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The Crystal Structure of 2,4,7-Trinitro-9-fluorenone

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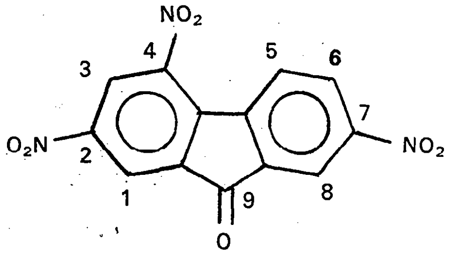
The crystal structure of 2,4,7-trinitro-9-fluorenone, $C_{13}H_5N_3O_7$, has been determined. The crystals are monoclinic, space group $P2_1/n$; cell dimensions are $a=22{\cdot}470$ (3), $b=5{\cdot}652$ (1), $c=10{\cdot}278$ (2) Å, $\beta=105{\cdot}51$ (1)°; $Z=4$; $D_m=1{\cdot}692$ and $D_x=1{\cdot}675$ g.cm^{-3}. An initial set of three-dimensional X-ray data was obtained using Cu radiation with a manually operated General-Electric diffractometer; a second set was measured using Mo radiation with a computer controlled Picker diffractometer. The structure was solved with direct methods; refinement by full-matrix least-squares calculations gave an R index of 0·057 (weighted $R=0{\cdot}045$) for the Mo data. Anisotropic temperature factors were used for the carbon, nitrogen and oxygen atoms while the hydrogen atoms were refined with isotropic terms. The fluorene nucleus is planar. The bond lengths indicate that there is little interaction between the benzene rings, or between the rings and the carbonyl group. Because of steric crowding, the C(4) nitro group is twisted out of the C(1)–C(2)–C(3)–C(4)–C(4*a*)–C(9*a*) benzene ring plane by 34°. A 23° r.m.s. rigid body libration of the C(7) nitro group about the C(7)–N bond was found.

Introduction

There has been some interest in our laboratories in the valence characteristics of fulvalenes containing the fluorenylidene moiety. With the goal in mind of forming a basis for future comparisons with possible charge separated fluorenylidene-fulvalenes, the crystal structure of 2,4,7-trinitro-9-fluorenone (TNF) is reported and its structural features are compared with those of known fluorene derivatives. TNF has been used routinely to prepare molecular complexes of polynuclear aromatic hydrocarbons since its first utilization by Orchin & Woolfolk (1946). TNF's behavior as a strong charge transfer acceptor has been described (Nepras & Zahradnik, 1964) and an extensive table of its π-complex derivatives, along with their characteristic powder X-ray patterns, has also been published (Hofer, Peebles & Bean, 1963).



Experimental

Commercially available crystals of TNF (Eastman) were used throughout. The yellow blade-like crystals are monoclinic and systematic absences from equi-inclination Weissenberg and precession photographs indicated the space group $P2_1/n$. The Bragg angles for 14 reflections were measured manually on a Picker FACS-I diffractometer with Mo $K\alpha$ radiation; the unit-cell parameters determined from these data by the method of least-squares are reported in Table 1. The crystal density was determined by the neutral buoyancy method in aqueous $ZnBr_2$.

Table 1. *Physical constants and crystal data for* 2,4,7-*trinitro-9-fluorenone*

Molecular formula	$C_{13}H_5N_3O_7$
Molecular weight	315·03
Melting point	173–5 °C (uncorrected)
Habit	Yellow, blade-like crystals
Monoclinic cell parameters	($\lambda=0{\cdot}7107$ Å)
a	22·470 (3) Å
b	5·652 (1)
c	10·278 (2)
β	105·51 (1)°
D_{measd}	1·692 g.cm^{-3}
$D_{\text{X-ray}}$	1·673
Systematic absences	($h0l$): $h+l=2n+1$
	($0k0$): $k=2n+1$
Space group	$P2_1/n$
Z	4
V	1257·7 Å^3
μ (Mo $K\alpha$)	1·42 cm^{-1}

An initial set of intensity data (Table 2) was collected using a manually operated General-Electric XRD-6 diffractometer with Cu radiation. Observed reflections were defined as those peaks noticeably greater than background on a strip chart recording of intensity. Additional intensity data (Table 2) were collected from a second crystal using a Picker FACS-I diffractom-

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eter with Mo radiation. A reflection was designated observed if it was at least 2·5$\sigma(I)$ above background. The standard deviations in intensity, $\sigma(I)$, were calculated from $\sigma(I)=[C_I+K^2(C_{B1}+C_{B2})]^{1/2}$, where C_I is the total scan count, C_{B1} and C_{B2} are the two background counts and K is the ratio of the scan time to the total background time.

