

93. *Dipole Moment and Structure of Organic Compounds. Part XV.*
The Electric Moments of Some Chlorinated Naphthalenes.

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THIS is a continuation of work already published (Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884) and was undertaken in order to try to settle the following points: (a) Is the moment of a substituted naphthalene the same as that of a substituted benzene? (b) Is the moment of an α - different from that of a β -substituted naphthalene? (c) Is there any evidence from the dipole data of the fixation of double and single bonds in naphthalene? (d) Does the introduction of a chlorine atom in one ring have any influence on the other ring?

Existing evidence concerning the structure of naphthalene is confusing. From X-ray investigations (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 674) it appears that naphthalene is centrosymmetric. De Laszlo (*J. Amer. Chem. Soc.*, 1928, **50**, 892), from absorption spectra, concluded that the two neighbouring β -positions (2 and 3) were not quite equivalent to one another, but that positions 2 and 6 were exactly equivalent. From chemical evidence there appears to be a marked difference between the α - and the β -positions, as is shown, e.g., by diazo-coupling to β -hydroxy- and β -amino-naphthalene (see Fieser and Lothrop, *ibid.*, 1935, **57**, 1459, and references therein). According to Pauling and his co-workers (Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362; Sherman, *ibid.*, 1934, **2**, 488), the naphthalene molecule should be considered as a resonance hybrid of 42 canonical structures. Easily the most important are the three unexcited Kekulé-type structures, and of these the symmetrical one, which has a double bond common to both rings, makes a 50% greater contribution to the wave function than either of the two unsymmetrical ones.

The electric moments of a number of naphthalene derivatives have already been measured, but the results in some cases were sufficiently discordant to require a careful redetermination. For all β -substituted derivatives, however, the moment appears to be somewhat larger than that of the α -isomeride, and this led Parts (*Z. physikal. Chem.*, 1930, *B*, **10**, 264) and Nakata (*Ber.*, 1931, **64**, 2059) to conclude that substituents in the β -position in naphthalene are aliphatically bound, or at any rate less aromatically bound than those in the α -position.

For the 1 : 4-, 1 : 5-, and 2 : 6-disubstituted naphthalenes, a moment indistinguishable from zero has been found by some workers, but others have found small but finite moments for some of them (Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1931, **53**, 2069; Bergmann and Engel, *Z. Elektrochem.*, 1931, **37**, 563; Nakata, *loc. cit.*; Weissberger and Sängewald, *Z. physikal. Chem.*, 1933, *B*, **20**, 146; Weissberger, Sängewald, and Hampson, *loc. cit.*). Nakata, for example, found 1 : 5-difluoro- and 1 : 4-dichloro-naphthalene to be non-polar, but 2 : 6-dichloronaphthalene had a small moment, and hence he concluded that the two rings were bent about the common C-C bond.

In cases such as this, where a differentiation between a small moment and one of zero is very important, great care must be taken over the measurement. To obviate the

experimental difficulty of measuring small moments, Nakata used disubstituted derivatives in which the two substituents were different, but owing to the non-additivity of group moments (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, 140, 562) this method cannot be considered satisfactory.

EXPERIMENTAL.

Materials.— α - and β -Chloronaphthalene were prepared from the purified amines by the Sandmeyer reaction (Scheid, *Ber.*, 1901, 34, 1813), followed by steam-distillation, treatment with caustic alkali, and distillation : α -chloronaphthalene, b. p. 255.5—256.0°; β -chloronaphthalene, m. p. 59.5—60.0°.

