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Structure of Fluorene, C₁₃H₁₀, at 159 K

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Abstract. $M_r = 166.22$, orthorhombic, *Pnma*, $a = 8.365$ (3), $b = 18.745$ (4), $c = 5.654$ (2) Å, $V = 886.4$ (5) Å³, $Z = 4$, $F(000) = 352$, $D_x = 1.25$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 159$ K, $\mu = 0.654$ cm⁻¹, 1250 unique reflections, $R = 0.043$. The fluorene molecule has mirror symmetry, but is slightly non-planar. The asymmetric unit [C(1) through C(7)], however, is planar, giving the molecule a 'V' shape (dihedral angle 1.3°). The crystal is well ordered.

Introduction. The crystal structure of dibenzofuran has been recently shown to exhibit a disorder such that 9% of the molecules adopt an alternative orientation (Reppart, Gallucci, Lundstedt & Gerkin, 1984). In view of that result, it was of interest to determine whether fluorene, a molecule of quite similar geometry, might also manifest a disordered crystal structure.

The only previously reported quantitative study of the fluorene structure was by Burns & Iball (1955), who used Fourier projections and least-squares refinement for the $0kl$, $h0l$ and $hk0$ zones to determine the atomic coordinates. On the basis of this limited analysis, these authors reported no disorder.

We report here the first complete three-dimensional analysis of the fluorene crystal structure.

Experimental. Commercial fluorene (Eastman, #598) purified by vertical zone refining, 250 passes; clear, colorless crystal taken from center of ingot, cut into parallelepiped, $0.53 \times 0.59 \times 0.60$ mm. Syntex P1 diffractometer, LT-1 low-temperature attachment. Set-

ting angles for 25 reflections ($19^\circ < 2\theta < 31^\circ$) used to determine unit-cell constants and crystal orientation. Temperature measured at cold-stream exit nozzle during data collection and at crystal site after data collection with a Fluke 2100A digital thermometer (type *K* thermocouple). The temperature measured at the site of the crystal was 159 K, estimated uncertainty ± 2 K. Data collected for 3278 reflections with $+h$, $+k$, $\pm l$. ω - 2θ scan, $4^\circ < 2\theta < 60^\circ$, scan range $2\theta \text{ Mo } K\alpha_1 - 1.0^\circ$ to $2\theta \text{ Mo } K\alpha_2 + 1.1^\circ$, background/scan-time ratio 0.5. 1250 unique reflections, $R_{\text{int}} = 0.02$, 1017 reflections with $I > 3\sigma$, used in refinement. Uncertainties assigned using $\sigma_I^2 = R^2(C + 4B) + (0.02I)^2$; C total counts, R scan rate, B total background counts, I intensity. Six standard reflections (022, 051, 131, 191, 231, 270), maximum intensity variation 6%. No absorption correction. Systematic absences as well as the results from the zero-moment test of Howells, Phillips & Rogers (1950) suggested that the space group had not changed from that of the room-temperature structure, *Pnma*. Least-squares refinement using *SHELX76* (Sheldrick, 1976); $\sum w(|F_o| - |F_c|)^2$ minimized, $w = \sigma_F^{-2}$. Initial C positions taken from Burns & Iball (1955), H-atom positions from $F_o - F_c$ map. Final refinement cycle: $R = 0.043$, $wR = 0.045$, $S = 2.9$, max. $\Delta/\sigma = 0.004$, max. and min. peak heights on final $F_o - F_c$ map 0.24 and -0.21 e Å⁻³, with peaks located near bond centers and troughs located near the centers of the rings of the molecule. Scattering factor for C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Discussion. The final positional parameters and equivalent isotropic temperature factors are given in Table 1.* The atomic numbering scheme is given in Fig. 1(a). Interatomic distances and angles are given in Table 2.

The fluorene molecule possesses mirror symmetry, with the mirror plane passing through C(7) and bisecting the C(6)–C(6') bond. While the entire molecule is not planar, the asymmetric unit [C(1) through C(7)] is planar, giving the molecule a 'V' shape as shown in Fig. 1(b). The dihedral angle between these two least-squares planes in the molecule is 1.3°. In contrast, Burns & Iball (1955) found the fluorene molecule to be planar at room temperature within their (larger) uncertainty.

