

dication that the excited structures which give the major contribution to absorption are closely related to those which contribute to the ab-

sorption of the substituted benzaldehydes.

URBANA, ILLINOIS

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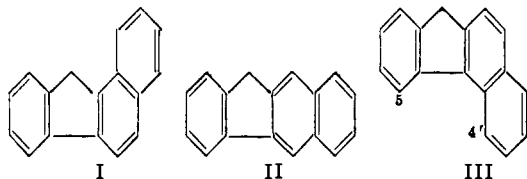
[CONTRIBUTION FROM THE WEIZMANN RESEARCH CENTER, REHOVOTH, ISRAEL, AND THE U. S. BUREAU OF MINES PITTSBURGH, PENNA.]

## Structure of the Benzfluorenes and Benzfluorenones

BY MILTON ORCHIN<sup>1</sup> AND ROBERT A. FRIEDEL<sup>2</sup>

### Introduction

Of the three possible benzfluorenes, I-III, 1,2-benzfluorene, I, and 2,3-benzfluorene, II, have strikingly similar chemical and physical properties and ultraviolet spectra. 3,4-Benzfluorene, III, is however considerably different from its isomers. The benzfluorenes, I and II, are high melting, difficult to separate and relatively insoluble. They both form unstable pic-



rates and trinitrobenzene complexes in the ratio of 2 moles of polynitro compound to 1 mole of hydrocarbon. The benzfluorene, III, is much lower melting, relatively soluble, easily separated from its isomers and forms stable molecular complexes in a molar ratio of 1:1.

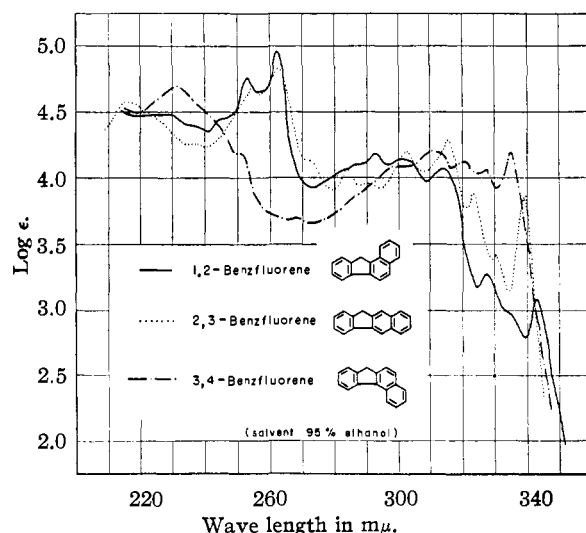


Fig. 1.—Ultraviolet spectra of the benzfluorenes.

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### Discussion

A possible explanation of the contrasting properties of the benzfluorenes is revealed in a comparison of them with the phenylnaphthalenes. Both I and II may be considered as 2-phenylnaphthalene derivatives while III may be considered as a derivative of 1-phenylnaphthalene. The ultraviolet absorption spectra of the three isomers (Fig. 1) show that although some dissimilarity exists between the spectra of I and II in the 270–300  $m\mu$  region, on the whole the spectra of I and II are quite similar and differ from that of III in a manner analogous to the difference in spectra between 1- and 2-phenylnaphthalene.<sup>3</sup> Thus it will be noted that I and II have strong absorption bands in the 260  $m\mu$  region, a feature also characteristic of the spectrum of 2-phenylnaphthalene, while the spectrum of the 3,4-benzfluorene, III, exhibits a minimum in this region similar to that shown by 1-phenylnaphthalene.

