The residue left after the methyl benzoate had been distilled with steam was extracted with ether. The ethereal solution was freed from acid by extraction with bicarbonate, then shaken with saturated aqueous copper acetate. It deposited a greenish-yellow copper compound which on acidification turned into a pale yellow solid crystallizing in plates melting at 129°. As the yield of this product was only 0.11 g. it seemed wise to synthesize benzoyl anisoyl methane for comparison. This was readily accomplished by adding bromine to benzal acetyl anisole, boiling the dibromide with sodium alcoholate and digesting the resulting ethoxyl compound with acetic acid

$$C_6H_5CHBrCHBrCOC_6H_4OCH_3 \longrightarrow C_6H_5C(OC_2H_5){=}CHCOC_6H_4OCH_3 \longrightarrow C_6H_5COCH_2COC_6H_4OCH_3$$

Both the diketone obtained in this manner and a mixture of the synthetic and the ozonization product melted at 129°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.5; H, 5.6.

The ethoxyl compound corresponding to the methoxyl compound VIII.—For the sake of comparison, the low-melting cyclopropane derivative was treated also with sodium ethylate. It dissolved just as readily but the product separated much more slowly. It was recrystallized from absolute ethyl alcohol from which it separated in colorless cubical prisms melting at 89–90°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.6; H, 6.4. Found: C, 80.6; H, 6.5.

Summary

The paper contains:

1. A method for the preparation of cyclopropane derivatives in which a tertiary nitro group is attached to one of the carbon atoms of the ring.
2. An account of the behavior of cyclopropane derivatives of this type toward bases.

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[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORY OF THE DEPARTMENT OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE RELATIONS BETWEEN SOME PHYSICAL PROPERTIES AND THE CONSTITUTION OF CERTAIN NAPHTHALENE DERIVATIVES

BY HENRY DE LASZLO

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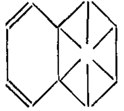
The structural formula of naphthalene is a vexing problem that has called forth a number of suggestions, more especially in recent years. Harries,[1] Mayer and Bansa,[2] and others suggest an aromatic olefinic structure . Willstätter[3] was inclined to support this view, but admitted later[4] that it is not necessarily right. On the other hand, v. Wein-

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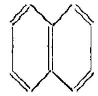
[1] Harries, *Ann.*, **343**, 337 (1905).

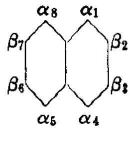
[2] Mayer and Bansa, *Ber.*, **54**, 19 (1921).

[3] Willstätter, *Ber.*, **44**, 3430 (1911).

[4] Willstätter, *Ber.*, **56**, 1407 (1923).

berg[5] is strongly in favor of the absolutely symmetrical, non-rigid Erlenmeyer-Graebe formula  based on his experience in the formation of azo colors. This view is supported by Lesser[6] on purely chemical grounds in the case of the same molecule. Lastly, v. Auwers[7,8] produces evidence for a formula in which the α and β positions are optically and chemically equivalent, both halves of the molecule being of the same type. It will be shown later that our results agree substantially with those obtained by v. Auwers.

The examination of the absorption spectra of a number of mono-substitution products of naphthalene[9] showed that the alpha derivatives were optically clearly differentiated from the beta compounds, the spectra of the latter being more like that of the parent body[10] than the former. This fact, among others, led us to measure the absorption spectra of the ten isomeric dichloronaphthalenes, both in vapor and solution. Throughout this paper we designate the position of the chlorine atoms in the naphthalene skeleton as shown, since we find that this expresses the optical characteristics of the isomers better than numbering alone. We hoped thus to obtain evidence as to whether the two halves of the naphthalene molecule were symmetrically built or not.



Technique.—The ten dichloronaphthalenes were kindly lent to me by Professor Palmer Wynne of Sheffield University, England. These substances had been prepared synthetically in the course of Armstrong and Wynne's[11] researches, so that there can be no doubt as to their chemical structure. They were all recrystallized at least three times from optically pure hexane,[12] and were thus obtained in perfectly white crystals which, however, could be easily differentiated. We hope later to prepare some more material, and then endeavor to grow crystals large enough for both x-ray and crystallographic investigation. These purified specimens have proved to be very stable when exposed to both light and air.

