the potential function chosen) of the observed configuration of 19·3°. It is not necessary to invoke the possibility of either an internal C–H···O bond or the influence of intermolecular packing forces in order to explain the considerable intramolecular crowding involved in this configuration. The mild propeller shape of the fluorene framework, and the angular strain present in the C–C–N bond angles at C(2), as well as a difference of 8° in the two C–C–H bond angles at C(2′) predicted by the potential function computations, all represent strain incurred by the molecule in order to allow the nitro group at C(2) closer to the plane. It is somewhat surprising that the nitro group is 30° closer to the plane than that found in 1,5-dinitronaphthalene. Possibly, the larger, less conjugated fluorene system undergoes angular and out-of-plane deformation more easily thus favoring an equilibrium configuration which has greater components of repulsion and strain energy balanced by an increase in resonance energy.

An edge-on view of the structure down the *b*-axis is shown in Fig. 3. As in fluorene itself (Burns & Iball, 1955) there is a herringbone packing arrangement. Molecular planes make angles of 129·5° and 50·5° with the *a* axis, a deviation of 0·5° from the intensely diffracting (302) planes. All close approaches in the structure involve the nitro groups except for a C···C contact of 3·56 Å between atoms C(2) of adjacent parallel pairs such as molecules 2 and 4. These paired molecules, related by *c*-glide planes perpendicular to the *b* axis, also have approaches of 3·01 Å for O(4)···C(4), 3·08 Å

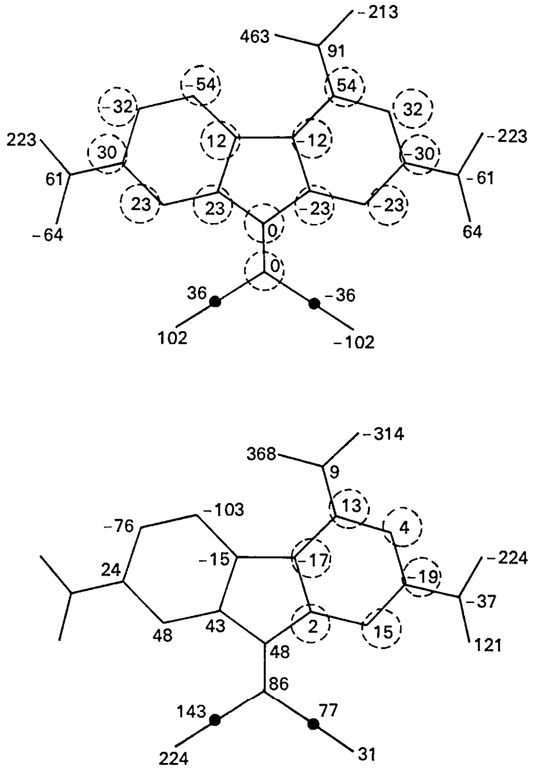

Fig. 2. Atomic deviations in units of 0·001 Å from least-squares planes fit to the positions of the fluorene moiety (upper figure) and to those of an outer benzene ring (lower figure). Circled deviations are those of plane-defining atoms.

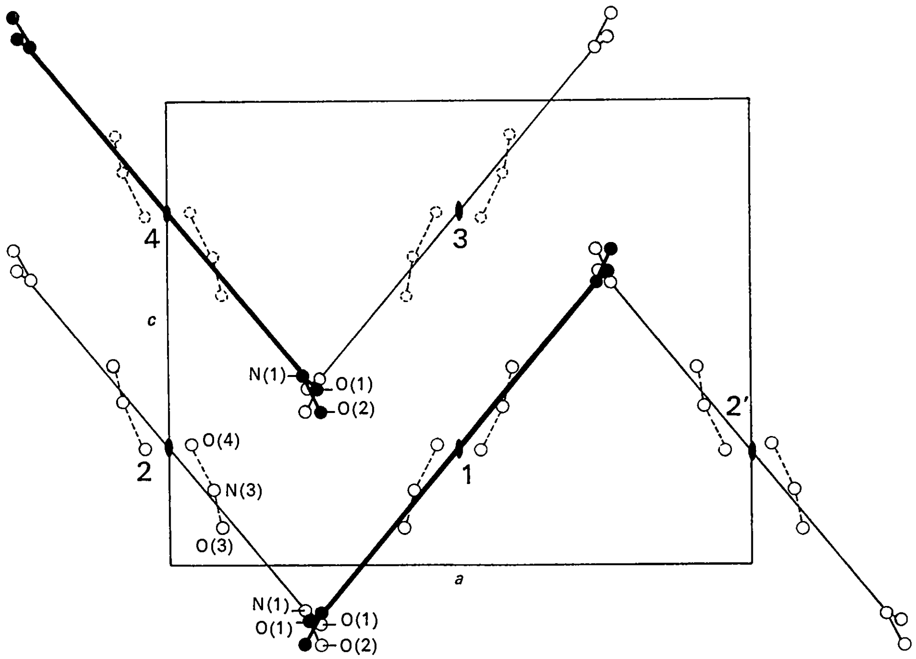

Fig. 3. Edge-on view of the structure down the *b* axis. Overall molecular planes are represented by lines; the positions of the nitro groups are shown in projection onto the *ac* plane. Each of the two possible sites for the disordered nitro group is shown as occupied .The centers of molecules 1 and 4 (thick lines) are roughly 3 Å above the *ac* plane. Those of molecules 2 and 3 (and 2′) are 3 Å below the *ac* plane. Pairs 1 and 2 are oriented with the dicyano group pointing down; pairs 3 and 4 with this group pointing up.

for O(4)···N(1), 3·00 Å for O(4)···O(2) and 3·06 Å for N(3)···O(2). Between molecules such as 1 and 2, which are related by *b*-glide planes perpendicular to the *a* axis, there are O(3)···O(1) distances of 2·88 Å and a distance of 2·40 Å between the hydrogen atom on C(3) (ideally placed) and O(1). All of the above contacts which involve O(1) or O(2) are equivalent to/or somewhat larger than the usually quoted van der Waals radii and would be from 0·1 to 0·2 Å longer if the nitro group in question were in the molecular plane rather than rotated by 7·8° from planarity. Molecules such as 1 and 4, which are related by the twofold screw axis at $\frac{1}{4},\frac{1}{4},z$, have a close approach of 3·26 Å for O(2)··· C(9). Molecules related by the *b*-axis translation make contact through an N(2)···O(3) distance of 2·89 Å. Those intermolecular contacts which are changed by assuming various combinations of ordered nitro group positions are well beyond the sum of the pertinent van der Waals radii. These results are consistent with the assumption of random occurrence of a nitro group at C(2) or C(2′).

R.M.S. components of the anisotropic thermal motion are listed in the final three columns of Table 1. The oxygen and nitrogen atoms exhibit the largest anisotropy. The spatial orientations of the ellipsoids (results not listed) are of doubtful significance in view of the disorder and the refinement of individual scale factors. No serious attempt to analyze the character of the molecular motion or to correct the bond distances seems warranted.

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