In 1-phenylnaphthalene there is unquestionably

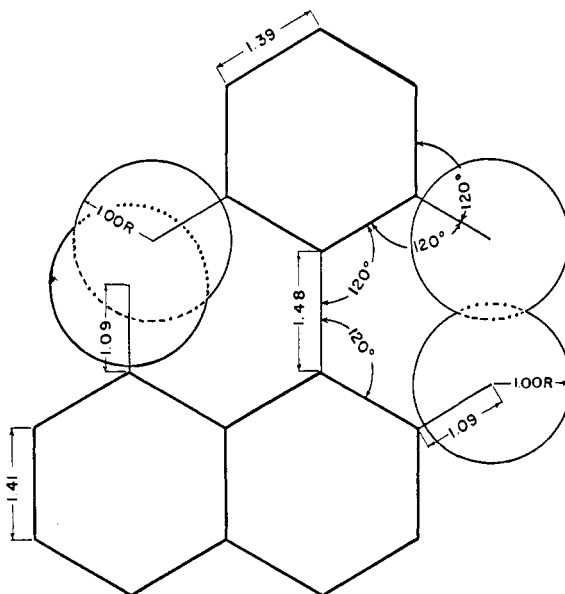


Fig. 2.—Planar representation of 1-phenylnaphthalene.

(3) Friedel, Orchin and Reggel, *THIS JOURNAL*, **70**, 199 (1948). The relationship of the spectra of the benzfluorenes and the phenylnaphthalenes has been commented on previously by Jacobs, Craig and Lavin, *J. Biol. Chem.*, **141**, 51 (1941).

steric interference between the hydrogen atoms at the 2'- and 8-positions which inhibits coplanarity. Figure 2 shows the probable extent of the hydrogen overlap at these positions in the planar model. The non-planar structure which is favored because of this interference probably explains the low melting point of 1-phenylnaphthalene as compared to 2-phenylnaphthalene. In view of the spectral resemblance of 3,4-benzfluorene III, to 1-phenylnaphthalene and the relatively low melting point of III, it is of interest to consider the hydrogen overlap in the structure of the latter and to consider also the structure of fluorene.

Cook and Iball concluded from an X-ray crystal study of fluorene, that the fluorene molecule is not planar but that the planes of each six-membered ring are inclined at an angle of  $20^\circ$  to that of the five-membered ring and at about  $40^\circ$  to each other (*cis*-form).<sup>4</sup>

Hughes, LeFèvre and LeFèvre, on the basis of dipole measurements in solution at first proposed a planar model of fluorene.<sup>5a</sup> They pointed out that if it is assumed that the five-membered ring is regular with internal angles of  $108^\circ$ , then the aromatic rings must be distorted  $12^\circ$  from a diphenyl structure and this requires the external angles around the diphenyl linkage to be  $132^\circ$ . These authors later stated<sup>5b</sup> that their measurements did not exclude the possibility of a non-planar structure in which the diphenyl linkage is distorted  $8^\circ$  (irregular pentagon) and the planes of the benzene ring are bent at about  $20^\circ$  either *cis* or *trans*. Figure 3 shows a planar model of 3,4-benzfluorene using angles and carbon to carbon distances which we regard as most probable if fluorene were planar.<sup>6</sup> In such a planar model there is only a minor amount of overlap between hydrogens at 4' and 5 compared to the overlap in 1-phenylnaphthalene (Fig. 2). This is an additional incentive to favor a non-planar form for fluorene since in either the non-planar model suggested by Cook or inferred by Hughes, LeFèvre and LeFèvre, the interference of the hydrogens in III would be larger and of the magnitude involved in the overlap in 1-phenylnaphthalene. This overlap would cause strain which is additional to that present in the other benzfluorenes, I and II, and may tend to rotate

the phenyl ring about the diphenyl linkage (as in the case with 1-phenylnaphthalene) so that the five-membered ring itself may become slightly non-planar. In any case, the postulated hydrogen overlap and the strain which it effects are now proposed to explain the relation between the spectra of 3,4-benzfluorene, III, and 1-phenylnaphthalene on the one hand and the other two benzfluorenes and 2-phenylnaphthalene on the other.