All the solution spectra were taken with hexane[12] as the solvent, using V. Henri's technique[13] for obtaining the molecular extinction coefficients (Σ). We sought to increase the accuracy of this method, which depends on the constancy of the source of

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[5] A. v. Weinberg, *Ber.*, **54**, 2168 (1921).

[6] Lesser, *Ber.*, **58**, 2109 (1925).

[7] K. v. Auwers and Frühling, *Ann.*, **422**, 206 (1921).

[8] K. v. Auwers and Krollpfeiffer, *Ann.*, **430**, 243 (1923).

[9] H. de Laszlo, *Proc. Roy. Soc.* (*London*), 111, 355 (1926).

[10] H. de Laszlo, *Z. physik. Chem.*, **118**, 371 (1925).

[11] Armstrong and Wynne, *Chem. News*, **59**, 189 (1889); **60**, 58 (1889); **61**, 273 (1890); **93**, 76, 70 (1906).

[12] V. Henri and Castille, *Bull. soc. chim. biol.*, **6**, 299 (1924).

[13] V. Henri, "Études de photochemie," Gauthier-Villars, Paris, 1919.

light, by inserting a rotating spark gap[14] in series with the one used in the experiment. To obtain a good continuous source of ultraviolet light, we supplemented the under-water spark, in which duralumin electrodes were used, by a gas-filled tungsten lamp which was made up for us through the kindness of Mr. A. L. Kimball, Jr., of the General Electric Company, Schenectady. The lamp consisted of a piece of tungsten ribbon (T) about 2 cm. long, 1.5 mm. wide, and 0.1 mm. thick, welded to two stout tungsten or nickel supports (S). The light issued through a fused quartz window (W) (3 cm. diam.) which was attached by means of a graded seal (G) to the body of the lamp at about 5 inches from the filament, to avoid deposition of tungsten by evaporation. It took about 18–20 amperes at 6 volts to run it. In order to bring it up to its maximum brightness, the filament was compared with that of a standard gas-filled lamp on a photometer bench and the current increased until they were equally bright. The experimental lamp was then run with a 10–15% current overload at about 300° below the melting point of tungsten. We were thus enabled to get a perfectly continuous blackening of the photographic plate down to 2500 Å., it proving especially satisfactory around 3000 Å.

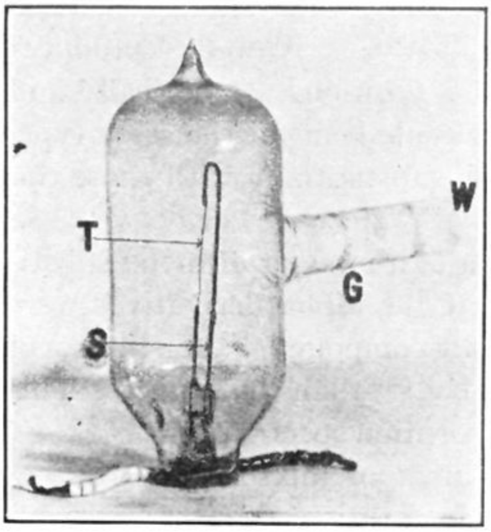

Fig. 1.

The vapor spectra were examined in an improved form of apparatus (see Fig. 2) over that described previously.[10] It was entirely constructed of fused quartz. The spaces (A) are evacuated, thus preventing condensation of the substance on the transparent windows (B). The outside is heated with Chromel wire, the mercury in the interannular space T being there to distribute the heat, thus bringing the vapor tube E to a constant temperature for any specified current. The material is inserted through a

