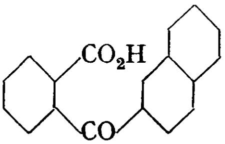
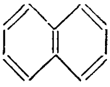
75. *Remarks on the Structure of Naphthalene.*

By Ernst Bergmann and Jehuda Hirshberg.

In spite of all the available information regarding the structure of the naphthalene system, we have neither definite knowledge nor even very exact data. One of the most striking features is the fact that a 2-hydroxy- or 2-amino-naphthalene couples with diazo-compounds exclusively in the 1- and not in the 3-position; *i.e.*, with regard to a 2-position, the 1- but not the 3-position behaves like an *o*-position. Furthermore, cyclisation of a suitable β-substituted naphthalene, *e.g.*, (I), usually involves the α-position, although the competitive cyclisation may be effected under different conditions.



(I.)



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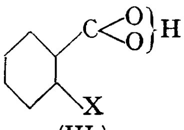

(III.)

(1) The first phenomenon has never been tested quantitatively. The present communication deals with the dissociation constants of *o*-chlorinated naphthoic acids: we obtained the following data for p_K, the measurements being carried out in acetone–water (1 : 1) as solvent for reasons of solubility.

Acid.	p_K.	Acid.	p_K.
1-Naphthoic	4·80	2-Naphthoic	4·67
2-Chloro-1-naphthoic	3·90	1-Chloro-2-naphthoic	3·80
8-Chloro-1-naphthoic	4·05	3-Chloro-2-naphthoic	4·37

The first conclusion to be drawn from these data is that the influence of a chlorine atom in the 1-position on the constant of the 2-naphthoic acid is the same as that of a 2-chlorine atom on the 1-naphthoic acid: the ratio between the respective constants is nearly the same (1·23) for both pairs. On the other hand, the chlorine atom in position 3 has a much smaller influence on the 2-naphthoic acid, which confirms the more qualitative assumption of organic chemists.

It is not easy to explain these results in terms of the theory of aromatic nuclei; it may be that the naphthalene system is not aromatic in the benzenoid sense. If we assume that in benzene there is no real difference between the various linkages of the nucleus, we may conclude that in naphthalene there are double and single bonds in the purely aliphatic sense, and that they have a fixed position and do not undergo any rearrangement. The further necessary assumption that an influence of the observed type is transmissible only through a double, not through a single, bond leads to a formula like (II) for naphthalene. [The validity of that assumption may be based on the consideration that in the system (III) two single bonds lie between the polar halogen bond (C–X) and the place of the dissociation: the transmission of polar effects through such systems of linkages has been treated theoretically by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668).] The same conclusion has been reached by Fieser and Lothrop (*J. Amer. Chem. Soc.*, 1935, **57**, 1459; cf. quinoline, Le Fèvre, J., 1935, 1470). According to the wave-mechanical treatment of the naphthalene molecule (Sherman, *J. Chem. Physics*, 1934, **2**, 488; cf. Kohlrausch, *Ber.*, 1935, **68**, 893), the above structure makes a considerably greater contribution to the wave function than any of the other possible structures (compare also Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2708).

According to that hypothesis, the influence concerned is not due to " steric hindrance," but is a merely " inductive effect "; any effect transmitted outside the nucleus should be the same for the 1 : 2- and the 2 : 3-position. Then, the influence of the 8-chlorine atom on the dissociation constant of 1-naphthoic acid, which is nearly as great as when it is in the 2-position, should be a really steric one, since no effect should be transmitted along the path from the 1- to the 8-position (3 single bonds).