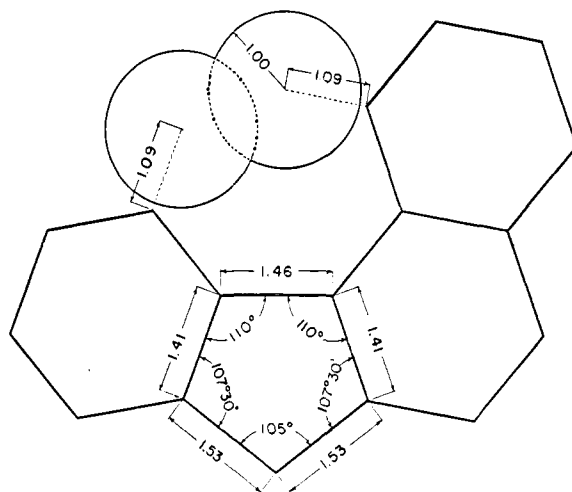


Fig. 3.—Planar representation of 3,4-benzfluorene.

The interesting differences observed with complex compound formation in this series, the data for which are found in Table I, are deserving of comment. The benzfluorenes, I and II, related to 2-phenylnaphthalene, form with 1,3,5-trinitrobenzene (T. N. B.) and with picric acid, complexes containing two moles of the polynitro compound. These complexes dissociate very readily. 2-Phenylnaphthalene also forms a 2:1 T. N. B. and its picrate is so unstable as to elude isolation. On the other hand, 3,4-benzfluorene, III, forms stable, sharp melting complexes with these nitro compounds in a molar ratio of 1:1.<sup>7</sup> These differences may be due to the smaller overall volume of 3,4-benzfluorene as compared to its isomers or they may be related to the strain differences discussed above which tend to make 3,4-benzfluorene less planar than its isomers. It will be noted that all the hydrocarbons in Table I form stable, high melting complexes with 2,4,7-trinitrofluorenone<sup>8</sup> (T. N. F.), in a 1:1 ratio. This fact may be due to some geometrical features of T. N. F. which permits its closer approach to relatively similar hydrocarbons or to the fact that T. N. F. is a relatively large molecule with widely separated positive centers. Observations

(4) Cook and Iball, *Chem. and Ind.*, 467 (1936). These authors point out that the non-planar configuration of fluorene does not necessarily demand the existence of stereoisomeric fluorenes because sufficient elasticity to oscillate may be possessed. Fieser and Joshi, *THIS JOURNAL*, **62**, 957 (1940), prepared 9-hydroxy-9-methyl-3,4-benzfluorene, which if 3,4-benzfluorene were non-planar, should exist as two racemic mixtures, each of which is resolvable. However, they isolated only one product in 85% yield.

(5) (a) Hughes, LeFèvre and LeFèvre, *J. Chem. Ind.*, **545**, 581 (1936); (b) *J. Chem. Soc.*, 202 (1937).

(6) The planar models of fluorene given by Hughes, LeFèvre and LeFèvre, ref. 5b, and by Pinck and Hilbert, *THIS JOURNAL*, **59**, 8 (1937), are not drawn accurately to scale. In the latter case, if the model is drawn with the bond lengths indicated and the angles about the diphenyl linkage as  $107.5^\circ$ , the angle at the methylene group is about  $104^\circ$  and not  $110^\circ$ .

(7) Attempts to prepare complexes with 1-phenylnaphthalene were unsuccessful in all cases but melting point-composition diagrams are needed before it can definitely be decided whether compound formation occurs.

(8) (a) Orchin and Woolfolk, *THIS JOURNAL*, **68**, 1727 (1946); (b) Orchin, Reggel and Woolfolk, *ibid.*, **69**, 1225 (1947).

made in this and other laboratories<sup>9</sup> indicate that in general, T. N. F. is to be preferred over other polynitro compounds for complex compound formation in the polycyclic series.

TABLE I  
TABLE OF PROPERTIES

Name	Hydrocarbons				Ketones	
	M. p., °C.	Picric acid <sup>a</sup> com- plex	T. N. B. com- plex	T. N. F. com- plex	M. p., °C.	T. N. B. com- plex
2-Phenylnaphthalene	103	...	2:1	1:1	...	...
		127	145	215	126	
1,2-Benzfluorene	186	2:1	2:1	1:1	135	1:1
		122	139	222	124	
2,3-Benzfluorene	214	2:1	2:1	1:1	155	1:1
		131	155	192	128	
3,4-Benzfluorene	127	1:1	1:1	1:1	160	1:1

<sup>a</sup> The top number under the various complexes is the melting point; below it is the ratio of moles polynitro component to moles of compound.