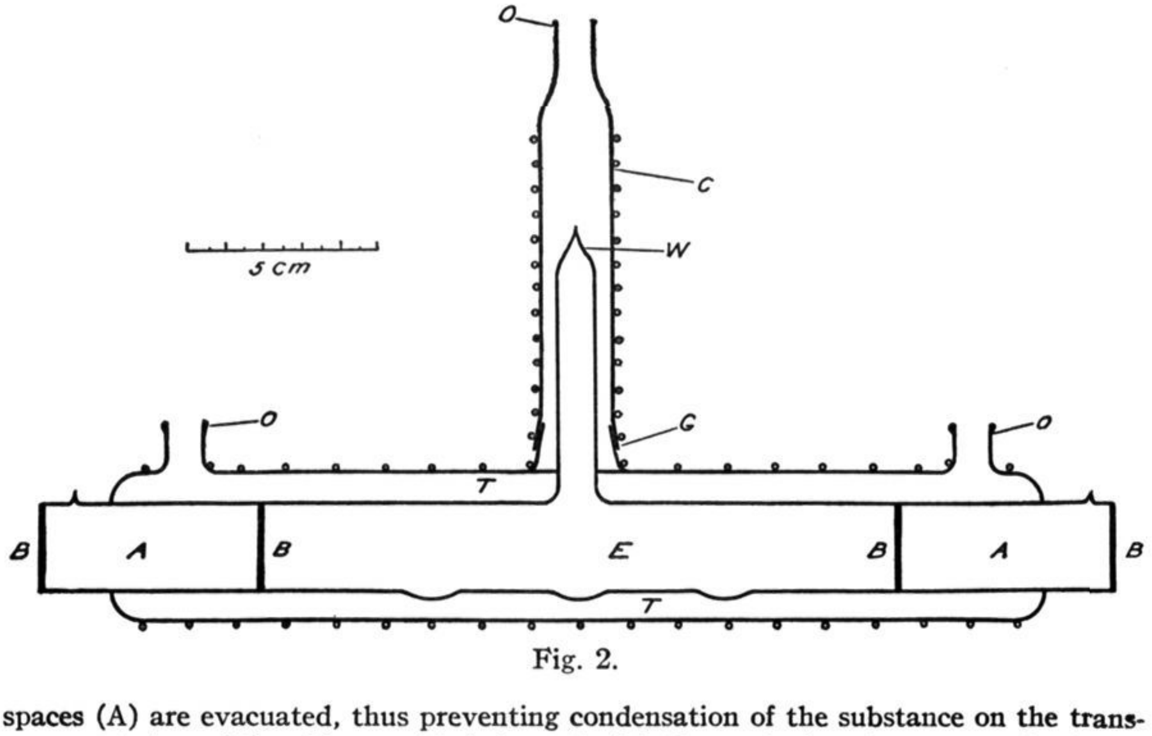

Fig. 2.

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[14] H. de Laszlo, THIS JOURNAL, **49,** 2107 (1927); *Ind. Eng. Chem.*, **19,** 1366 (1927).

side tube (W) which is sealed off after evacuating. A tube C is then fitted over a ground joint (G), the space between G and W being filled with mercury. C is heated about 50° higher than the rest of the apparatus by winding the Chromel closer. This insures that the substance does not distil into the side tube. Photographs are taken at every 10°, the temperature being measured with a thermocouple inserted through O. The openings O,O,O are connected to a three-way tube which leads to an exhaust line, so that mercury vapor does not enter the laboratory. The optical equipment consisted of a Hilger E_2 quartz spectrograph, the wooden back of which had been changed to metal owing to warping through atmospheric influence.

The results of our researches are shown graphically on Figs. 3, 4 and 5. Tables I, II and III give the exact position (λ) and intensity (Σ) of the bands both in vapor and solution.

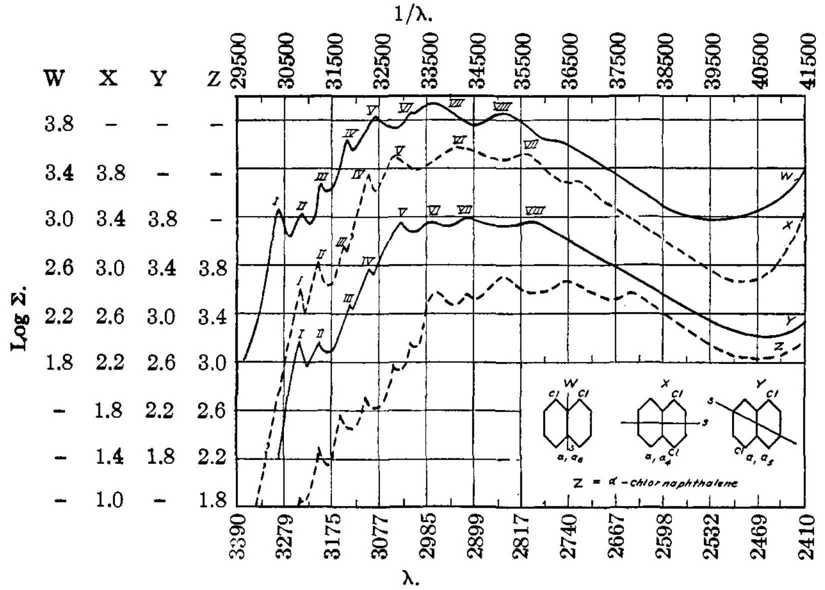

Fig. 3.