Table 2. *X-ray measurement data for 2,4,7-trinitro-9-fluorenone*

	First data set	Second data set
Radiation (λ)	Cu $K\alpha$ (1·5418 Å)	Mo $K\alpha$ (0·7107 Å)
Filter	Ni foil	highly oriented graphite monochromator
Crystal size	0·33 × 0·11 × 0·07 mm	0·38 × 0·12 × 0·05 mm
Crystal mounting	Parallel to **b**	
Diffractometer	General-Electric Picker FACS-I XRD-6	
X-ray detection	Scintillation detector with pulse height analyzer	
Collection method	2θ–θ scan	
2θ scan range	3·33°	1·8° + 0·692° tan θ
2θ scan speed	2° min^{-1}	0·5° min^{-1}
Background: time of stationary count at beginning and end of each scan	20 sec	40 sec
2θ (sin θ/λ) maximum	140° (0·6095)	50° (0·5947)
Number of unique data measured	2384	2211
Number of observed data	1108	1001

The structure was solved using the Cu intensity data.* The data were reduced in the normal way and scale, temperature and normalized structure factors ($|E|$) were computed. The phases of the 60 largest $|E|$'s were determined as functions of three reflections (411, 10,3,4, 745) required for origin definition using the X-ray System's direct methods subprogram *PHASE*. The subprogram uses both $\sum_2$ relationships ($S_iS_jS_k \simeq +1$, where $S_l=\cos\alpha_l$), in which all three reflections ($i, j, k \le 60$) are contained within the set of 60, and 'relationships of the second kind' ($S_iS_jS_kS_l \simeq +1$, $i, j, k, l \le 60$). These equations are developed from two $\sum_2$ relationships, each having two reflections which are members of the basic set and one common reflection which is outside the set. For example, the combination of $S_iS_jS_m \simeq +1$ and $S_kS_lS_m \simeq +1$ ($m > 60$) would give the preceding 'relationship of the second kind'. This initial set of 60 phases was then expanded to a total of 361 phases (177+, 184−) by the straightforward application of the $\sum_2$ equations. An E map computed with these 361 terms revealed the 23 C, O and N atoms; a structure-factor calculation using all of the observed data gave an initial residual ($R=\sum||F_o|-|F_c||/\sum|F_o|$) of 0·35.

The structural parameters were refined by the method of full-matrix least-squares. The final refinement cycles used anisotropic temperature factors for C, N and O,

Table 3. *Atomic fractional coordinates* (× 10^4) *and temperature factors* (× 10^3 Å^2)

Estimated standard deviations are given in parentheses.
The anisotropic temperature factors are in the form $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{23}klb^*c^*)]$.
Fractional coordinates for the hydrogen atoms are × 10^3.