The ultraviolet absorption spectra of the benzfluorenones (Fig. 4) show an interesting reversal as compared to the parent benzfluorenes. Whereas

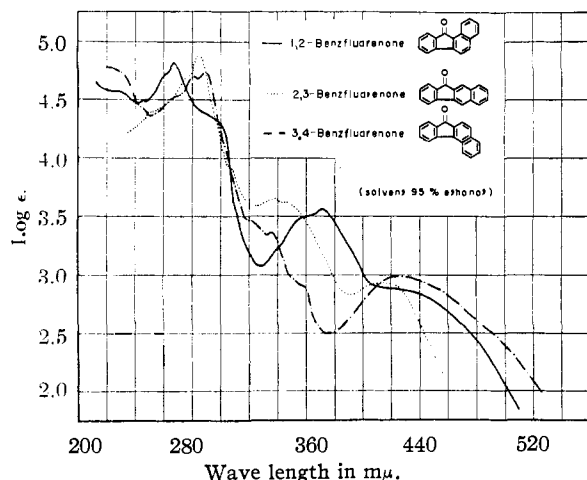


Fig. 4.—Ultraviolet spectra of the benzfluorenones.

in the hydrocarbon series, 3,4-benzfluorene exhibits a spectrum different from that of the other two isomers, in the ketone series 1,2-benzfluorenone has the spectrum which is easily distinguished from that of its isomers. This may be due to interaction between the carbonyl group at position 9 and the hydrogen on carbon 1' giving rise to weak internal hydrogen bonding and incipient six-membered ring formation. The two main absorption maxima in the spectrum of 1,2-benzfluorenone are located at shorter wave lengths as compared to these maxima in the spectra of its isomers. This indicates less carbonyl contribution in the case of the 1,2-benzfluorenone as indeed would be expected if the oxygen were partially involved in hydrogen bonding. It will

(9) For example, Newman and Hart, *THIS JOURNAL*, **69**, 298 (1947); Cheronis and Entrikin, "Semimicro Qualitative Analysis," Thomas Y. Crowell, New York, N. Y., 1947, pp. 311, 314.

be noted from Table I that this ketone is the lowest melting of the isomers.

**Acknowledgment.**—The authors wish to thank Mr. Martin Michael for expert drafting aid and Mrs. Lois Harnack for assistance with the spectral measurements.

### Experimental<sup>10</sup>

**1,2-Benzfluorenone.**—This compound was prepared on a large scale by a new method which will be reported later.<sup>11</sup> It had a melting point of 134.5–135.0°.

The complex with 1,3,5-trinitrobenzene was prepared in the usual way in ethanol solution and the complex separated as yellow-orange needles, m. p. 125.0–126.0°. Recrystallization from ethanol resulted in a less pure material. The material isolated in the first crop was used for analysis. *Anal.* Calcd. for  $C_{23}H_{13}N_3O_7$ : C, 62.3; H, 3.0. Found: C, 62.3; H, 3.0.

**2,3-Benzfluorenone.**—A small sample of this compound was secured from Professor L. F. Fieser.<sup>12</sup> The preparation of a complex with 4 mg. of this material and double the molar proportions of 1,3,5-trinitrobenzene was attempted. The first crops isolated were unchanged trinitrobenzene but later crops consisted of the complex. One recrystallization of the complex gave yellow prisms, softening at 117° and m. p. 124°. Ultraviolet absorption spectra analysis showed this complex to consist of 49 molar per cent. trinitrobenzene and 51 molar per cent. ketone.

**3,4-Benzfluorenone.**—This compound was also the generous gift of Professor L. F. Fieser.<sup>13</sup>

The complex with 1,3,5-trinitrobenzene was prepared in ethanol; the complex separated in yellow gold needles, which after recrystallization from ethanol had a melting point of 128.0–128.4°. *Anal.* Calcd. for  $C_{23}H_{13}N_3O_7$ : C, 62.3; H, 3.0. Found: C, 62.3; H, 2.6. The complex was much lighter in color than the ketone itself.