General Characteristics.—The curves and tables show: (A) that all the absorption spectra can be divided into two distinct parts, each possessing entirely different properties. (B) Two common frequency intervals Δ_1 and Δ_2 occur in all the isomers. (C) The spectra are of three definite types, each of which is represented in Figs. 3, 4 and 5.

(A). Part I between λ 3295 Å. and λ 2980 Å. consists of a number of narrow, clearly defined bands whose maxima may be determined with an accuracy of ±1 Å. These, according to present-day theory, are due to the quantized vibration of certain atoms or groups of atoms in the molecule.

Part II between λ 3080 Å. and λ 2530 Å. is of a very different character. The bands are between 50 Å. and 100 Å. wide, their maxima being difficult to measure with an accuracy greater than ±3 Å. We are as yet not certain what gives rise to this type of band, but it is suggested that the molecule becomes activated by quanta received from the light source used in these determinations and that those electron orbits which hold the atoms of the molecule together are altered, thus causing a general rearrangement of the structure in order to bring the molecule into equilibrium again. But this new state is not as stable as the first and becomes labile, for the molecule will be constantly changing its form between certain limits; vibrational quantization ceases and the bands become broad.

These spectra possess two more properties which make it easy to separate them into two parts.

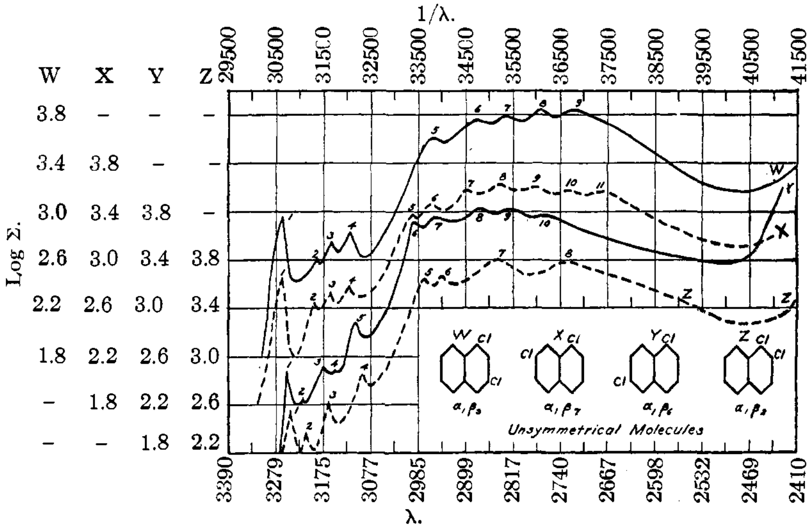

Fig. 4.

(a) We have found, as in the case of the mono-derivatives of naphthalene, that the vapor bands reproduce the hexanic solution bands both in relative position and intensity, except that the latter are shifted towards the red with respect to the former. This shift (δ) is a constant for each part of the spectrum of every isomer, and the various values are shown in Table IV. This rule has been found to hold rigorously in the case of substances whose vapor spectra do not show any fine structure. *But δ is widely different for both parts, it being always larger for Part II than Part I.* We have sometimes used this observation as a check on the exact position of some band that is but faintly distinguishable in solution or *vice versa.* How useful this may be is seen in the case of $\alpha_1\beta_7$ and $\alpha_1\beta_8$. Here both solution spectra were practically identical, especially in Part I. This, coupled with the fact that their melting points differed by but 1°, led to the supposition that they were perhaps not pure. However, on photographing the vapor spectra, δ for Part II of $\alpha_1\beta_7$ was found to be about double that for $\alpha_1\beta_3$, thus clearly showing that no such error had arisen.

(b) The molecular absorption coefficient (Σ) of Part II is about ten times stronger than Part I, which again supports the theory that the molecule becomes unstable on activation, for it has been found that those bodies which are chemically the most unsaturated or unstable have the strongest ultraviolet absorption bands.

No case of fine structure of the vapor bands could be found. This is interesting, as traces of such were noted for some of the bands of the monochloronaphthalenes. Thus rotational quantization ceases with the introduction of the second chlorine atom.

