35. *The Structure of Some Derivatives of Fluorene and Fluorenone.*

By E. D. Hughes, C. G. Le Fèvre, and R. J. W. Le Fèvre.

No undisputed space formula for fluorene and its derivatives has yet been assigned. Mills, Palmer, and Tomkinson (J., 1924, **125**, 2365) were of the opinion that a strainless configuration for the fluorene molecule could be achieved by the planes of the benzene rings becoming inclined to the 5-ring. The stereochemical implications of such a non-planar structure have been widely investigated, with somewhat equivocal results, reviewed by Cook and Iball (*Chem. and Ind.*, 1936, **55**, 467). From their summary it is obvious that the authenticity of allegedly geometrically isomeric 9-substituted fluorenes is highly doubtful, and that no unquestioned resolution of an unsymmetrically substituted fluorene into optical isomers has yet been made.

Some physical data are on record having a bearing on the present question. Hengstenberg and Mark (*Z. Krist.*, 1929, **70**, 289) and Cook and Iball (*loc. cit.*) examined crystalline fluorene by means of *X*-rays. The observations are apparently not identical. The latter authors, however, state that they can reconcile their results with a space formula for the molecule in which the aromatic nuclei are flat regular hexagons inclined at 20° about the common links to the plane of the pentagonal ring to which they are attached.

This paper records certain dipole-moment determinations (Table I) and contains a discussion of their significance in relation to the general problem.

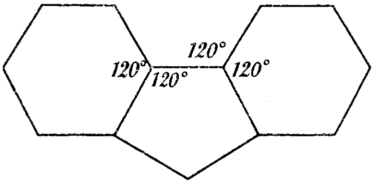
Possible Spatial Configurations.—In attempting to consider the above results, it at once becomes obvious that in default of definite experimental evidence certain assumptions have to be made. We will, therefore, begin by supposing the five-membered ring to be regular, *i.e.*, with all its angles 108°, and since 120° is the internal angle of each aromatic ring, it follows that (*if the molecule remains planar*) the aromatic rings are distorted by 12° from a diphenyl-containing structure (I), thus presenting form (II). It is noteworthy that structure (I) is not only unlikely in view of the strain imposed on the 5-membered

TABLE I.

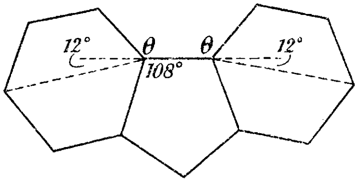
Substance.	P_T.	$[R_L]_D$.	μ, found.
Fluorene	70	56	0·82
* 2 : 7-Dinitrofluorene	137	78	*ca.* 1·7
2 : 5- „	1100	68	7·06
2 : 7-Dibromofluorene	73	72	0·22
Fluorenone	289	57	3·35
2-Nitrofluorenone	816	63	6·04
2 : 7-Dinitrofluorenone	547	70	4·80
* 2 : 5- „	830	70	*ca.* 6
2 : 7-Dibromofluorenone	481	73	4·44

* Owing to the limited solubility of these substances (maximum f_1 *ca.* 0·0002), the $^{\infty}P_T$ should be regarded as being only an approximation.

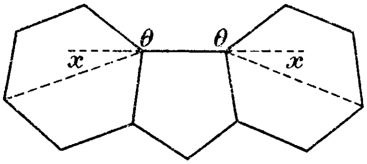
ring but is definitely excluded by our experimental results (*e.g.*, the non-identity of the moments of fluorenone and its 2 : 7-disubstituted derivatives).



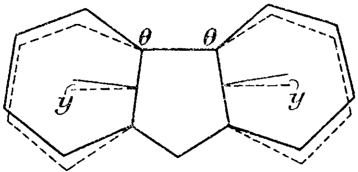
(I.)



(II.)



(IIa.)



(IIb.)

Formula (II), however, requires that the external angle, θ, common to the 5- and each 6-membered ring, must be 132°. *A priori* little is known regarding the possibility of this, but we note that the natural external angles for regular pentagons and hexagons are 126° and 120° respectively. One might, therefore, expect the external angle to become *ca.* 123° by a *cis-* or *trans*-rotation (illustrated in II*b*) of the six-membered rings through *ca.* 30° around the links common to them and the 5-membered ring. Adopting this configuration, we have calculated (cf. Table II) the dipole moments of the substances examined, taking the moments of the $-NO_2$ and $-Br$ groups as 4·17 and 1·64 respectively. These are the moments found for 4-nitrodiphenyl and 4-bromodiphenyl (Le Fèvre and Le Fèvre, J., 1936, 1130); in assuming these values we dispense with the necessity of calculating in each case the moments induced in the polarisable nuclei by the principal moment. This we feel justified in doing since fluorene and diphenyl are not greatly dissimilar in their molecular form and polarisability.* The values of the moments due to the $\cdot CH_2\cdot$ group in fluorene and the $:C{=}O$ group in fluorenone, used in these calculations, were obtained by direct measurement on the two substances.