	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1983 (2)	−2444 (10)	4600 (5)	44 (3)	36 (3)	59 (3)	−4 (3)	17 (3)	−4 (3)
C(2)	1797 (2)	−2977 (9)	5739 (5)	50 (3)	37 (4)	44 (3)	0 (3)	6 (3)	1 (3)
C(3)	1354 (2)	−1770 (9)	6150 (4)	46 (3)	39 (3)	38 (3)	−5 (3)	10 (2)	5 (3)
C(4)	1085 (2)	185 (9)	5374 (4)	34 (3)	35 (3)	38 (2)	−6 (3)	13 (2)	−8 (3)
C(4*a*)	1239 (2)	816 (9)	4204 (4)	36 (3)	39 (3)	37 (2)	−5 (3)	10 (2)	0 (3)
C(4*b*)	134 (2)	2720 (9)	3135 (4)	37 (3)	41 (3)	39 (3)	−4 (3)	15 (2)	0 (3)
C(5)	590 (2)	4461 (10)	2929 (4)	44 (3)	60 (4)	39 (3)	8 (3)	17 (2)	7 (3)
C(6)	515 (2)	5979 (9)	1814 (4)	47 (3)	48 (4)	46 (3)	3 (3)	12 (3)	−3 (3)
C(7)	888 (2)	5634 (10)	952 (4)	56 (3)	50 (4)	36 (3)	−3 (3)	8 (3)	15 (3)
C(8)	1316 (2)	3845 (10)	1090 (4)	54 (4)	55 (4)	44 (3)	−3 (3)	21 (3)	6 (3)
C(8*a*)	1384 (2)	2437 (9)	2205 (4)	46 (3)	37 (3)	42 (3)	−2 (3)	15 (2)	3 (3)
C(9)	1803 (2)	336 (10)	2589 (5)	45 (3)	44 (4)	50 (3)	−7 (3)	19 (3)	−1 (3)
C(9*a*)	1699 (2)	−505 (9)	3868 (4)	40 (3)	31 (3)	44 (3)	0 (3)	14 (2)	4 (3)
N(1)	2081 (2)	−5133 (8)	6548 (4)	64 (3)	56 (3)	51 (3)	−1 (3)	−2 (3)	−1 (3)
N(2)	629 (2)	1465 (10)	5891 (4)	43 (3)	66 (4)	35 (2)	1 (3)	12 (2)	3 (3)
N(3)	808 (3)	7246 (11)	−217 (5)	75 (4)	68 (4)	55 (3)	5 (4)	15 (3)	19 (3)
O(1)	2486 (2)	−6116 (8)	6176 (4)	102 (4)	61 (3)	84 (3)	38 (3)	24 (3)	15 (3)
O(2)	1892 (2)	−5678 (7)	7505 (4)	79 (3)	53 (3)	63 (2)	0 (3)	7 (2)	24 (2)
O(3)	319 (2)	372 (7)	6506 (3)	72 (3)	85 (3)	64 (2)	0 (3)	41 (2)	19 (2)
O(4)	590 (2)	3637 (7)	5715 (3)	73 (3)	43 (3)	61 (2)	9 (2)	27 (2)	3 (2)
O(5)	533 (3)	9049 (9)	−237 (4)	169 (5)	80 (4)	89 (3)	44 (4)	54 (3)	48 (3)
O(6)	1025 (3)	6662 (11)	−1106 (5)	197 (6)	175 (6)	99 (3)	91 (5)	104 (4)	85 (4)
O(7)	2151 (2)	−434 (6)	1975 (3)	69 (3)	51 (3)	73 (2)	6 (2)	46 (2)	6 (2)
H(1)	229 (2)	−335 (7)	432 (3)	56 (12)					
H(3)	120 (2)	−223 (7)	698 (3)	53 (12)					
H(5)	32 (1)	475 (5)	351 (3)	22 (9)					
H(6)	22 (2)	725 (6)	174 (3)	50 (11)					
H(8)	158 (1)	369 (6)	42 (3)	28 (9)					

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* All calculations were performed on a UNIVAC 1108 computer using the X-ray System (Stewart, 1970) and X-ray 84 (Hybl, 1970) systems of crystallographic programs.

Table 4. *Structure factor list*

The data are listed in blocks with constant *h* and *k*. Within each block, the columns are *l*, $10F_o$ and $10F_c$. The unobserved data are identified with an asterisk (*).

isotropic terms for H, and gave a residual of 0·095 for all observed Cu data. The quantity minimized in the least-squares calculations was $\sum w(|F_o|-|F_c|)^2$ with $w=1$.

The final Cu data atom parameters formed the starting point for structure refinement using the Picker Mo data. Weights, w, equal to $1/\sigma^2(F_o)$ were used in the refinement; the 'unobserved' data were included in the

Table 4 (*cont.*)