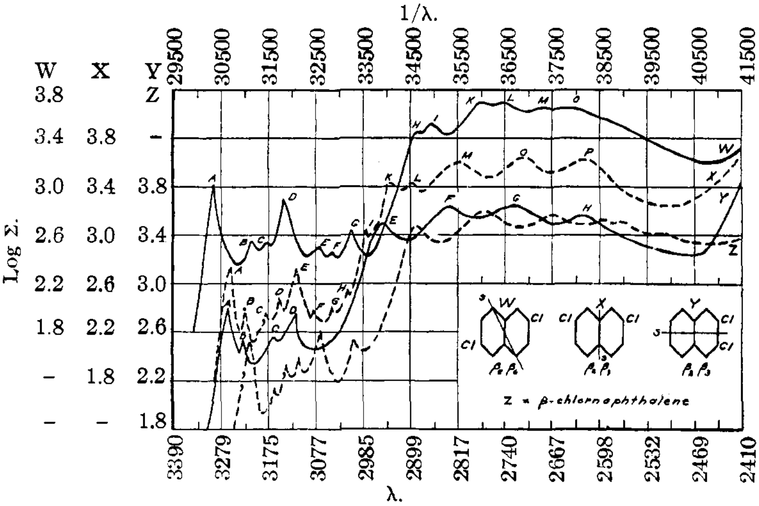

Fig. 5.

The first band that was found in Part I of each of the ten isomers corresponds to the characteristic band (c) of naphthalene (32605 cm.$^{-1}$, $\Sigma = 320$). It shifts in the spectrum between the limits λ 3292 Å. and λ 3245 Å., and is most clearly marked in the case of the β,β and α,β derivatives.

Going out from this band we find a common frequency interval Δ_1 varying from 1400 to 1450 cm.$^{-1}$. The only exception to this is the $\alpha_1\beta_2$ compound which shows one of 1530 cm.$^{-1}$. The same interval in naphthalene was found to be 1458 cm.$^{-1}$, so that the introduction of two chlorine atoms in one or both halves of the molecule would seem to make but little difference. The origin must lie in certain quantized electron jumps belonging to such an atom or groups of atoms as are unlikely to be affected to any great extent by the introduction of two substituents of fairly high atomic weight and negative moment. This might, therefore, originate in the $>C=C<$ linkage which acts as a pivot for both halves of the molecule.

A smaller interval Δ_2 of amazing regularity was found among most of the members of this group. This varied from 395 – 530 cm.$^{-1}$. Naphthalene has one of 474 cm.$^{-1}$ which lies nearly midway between the above limits. Here, however, there is a distinct difference depending on whether the chlorine atoms are in one or both rings. The results for Δ_1 and Δ_2 are summarized in Table IV. It is useless at present to theorize on the origin of these intervals; but we feel that much light would be thrown on the question by measuring the absorption spectra of (a) the twenty di-substituted naphthalenes, where both substituents were either fluorine or bromine atoms and (b) where fluorine and bromine are both present in the molecule in all the possible fourteen combinations. One might thus get some clue as to the mechanism of their formation by observing what changes were then wrought in the frequency intervals by such atoms of the same type but widely different atomic weights and electric moments under these several conditions.

(c) On examining the curves of the solution spectra we find that they may be divided into three clearly differentiated groups, the members of each group being of the same general type, namely, α,α, α,β and β,β. Besides this we will see how the average Σ rises in steps from β,β to α,α and conversely how the breadth of Part I decreases. The former property may be brought into line with the fact that Σ rises with the instability of the compound. α,α derivatives are more readily oxidized than β,β.

	Average Σ		
	Part I	Part II	Breadth, Part I
(a) α,α	1500	7000	1500 cm.$^{-1}$
(b) α,β	500	5000	2200 cm.$^{-1}$
(c) β,β	400	3500	3000 cm.$^{-1}$

We will now attempt to analyze successively each member of the three groups.