It will be observed that for neither the *trans*- nor the *cis*-form is there good agreement. However, it might be urged that a deflection of the order 30° must be regarded as an upper limit, because if this value be increased the common external angle θ will become too small (*i.e.*, less than 123°) and a redevelopment of strain will occur in it. Since a non-planar molecule of this type, however, already contains strain due to the distortion of two of the external carbon valency directions of each benzene ring from their normal plane, a tendency towards a strainless form may exist in which the deflection is intermediate between 0° and 30°. The remainder of the calculations in Table II were accordingly made; the value of μ, found, is added in parentheses after the name of each substance.

* Cf. footnote on p. 206.

TABLE II.

Deflection.	μ, calc. *trans.*	μ, calc. *cis.*	Deflection.	μ, calc. *trans.*	μ, calc. *cis.*	Deflection.	μ, calc. *trans.*	μ, calc. *cis.*	Deflection.	μ, calc. *trans.*	μ, calc. *cis.*
2 : 7-Dinitrofluorene (1·7 *).			2 : 7-Dibromofluorene (0·2).			2-Nitrofluorenone (6·0).			2 : 5-Dinitrofluorenone (6 *).		
0°	0·9	0·9	0°	0·1	0·1	0°	5·9	5·9	0°	5·4	5·4
10	0·9	1·6	10	0·1	0·5	10	5·9	5·9	10	5·4	5·4
20	1·1	2·7	20	0·1	1·0	20	5·9	5·9	20	5·3	5·3
30	1·2	3·8	30	0·0	1·4	30	6·0	6·0	30	5·3	5·3
2 : 7-Dinitrofluorenone (4·8).			2 : 7-Dibromofluorenone (4·4).			2 : 5-Dinitrofluorene (7·1).					
0	5·1	5·1	0	4·0	4·0	0	6·7	6·7			
10	5·1	5·2	10	4·0	4·1	10	6·6	6·6			
20	5·2	5·8	20	4·1	4·2	20	6·6	6·6			
30	5·4	6·5	30	4·2	4·4	30	6·5	6·5			

* Cf. Table I.

It is seen that no *one* form adopting a deflection value between + 30° and — 30° (*trans*- and *cis*-extremes) can be considered as suggesting a spatial structure typical of the series.

We have already written a brief note (*Chem. and Ind.*, 1935, **55**, 545) in which it was pointed out that the dipole moment we obtain in *benzene solution* for 2 : 7-dinitrofluorenone is considerably smaller than that calculated on a basis of Cook and Iball's structure, that is, our 20° *cis*-deflection. We appreciate that Cook and Iball advance their non-planar configuration for *solid fluorene*, and that this non-agreement need not indicate more than that a non-planar molecule of the type they describe cannot exist in solution. Essentially the same comment has been made by Cook and Iball (*loc. cit.*) on the incompatibility of the extant stereochemical evidence and their suggested structure.

The effect of the variation of one of the basic assumptions made above should now be mentioned : if in the transition of (I) into (II) an angle (x in II*a*) *less* than 12° were involved (*i.e.*, if the hypothesis of a regular pentagon were abandoned) the strain on the external angle would be less and the consequent departure of the molecule from one plane (y in II*b*) need not be so great. The corresponding calculated results are in Table III.

TABLE III.