H,4,6		
-14	72•	58
-15	96	-104
-16	68•	4
-17	71	-64
-18	39•	48
-19	34•	-44
H,4,7		
0	24•	46
1	26•	-41
-1	119	-120
2	58•	6
-2	41•	-43
3	54•	15
-3	43•	17
4	31•	84
-4	41•	-55
5	35•	11
-5	47•	-34
6	30•	18
-6	103	-85
7	71•	22
-7	68•	35
8	35•	-2
-8	84	-78
9	71•	-7
-9	37•	9
10	75•	5
-10	114	139
-11	146	162
-12	68•	5
-13	28•	-32
-14	33•	-43
-15	32•	-15
-16	67•	6
-17	51•	23
-18	30•	-21
H,4,8		
0	42•	-24
1	26•	6
-1	40•	-35
2	44•	11
-2	102	101
3	71•	23
-3	48•	-58
4	34•	7
-4	82	91
5	71•	13
-5	32•	-37
6	53•	-20
-6	36•	77
7	36•	-15
-7	39•	-5
-8	97	-97
-9	71•	-9
-10	31•	-92
-11	47•	27
-12	45•	11
-13	43•	10
-14	69•	-5
-15	32•	57
-16	71•	-28
H,4,9		
0	35•	26
1	30•	43
-1	70•	31
2	28•	42
-2	50•	40
3	60•	14
-3	95	-84
-4	61•	-39
-5	47•	-32
-6	41•	6
-7	42•	9
-8	49•	67
-9	68•	45
-10	73•	-26
-11	69•	-15
-12	31•	22
-13	70•	-22
H,5,0		
1	42•	43
2	79•	-22
3	41•	-1
4	41•	23
5	62•	-37
6	144	144
7	47•	44
8	36•	-72
9	57•	-34
10	94	-97
11	41•	-50
12	94	-86
13	40•	-5
14	60•	50
15	76•	26
16	53•	9
17	34•	4
H,5,1		
0	67•	-22
1	79•	-15
-1	39•	-27
2	34•	-70
-2	67•	-33
3	32•	25
-3	123	-131
4	76•	9
-4	46•	-65
5	35•	83
-5	159	154
6	38•	-18
-6	168	170
7	110	-150
-7	101	101
8	72•	-21
-8	73•	-17
9	64•	70
-9	56•	23
10	35•	59
-10	37•	20
11	91	102
-11	74•	-36
12	48•	7
-12	36•	-63
13	73•	-12
-13	39•	-34
14	76•	28
-14	45•	-9
15	49•	20
-15	34•	-65
16	75•	-1
-16	73•	-3
-17	39•	-59
H,5,2		
0	100	77
1	136	-143
-1	35•	39
2	246	243
-2	119	-103
3	113	-135
-3	184	166
4	59•	5
-4	76•	2
5	37•	-82
-5	76•	-28
6	80	-65
-6	249	-235
7	116	140
-7	84	-87
8	38•	-1
-8	31•	-56
9	48•	-25
-9	187	206
10	96	-103
-10	100	102
11	50•	23
-11	35•	-6
12	57•	-1
-12	46•	-5
13	74•	28
-13	73•	-18
14	74•	-32
-14	95	79
15	50•	20
-15	74•	-63
-16	73•	5
-17	71•	-9
H,5,3		
0	132	-128
1	76•	3
-1	133	104
2	73	-52
-2	39•	-53
3	52•	-61
-3	132	-131
4	88	83
-4	46•	-12
5	86	-87
-5	74•	37
6	74•	8
-6	131	120
7	36•	43
-7	146	144
8	37•	63
-8	46•	29
9	43•	11
-9	45•	-13
10	49•	24
-10	107	-115
11	74•	-17
-11	142	150
12	75•	13
-12	90	89
13	47•	35
-13	37•	-79
14	54•	-38
-14	38•	14
-15	76•	-26
-16	74•	34
-17	48•	-53
H,5,4		
0	30•	12
1	38•	-53
-1	42•	-11
2	39•	1
-2	164	163
3	90	-115
-3	75•	-18