**1,2-Benzfluorene, I.**—This compound was prepared by reduction of the corresponding benzfluorenone with phosphorus and hydriodic acid, essentially according to the directions of Graebe.<sup>14</sup> Crystallization from ethanol gave small colorless crystals, m. p. 185.4–186.0°.

The picrate has been prepared previously<sup>15</sup> and has been shown to consist of 2 moles of picric acid to 1 mole of hydrocarbon.

The trinitrobenzene complex was obtained from ethanol as small yellow crystals, m. p. 144.0–145.0°. *Anal.* Calcd. for  $C_{29}H_{18}N_3O_{12}$ : N, 13.1. Found: N, 13.9.

The complex with 2,4,7-trinitrofluorenone separated as red crystals which after crystallization from benzene-ethanol had a melting point of 213.5–215.5°. *Anal.* Calcd. for  $C_{30}H_{17}N_3O_7$ : C, 67.8; H, 3.2. Found: C, 68.0; H, 3.3.

**2,3-Benzfluorene, II.**—The properties of this compound have been reported by us previously.<sup>8b</sup>

The picrate was made from the hydrocarbon and picric acid in petroleum ether and recrystallized from petroleum-ether (90–100°) whereupon it separated as yellow-orange crystals, softening at 118° and melting at 121.8–122.5°. *Anal.* Calcd. for  $C_{29}H_{18}N_3O_{14}$ : C, 51.6; H, 2.7. Found: C, 51.8; H, 3.1.

The complex with 1,3,5-trinitrobenzene was obtained from petroleum ether (90–100°) as bright yellow plates, m. p. 138.0–139.0°. *Anal.* Calcd. for  $C_{23}H_{13}N_3O_{12}$ : N, 13.1. Found: N, 13.6.

(10) All melting points corrected. All analyses are microanalyses by Mr. G. L. Stragand, University of Pittsburgh.

(11) We wish to thank Mr. Leslie Reggel for this preparation and for other valuable assistance with a portion of the experimental work.

(12) Fieser and Gates, *THIS JOURNAL*, **62**, 2335 (1940).

(13) Fieser and Joshel, *ibid.*, **62**, 957 (1940).

(14) Graebe, *Ber.*, **29**, 828 (1896).

(15) Graebe, *Ann.*, **335**, 135 (1904), gives a melting point of 127.5° and Cook and Hewett, *J. Chem. Soc.*, 365 (1934), give a melting point of 124–126°.

In this series of 2:1 complexes it is desirable to avoid the use of ethanol as a solvent. Chloroform or petroleum ether is more satisfactory for the isolation of the unstable complexes.

The 2,4,7-trinitrofluorenone complex has been reported previously<sup>8b</sup> but its analysis did not correspond to any simple molar ratio. This conclusion was reached on the basis of several nitrogen analyses at different laboratories, all of which checked but all of which we have found subsequently to be in error. The carbon and hydrogen analyses showed the complex to be a 1:1 combination. *Anal.* Calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O<sub>7</sub>: C, 67.8; H, 3.2. Found: C, 68.1; H, 3.5.

**3,4-Benzfluorene, III.**—An attempted reduction of 3,4-benzfluorenone with phosphorus and iodine in acetic acid resulted in the almost complete recovery of the ketone. It was then successfully reduced by the Huang-Minlon<sup>16</sup> modification of the Wolff-Kishner reaction. A solution of 0.317 g. of the ketone, 0.5 cc. of 85% hydrazine hydrate, 0.4 g. of sodium hydroxide and 25 cc. of ethylene glycol was refluxed for two hours. During this time the yellow solid became red and gradually went into solution; then all the red color disappeared leaving a clear yellow solution. At the end of the two hours, the condenser was removed and the contents boiled in the open until the temperature in the flask was 200°. The condenser was replaced and the solution refluxed two hours, cooled and poured into ice and hydrochloric acid. The precipitate was dried and crystallized from ethanol. The first crop (0.19 g.) separated as nearly colorless plates tinged with a pink color, m.p. 122.6–124.0°. The second crop (0.05 g.) had about the same melting point. On recrystallization of the first crop from benzene-alcohol a small amount of insoluble material was noted and separated. This melted at 241.5–244.0° and was probably the hydrazone of the benzfluorenone.