1 : 6-Dichloronaphthalene was obtained from naphthalene-1 : 6-disulphonyl chloride (Armstrong and Wynne, *Chem. News*, 1890, 62, 164); m. p. 48—49°. More satisfactory is the preparation from 1 : 6-diaminonaphthalene, obtained in a yield of 72% by reduction of 5-nitro-2-aminonaphthalene (Friedlander and Zsymanski, *Ber.*, 1892, 25, 2080). The diamine (4.8 g.) was finely dispersed in hydrochloric acid (25 c.c. concentrated acid and 25 c.c. water) and, after cooling in an ice-bath and addition of ice (80 g.), tetrazotised by sodium nitrite (4.2 g.) in water (8 c.c.). The solution was poured into cuprous chloride (20 g.) in concentrated hydrochloric acid (100 c.c.), slowly heated to 60°, filtered, and the residue steam-distilled after addition of caustic soda. The solid distillate had the correct m. p. but was rather yellow; it was therefore dissolved in light petroleum, decolorised (charcoal), the ether evaporated, and the colourless solid recrystallised from alcohol, 1.4 g. (24%) of colourless needles, m. p. 48.5—49.0°, being obtained.

1 : 7-Dichloronaphthalene. A sample, for which we thank I. G. Farbenindustrie A.-G., was repeatedly crystallised from benzene and from alcohol, forming colourless needles, m. p. 63.5—64.5°, undepressed on admixture with a specimen for which we are grateful to Professor W. P. Wynne.

1 : 8-Dichloronaphthalene. 1 : 8-Diaminonaphthalene (15.8 g.) in hydrochloric acid (80 c.c. conc. acid and 50 g. ice) was quickly tetrazotised and treated with cuprous chloride under conditions parallel to the above, benzene being added to prevent formation of froth. The mixture was slowly heated to boiling until the benzene was distilled off, then steam-distilled, and the solid distillate triturated in the cold with aqueous potassium hydroxide, filtered off, and steam-distilled after addition of caustic potash. The solid distillate was recrystallised from alcohol (11.9 g., 59%), colourless needles, m. p. 87—89°, and finally from hexane, m. p. 89.0—89.5°.

2 : 3-Dichloronaphthalene. We thank Messrs. Imperial Chemical Industries Ltd. for a pure sample (m. p. 119.5—120.5°) which gave no depression in m. p. with a specimen kindly supplied by Professor W. P. Wynne.

The other dichloronaphthalenes were either identical with, or prepared by the same methods as, the substances described in previous papers (Weissberger and Sängewald; Weissberger, Sängewald and Hampson, *loc. cit.*).

Measurements.—The data for the determination of dipole moments are in the following tables, where the symbols have their usual significance. All the measurements were carried out in benzene solution at 25.0°.

f_2 .	d .	ϵ .	n^2 .	P_2 .	ϵP_2 .	f_2 .	d .	ϵ .	n^2 .	P_2 .	ϵP_2 .
α -Chloronaphthalene.						β -Chloronaphthalene.					
0.029580	0.8882	2.3878	2.27775	97.11	50.24	0.023294	0.8848	2.3765	2.27285	105.75	50.27
0.019137	0.8833	2.3464	2.27008	96.80	49.76	0.018187	0.8825	2.3539	2.26975	105.95	50.31
0.011181	0.8795	2.3160	2.26542	97.18	50.14	0.008761	0.8781	2.3118	2.26361	106.27	50.27
0.010505	0.8792	2.3133	2.26531	97.15	50.69						
1 : 2-Dichloronaphthalene.						2 : 3-Dichloronaphthalene.					
0.018511	0.8879	2.4426	2.27302	174.8	55.43	0.013535	0.8841	2.4059	2.26808	185.08	54.51
0.013853	0.8844	2.4007	2.26929	176.5	55.43	0.010262	0.8816	2.3730	2.26537	184.95	54.20
0.006468	0.8787	2.3330	2.26375	179.5	56.84	0.007617	0.8796	2.3476	2.26361	186.40	54.47
						0.006162	0.8785	2.3334	2.26248	186.95	54.32
1 : 5-Dichloronaphthalene.						1 : 3-Dichloronaphthalene.					
0.010398	0.8815	2.2809	2.26661	55.20	55.54	0.010688	0.8818	2.3289	2.26641	120.9	55.56
0.009691	0.8810	2.2808	2.26586	55.57	55.16	0.008536	0.8802	2.3179	2.26466	121.5	55.45
0.005454	0.8777	2.2766	2.26244	54.16	55.39	0.008244	0.8798	2.3154	—	120.6	—

