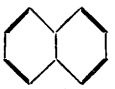
96. *The Structure of Aromatic Compounds. Part II.*

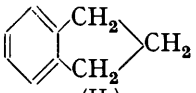
By Neil Campbell, W. Anderson, and J. Gilmore.

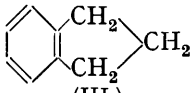
The results of a previous paper on the structure of aromatic hydrocarbons (Part I, McLeish and Campbell, J., 1937, 1103) have been revised in terms of the resonance theory. The halogen reactivity of halogenonitro-compounds of styrene, phenanthrene, diphenyl, hydrindene, fluorene, and acenaphthene has been measured, and the results correlated with the fine structure of the compounds.

The problem of the structure of the aromatic polycyclic hydrocarbons has recently been revised in terms of the theory of resonance (for summary, see Taylor and Brockway, *Ann. Reports*, 1937, 196). Naphthalene may accordingly be represented by (I) as the resultant of the three unexcited structures, the heavy lines indicating those bonds with greater

double-bond character. Hydrindene has forms (II) and (III) as the main contributing structures, and its chemical properties may be accounted for by the slight predominance of (II) (Sutton and Pauling, *Trans. Faraday Soc.*, 1935, **31**, 939). It is therefore necessary to abandon the theory of fixed structures, and to conclude that polycyclic aromatic compounds


(I.)

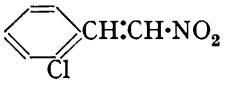

(II.)

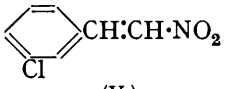

(III.)

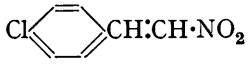
are resonance hybrids, the chemical properties of which are explained by the non-equivalence of the carbon–carbon linkages. This accounts for the reactivity of 2-bromo-1-nitro- in contrast to the non-reactivity of 2-bromo-3-nitro-naphthalene; for the much greater reactivity of 5-bromo-6-nitro- than of 4-bromo-5-nitro-hydrindene (Part I, *loc. cit.*), and for the findings of Lindner, Sellner, Hofmann, and Hager (*Monatsh.*, 1939, **72**, 335) and of Evans and Sandin (*J. Amer. Chem. Soc.*, 1939, **61**, 2916).

In the present research the method used to determine the fine structure of aromatic compounds (Part I, *loc. cit.*) has been applied to certain other compounds, and the effect of methyl groups on the bromine reactivity of bromonitro-compounds has been studied. The reactivities were measured as before by the piperidine method, and the results are given in the table.

The reactivity of 9-bromo-10-nitrophenanthrene and the non-reactivity of 3-bromo-4-nitroacenaphthene supply evidence for the essential correctness of Fuson's vinylogy theory (*Chem. Reviews*, 1935, **16**, 1). The former contains the Br·Ç—Ç·NO_2 fragment in which the carbon–carbon linkage has 4/5 double-bond character, and in the latter compound the bromo- and the nitro-group, although in many respects *ortho* to one another, are not


(IV.)


(V.)


(VI.)

separated by the bond system necessary for reactivity. Further support for Fuson's theory is obtained from the reactivities of *o*-bromo-ω-nitrostyrene and the three isomeric chloro-ω-nitrostyrenes (IV), (V), and (VI). As was anticipated, only the *m*-compound was non-reactive. The results of the hydrolysis of the ω-bromonitrostyrenes (Dann, Howard, and Davies, J., 1928, 605) also support the theory.

It was of interest to measure the reactivities of 2-bromo- and 4-bromo-α-nitrostilbene, but attempts to obtain these compounds by condensing phenylnitromethane with the necessary aldehyde by the method of Knoevenagel and Walter (*Ber.*, 1904, **37**, 4502) yielded either 3 : 5-diphenyl-4-bromophenyl- or 3 : 4-diphenyl-5-bromophenyl-*iso*oxazoles depending on the mechanism of formation (Heim, *Ber.*, 1911, **44**, 2016; Kohler and Barrett, *J. Amer. Chem. Soc.*, 1924, **46**, 2106; Worrall, *ibid.*, 1935, **57**, 2299; Ruggli and Hegedüs, *Helv. Chim. Acta*, 1939, **22**, 405).