(2) Similar conclusions may be drawn from dipole data. For 1 : 8-disubstituted naphthalenes, the following data were obtained:

	μ.	μ'.		μ.	μ'.
1-*Chloro*-8-*fluoronaphthalene*	2·86	3·01	1-Chloro-8-iodonaphthalene	2·55	2·86
1 : 8-Dichloronaphthalene	2·78	3·12	1 : 8-Dinitronaphthalene	7·87	7·96
1-Chloro-8-bromonaphthalene	2·64	3·05			

Since theoretically the moment of these naphthalene derivatives is equal to the sum (μ') of the substituent moments (the moment values used for F, Cl, Br, I, NO_2 are 1·45, 1·56, 1·49, 1·30, 3·96 respectively), the data give immediately a measure of the respective influences. If it is assumed that the difference between μ and μ' is due to a real valency deflexion, the angle between the halogen valencies is nearly proportional to the atomic radii of the halogens (96 : 114 : 120 : 120), but that consideration has only a formal value, and it would be interesting to determine the places of the halogen atoms by the method of electronic diffraction (for *o*-di-iodobenzene, see Hendricks, Maxwell, Mosley, and Jefferson, *J. Chem. Physics*, 1933, **1**, 549; cf. Schopp and Wolf, *Chem. Zentr.*, 1935, II, 2040).

The dipole moment of 1 : 8-dinitronaphthalene is nearly equal to the theoretical value —the small deviation may be due to experimental errors, since the compound is very sparingly soluble. The reason for this striking result may be that the nitro-groups do not lie in the plane of the nucleus, but in a perpendicular one, so that the steric disturbance is very small. Solvent effects, which may always invalidate discussion of dipole moments, will not greatly affect the above conclusions.

(3) The speed of alkaline hydrolysis of the methyl chloronaphthoates may also give a qualitative clue to the structural features of the naphthalene system. The measurements were carried out in methyl alcohol as solvent, and time was recorded in minutes :

Methyl 1-naphthoate	$k_{60^\circ} = 0{\cdot}0206$	Methyl 1-*chloro-2-naphthcate*	$k_{62^\circ} = 0{\cdot}0354$
,, 2-chloro-1-naphthoate	$k_{60^\circ} = 0$ *	,, 3-chloro-2-naphthoate	$k_{63^\circ} = 0{\cdot}0687$
,, 8-*chloro*-1-*naphthoate*	$k_{60^\circ} = 0$	,, benzoate †	$k_{60^\circ} = 0{\cdot}0490$
,, 2-naphthoate	$k_{59^\circ} = 0{\cdot}0153$	,, *o*-chlorobenzoate ‡	$k_{61^\circ} = 0{\cdot}0368$

* The stability of this ester towards hydrolysis and the lability of the 3-chloro-isomeride were recorded by Meyer (*Ber.*, 1895, **28**, 182).

† Cf. Treu, Diss., Hamburg, 1926.

‡ Studied by Kellas (*Z. physikal. Chem.*, 1897, **24**, 243) under similar conditions.

The absolute magnitude of the constants for methyl 1- and 2-naphthoates cannot readily be explained; for the α-compound, the depression with regard to the methyl benzoate constant may be due to the *o*-position being blocked by the second nucleus (cf. methyl *o*-chlorobenzoate), but the still lower value for the β-isomeride cannot be accounted for. The case is complicated by the fact that chlorination of methyl 2-naphthoate in the 1- and especially in the 3-position raises the hydrolysis constant. Such a rise would be expected only for the 3-chlorinated ester by analogy with methyl chloroacetate and acetate (cf. Freudenberg, " Stereochemie," 1932, p. 485) or similar pairs; that view would support the naphthalene formula discussed above.

That the 2-chlorination of methyl 1-naphthoate makes the resulting ester inaccessible to the hydrolytic agent, may be explained by the double ortho-substitution; but the behaviour of the 8-chloro-derivative is inexplicable, since the introduction of the chlorine atom merely enlarges the size of the ortho-substituent (the second nucleus) already present. It is obvious that we are dealing with a specific relation between the 1 : 8-substituents, and, in contrast to the p_K data, the hydrolysis data are not amenable to mathematical analysis, owing to the overlapping of various factors (8-*chloro*-1-*naphthonitrile* has an abnormally high dipole moment, 5·70, instead of the maximum theoretical value 5·47, which shows that 1 : 8-naphthalene derivatives are anomalous).