f_2	d	ϵ	n^2	P_2	ϵP_2	f_2	d	ϵ	n^2	P_2	ϵP_2
1 : 4-Dichloronaphthalene.						1 : 6-Dichloronaphthalene.					
0·013770	0·8841	2·2879	2·26860	59·80	54·63	0·014161	0·8848	2·3239	—	97·35	—
0·010420	0·8816	—	2·26632	—	55·00	0·011094	0·8825	2·3126	—	97·26	—
0·008659	0·8802	2·2823	2·26503	59·80	55·19	0·008394	0·8805	2·3031	—	97·56	—
0·006439	0·8785	2·2797	2·26295	59·40	54·51	0·014416	0·8846	—	2·26831	—	54·73
						0·012975	0·8836	—	2·26720	—	54·62
						0·011299	0·8740	—	2·26621	—	54·93
1 : 7-Dichloronaphthalene.						1 : 8-Dichloronaphthalene.					
0·013909	0·8842	2·5072	2·26811	183·4	54·96	0·022350	0·8912	2·5337	2·27637	206·8	55·90
0·013005	0·8835	2·3993	2·26735	184·6	54·96	0·018215	0·8879	2·4863	2·27305	208·9	55·11
0·007796	0·8798	2·3483	2·26372	184·9	54·93	0·009633	0·8812	2·3870	2·26598	213·9	55·28
0·005295	0·8779	2·3251	2·26185	188·4	54·88	0·007927	0·8798	2·3682	2·26455	217·2	55·35
2 : 6-Dichloronaphthalene.						2 : 7-Dichloronaphthalene.					
0·015300	0·8851	2·2842	2·26932	55·64	55·20	0·012554	0·8831	2·3212	2·26706	101·17	55·03
0·013413	0·8837	2·2828	2·26794	55·71	55·27	0·011712	0·8825	2·3192	2·26664	102·69	55·24
0·012634	0·8831	2·2824	2·26740	55·87	55·26	0·008653	0·8803	2·3071	2·26446	102·88	55·43
0·010410	0·8814	2·2806	2·26570	55·95	55·42	0·005546	0·8779	2·2948	2·26185	103·23	54·81

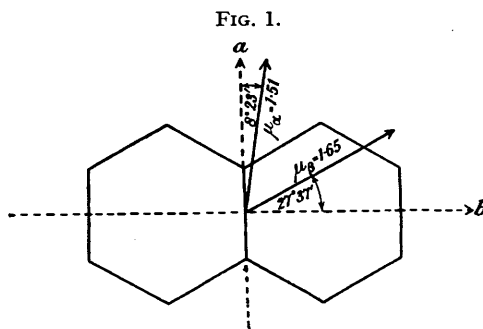
Substance.	P_2	ϵP_2	$\Delta + 0P_2 = P_2 - \epsilon P_2$	$\mu, D.$
1-Chloronaphthalene	97·5	50·2	47·3	1·51
2-Chloronaphthalene	106·6	50·3	56·3	1·65
1 : 2-Dichloronaphthalene	181·9	55·4	126·5	2·47
1 : 3-Dichloronaphthalene	121·0	55·5	65·5	1·78
1 : 4-Dichloronaphthalene	59·7	54·9	4·8	0·48
1 : 5-Dichloronaphthalene	55·1	55·3	—	0
1 : 6-Dichloronaphthalene	97·8	54·8	43·0	1·44
1 : 7-Dichloronaphthalene	189·5	54·9	134·6	2·55
1 : 8-Dichloronaphthalene	220·0	55·2	164·8	2·82
2 : 3-Dichloronaphthalene	189·0	54·4	134·6	2·55
2 : 6-Dichloronaphthalene	55·8	55·3	—	0
2 : 7-Dichloronaphthalene	103·5	55·1	48·4	1·53

DISCUSSION.