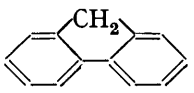
	Removal of bromine, %.			Removal of bromine, %.	
	1 Hr.	24 Hrs.		1 Hr.	24 Hrs.
9-Bromophenanthrene	0	0	*2-Bromo-3-nitrofluorene*	50	97
9-Bromo-10-nitrophenanthrene	69	100	3-Bromoacenaphthene	—	0
o-*Bromo-ω-nitrostyrene*	—	34	*3-Bromo-2-nitroacenaphthene* ...	68	100
o-*Chloro-ω-nitrostyrene*	—	13 *	3-Bromo-4-nitroacenaphthene	—	0
m-*Chloro-ω-nitrostyrene*	—	0 *	*4-Bromo-1-nitroacenaphthene* ...	—	2
p-*Chloro-ω-nitrostyrene*	—	8 *	*o*-Bromonitrobenzene	53	96
4-Bromodiphenyl	—	0	*m*-Bromonitrobenzene	—	0
2-Bromo-4′-nitrodiphenyl	—	0	*p*-Bromonitrobenzene	96	104
4-Bromo-4′-nitrodiphenyl	—	0	2-Bromo-3-nitrotoluene	1	4
4-*Bromo-3-nitrodiphenyl*	78	98	4-Bromo-3-nitrotoluene	13	91
4-Bromo-2′-nitrodiphenyl	—	0	2-Bromo-4-nitrotoluene	0	0
3-Bromo-4′-nitrodiphenyl	—	0	2-Bromo-5-nitrotoluene	—	8
4-Bromo-5-nitrohydrindene ...	—	7	5-Bromo-2-nitrotoluene	0	51
2-Bromofluorene	—	0	3-Bromo-4-nitrotoluene	54	99
2-Bromo-7-nitrofluorene	—	0			

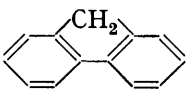
* 48 Hours.

The non-reactivity of 2-bromo-4'-, 4-bromo-4'-, and 4-bromo-2'-nitrodiphenyl, and of 2-bromo-7-nitrofluorene shows that the influence of the nitro-groups is not transmitted from one ring to the other. This supports the conclusion of Le Fèvre and Turner (J., 1928, 246) on the independence of the two nuclei in the diphenyl molecule.

Previous measurements of the reactivity of 4-bromo-5-nitrohydrindene (McLeish and Campbell, *loc. cit.*) were not satisfactory, as the compound was not pure. We have repeated the preparation, and obtained on fractional distillation an oil which, when immersed in carbon dioxide–ether, yielded a crystalline compound, m. p. about 20°. The compound was found to be slightly reactive, thus confirming our previous result.

The reactivities of some bromonitroacenaphthenes and fluorenes were measured, but the results are not conclusive, as all the required compounds were not obtained. The pronounced reactivity of 3-bromo-2-nitroacenaphthene suggests that acenaphthene contains a nucleus similar to that of naphthalene (I). This is to be expected, for acenaphthene has the same resonance energy as naphthalene (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606). The reactivities of the fluorene compounds and the substitution reactions of compounds such as 2-aminofluorene point to the structure (VII), but the similarity of fluorene to indene and *cyclo*pentadiene (Thiele and Henle, *Annalen*, 1906, **347**, 290) supports structure (VIII). It is therefore reasonable to conclude that fluorene is a resonance hybrid of forms such as (VII) and (VIII), and Lothrop's results (*J. Amer. Chem. Soc.*, 1939, **61**, 2115) from a study of 2-hydroxyfluorene can be explained in this way. The results of Pauling and Sherman (*loc. cit.*) show that fluorene is indeed a resonance hybrid, the main contributing forms being the Kekulé structures.