4	76•	40
-4	32•	-69
5	43•	71
-5	84	86
6	73•	-22
-6	44•	-19
7	35•	46
-7	102	-112
8	45•	-12
-8	30•	60
9	73•	9
-9	32•	59
10	47•	-16
-10	183	-197
11	38•	10
-11	81	81
12	45•	-9
-12	56•	4
-13	83	-92
-14	37•	49
-15	73•	-7
-16	36•	-33
-17	83	59
H,5,5		
0	63•	-9
1	37•	2
-1	132	-114
2	54•	8
-2	75•	-9
3	76•	29
-3	50•	-31
4	39•	34
-4	40•	52
5	110	118
-5	96	-114
6	50•	-44
-6	74•	-16
7	50•	12
-7	89	-92
8	73•	-23
-8	32•	79
9	73•	-14
-9	146	148
10	76•	14
-10	37•	-103
-11	113	119
-12	60•	6
-13	74•	-48
-14	44•	54
-15	71•	14
-16	75•	-25
H,5,6		
0	39•	48
1	48•	-20
-1	35•	-15
2	36•	-7
-2	54•	19
3	64•	-25
-3	91	68
4	38•	-53
-4	126	122
5	34•	-47
-5	42•	16
6	31•	11
-6	48•	41
7	47•	38
-7	57•	33
8	76•	-19
-8	47•	-65
-9	98	-72
-10	73•	-46
-11	43•	11
-12	38•	-19
-13	49•	-30
-14	45•	12
-15	53•	-23
H,5,7		
0	34•	-22
1	74•	-2
-1	42•	-32
2	76•	-8
-2	75•	-6
3	35•	42
-3	76•	-13
4	38•	17
-4	76•	20
-5	36•	38
-6	33•	68
-7	91	-82
-8	73•	8
-9	73•	-13
-10	30•	23
-11	33•	-20
-12	33•	-58
-13	39•	13
H,5,8		
-1	74•	-1
-2	40•	-11
-3	49•	-36
-4	82	-56
-5	49•	31
-6	97	110
-7	45•	67
-8	41•	58
H,6,0		
0	89	-98
1	84•	-6
2	70•	3
3	80•	-49
4	57•	36
5	44•	-3
6	74•	9
7	79•	23
8	38•	8
9	63•	-36
10	79•	5
11	77•	19
H,6,1		
0	74	59
1	48•	13
-1	174	-151
2	83•	1
-2	33•	49
3	50•	77
-3	122	-112
4	83•	39
-4	38•	35
5	42•	21
-5	39•	58
6	38•	-16
-6	90	-84
7	36•	14
-7	60•	54
8	79•	-25
-8	77•	-10
9	49•	39
-9	78•	-15
10	40•	-16
-10	55•	-29
-11	48•	10
-12	36•	-5
H,6,2		
0	42•	39
1	120	-133
-1	82•	1
2	50•	-53
-2	133	106
3	81•	-8
-3	113	93
4	79•	2
-4	83	-75
5	48•	-36
-5	33•	70
6	81•	-3
-6	48•	7
7	77•	6
-7	45•	-45
8	59•	44
-8	78•	1
9	36•	61
-9	50•	-1
-10	56•	3
-11	79•	-31
-12	49•	-9
H,6,3		
0	87	78
1	112	94
-1	111	-86
2	84•	0
-2	86	-85
3	81•	-7
-3	95	-73
4	37•	12
-4	47•	13
5	44•	30
-5	113	90
6	81•	4
-6	125	121
7	78•	4
-7	43•	-24
8	32•	-68
-8	44•	-71
-9	37•	53
-10	77•	7
-11	33•	-101
H,6,4		
0	71	-64
1	80•	-25
-1	80•	3
2	84•	-65
-2	46•	84
3	84•	36
-3	85	72
4	82•	-2
-4	79•	-1
5	49•	-4
-5	87	-94
-6	63•	-24
-7	61•	64
-8	83	73
-9	34•	-26
-10	43•	29
H,6,5		
0	69•	10
1	61•	-4
-1	80•	4
2	44•	47
-2	84	-19
-3	54•	-21
-4	32•	33
-5	40•	8
-6	32•	-26
-7	79•	9
-8	46•	-7