EXPERIMENTAL.

Materials.—1-Naphthoic acid and 1 : 8-dinitronaphthalene were commercial samples, recrystallised from dilute acetic acid and pyridine, respectively; m. p.'s 161°, 171°. 2-Naphthoic acid was prepared according to Salkind (*Ber.*, 1934, **67**, 1031), m. p. 182°; and 2-chloro-1-naphthoic acid according to Rabe (*Ber.*, 1889, **22**, 394), m. p. 151—152° from benzene (yield 27%).

3-*Chloro*-2-*naphthoic acid.* Commercial 3-amino-2-naphthoic acid (68 g.) was converted into the hydrochloride by heating with concentrated hydrochloric acid (300 c.c.), diazotised with sodium nitrite (27 g.), and slowly poured into a cold solution of cuprous chloride (copper filings, 180 g.; copper chloride, 20 g.; concentrated hydrochloric acid, 80 c.c.; water, 20 c.c.). The precipitate was purified by dissolving it in sodium carbonate solution and acidifying (yield, nearly quantitative); m. p. 212—213° (Hosaeus, *Ber.*, 1893, **26**, 668, gives 216°) from benzene. Esterification (*Ber.*, 1901, **34**, 4161) by heating with ethyl alcohol in a stream of hydrogen chloride proceeded normally; b. p. 195—197°/18 mm., from light petroleum, m. p. 57—59° (Found : C, 66·3; H, 4·7. $C_{13}H_{11}O_2Cl$ requires C, 66·7; H, 4·7%).

1-*Chloro*-2-*naphthoic acid.* 1-Hydroxy-2-naphthoic acid was converted into 1-chloro-2-naphthoyl chloride by means of phosphorus pentachloride (Strohbach, *Ber.*, 1901, **34**, 4161). The chloro-chloride was treated for 3 hours with its own weight of boiling methyl alcohol, and the resulting crude ester (b. p. 189—193°/17·5 mm.) was hydrolysed by boiling 15% methyl-alcoholic potassium hydroxide. The potassium salt was dissolved in warm water, and the solution acidified, the acid forming white needles, m. p. 195° (yield, 46%) from 50% acetic acid (Wolffenstein, *Ber.*, 1888, **21**, 1190, gives 196°).

8-Chloro-1-naphthoic acid was prepared from its nitrile (see below) by conversion into the amide and hydrolysis of the latter (Kalb, *Ber.*, 1914, **47**, 1726). It was obtained as an oil, crystallising on standing, and was recrystallised from benzene; yellowish crystals, m. p. 169—170° (Kalb gives 167°).

1-*Chloro*-8-*fluoronaphthalene*. 8-Chloro-1-naphthylamine (30 g.) was diazotised in concentrated hydrochloric acid (41·5 c.c.) with sodium nitrite (13 g.), and the filtered solution mixed with borofluoric acid (140 c.c.; 40%); the precipitated *diazonium borofluoride* had m. p. 106—107° (decomp.) (yield, 32 g.; 80%) (Found, by the method of Wilke-Dörfurt and Balz, *Ber.*, 1927, **60**, 116: N, 10·3. $C_{10}H_6N_2ClF_4B$ requires N, 10·4%). Thermal decomposition gave 1-*chloro*-8-*fluoronaphthalene* in 50% yield; b. p. 130—132°/12·5 mm., m. p. 44° (Found: C, 66·8; H, 3·5. $C_{10}H_6ClF$ requires C, 66·5; H, 3·3%).

1 : 8-*Dichloronaphthalene*. The diazo-solution prepared as above was introduced slowly into a boiling solution of cuprous chloride (copper sulphate, 125 g.; water, 250 c.c.; sodium chloride, 60 g.; copper turnings, 65 g.; concentrated hydrochloric acid, 500 c.c.), and the product isolated by steam distillation; m. p. 84—85° from alcohol (Altenberg, *Ber.*, 1876, **9**, 1732, gives 83°); yield, 17·5 g. (52%).