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39571 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

For C atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. Standard deviations are in parentheses.

	x	y	z	U_{eq}/U_{iso}
C(1)	7327 (1)	3126.5 (6)	6235 (2)	290 (3)
C(2)	7511 (2)	3849.2 (7)	6676 (2)	373 (4)
C(3)	6805 (2)	4332.6 (7)	5147 (3)	423 (4)
C(4)	5932 (2)	4102.0 (7)	3210 (3)	414 (4)
C(5)	5747 (1)	3378.3 (7)	2749 (2)	356 (3)
C(6)	6452 (1)	2892.5 (6)	4277 (2)	270 (3)
C(7)	7971 (2)	2500	7597 (3)	331 (5)
H(2)	8140 (17)	4008 (7)	8082 (25)	473 (41)
H(3)	6900 (15)	4853 (8)	5481 (24)	481 (40)
H(4)	5444 (17)	4458 (8)	2142 (25)	539 (44)
H(5)	5148 (17)	3214 (7)	1396 (23)	411 (37)
H(7)A	9178 (24)	2500	7651 (39)	511 (60)
H(7)B	7614 (24)	2500	9348 (32)	485 (56)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with standard deviations in parentheses

C(1)–C(2)	1.386 (2)	C(6)–C(6')	1.472 (3)
C(2)–C(3)	1.385 (2)	C(2)–H(2)	1.00 (1)
C(3)–C(4)	1.385 (2)	C(3)–H(3)	1.00 (1)
C(4)–C(5)	1.390 (2)	C(4)–H(4)	0.99 (1)
C(5)–C(6)	1.387 (2)	C(5)–H(5)	0.97 (1)
C(6)–C(1)	1.397 (2)	C(7)–H(7)A	1.01 (2)
C(7)–C(1)	1.504 (2)	C(7)–H(7)B	1.03 (2)
C(1)–C(2)–C(3)	118.7 (1)	H(2)–C(2)–C(1)	119.5 (8)
C(2)–C(3)–C(4)	120.9 (1)	H(2)–C(2)–C(3)	121.8 (8)
C(3)–C(4)–C(5)	120.7 (1)	H(3)–C(3)–C(2)	119.2 (8)
C(4)–C(5)–C(6)	118.5 (1)	H(3)–C(3)–C(4)	119.8 (8)
C(5)–C(6)–C(1)	120.7 (1)	H(4)–C(4)–C(3)	119.3 (8)
C(6)–C(1)–C(2)	120.5 (1)	H(4)–C(4)–C(5)	119.9 (8)
C(1)–C(6)–C(6')	108.3 (2)	H(5)–C(5)–C(4)	121.2 (8)
C(1)–C(7)–C(1')	102.7 (2)	H(5)–C(5)–C(6)	120.3 (8)
C(5)–C(6)–C(6')	131.0 (2)	H(7)A–C(7)–H(7)B	105 (1)
C(7)–C(1)–C(2)	129.1 (1)	H(7)A–C(7)–C(1)	111.9 (7)
C(7)–C(1)–C(6)	110.4 (1)	H(7)B–C(7)–C(1)	112.8 (6)

Symmetry code: (i) $x, \frac{1}{2}-y, z$.

A stereoview of the fluorene unit cell is shown in Fig. 2. The closest contact distance between molecules is 2.53 (2) \AA , between H(3) and H(4) atoms.

In contrast to the case of dibenzofuran, no disorder is apparent in the structure of fluorene at 159 K. The orientations and spacings of the molecules in this structure lead us to suggest that protons H(7)A and H(7)B of molecules disordered in the manner characteristic of dibenzofuran would give rise to very substantial repulsive interactions with the adjacent ordered molecules.

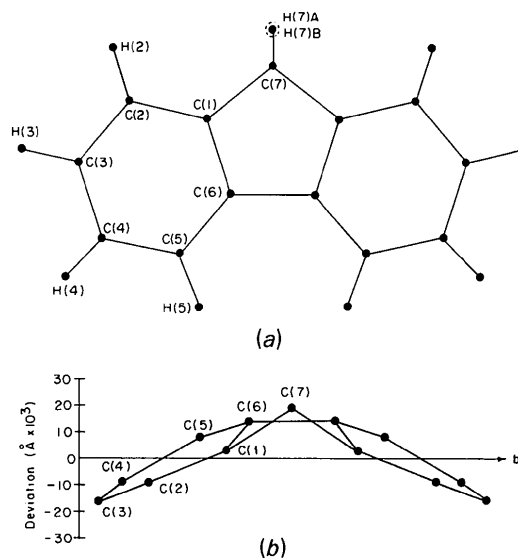


Fig. 1. (a) Atomic numbering scheme for fluorene atoms as listed in Table 1. (b) Deviation of the C-atom positions from the mean molecular plane of the fluorene molecule; uncertainties of the deviations are less than the symbol diameter.