(16) Huang-Minlon, *THIS JOURNAL*, **68**, 2487 (1946).

The soluble fraction gave pure 3,4-benzfluorene, m.p. 126.8–127.4°. <sup>17</sup>

The known mono-picrate<sup>17</sup> was obtained from ethanol as fine red needles, m.p. 131.4–132.2°.

The trinitrobenzene complex was obtained from benzene-alcohol as orange-yellow crystals, m.p. 154.2–155.2°. *Anal.* Calcd. for C<sub>23</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>: C, 64.3; H, 3.5. Found: C, 64.5; H, 3.5.

The trinitrofluorenone complex separated from benzene-alcohol as fine, light red needles, m.p. 191.8–192.8°. *Anal.* Calcd. for C<sub>30</sub>H<sub>17</sub>N<sub>3</sub>O<sub>7</sub>: C, 68.8; H, 3.2. Found: C, 67.6; H, 2.9.

**2-Phenylnaphthalene** and its complex with 2 moles of trinitrobenzene has been described previously<sup>8</sup> as has the complex with trinitrofluorenone.<sup>8b</sup>

### Summary

The physical properties and ultraviolet absorption spectra of the three benzfluorenes and the three benzfluorenes were determined and significant features discussed. The molecular complexes formed between these compounds and various polynitro compounds were prepared and studied. In nearly all respects the behavior of 1,2- and 2,3-benzfluorene was similar but 3,4-benzfluorene differed from its isomers. It is proposed that the differences stem from the possibility of hydrogen overlap in the 3,4-benzfluorene molecule which may cause it to assume a less planar structure than its isomers.

(17) Cook, Dansl, Hewett, Iball, Mayneord and Roe, *J. Chem. Soc.*, 1319 (1935), give the melting point of the hydrocarbon as 124–125° and the melting point of its picrate as 130–131°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

## Isomerism of Sulfanylamino Guanidines<sup>1</sup>

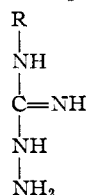
BY ALBERT H. GREER,<sup>1a</sup> DENNIS L. KERTESZ<sup>2</sup> AND G. B. L. SMITH<sup>3</sup>

A sulfanylamino guanidine melting at 208–210° was prepared by Winnek, *et al.*,<sup>4</sup> by condensation of N<sup>4</sup>-acetylsulfanylyl chloride with S-methylthiourea or with cyanamide, followed by hydrazinolysis or hydrazination and deacetylation. More recently, Owades<sup>5</sup> has obtained the same sulfanylamino guanidine by the catalytic hydrogenation of N<sup>4</sup>-acetylsulfanylnitroguanidine and subsequent deacetylation. Prior to this, Kertesz<sup>6</sup> had prepared another sulfanylamino guanidine melting at 298–300° by condensing *p*-nitro-

benzenesulfonyl chloride with aminoguanidine, and reducing the product by catalytic hydrogenation. We have now prepared a third sulfanylamino guanidine melting at 188–190°.

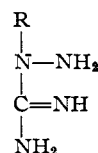
It is evident that three structural isomers of sulfanylamino guanidine are possible, as follows

R = sulfanylyl



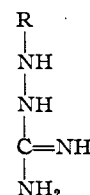
1-Sulfanylyl-3-aminoguanidine

I



1-Sulfanylyl-1-aminoguanidine

II



Sulfanylamido-guanidine

III

The above does not include the tautomeric isomers for which formulas can be written. Isomer I has three tautomers, isomer III has two, and isomer II only one.<sup>4</sup>

The present paper describes the preparation

(1) Abstracted from parts of the theses submitted by Albert H. Greer (M.S. Chem., 1945) and Dennis L. Kertesz (Ph.D., 1941) to the Graduate Faculty of Polytechnic Institute of Brooklyn.

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(4) Winnek, *et al.*, *THIS JOURNAL*, **64**, 1682 (1942).

(5) J. Owades, M.S. Thesis, Polytechnic Institute of Brooklyn, 1944.

(6) D. Kertesz, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1941.