Substance.	μ, calc. *trans*-Config.	μ, calc. *cis*-Config.	μ, calc. *trans*-Config.	μ, calc. *cis*-Config.	μ, calc. *trans*-Config.	μ, calc. *cis*-Config.
	$x = 4°$; $y = 0°$.		$x = 4°$; $y = 10°$.		$x = 4°$; $y = 20°$.	
2 : 7-Dinitrofluorene	0·2	0·2	0·2	1·3	0·0	2·5
2 : 7-Dinitrofluorenone	3·9	3·9	4·0	4·1	4·1	4·8
2 : 7-Dibromofluorene	0·6	0·6	0·6	0·8	0·5	1·1
2 : 7-Dibromofluorenone	3·6	3·6	3·6	3·8	3·7	3·8
2-Nitrofluorenone	5·5	5·5	5·5	5·5	5·6	5·6
2 : 5-Dinitrofluorene	7·4	7·4	7·3	7·3	7·3	7·3
2 : 5-Dinitrofluorenone	6·0	6·0	6·0	6·0	5·9	5·9
	$x = 8°$; $y = 0°$.		$x = 8°$; $y = 10°$.		$x = 8°$; $y = 20°$	
2 : 7-Dinitrofluorene	0·3	0·3	0·4	1·3	0·5	2·5
2 : 7-Dinitrofluorenone	4·5	4·5	4·5	4·7	4·7	5·3
2 : 7-Dibromofluorene	0·4	0·4	0·4	0·6	0·3	1·0
2 : 7-Dibromofluorenone	3·8	3·8	3·8	3·8	3·9	4·0
2-Nitrofluorenone	5·7	5·7	5·7	5·7	5·8	5·8
2 : 5-Dinitrofluorene	7·0	7·0	7·0	7·0	6·9	6·9
2 : 5-Dinitrofluorenone	5·7	5·7	5·7	5·7	5·6	5·6

It can be seen that here again no general solution emerges for any one form although the experimental figures seem to fit less badly the configurations with $x = 8°$ and $y = 10$—20°. We note that for the latter value ($y = 20°$) the external angle is practically strainless ($\theta = 124°$), and that the results would not be in great disagreement with the existence of these molecules in solution as a mixture of *cis*- and *trans*-strainless forms.

Finally, we have considered the possibility that each derivative has a different structure, intermediate between two extreme forms in which the benzene rings are not regular hexagons but have some less symmetrical form. On this hypothesis the 2 : 4 : 5 : 7-C–H valency directions will differ by $\pm\phi°$ respectively from those which they would otherwise have in a symmetrical molecule. We will illustrate the applicability of the proposal to the flat structure specified under (II) above. We find that if $\phi = 7\frac{1}{2}°$ the experimental results can just be included in the range of the calculated figures (cf. Table IV).

TABLE IV.

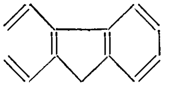
Substance.	μ, calc., for $\phi = +7\frac{1}{2}°$.	μ, found.	μ, calc., for $\phi = -7\frac{1}{2}°$.
Fluorene	—	0·82	—
* 2 : 7-Dinitrofluorene	0·17 ↑	*ca.* 1·7	1·96 ↓
2 : 5- "	7·31	7·06	5·87
2 : 7-Dibromofluorene	0·56 ↑	0·22	0·28 ↓
Fluorenone	—	3·35	—
2-Nitrofluorenone	5·55	6·04	6·16
2 : 7-Dinitrofluorenone	4·00	4·80	6·13
* 2 : 5- "	5·95	*ca.* 6	4·73
2 : 7-Dibromofluorenone	3·61	4·44	4·45

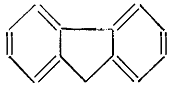
* Cf. footnote to Table I.

(In certain cases for the purpose of comparison attention has to be paid to the direction in which the calculated resultant moment lies. This is indicated by arrows. The direction of the μ_{-CH_2} is taken as ↑ and the $\mu_{C=O}$ as ↓.)

This value for ϕ coincides with one which can be forecast from an application to formulæ (III*a*) and (III*b*) of the argument which Mills and Nixon (J., 1930, 2510) have used fruitfully in the cases of 5-hydroxyhydrindene and *ar*-tetrahydro-β-naphthol, namely, that the

(III*a*.)





(III*b*.)

C–H valency directions in such molecules will make, alternately, greater and smaller angles with their adjacent C–C bonds. The magnitudes of these angles are uncertain; for a six-membered ring they should result from the distribution of 5° of strain over two angles of 125° and 110° each; 127½° and 112½° thus seem a fair choice; ϕ in (III*a*) and (III*b*) therefore becomes ± 7½°.

General Conclusions.—(1) Although our results do not point to one specific configuration, certain structures are definitely inapplicable. (2) The hypotheses that these compounds exist in solution as a mixture of non-planar forms of the type $x = 8°$, $y = 20°$ considered above, or that they are flat degenerate forms between the extremes (III*a*) and (III*b*), are not excluded.