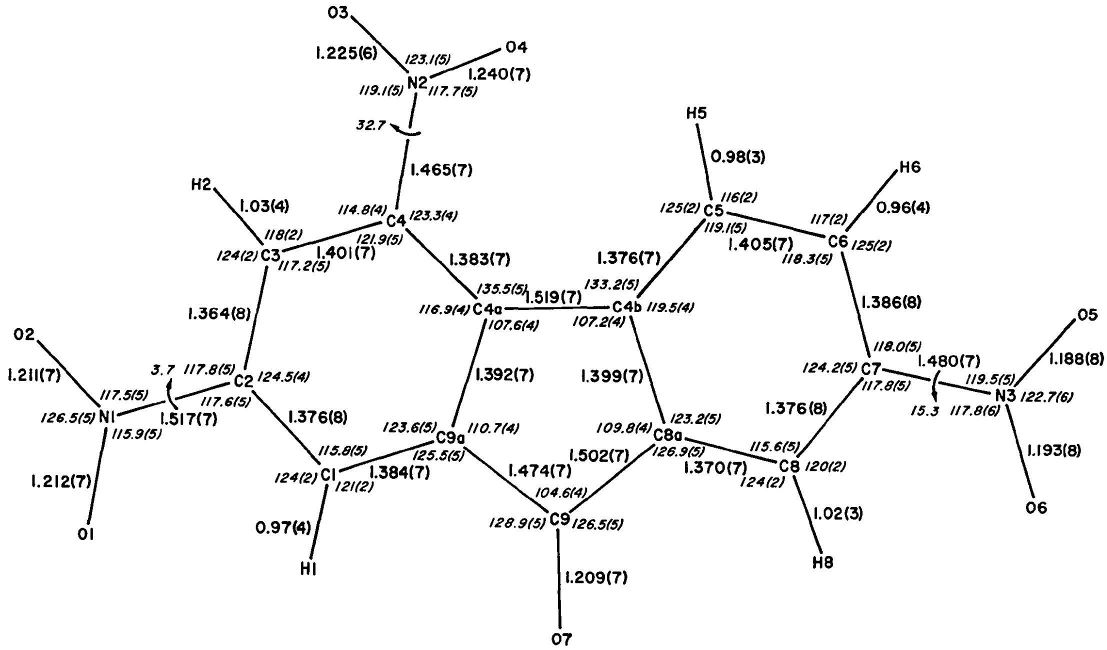

Fig. 1. Bond lengths (Å) and angles (°) for 2,4,7-trinitro-9-fluorenone. Estimated standard deviations are given in parentheses.

calculations only in those cases in which $I_c > 2\cdot5\sigma(I_o)$. The final R index was 0·057 and the weighted R index $\{[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ was 0·045. The scattering factors used for C, N and O were from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); for H from Stewart, Davidson & Simpson (1965).

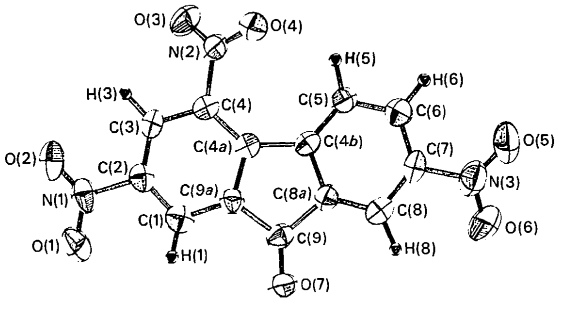

Fig. 2. A thermal ellipsoid drawing (Johnson, 1965) viewed normal to the plane of the five-membered ring. 50% probability ellipsoids were used for C, N and O with 0·1 Å spheres for H.

Discussion

The atom parameters and the structure-factor list derived from the Mo intensity data are given in Tables 3 and 4, bond distances and angles for TNF are shown in Fig. 1 and the relative magnitudes of the temperature ellipsoids are depicted in Fig. 2. There are no significant bond length differences between 2,4,7-trinitro-9-fluorenone and other known fluorenes: *viz.* fluorene (Burns & Iball, 1954), 2,4,7-trinitro-9-dicyanomethylenefluorene (Silverman, Krukonis & Yannoni, 1967), 2,7-dinitro-9-dicyanomethylenefluorene (Silverman, Krukonis & Yannoni, 1968), 2-bromo-9-fluorenone (Griffiths & Hine, 1970*a*), 2-bromo-9-diazofluorene (Griffiths & Hine, 1970*b*) and 9-fluorenone (Luss & Smith, 1972). TNF shows the longest biphenyl linkage [C(4*a*)–C(4*b*) = 1·519 Å] of the six compounds. This distance and the normal C(8*a*)–C(9) and C(9)–C(9*a*) lengths of 1·502 and 1·474 Å indicate that there is little interaction between benzene rings or between the rings and the C(9) carbonyl. The enlarged C–C–C angle at C attached to NO_2 is a common feature in the nitrofluorenes and in other nitro-aromatic compounds (Carter, McPhail & Sim, 1966).

The crystal structure of fluorene was originally investigated because of the possibility that the molecule was not planar and that optical isomers of unsymmetrical derivatives could be found (Burns & Iball, 1954). Two independent studies have verified the molecule's planarity (Burns & Iball, 1954, 1955; Brown & Bortner, 1954) as has subsequent work on several fluorene derivatives (*vide supra*). The greatest deviation from planarity was found in 2,4,7-trinitro-9-dicyanomethylenefluorene (Silverman, Krukonis & Yannoni, 1967) in which the benzene rings show a 3·2° propeller-like twist. Table 5 presents the least-squares plane data for the entire carbon skeleton, the two benzene rings and the central five-membered ring of TNF. There are no significant deviations from the basic planarity of the fluorene moiety. The angle between the planes of the two benzene rings is 1·5° and the angles between the planes of the C(1)–C(2)–C(3)–C(4)–C(4*a*)–C(9*a*) and C(4*b*)–C(5)–C(6)–C(7)–C(8)–C(8*a*) rings and the plane of the central ring are 1·0 and 1·5° respectively.