(VII.) 



(VIII.)

Most efforts to prepare fluorene derivatives substituted in position 1 have been unsuccessful (*e.g.*, Eckert and Langecker, *J. pr. Chem.*, 1928, **118**, 277). An attempt was made to prepare 1 : 2-substituted derivatives by the method used to prepare 2-bromo-3-aminonaphthalene (Part I, *loc. cit.*). Bromination of 2-*p*-toluenesulphonamidofluorene yielded, however, the 3 : 7-dibromo-compound. Similarly, bromination of 2-acetamidofluorene yielded 3 : 7-dibromo-2-acetamidofluorene.

The presence of a methyl group was shown to decrease the halogen reactivity in the bromonitrotoluenes. This influence has already been noted (*e.g.*, Kenner, J., 1914, **105**, 2717), but no adequate explanation has yet been given (cf. Lindemann and Pabst, *Annalen*, 1928, **462**, 24).

2-*p*-Toluenesulphonamidotoluene was brominated in the hope that the bromine would substitute in the 3-position, and from this compound 3-bromo-2-nitrotoluene could be prepared. Bromination, however, was shown to occur in position 5.

Experimental.

Unless otherwise stated, the methods of preparation and the properties of the compounds used are those given in the literature. Hodgson and Walker's diazotisation method (J., 1933, 1620) was used, and the amino-group was converted into the nitro-group by the method of Hantzsch and Blagden (*Ber.*, 1900, **33**, 2554). The purity of all compounds was checked by the sharpness of their m. p.'s on the Kofler micro-apparatus (*Mikrochem.*, 1934, **15**, 242). Sublimations were effected on this apparatus. All analyses were done by Mr. Brown, Edinburgh.

Halogeno-ω-nitrostyrenes.—Various methods were investigated for the condensation of nitromethane and aromatic aldehydes. The use of zinc chloride (Posner, *Ber.*, 1898, **31**, 656) was very unsatisfactory. Amines (Knoevenagel and Walter, *loc. cit.*) yielded better results, and it is noteworthy that, although neither *n*-butylamine nor piperidine gave appreciable yields, yet a mixture of the two was an effective condensing agent. The most satisfactory results were obtained with alcoholic potassium hydroxide (Thiele, *Ber.*, 1899, **32**, 1293; Remfrey, J., 1911, **99**, 282), the modification of Thiele and Haeckel (*Annalen*, 1902, **325**, 7) being finally adopted.

o-*Chloro*-ω-*nitrostyrene* was prepared by cooling *o*-chlorobenzaldehyde (3 g.) and nitromethane (2·2 g.) in a freezing mixture, and carefully adding sodium hydroxide (1·5 g.) in water (3 c.c.). After an induction period, a bulky white precipitate separated, and methyl alcohol was added if the mixture became too thick to stir. The reaction was complete when a sample gave a clear solution with water. Addition of concentrated hydrochloric acid (20 c.c.) and water (10 c.c.) yielded yellow crystals which, after being washed with water, were crystallised from alcohol; m. p. 47° (Found : Cl, 19·6. $C_8H_6O_2NCl$ requires Cl, 19·1%). By similar methods were obtained the m-*chloro*- and the p-*chloro*-compounds, yellow crystals, m. p. 48—49° (Found : Cl, 20·0%), and elongated yellow prisms, m. p. 113—114° (Found : N, 7·0; Cl, 18·4. $C_8H_6O_2NCl$ requires N, 6·1; Cl, 19·1%), respectively. The yields in all cases were good.

o-Bromobenzaldehyde was prepared by a method similar to that of Brady and Lahiri (J., 1934, 1956). The 2 : 4-*dinitrophenylhydrazone* separated from tetralin in orange needles, m. p. 199—200° (Found : N, 15·3. $C_{13}H_9O_4N_4Br$ requires N, 15·3%). o-*Bromo*-ω-*nitrostyrene* was obtained in 50% yield by keeping *o*-bromobenzaldehyde (1 g.) and nitromethane (0·33 g.) for 3 days with one drop each of piperidine and *n*-butylamine; yellow crystals (alcohol), m. p. 86° (Found : Br, 34·2. $C_8H_6O_2NBr$ requires Br, 34·7%).