The Dipole Moments of Fluorene and Fluorenone.—The moments observed for these compounds are unexpectedly high when considered in the light of those of diphenylmethane ($\mu = 0{\cdot}23$; Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, **143**, 147) and benzophenone ($\mu = 2{\cdot}99$; Müller, *Physikal. Z.*, 1933, **34**, 689) respectively. An important contrast between fluorene and diphenylmethane is, however, the much greater reactivity of the hydrogen atoms of the methylene group in the former hydrocarbon; compare the formation of sodium and potassium derivatives by melting with the corresponding alkali hydroxides (Weissgerber, *Ber.*, 1901, **34**, 1659; 1908, **41**, 2914). In this respect it resembles indene (Weissgerber, *Ber.*, 1909, **42**, 572) and the parent compound *cyclo*pentadiene (Thiele, *Ber.*, 1901, **34**, 68). An explanation of this reactivity has been advanced by Goss and Ingold (J., 1928, 1268) depending on the fact that in the *cyclo*pentadiene ring the electrons requisite for the stabilising sextet (supplied by the three olefinic bonds in benzene) can only be provided by the partial appropriation of the bonding electrons of one of the methylene hydrogen atoms. This hydrocarbon and its derivatives therefore have properties analogous to those of an acid in so far as one of their hydrogen atoms is predisposed to leave the molecule as a proton. It is therefore not incompatible with this to find that in fluorene the H⟶C dipoles evidently have a value several times greater than they possess in an ordinary methylene group.

Between fluorene and fluorenone, on the one hand, and diphenylmethane and benzophenone, on the other, there exists the further difference that in the former compounds the benzene rings are fixed close to the same plane as the 9-carbon atom, whilst in the latter pair the rings are free to undergo rotation, etc.,* about the links by which they are attached to the central carbon atom. The consequence of this is that in both fluorene and fluorenone, since the chief moment of the molecule in both cases operates through the 9-position and *in the plane* to which reference has just been made, circumstances are so arranged that the induction of subsidiary moments in the polarisable benzo-nuclei can occur almost to the maximum extent possible.

The magnitudes of these induced moments can be calculated if the value of the chief moment, the polarisability of the structure in which the induction occurs, the distances between the mass centre of the latter and the point of operation of the inducing dipole, the dielectric constant of the intervening medium, etc., are known.

In the case of fluorenone the chief moment is the bond moment appropriate to the ketonic linkage, *viz.*, 2·5 (Sidgwick, " The Covalent Link in Chemistry," 1933, 153). Thus on the basis of a flat model in which two regular hexagons of side 1·42 A. are fused to a regular pentagon of the same side length, in which the polarisability of the benzene rings is that found by Stuart and Volkmann (*Ann. Physik*, 1933, **18**, 121) for the benzene molecule in its plane, we have : †

moment induced at mass centre of attached nuclei in direction parallel to the direction of the ketonic link

$$= \frac{\text{polarisability} \times \text{inducing moment}}{(\text{distance})^3} (3 \cos^2 \beta - 1) \frac{(\varepsilon + 2)}{3\varepsilon}$$

where β = angle between line joining mass centre to seat of dipole and direction of dipole. Calculation shows that

$$\beta = 38{\cdot}9^\circ,\ \text{distance} = 3{\cdot}34\ \text{A.};$$

hence if ε is taken as 2·3,

$$\mu\ \text{induced} = 0{\cdot}42\ \text{unit}$$

Therefore, molecular resultant = $2{\cdot}5 + 2 \times 0{\cdot}42 = 3{\cdot}34$ units.

This is in excellent agreement with the value, 3·35, found experimentally. A similar calculation cannot be carried out in the case of fluorene owing to the uncertainty of the value to be taken for the moment of the methylene group in view of the abnormal chemical behaviour of this radical.

Previous Measurements.—Four of the present compounds had been studied by Bergmann, Engel, and Hofmann (*Z. physikal. Chem.*, 1932, *B*, **17**, 92), and their results are tabulated beside ours :

	B., E., & H.		Present authors.	
Substance.	$[R_L]_D$.	μ.	$[R_L]_D$.	μ.
Fluorene	60	0·28 ~ 0	56	0·82
2 : 7-Dibromofluorene	75	0	72	0·22
Fluorenone	63	3·29	57	3·35
2-Nitrofluorenone	94	5·44	63	6·04

In our work, because of the limited solubility of most of the substances, refractivities were not directly measured; instead, they were calculated from the experimental values

---

* In the cases of the diphenyl compounds mentioned on p. 203, it will be realised that free rotation of the remote phenyl group will not affect either the magnitudes or the directions of the moments induced therein, because both induced and inducing moments lie along the same axis. The situation is different with the fluorene derivatives : here the inducing and resultant moments induced in the side rings lie along directions which are neither collinear nor parallel. Because of the anisotropy of polarisability of the benzene rings, therefore, the induced moments will vary with the process of tilting the 6-rings out of the plane of the central 5-ring.