Table 5. *Least-squares planes and deviations* (Å)

	Plane 1	Plane 2	Plane 3	Plane 4
C(1)	−0·012*	0·004*	−0·040	−0·016
C(2)	−0·012*	−0·003*	−0·026	−0·030
C(3)	−0·011*	−0·008*	−0·004	−0·044
C(4)	0·032*	0·013*	0·046	−0·002
C(4*a*)	0·013*	−0·014*	0·014	−0·007
C(4*b*)	0·011*	−0·038	0·014*	−0·007*
C(5)	−0·034*	−0·102	−0·014*	−0·061
C(6)	−0·019*	−0·105	−0·002*	−0·039
C(7)	0·020*	−0·063	0·018*	0·017
C(8)	0·002*	−0·062	−0·017*	0·009
C(8*a*)	0·017*	−0·038	−0·001*	0·017*
C(9)	−0·029*	−0·053	−0·060	−0·020*
C(9*a*)	0·023*	0·010*	0·003	0·018*
N(1)	−0·092	−0·054	−0·114	−0·109
N(2)	0·082	0·051	0·117	0·031
N(3)	0·040	−0·061	0·035	0·044
O(1)	−0·051	0·001	−0·090	−0·053
O(2)	−0·169	−0·124	−0·179	−0·198
O(3)	−0·470	−0·494	−0·423	−0·531
O(4)	0·721	0·674	0·764	0·668
O(5)	0·306	0·187	0·314	0·301
O(6)	−0·214	−0·324	−0·235	−0·196
O(7)	−0·077	−0·095	−0·127	−0·055

Plane 1: $12·9344x+3·4825y+3·7416z=3·4467$.
Plane 2: $13·0742x+3·4130y+3·7960z=3·5083$.
Plane 3: $12·6560x+3·5178y+3·8341z=3·4530$.
Plane 4: $13·1468x+3·4674y+3·6443z=3·4512$.

* Atom used for definition of the plane.