Condensation of o- *and* p-*Bromobenzaldehydes and Phenylnitromethane.*—*o*-Bromobenzaldehyde (1 g.), phenylnitromethane (0·74 g.), methylamine hydrochloride (0·1 g.), sodium carbonate (0·04 g.), and a few drops of ethyl alcohol were heated under reflux for 24 hours. Crystals separated, which were crystallised several times from ligroin; m. p. 135°, yield 0·5 g. The compound was a *diphenyl*-o-*bromophenylisooxazole* (Found : C, 67·4; H, 4·2; N, 3·8; Br, 20·1. $C_{21}H_{14}ONBr$ requires C, 67·0; H, 3·7; N, 3·7; Br, 21·3%). *p*-Bromobenzaldehyde similarly yielded 0·5 g. of an *isomer*, m. p. 175° (Found : N, 3·9; Br, 19·6%), which sublimed in needles and then had m. p. 180°.

4-*Nitrodiphenyl.*—The method of Fichter and Sulzberger (*Ber.*, 1904, **37**, 881) required modification. 4-Acetamidodiphenyl was prepared by suspending 4-aminodiphenyl (200 g.) in benzene (200 c.c.) and adding acetic anhydride (120 g.) carefully, the mixture being cooled with running water. After 15 minutes the acetamido-compound was separated, well washed with water, and when thoroughly dry was sufficiently pure for the next stage. 4-Acetamidodiphenyl (180 g.) was dissolved in glacial acetic acid and the solution warmed to 70° on the water-bath. Fuming nitric acid (200 g., *d* 1·51) mixed with an equal volume of glacial acetic acid was gradually added, with good stirring. The mixture was kept at 70° for 1 hour, and then poured into twice its volume of cold water. 3-Nitro-4-acetamidodiphenyl separated, and crystallised from alcohol in yellow needles (200 g.), m. p. 132° (lit., 132°). The compound was suspended in boiling alcohol (1 l.), and potassium hydroxide (100 g.) in water (125 c.c.) added. A mass of dark red crystals separated after a few minutes, and was purified by washing with 30% aqueous alcohol. Yield, 166 g., m. p. 167—169° (lit., 169°). 3-Nitro-4-aminodiphenyl (160 g.) was added to a mixture of 95% alcohol (390 c.c.) and concentrated sulphuric acid (58 c.c.), and the mixture heated until a clear solution was obtained. The mixture, cooled and vigorously stirred, was diazotised in the usual manner, and kept at room temperature for 3 hours. Copper bronze (6 g.) was then added in portions, the mixture being kept in cold water. The temperature rose to 40°, and nitrogen and acetaldehyde were copiously evolved. The alcohol was removed by distillation, and the residue distilled in a current of superheated steam, the flask being immersed in an oil-bath maintained at 210°. The 4-nitrodiphenyl crystallised from alcohol in yellow needles (60 g.), m. p. 62° (lit., 62°).

4-*Bromo*-3-*nitrodiphenyl.*—Prepared from 3-nitro-4-aminodiphenyl (6·5 g.) by diazotisation, this *compound* crystallised from light petroleum (b. p. 40—60°) in long yellow prisms (4·5 g.), m. p. 41—42° (Found : N, 4·9; Br, 27·6. $C_{12}H_8O_2NBr$ requires N, 5·0; Br, 28·7%).

5-*Bromo*-2-*nitrodiphenyl.*—The amino-group of 5-bromo-2-aminodiphenyl was converted into the nitro-group, and the resulting compound crystallised from ligroin in light brown needles, m. p. 230°; yield 2%. This compound is believed to be 5-*bromo*-2-*nitrodiphenyl*, but its m. p. is abnormally high (Found : N, 5·3; Br, 28·9%).