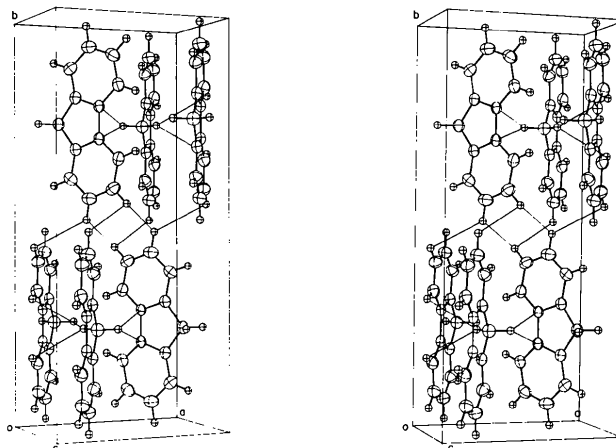


Fig. 2. Stereoview of the fluorene unit cell drawn using ORTEPII (Johnson, 1971). Also shown are the closest intermolecular contact distances.

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Note added in proof. After this article was accepted for publication, a work reporting the structure of fluorene at 295 K (Belsky, Zavodnik & Vozzhennikov, 1984) was brought to our attention. The bond lengths and angles reported therein are in very good agreement with those given for the present study, with the exception that Belsky *et al.* give the C(6)–C(6^l) bond length as 1.491 (8) Å. While the 0.019 (9) Å difference in this bond length is of questionable significance, it may also be a direct consequence of slightly different conformations of the fluorene molecule at 159 and 295 K.

A major point of disagreement in the interpretations of these structures concerns the planarity of the fluorene molecule: Belsky *et al.* report that the molecule is planar at room temperature, whereas we have determined that only the asymmetric unit is planar at 295 K, as well as at 159 K. The values of χ^2 calculated for each of the planes in question are presented in Table 3. Since $\chi^2_{0.01,10}$ is less than the calculated value at each temperature, the departures from planarity of the C atoms in the fluorene molecule are statistically significant at the 99% confidence level. However, the planarity of the asymmetric unit at each temperature is clearly evident from Table 3, and we therefore conclude that the molecule is 'V' shaped at both 159 and 295 K. The angle between the two planes in the molecule is

Table 3. χ^2 values for some least-squares planes in the fluorene molecule; ν represents the number of degrees of freedom

Plane	ν	χ^2 (calc.)			
		Present work	Belsky <i>et al.</i>	$\chi^2_{0.01,\nu}$	$\chi^2_{0.5,\nu}$
Molecule	10	280	24.7	23.21	9.34
Asymmetric unit	4	2.4	2.2	13.28	2.37

0.77 (20)° calculated from the data obtained at room temperature, in contrast to the value of 1.28 (4)° given above for the molecule at low temperature. Owing to the lower precision of the results at 295 K, the significance of the small difference between these two angles is again questionable. However, a decrease in the C(6)–C(6^l) bond length is consistent with an increase in the dihedral angle of the fluorene molecule at lower temperature.

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The Structure of Benzyl *N*-(*tert*-Butoxycarbonyl)oxamate, C₁₄H₁₇NO₅

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Abstract. $M_r = 279.3$, monoclinic, $P2_1/c$, $a = 11.089$ (2), $b = 13.751$ (2), $c = 10.145$ (2) Å, $\beta = 111.0$ (4)°, $V = 1444.2$ Å³, $D_m = 1.23$, $D_x = 1.284$ Mg m⁻³, $Z = 4$, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 0.78$ mm⁻¹, $F(000) = 592$, $T = 295$ K, $R = 0.040$ for 2227 observed reflections. The formation of this compound corroborates the Collins reaction which, by oxidation of *N*-butoxycarbonyl- and *N*-benzyloxy-carbonylserine amides and esters, yields the corresponding diamides and amide esters of oxalic acid. The

molecule is basically an amide ester of oxalic acid. The ester is a nearly planar benzyl group inclined by about 43 (1)° to the plane of the carboxylic group of atoms. The distance, 1.533 (2) Å, separating the carboxylic and the amide groups is unusually long for a C(sp²)–C(sp²) type bond. This, however, is consistent with the fact that the carboxylic plane is 90 (1)° to the amide group. The latter is coplanar with the terminal butoxycarbonyl group. A dimer is formed by hydrogen bonding of the amide groups of two adjacent molecules.

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