Concerning the sources of error inherent in the method used, it would appear that atom polarisation in this series of compounds is negligible. The difference between P_2 and ϵP_2 for 1 : 5- and 2 : 6-dichloronaphthalene, which one would expect to be non-polar, is certainly less than 1 c.c., and a similar small difference has been found for naphthalene itself (Parts, *loc. cit.*). The other source of error is the solvent effect, and since all these substances were measured in one solvent under the same conditions the results are probably strictly comparable (Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945).

Significance of Results.—Since the moments of 1 : 5- and 2 : 6-dichloronaphthalene are zero within the experimental error, the small value found for the 1 : 4-derivative has some significance and indicates that the moment of an α -substituted naphthalene is not quite parallel to the a -axis of the naphthalene molecule (see Fig. 1). This could arise either if the α -substituent itself were not directed as from the centre of the ring, or if this substituent were so directed, but induced a moment in the rest of the molecule which had a component along the b -axis. Also, the difference in moment of the α - and β -monochloronaphthalenes can be explained either by the moment of the C-Cl link in the two positions being different, or by a polarisation of the rest of the molecule by this link (Weissberger, Sängewald, and Hampson, *loc. cit.*).

In order to determine the direction of the resultant moment of the α - and the β -monochloro-derivatives relative to the a - and the b -axis of the naphthalene molecule, consider



that these resultants are each made up of two components along these principal axes. This introduces four unknowns which can be determined by solving four equations set up from four of the measurements. Besides the two monochloro-derivatives, the two dichloro-derivatives chosen for setting up these equations were the 1 : 6- and the 2 : 7-compound, since in these the chlorine atoms are far apart and so the Smallwood-Herzfeld effect (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) is negligible. Of course, this method of treatment presupposes that the moment of the disubstituted compound is the vector sum of the component moments of the monosubstituted compounds. This assumption is probably not strictly correct, but if the result which it gives enables the values of the moments of the other dichloronaphthalenes to be calculated correctly, then one is justified in using this method.

If the component moments along the a and the b axis for the α -compound are x and y , and for the β -compound p and q , the equations are

$$\begin{aligned} x^2 + y^2 &= 1.51^2 & p^2 + q^2 &= 1.65^2 \\ 2p &= 1.53 & (a-p)^2 + (q-b)^2 &= 1.44^2 \end{aligned}$$

from which $x = 1.494$, $y = 0.22$, $p = 0.765$, $q = 1.462$. In other words the measured moments 1.51 and 1.65 of α - and β -monochloronaphthalene are inclined at angles $8^\circ 23'$ and $27^\circ 37'$ to the principal axes of the naphthalene molecule, as shown in Fig. 1. Using these values to calculate the moments of the other dichloronaphthalenes, we obtain the results shown below.

Substance.	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$	$\mu_{\text{obs.}}/\mu_{\text{calc.}}$
1 : 7-Dichloronaphthalene.....	2.57	2.55	0.99
1 : 3-Dichloronaphthalene.....	1.83	1.78	0.97
1 : 8-Dichloronaphthalene.....	2.99	2.82	0.94
1 : 2-Dichloronaphthalene.....	2.82	2.47	0.87
2 : 3-Dichloronaphthalene.....	2.92	2.55	0.87
1 : 4-Dichloronaphthalene.....	0.44	0.48	0.92

The small difference between $\mu_{\text{obs.}}$ and $\mu_{\text{calc.}}$ for the 1:4-compound is, of course, meaningless in a moment of this magnitude. Of the others, the differences can all be explained by a Smallwood-Herzfeld effect, the ratio of $\mu_{\text{obs.}}/\mu_{\text{calc.}}$ approaching unity as the distance apart of the two chlorine atoms increases. The value of $\mu_{\text{obs.}}/\mu_{\text{calc.}}$ for 1:2- and 2:3-dichloronaphthalene might be expected to be the same as that of $\mu_{\text{obs.}}/\mu_{\text{calc.}}$ for 1:2-dichlorobenzene. The value of the latter is 0.86 (from Müller's polarisation data, *Physikal. Z.*, 1933, **34**, 689). Similarly, the value of $\mu_{\text{obs.}}/\mu_{\text{calc.}}$ for 1:3-dichlorobenzene is 0.97, in agreement with the value found for 1:3-dichloronaphthalene.