2-*Bromo*-3-*nitrofluorene.*—Prepared by diazotisation of 3-nitro-2-aminofluorene, this *compound* formed dark red needles from glacial acetic acid, m. p. 120—121° (Found : N, 5·0; Br, 28·4. $C_{13}H_8O_2NBr$ requires N, 4·8; Br, 27·6%).

3 : 7-*Dibromo*-2-*aminofluorene.*—Equimolecular quantities of 2-bromo-7-aminofluorene and *p*-toluenesulphonyl chloride in pyridine were mixed, kept overnight, and poured into dilute hydrochloric acid. The resulting 2-*bromo*-7-p-*toluenesulphonamidofluorene* was obtained as elongated prisms (*iso*propyl alcohol or carbitol), m. p. 211° (Found : N, 3·8. $C_{20}H_{16}O_2NBrS$ requires N, 3·4%). This compound (1 g.) was dissolved in chloroform (50 c.c.), and bromine

(0·4 g.) in chloroform (10 c.c.) added. The solution was heated on the water-bath for 1 hour and the chloroform removed by distillation. The residual oil on trituration with alcohol yielded a solid which crystallised from carbitol in needles, m. p. 203°, identical (mixed m. p.) with the dibromosulphonamido-compound, m. p. 203°, prepared below.

2-Aminofluorene (5 g.) and *p*-toluenesulphonyl chloride (6 g.) in pyridine were heated for 1 hour under reflux. 2-p-*Toluenesulphonamidofluorene* was isolated in the usual way, and crystallised from glacial acetic acid or carbitol in colourless prisms (7 g.), m. p. 157—158° (Found : N, 4·4. $C_{20}H_{17}O_2NS$ requires N, 4·4%). This compound (7 g., 1 mol.) was dissolved in chloroform, bromine (6·7 g., 2 mols.) added, and the mixture heated on the water-bath for ½ hour. The chloroform was removed by distillation, and the resulting 3 : 7-*dibromo*-2-p-*toluenesulphonamidofluorene* crystallised several times from alcohol; m. p. 203°; yield, 8·7 g. (Found : N, 2·8; Br, 31·3. $C_{20}H_{15}O_2NBr_2S$ requires N, 2·8; Br, 32·4%). The compound was hydrolysed by dissolving it in concentrated sulphuric acid at 40° and pouring it into water. The white flocculent precipitate obtained was triturated with 30% sodium hydroxide. 3 : 7-*Dibromo*-2-*aminofluorene* crystallised from alcohol in prisms, m. p. 135°; yield, almost theoretical (Found : N, 4·1; Br, 48·7. $C_{13}H_9NBr_2$ requires N, 4·1; Br, 47·2%).

3 : 7-*Dibromofluorene*.—3 : 7-Dibromo-2-aminofluorene (2 g.) was diazotised, the solution diluted with an equal volume of alcohol, warmed to 80°, and poured into water when the evolution of gas had ceased. The precipitated 3 : 7-*dibromofluorene* was recrystallised from methyl alcohol; m. p. 129°; yield, 0·5 g. (Found : Br, 48·1. $C_{13}H_8Br_2$ requires Br, 49·4%). Further purification by repeated sublimation yielded prisms or needles, m. p. 133°.

3 : 7-*Dibromofluorenone*.—3 : 7-Dibromofluorene (0·2 g.) was boiled under reflux for 3 hours with sodium dichromate (1 g.) and acetic acid (2 c.c.). The mixture was cooled, diluted with water, and the yellow precipitate crystallised from glacial acetic acid; m. p. 200°; yield, 80% (Found : Br, 47·5. $C_{13}H_6OBr_2$ requires Br, 47·3%).