1-*Chloro*-8-*bromonaphthalene*. 8-Chloro-1-naphthylamine (52 g.) was dissolved in a solution of cuprous bromide (copper sulphate, 35 g.; potassium bromide, 116 g.; copper filings, 30 g.; concentrated sulphuric acid, 19 c.c.; water, 300 c.c.) and diazotised with sodium nitrite (22 g.). Extraction with ether and distillation in a vacuum gave the desired product, which was purified from light petroleum; m. p. 94—95°; yield 7 g. (17%) (I. G. Farbenind. give m. p. 87—88°; see *Chem. Zentr.*, 1930, II, 1466). Guareschi and Biginelli's compound of m. p. 119—119·5° (*Gazzetta*, 1887, **16**, 152) cannot be this 1-chloro-8-bromo-compound, but may be the otherwise unknown 1 : 5-derivative.

1-*Chloro*-8-*iodonaphthalene*. To the diazo-solution prepared as for the corresponding fluoro-compound, 50 g. of potassium iodide were added slowly. The mixture was heated on the water-bath for 1 hour, the brown precipitate dissolved in ether, the solution shaken with sodium thiosulphate, and the ether evaporated. Distillation in a vacuum (b. p. 197—198°/19 mm.) and recrystallisation from alcohol gave the pure product; m. p. 79—80°; yield 14 g. (28%) (0·1804 g. gave 0·2376 g. of AgCl + AgI. Calc. for $C_{10}H_6ClI$: 0·2365 g. AgCl + AgI) (compare Vieth, *Annalen*, 1875, **180**, 319).

8-*Chloro*-1-*naphthonitrile*. The diazo-solution prepared as above was mixed with a solution of 42·5 g. of potassium cuprocyanide. After 12 hours, the mixture was heated for 2 hours on the water-bath, the product isolated by suction, dried, and distilled in a vacuum; b. p. 242—244°/15·5 mm. Repeated crystallisation from alcohol gave silky needles, m. p. 145—146°; yield, 22% (Found: C, 70·5; H, 3·2. $C_{11}H_6NCl$ requires C, 70·6; H, 3·2%).

Methyl 1-naphthoate was obtained in quantitative yield from 1-naphthoic acid (10 g.) and methyl alcohol (200 c.c.) by heating for 2 hours in a stream of hydrogen chloride; b. p. 165°/17 mm. (Found: C, 77·2; H, 5·7. Calc.: C, 77·4; H, 5·4%). Methyl 2-naphthoate, prepared in the same way, was recrystallised from methyl alcohol; m. p. 76°. Methyl 2-chloro-1-naphthoate was prepared from the acid by means of ethereal diazomethane solution. The distilled ester (b. p. 176—180°/18·5 mm.) crystallised immediately and, after trituration with light petroleum, had m. p. 50° (Rabe, *Ber.*, 1889, **22**, 394).

Methyl 8-*chloro*-1-*naphthoate* was prepared in the same way (5 g. acid, 1 g. diazomethane); b. p. 188—189°/16·2 mm. (Found: C, 65·2; H, 4·2. $C_{12}H_9O_2Cl$ requires C, 65·4; H, 4·1%); and the 1-*chloro*-2-*naphthoate*, similarly prepared, afforded white needles, m. p. 48—49° (Found: Cl, 16·3. $C_{12}H_9O_2Cl$ requires Cl, 16·1%), from light petroleum.

Methyl 3-*chloro*-2-*naphthoate*. This was obtained by use of diazomethane, and also from 3-chloro-2-naphthoyl chloride (Strohbach, *Ber.*, 1901, **34**, 4159) by reaction with 5 times its weight of methyl alcohol. It crystallised spontaneously on evaporation and was purified from methyl alcohol; m. p. 58—59° (Ullmann, *Ber.*, 1918, **51**, 22, gives 58°).