It would appear, therefore, that this method of treatment is satisfactory, and it remains now to try to explain the difference in the moments of α - and β -monochloronaphthalenes.

One possibility (Weissberger, Sägewald, and Hampson, *loc. cit.*) is that the C-Cl moment is the same in the two positions and is directed as from the centre of the ring, but that, in addition, the substituent sets up an induced moment in the system which is directed from the unsubstituted ring. This problem has since been discussed by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 188), and we are indebted to him for his helpful advice.

A monosubstituted naphthalene molecule may be regarded as a substituted benzene molecule to which a polarisable system has been attached. This system consists of four aromatic C-H groups, and its polarisability α has been assumed to be two-thirds of that of a benzene ring. This is justified, since the aromatic character of the ring is preserved. The moment μ of the substituent will induce moments μ_x and μ_y at the mass centre of this polarisable system, μ_x and μ_y being respectively parallel and perpendicular to the inducing moment μ (see Figs. 2 and 3). Now μ_x and μ_y are respectively equal to $\{(\epsilon + 2)/3\}\alpha E_x$ and $\{(\epsilon + 2)/3\}\alpha E_y$, ϵ being the dielectric constant of the medium and E_x and E_y being the components of the field in the directions x and y . Also, since E_x and E_y are respectively equal to $\mu(3 \cos^2 \Theta - 1)/\epsilon r^3$ and $\mu \cdot 3 \sin \Theta \cos \Theta/\epsilon r^3$ (Frank, *loc. cit.*, p. 176), μ being the inducing moment, r the distance between the inducing moment and the polarisable centre, and Θ the angle between the directions of μ and r , then μ_x and μ_y can be evaluated in terms of ϵ , α , μ , Θ , and r . In order to determine r , it is necessary to locate the position of

the inducing dipole; this cannot be done with certainty, but in the following calculations it is assumed to be at the point of contact of the carbon and the chlorine atoms. Using as standard data throughout $\epsilon = 2.27$, $\mu = 1.55$, $\alpha = 2/3 \times 12.5 \times 10^{-24} = 8.33 \times 10^{-24}$,* and $C_{ar}-C_{ar} = 1.40 \text{ \AA.}$, we obtain the following results.

	$r, \text{ \AA.}$	$\theta.$	$\mu_x.$	$\mu_y.$
α -Chloronaphthalene	3.69	55°17'	-0.004*	0.226
β -Chloronaphthalene	4.96	17°47'	0.114	0.058

* *I.e.*, in the opposite direction to that shown in Fig. 2.

Taking into account these induced moments, one calculates that the resultant moments of α - and β -chloronaphthalene are 1.56 and 1.66, respectively, inclined at angles of 8°19' and 28° to the a - and the b -axis of the naphthalene molecule. These results are in good agreement with those deduced on p. 396 from the experimentally determined dipole data. It follows that the moment of 1 : 4-dichloronaphthalene can be completely explained by a polarisation effect of the two C-Cl moments on the unsubstituted ring (moment : calc., $2\mu_y = 0.45$; obs. = 0.48) and that the difference in moment of α - and β -chloronaphthalene, as also that between those of the 1 : 6- and 2 : 7-, and the 1 : 2- and 2 : 3-dichloronaphthalenes, can be explained by the different polarising influence of the C-Cl bond in the α - and the β -position.

FIG. 2.
 α -Chloronaphthalene.