Bromination of 2-*Bromo*-7-*acetamidofluorene*.—2-Bromo-7-aminofluorene (1 g.) was dissolved in boiling tetralin and acetic anhydride (2 c.c.) added. A solid separated immediately, and was purified by sublimation or by crystallisation from carbitol, forming prisms, m. p. 229—231° (Found : N, 5·0. $C_{15}H_{12}ONBr$ requires N, 4·6%). The *acetyl* compound was suspended in chloroform (20 c.c.), and bromine (0·3 g.) in chloroform (5 c.c.) added. Pyridine was then added until a clear solution was obtained, and this was kept at room temperature for 1 hour. The chloroform was removed by distillation, and the residue on treatment with dilute hydrochloric acid yielded a solid, which crystallised from carbitol in prisms, m. p. 263—265° (Found : Br, 41·0. $C_{15}H_{11}ONBr_2$ requires Br, 42·0%). The compound was identical with 3 : 7-*dibromo*-2-*acetamidofluorene* obtained by acetylation of 3 : 7-dibromo-2-aminofluorene in tetralin by acetic anhydride; it was further purified by sublimation, elongated prisms or needles, m. p. 272°, being obtained.

3-*Bromo*-4-*nitroacenaphthene*.—This compound was obtained by Dziewonski, Schoen, and Glazner (*Chem. Abstracts*, 1931, **25**, 1518) but no experimental details are available. 3-Bromoacenaphthene (8 g.) was dissolved in hot glacial acetic acid (40 c.c.), the solution quickly cooled to 10°, and vigorously stirred while concentrated nitric acid (5 c.c.) was slowly run in. 3-Bromo-4-nitroacenaphthene separated; it crystallised from alcohol in light yellow prisms, m. p. 155° (lit., 159—161°); yield, 65%.

4(?)-*Bromo*-1-*nitroacenaphthene*.—1-Nitroacenaphthene (5 g.) was dissolved in glacial acetic acid (25 c.c.), bromine (4 g.) added, and the solution heated to boiling; on cooling, it deposited 4-*bromo*-1-*nitroacenaphthene*, which was crystallised several times from alcohol; m. p. 157°; yield, 2 g. (Found : N, 5·3; Br, 28·7. $C_{12}H_8O_2NBr$ requires N, 5·0; Br, 28·7%). It sublimes in elongated prisms. By analogy with the bromination of the nitronaphthalenes, the bromine is believed to be in the 4-position.

3-*Bromo*-2-*nitroacenaphthene*.—This *compound* was prepared by the diazotisation of 2-nitro-3-aminoacenaphthene, and was crystallised first from alcohol and then from light petroleum (b. p. 80—100°), forming golden prisms, m. p. 143°; yield, 66% (Found : Br, 29·1%).

3-*Bromo*-4-*nitrotoluene*.—Prepared by the diazotisation of 3-bromo-4-aminotoluene (6 g.), this compound was purified by steam-distillation, followed by crystallisation from methyl alcohol; it formed pale yellow needles (2 g.), m. p. 36—37° (Found : Br, 36·7. Calc. for $C_7H_6O_2NBr$: Br, 37·0%).

Bromination of 2-p-*Toluenesulphonamidotoluene*.—*o*-Toluidine (15 g.) and *p*-toluenesulphonyl chloride (27 g.) were dissolved in pyridine (140 c.c.), bromine (7·1 c.c.) added, and the solution kept overnight. The product, isolated by the usual procedure, crystallised from alcohol in prisms, m. p. 136°; yield, theoretical. The 5-*bromo*-p-*toluenesulphonamidotoluene* was identical

with that prepared by the interaction of *p*-toluenesulphonyl chloride with 5-bromo-*o*-toluidine (Found : Br, 23·2. $C_{14}H_{14}O_2NBrS$ requires Br, 23·5%).

Thanks are expressed to the Carnegie Trust for the Universities of Scotland for the award of a Teaching Fellowship to one of us (N. C.).

UNIVERSITY OF EDINBURGH. [*Received, November* 16*th*, 1939.]