Methyl *o*-chlorobenzoate, prepared according to Kellas (*loc. cit.*), had b. p. 119·5—120·5°/24·4 mm.

Measurements.—The dissociation constants of the halogenated naphthoic acids were determined by the method of "half-titration" from electrometrical titrations, the Cambridge Potentiometer apparatus and glass electrodes being used. The dipole measurements were carried out in benzene solution by the methods adopted in our laboratory (Bergmann, Engel, and Sándor, *Z. physikal. Chem.*, 1930, *B*, **10**, 113, where the significance of the symbols in the following tables is explained). The refractive indices were determined with the Zeiss interferometer.

The hydrolysis of the esters was effected by means of methyl-alcoholic potassium hydroxide solution. The ester was weighed into a 100-c.c. measuring flask, the equivalent amount of the hydroxide solution added from a burette, then most of the methyl alcohol, and the mixture was kept in the thermostat for 5 minutes and then diluted to the mark. After definite time intervals,

f.	$\overline{M}$.	ρ.	ϵ.	n^2.	$P_{\frac{1}{2}}$.	$P_{E\frac{1}{2}}$.	P.	P_E.	P_{A+O}.
				1-*Chloro*-8-*fluoronaphthalene*; t = 19·4°.					
0	78	0·8794	2·2852	2·2852	26·603	26·603	—	—	→
0·00994	79·018	0·8857	2·4077	2·2927	28·493	26·866	216·90	53·15	163·75
0·01221	79·252	0·8872	2·4343	2·2943	28·894	26·924	214·25	52·91	161·34
0·01458	79·494	0·8887	2·4634	2·2954	29·328	26·978	213·60	52·93	161·67
0·01931	79·979	0·8917	2·5157	2·2999	30·107	27·115	208·07	53·14	155·93
				P^{∞}_{A+O} = 172·0; μ = 2·86 D.					
				1 : 8-*Dichloronaphthalene*; t = 14·5°.					
0	78	0·8851	2·2951	2·2951	26·449	26·449	—	—	→
0·01109	79·319	0·8941	2·4318	2·3060	28·660	26·906	225·94	67·68	158·25
0·01324	79·575	0·8959	2·4610	2·3082	29·090	26·971	226·76	65·95	160·81
0·01525	78·814	0·8975	2·4778	2·3105	29·348	27·036	216·65	65·00	151·65
0·03923	82·669	0·9270	2·7708	2·3299	33·102	27·391	196·03	(50·48)	145·58
				P^{∞}_{A+O} = 166·0; μ = 2·78 D.					
				1-*Chloro*-8-*bromonaphthalene*; t = 13·5°.					
0	78	0·8863	2·2972	2·2972	26·566	26·566	—	—	→
0·00692	79·130	0·8947	2·3802	2·3045	27·869	26·805	215·07	61·14	153·93
0·00944	79·543	0·8962	2·4081	2·3075	28·353	26·943	215·90	66·49	149·41
0·01318	80·153	0·9001	2·4581	2·3118	29·126	27·092	220·87	66·50	154·37
0·01622	80·650	0·9032	2·4912	2·3154	29·647	27·217	216·60	66·73	149·87
				P^{∞}_{A+O} = 157·5; μ = 2·64 D.					
				1-*Chloro*-8-*iodonaphthalene*; t = 13·6°.					
0	78	0·8862	2·2970	2·2970	26·566	26·566	—	—	→
0·00603	79·268	0·8963	2·3629	2·3052	27·628	26·813	202·63	67·42	135·21
0·00875	79·841	0·9009	2·3912	2·3092	28·079	26·926	199·42	67·71	131·71
0·01194	80·513	0·9062	2·4293	2·3139	28·670	27·061	202·71	68·01	134·70
0·01465	81·083	0·9071	2·4546	2·3180	29·187	27·284	205·46	75·54	129·92
				P^{∞}_{A+O} = 140·0; μ = 2·55 D.					
				8-*Chloro*-1-*naphthonitrile*; t = 18·8°.					
0	78	0·8801	2·2864	2·2864	26·599	26·599	—	—	→
0·00292	78·320	0·8816	2·4274	2·2895	28·640	26·705	727·6	64·8	662·8
0·00423	78·463	0·8821	2·4780	2·2909	29·350	26·753	677·7	64·3	613·4
0·00599	78·656	0·8833	2·5583	2·2928	30·442	26·817	669·6	63·9	605·7
0·00808	78·885	0·8844	2·6481	2·2950	31·626	26·894	649·4	63·8	585·6
				P^{∞}_{A+O} = 687·0; μ = 5·70 D.					
				1 : 8-*Dinitronaphthalene*; t = 14·1°.					
0	78	0·8857	2·2962	2·2962	26·569	26·569	—	—	→
0·00053	78·074	0·8860	2·3400	2·2964	27·207	26·589	1236·57	64·53	1172·04
0·00074	78·103	0·8861	2·3553	2·2968	27·492	26·602	1193·17	61·62	1131·55
0·00099	78·175	0·8862	2·3702	2·2970	27·657	26·626	1122·47	83·18	1039·29
0·00151	78·212	0·8865	2·3894	2·2976	27·926	26·700	922·33	(112·80)	809·53
				P^{∞}_{A+O} = 1330·0; μ = 7·87 D.					