TABLE I

ABSORPTION BANDS OF THE α,α-DICHLORONAPHTHALENES

$\alpha_1\alpha_8$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	I	3285	1150	30440	115°	3226	30630
	II	3238	1050	30880		3219	31070
	III	3193	1850	31320		3174	31510
	IV	3140	4400	31850		3121	32040
Pt. II	V	3078	6950	32410	90°	3027	33040
	VI	3021	7250	33110		2972	33650
	VII	2964	8350	33700		2908	34390
	VIII	2849	7150	35100		2899	34490

TABLE I (*Concluded*)

$\alpha_1\alpha_4$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	I	3245	620	30820	105°	3229	30970
	II	3205	1080	31200		3190	31350
	III	3151	1450	31740		3136	31890
	IV	3099	5500	32270		3085	32410
Pt. II	V	3048	7950	32810	70°	2980	33560
	VI	2926	9100	34180		2863	34930
	VII	2810	8350	35590		2752	36340
	VIII	2712	4900	36870		2651	37720

$\alpha_1\alpha_5$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	I	3244	620	30830	140°	3226	31000
	II	3199	605	31260		3181	31440
	III	3139	1200	31860		3121	32040
	IV	3097	2350	32290		3082	32450
Pt. II	V	3033	5600	32970	80°	2978	33580
	VI	2979	5750	33570		2926	34180
	VII	2915	6200	34310		2863	34930
	VIII	2799	5800	35730		2750	36380

(a) The α,α group shown on Fig. 3 is the least like the spectrum of naphthalene. On the other hand, it bears a marked resemblance to α-chloronaphthalene, whose absorption curve is given on the same figure for purposes of comparison. None of the bands are very well marked and the two parts of the spectrum form in general a smooth curve without any clear division.

It is of special interest to notice how similar are the first parts of $\alpha_1\alpha_4$ and $\alpha_1\alpha_5$. Here, in the first case, the two chlorine atoms are substituted in the same ring, and in the second case in both rings. This fact would seem to show that the two halves of the naphthalene molecule are symmetrically built, or at least that the α positions are optically as well as chemically equivalent to each other.

The (Δ_1) is about 1440 cm.$^{-1}$, (Δ_2) about 435 cm.$^{-1}$ when the chlorine atoms are in opposite halves, and 535 cm.$^{-1}$ when substituted in the same half.

	No.	Δ_1	No.	Δ_2	No.	Δ_2
$\alpha_1\alpha_8$	I–IV	= 1410 cm.$^{-1}$	I –II	= 440 cm.$^{-1}$	II–III	= 440 cm.$^{-1}$
$\alpha_1\alpha_4$	I–IV	= 1450 cm.$^{-1}$	II–III	= 540 cm.$^{-1}$	III–IV	= 530 cm.$^{-1}$
$\alpha_1\alpha_5$	I–IV	= 1460 cm.$^{-1}$	I –II	= 430 cm.$^{-1}$	III–IV	= 430 cm.$^{-1}$

TABLE II

ABSORPTION BANDS OF α,β-DICHLORONAPHTHALENES

$\alpha_1\beta_3$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt I	1	3264	915	30650	150°	3248	30790
	2	3187	400	31380		3173	31520
	3	3158	555	31670		3145	31800
	4	3120	675	32050		3107	32190

TABLE II (*Concluded*)

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. II	5	2949	4000	33910	85°	2901	34470
	6	2876	5500	34770		2834	35290
	7	2833	6050	35300		2788	35870
	8	2770	6700	36100		2730	36630
	9	2720	6600	36760		2680	37310
				$\alpha_1\beta_7$			
Pt. I	1	3264	730	30650	160°	3247	30800
	2	3195	455	31300		3180	31450
	3	3157	555	31680		3140	31830
	4	3120	620	32050		3106	32200
	5	2991	2400	33430		2975	33610
Pt. II	6	2960	2800	33780	95°	2860	34960
	7	2895	3800	34540		2799	35730
	8	2840	4300	35210		2748	36390
	9	2778	4000	36000		2690	37170
	10	2727	3800	36670		2641	37860
	11	2673	3700	37420		2590	38610
				$\alpha_1\beta_6$			
Pt. I	1	3253	300	30740	150°	3234	30920
	2	3219	185	31070		3201	31240
	3	3174	330	31510		3156	31690
	4	3151	305	31740		..	...
	5	3107	760	32190		3091	32360
Pt. II	6	2992	5050	33420	75°	2913	34340
	7	2957	5750	33820		2880	34720
	8	2876	6750	34770		2804	35660
	9	2885	6600	35370		2767	36140
	10	2764	5800	36180		..	...
				$\alpha_1\beta_2$			
Pt. I	1	3245	305	30820	135°	3226	31000
	2	3212	240	31130		3194	31310
	3	3162	435	31630		3145	31800
	4	3091	725	32350		3073	32530
Pt. II	5	2976	4500	33600	75°	2892	34580
	6	2943	4700	33980		2860	34960
	7	2842	6300	35150		2766	36150
	8	2731	6200	36610		2666	36510