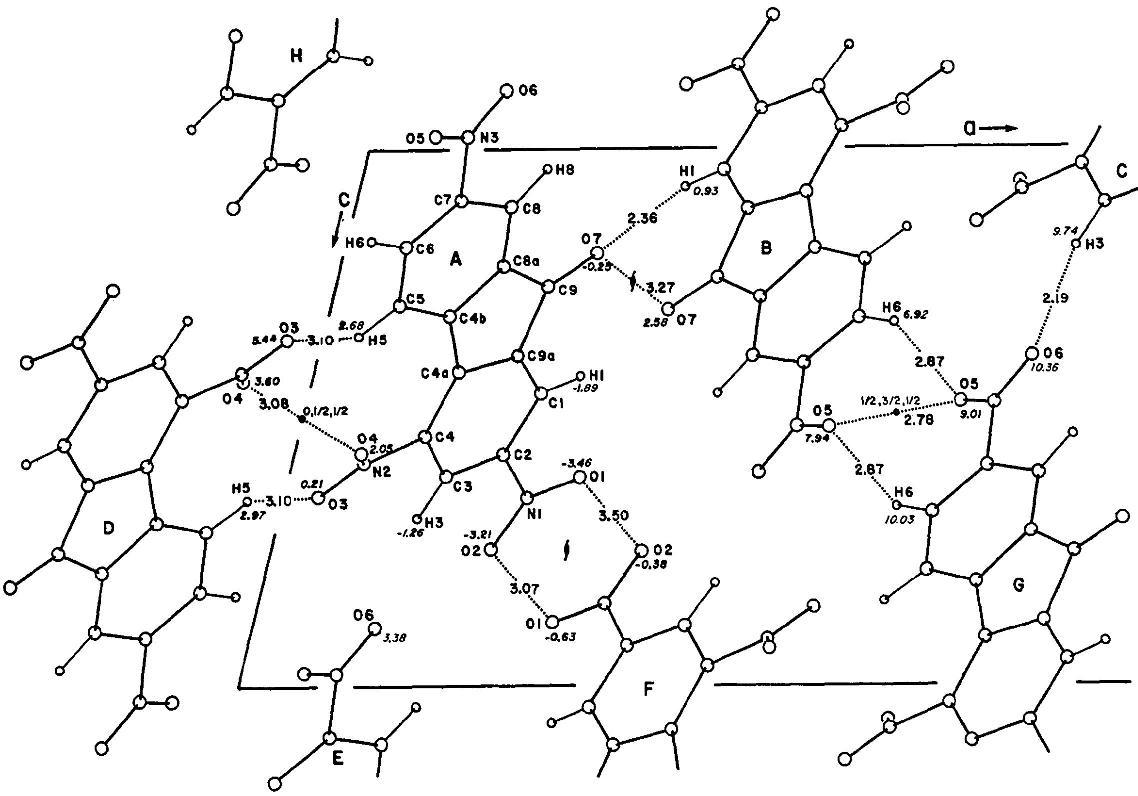

Fig. 3. Intermolecular contact diagram viewed along [010]. The distances shown are in Å. The relationships between the several illustrated molecules are: A at x, y, z; B at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; C at $\frac{1}{2}+x, 1\frac{1}{2}-y, -\frac{1}{2}+z$; D at $-x, 1-y, 1-z$; E at $x, y, 1+z$; F at $\frac{1}{2}-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; G at $\frac{1}{2}+x, 2\frac{1}{2}-y, \frac{1}{2}+z$.

The four atoms defining each nitro group are coplanar within experimental error. The twist angles for the C(2) and C(7) nitro groups are respectively 3·7 and 15·3° and are comparable with the angles found in 2,4,7-trinitro-9-dicyanomethylene [C(2)–NO_2 = C(7)–NO_2 = 7·8°] and 2,7-dinitro-9-dicyanomethylene fluorene [C(2)–NO_2 = C(7)–NO_2 = 17·6°]. Dashevskii, Struchkov & Akopyan (1966) have reported that an out-of-plane NO_2 rotation of 18° requires only 0·6 $kcal.mole^{-1}$, a value within the range of available thermal energy. The C(4)–NO_2 moiety, however, is appreciably more crowded than the other two NO_2's; the 32·7° C–N twist represents a stress energy of *ca.* 2·6 $kcal.mole^{-1}$. The close contact of this nitro group with the benzene ring is also responsible for the unequal C–C–N angles at C(4) (114·8 and 123·3°). A detailed discussion of nitro groups and crowding has been given by Silverman, Krukonis & Yannoni (1967).

A rigid-body analysis (Cruickshank, 1956) of the carbon atom portion of TNF has revealed isotropic translational and slightly anisotropic librational tensors. The largest component of the $\boldsymbol{\omega}$ tensor corresponds to a 3·1° r.m.s. libration about an axis which is essentially parallel to the C(9)–O(7) bond direction. Rigid-body analyses of the four atoms defining each of the nitro groups, has shown that, as expected, the largest librational components [C(2)–NO_2 = 13·2°; C(4)–NO_2 = 10·0°; C(7)–NO_2 = 23·0°] correspond to torsional motion about the C–N bond. The Busing & Levy (1964) riding-motion correction was applied to the N–O distances giving an average of 1·255 Å. The individual corrected lengths are N(1)–O(1) = 1·250, N(1)–O(2) = 1·230, N(2)–O(3) = 1·254, N(2)–O(4) = 1·260, N(3)–O(5) = 1·241 and N(3)–O(6) = 1·294 Å. The N(3)–O(6) correction clearly has been overestimated, stemming from the disproportionate size of the O(6) temperature factor (see Table 3 and Fig. 2).

A packing diagram viewed normal to the *ac* plane is shown in Fig. 3. The shortest contacts in the **b** direction are O(4)···C(3) = 3·08 and O(2)···O(4) = 3·03 Å with all other distances greater than 3·30 Å. The closest approaches more-or-less parallel to *ac* are O(7)···H(1) = 2·36 and O(6)···H(3) = 2·19 Å, the first of which is between molecules related by the twofold screw axis (*A* and *B*) while the second is between molecules (*C* and *G*) separated by unit translations along **b** and **c**. An analysis of the packing scheme does not provide a rationale for the large temperature factors of O(5) and O(6). Indeed, just the opposite might have been predicted since these atoms seem to be more involved in intermolecular interactions than the other nitro oxygens.

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