10 c.c. were run into ice-cold water and titrated with 0·1N-hydrochloric acid. In the following tables t is the time in minutes, a the initial concentration of alkali and ester in c.c. of 0·1N-acid per 100 c.c., and $a—x$ their concentration (in the same units) at time t. The velocity constants, therefore, are given by the equation $k = 100x/at(a - x)$.

Methyl α-*naphthoate.*

0·4966 G. of ester; a = 26·81; 60°.

t.	$a - x$.	k.	t.	$a - x$.	k.
11·5	26·6	0·0256	48·5	26·2	0·0179
23·0	26·4	0·0252	58·5	26·1	0·0173
33·0	26·3	0·0219	74·5	26·0	0·0156

k = 0·0206

Methyl β-*naphthoate.*

0·5158 G. of ester; a = 27·79; 59°.

t.	$a - x$.	k.	t.	$a - x$.	k.
46	27·0	0·0231	137	26·2	0·0161
76	27·0	0·0140	178	26·2	0·0098
108	26·6	0·0150	239	25·5	0·0136

k = 0·0153

Methyl 1-*chloro*-2-*naphthoate.*

0·5645 G. of ester; a = 25·60; 62°.

31	25·0	0·0225	202	21·2	0·0299
78	23·1	0·0404	347	18·9	0·0297
111	22·5	0·0361	498	15·1	0·0406
138	21·7	0·0379	1343	8·2	0·0459

k = 0·0354

Methyl 3-*chloro*-2-*naphthoate.*

0·5551 G. of ester; a = 25·17; 63°.

30	22·7	0·1073	201	17·5	0·0645
73	21·4	0·0714	343	16·5	0·0453
103	20·2	0·0706	489	12·2	0·0643
136	19·1	0·0691	1338	7·0	0·0574

k = 0·0687

Methyl o-*chlorobenzoate*. 0·5579 G. of ester; a = 32·86; 61°.

t.	*a* — *x*.	*k*.	*t*.	*a* — *x*.	*k*.	*t*.	*a* — *x*.	*k*.	*t*.	*a* — *x*.	*k*.
18·5	31·6	0·0656	37·0	31·4	0·0383	57·5	31·1	0·0300	81·5	30·5	0·0289
28·5	31·5	0·0372	46·0	31·2	0·0352	70·5	30·6	0·0319	95·0	30·3	0·0271

k = 0·0368

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