(b) The four α,β compounds shown in Fig. 4 possess a marked similarity. Thus $\alpha_1\beta_3$ and $\alpha_1\beta_7$ are nearly identical, although in the former both chlorines are in the same ring and in the latter in both rings. Similarly, $\alpha_1\beta_2$ and $\alpha_1\beta_6$ are not very unlike, yet here again the substituent atoms are distributed first on one side, then on both sides of the molecule. This should surely prove the symmetrical structure of the two halves of the molecule and the optical equivalence of the β_3 and β_7 as well as of the β_2 and β_6 positions.

Δ_1 recurs with its usual value except for $\alpha_1\beta_2$, which is far higher than for any of the others. Δ_2 is not so regular as in the α,α and β,β types. There is a considerable difference between the $\alpha_1\beta_7$ and $\alpha_1\beta_6$, as is borne out by the spectra. The values of Δ_2 for $\alpha_1\beta_3$ and $\alpha_1\beta_2$ may not be correct, but their similarity is striking and seems to agree with what was found above for the α,α group, in that Δ_2 *increases when the atoms are distributed between the two rings.*

	No.	Δ_1	No.	Δ_2
$\alpha_1\beta_3$	1–4	= 1400 cm.$^{-1}$	1–2	= 730 cm.$^{-1}$
$\alpha_1\beta_7$	1–4 4–5	= 1400 cm.$^{-1}$ = 1400 cm.$^{-1}$	2–3 3–4	= 380 cm.$^{-1}$ = 370 cm.$^{-1}$
$\alpha_1\beta_6$	1–5	= 1445 cm.$^{-1}$	2–3 4–5	= 440 cm.$^{-1}$ = 450 cm.$^{-1}$
$\alpha_1\beta_2$	1–4	= 1530 cm.$^{-1}$	3–4	= 720 cm.$^{-1}$

TABLE III

ABSORPTION BANDS OF THE β,β-DICHLORONAPHTHALENES

$\beta_2\beta_6$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	A	3292	1000	30380	155°	3272	30570
	B	3213	365	31120		3193	31320
	C	3183	345	31420		3164	31610
	D	3144	795	31810		3125	32000
	E	3072	325	32550		3053	32750
	F	3046	290	32830		3029	33010
	G	3008	440	33240		2992	33420
Pt. II	H	2893	2900	34570	110°	2829	35350
	I	2867	3350	34880		2804	35660
	K	2780	5000	35970		2720	36760
	L	2751	5000	36350		2692	37150
	M	2682	4600	37290		2623	38120
	O	2649	4450	37750		..	...

$\beta_2\beta_7$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	A	3256	550	30710	145°	3239	30870
	B	3223	250	31030		3207	31180
	C	3182	230	31430		3167	31580
	D	3151	310	31740		3134	31910
	E	3111	550	32140		3096	32300
	F	3080	240	32470		3065	32630
	G	3045	250	32840		3031	32990
	H	3015	365	33170		3000	33330
	I	2979	1150	33570		2965	33730
Pt. II	K	2934	2600	34080	85°	2866	34890
	L	2897	2600	34520		2831	35320
	M	2819	4000	35470		2756	36290
	O	2707	4350	36940		2650	37740
	P	2615	4200	38240		2560	39060

TABLE III (*Concluded*)

$\beta_2\beta_3$

	No.	Solution λ	Solution Σ	Solution 1/λ		Vapor λ	Vapor 1/λ
Pt. I	A	3260	635	30680	140°	3244	30840
	B	3226	350	31000		3209	31160
	C	3163	365	31630		3148	31770
	D	3115	575	32100		3100	32260
Pt. II	E	2947	3150	33930	90°	2878	34750
	F	2830	4350	35340		2766	36150
	G	2721	4350	36750		2662	37570
	H	2618	3650	38200		2563	39020

(c) The β,β group stands out by the clearness and persistence of the bands of Part I, which reminds one forcibly of parabenzene derivatives. Thus both *p*-dichlorobenzene[15] and *p*-xylene[16] have three very persistent and clear bands far stronger than the respective ortho and meta compounds. The resemblance to the curve of β-chloronaphthalene is very striking. In the case of $\beta_2\beta_6$ and $\beta_2\beta_7$ it seems to have broadened considerably and we obtain a double period for Δ_1. This is the same phenomenon that was found for β_2,β_6-dimethylnaphthalene.[17] Δ_1 is well represented and Δ_2 is likewise clearly marked.