† We consider the polarisability of a benzene ring as situated at its centre. A more detailed calculation might be made in which the CH groups are taken separately. We have recently made calculations on both bases for the somewhat similar case of xanthone. (See preceding paper.)

for fluorene (56) and fluorenone (57)—which can be obtained with a reasonable degree of accuracy—by subtraction of the refractive equivalents for the necessary number of hydrogen atoms, and addition of the appropriate atomic refractions for the substituent groups.

EXPERIMENTAL.

Preparation of Materials.—Fluorene was recrystallised from alcohol immediately before use, m. p. 114—115°. 2 : 7- and 2 : 5-Dinitrofluorenes were prepared as described by Courtot (*Ann. Chim.*, 1930, **14**, 5; compare Anantakrishnan and Hughes, J., 1935, 1607).

2 : 7-Dibromofluorene also was obtained by Courtot's method (*loc. cit.*) but was repeatedly recrystallised from ethyl acetate instead of carbon disulphide; m. p. 165° (Courtot gives 162—163°). The ketones were prepared in each instance by the oxidation of the purified corresponding fluorene derivative. They were finally recrystallised from acetic acid; their m. p.'s agreed with those recorded in the literature.

Measurements.—In the following tables, the symbols have their usual significance, ε being measured at approximately 1200 kc.; the temperature of measurement was 25° throughout, and the solvent, benzene.

f_1.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	$P_1f_1 + P_2f_2$.	P_1.
		Benzene.		
0	2·2725	0·87380	26·5863	—
		Fluorene.		
0·000488	2·2733	0·87398	26·6072	69·53
0·001706	2·2750	0·87444	26·6547	66·71
0·002714	2·2763	0·87484	26·6918	65·47
0·003550	2·2771	0·87515	26·7192	64·02
		2 : 7-*Dinitrofluorene.*		
0·000199	2·2736	0·87401	26·6082	136·2
0·000277	2·2740	0·87409	26·6164	134·7
0·000278	2·2741	0·87409	26·6178	139·8
		2 : 5-*Dinitrofluorene.*		
0·000107	2·2800	0·87394	26·6984	1072·7
0·000203	2·2848	0·87407	26·7703	932·7
0·000310	2·2897	0·87422	26·8437	856·9
0·000489	2·2969	0·87446	26·9520	773·9
		2 : 7-*Dibromofluorene.*		
0·001179	2·2739	0·87596	26·6399	72·04
0·001299	2·2741	0·87618	26·6462	72·67
0·001998	2·2750	0·87749	26·6781	72·49
0·003017	2·2761	0·87934	26·7231	71·92

f_1.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	$P_1f_1 + P_2f_2$.	P_1.
		Fluorenone.		
0·000902	2·2874	0·87428	26·8210	286·84
0·002414	2·3120	0·87513	27·2048	282·83
0·002999	2·3214	0·87545	27·3510	281·51
0·004199	2·3411	0·87607	27·6564	281·38
		2-*Nitrofluorenone.*		
0·000131	2·2793	0·87391	26·6892	815·30
0·000170	2·2813	0·87394	26·7194	807·75
0·000326	2·2896	0·87412	26·8428	814·67
0·000554	2·3014	0·87434	27·0189	807·36
		2 : 7-*Dinitrofluorenone.*		
0·000081	2·2752	0·87390	26·6281	543·21
0·000116	2·2764	0·87396	26·6462	541·70
0·000400	2·2858	0·87433	26·7910	538·38
0·000561	2·2911	0·87454	26·8723	536·01
		2 : 5-*Dinitrofluorenone.*		
0·000113	2·2775	0·87390	26·6640	712·39
0·000152	2·2785	0·87393	26·6802	644·12
0·000197	2·2791	0·87397	26·6907	555·83
0·000232	2·2795	0·87400	26·6980	508·18
		2 : 7-*Dibromofluorenone.*		
0·000067	2·2744	0·87392	26·6165	476·9
0·000143	2·2764	0·87407	26·6484	459·7
0·000334	2·2809	0·87443	26·7198	425·7
0·000545	2·2845	0·87489	26·7771	376·6

The authors are grateful to Professor Ingold for many helpful suggestions.

UNIVERSITY COLLEGE (UNIVERSITY OF LONDON).

[*Received, October 20th,* 1936.]