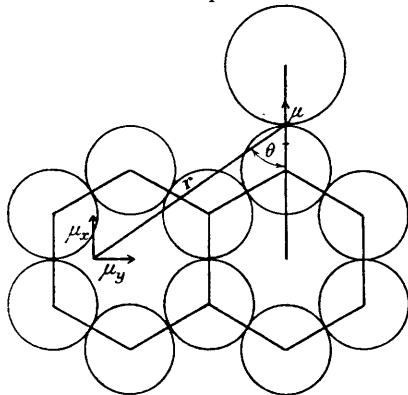
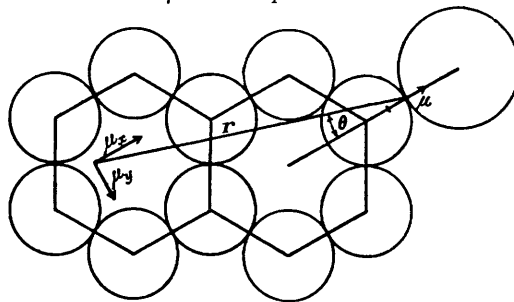


FIG. 3.
 β -Chloronaphthalene.



In these calculations it has been assumed throughout that the C-Cl moment in chloronaphthalene is 1.55, and by using this the value of 1.56 was deduced for the moment of α -chloronaphthalene. The experimental value is 1.51, and the discrepancy is rather outside the limits of experimental error. The explanation may be that the C-Cl moment in the α - is less than in the β -position, *i.e.*, in the α -position there is a greater mesomeric effect into the ring. This would be in accordance with the different chemical properties of α - and β -substituted naphthalenes, and also with the observation that the dissociation constant of α - is greater than that of β -naphthol.

If the polarisation theory developed above is correct, it should of course be applicable to other similar systems. Such a one is the series pyridine, quinoline, isoquinoline, acridine. The available dipole data (Rolinski, *Physikal. Z.*, 1928, 29, 658; Bergmann, Engel, and Meyer, *Ber.*, 1932, 65, 446; Le Fèvre and Smith, *J.*, 1932, 2810; Le Fèvre and Le Fèvre, *J.*, 1935, 1470) are reasonably concordant for this series of compounds, the order of the moments being isoquinoline > pyridine > quinoline > acridine. In applying calculations similar to those on p. 396 for the chloronaphthalenes, it is still more difficult in this case to locate the position of the inducing dipole, but qualitatively, at any rate, the theory predicts the above sequence. Similarly, the differences in moment between pyrrole, indole, and carbazole (Cowley and Partington, this vol., p. 47) can no doubt also be accounted for by this polarisation effect.

* For the value of the polarisability of benzene in the plane of the ring (12.5×10^{-24}), see Debye, "Handbuch der Radiologie," Vol. 6, p. 786, Leipzig, 1925, and Landolt-Börnstein-Roth, 5th ed.

CONCLUSIONS.

(1) Each C-Cl bond in the chloronaphthalenes is directed as from the centre of the ring; if there is any fixation of the single and the double bonds in naphthalene it is not revealed in the direction of the substituents (see Mills and Nixon, J., 1930, 2510).

(2) When a chlorine atom is substituted in the β -position in naphthalene, the C-Cl moment is the same, or very nearly the same, as in chlorobenzene. In the α -position it may be a little less, indicating a greater mesomeric effect into the ring.

(3) The moments of all the mono- and di-chlorinated naphthalenes can be accounted for on the basis of (1) and (2) if an additional polarisation effect is taken into account, the polar group inducing a moment in the rest of the system according to the polarisability of the system. In the dichloronaphthalenes, when the two chlorine atoms are close together, a part of this polarisation effect is a mutual effect of the two C-Cl bonds upon one another, *i.e.*, the well-known "ortho-effect" discussed by Smallwood and Herzfeld.

In the ortho-positions there may also be a steric factor.

The authors thank Imperial Chemical Industries Limited for a grant.

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[Received, February 3rd, 1936.]