	No.	Δ_1	No.	Δ_2
$\beta_2\beta_6$	A–D	= 1430 cm.$^{-1}$		
	B–E	= 1430 cm.$^{-1}$	C–D	= 390 cm.$^{-1}$
	C–F	= 1410 cm.$^{-1}$	F–G	= 390 cm.$^{-1}$
	D–G	= 1430 cm.$^{-1}$		
$\beta_2\beta_7$	A–D	= 1430 cm.$^{-1}$	B–C	= 400 cm.$^{-1}$
	D–I	= 1430 cm.$^{-1}$	D–E	= 400 cm.$^{-1}$
	B–F	= 1440 cm.$^{-1}$	H–I	= 400 cm.$^{-1}$
	C–G	= 1410 cm.$^{-1}$		
$\beta_2\beta_3$	A–D	= 1420 cm.$^{-1}$	C–D	= 470 cm.$^{-1}$

Δ_2 is nearly the same in the two isomers where the chlorines are on opposite halves of the molecule; but this value is smaller in $\beta_2\beta_3$ where the substituent atoms are adjacent.

Other Physical Properties of the Dichloronaphthalenes Refractive Indices.—We have just shown how one can divide these isomers into three types with the aid of their absorption spectra. The measurement of the specific exaltation of refractivity ($E\Sigma_{\mathrm{D}}^{20°}$) by v. Auwers and Krollpfeiffer[18] for a number of these compounds has given similar results. Unfortunately they did not measure the whole series so as to confirm their conclusions. As will be seen from Table IV, the $E\Sigma_{\mathrm{D}}^{20°}$ values are arranged in the following order, $\beta,\beta > \alpha,\beta > \alpha,\alpha$. Thus the effect previously noted by v. Auwers

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[15] Jan. Kalff, "Die Refractometrie der Chlorbenzolen," *Dissertation*, Amsterdam. 1924.

[16] Klingstedt, *Compt. rend.*, **175**, 1065 (1922).

[17] De Laszlo, *ibid.*, **180**, 203 (1925).

[18] K. v. Auwers and Krollpfeiffer, *Ann.*, **422**, 168 (1921).

TABLE IV

SOME PHYSICAL CONSTANTS OF THE DICHLORONAPHTHALENES

	δ in cm.$^{-1}$ Part I	δ in cm.$^{-1}$ Part II	Δ_1 in cm.$^{-1}$	Δ_2 in cm.$^{-1}$	$E\Sigma^{20°}_{D}$	M. p., °C. (Cl)$_2$	M. p., °C. (Br)$_2$	
$\beta_2\beta_6$	190	790	1425	390	...	135	158	[a]
$\beta_2\beta_7$	160	820	1430	400	...	120	...	
$\beta_2\beta_3$	160	810	1420	470	1.3	114	140	
$\alpha_1\alpha_5$	170	620	1455	430	0.9	107	131	
$\alpha_1\alpha_8$	190	600	1410	440	1.1	87	109	
$\alpha_1\alpha_4$	150	750	1445	530	0.9	68	82	
$\alpha_1\beta_7$	150	1180	1400	375	1.1	63	75	[b]
$\alpha_1\beta_3$	140	560	1400	730	...	62	64	
$\alpha_1\beta_6$	180	900	1445	445	...	49	61	
$\alpha_1\beta_2$	180	990	1530	720	1.0	35	67	
Naphthalene	260	505	1458	474	1.9	80.3		

[a] Symmetrical molecules.

[b] Unsymmetrical molecules.

that, in the case of the mono derivatives of naphthalene, the $E\Sigma$ value was always greater for the beta compounds is confirmed in the di-series. Judging from the previous values[18] found for the dichlorobenzenes, and xylenes, in which the para compounds had the highest $E\Sigma^{20°}_{D}$, we would likewise expect the $\beta_2\beta_6$ dichloronaphthalene to show a similar maximum in this respect, since its structure is comparable to a para-benzene derivative. As was the case with the absorption spectra, the values of $\alpha_1\alpha_4$ and $\alpha_1\alpha_5$ are identical where the chlorine atoms are in one, and later, in two rings. Hence v. Auwers deduces that naphthalene is a symmetrical system in which the four α and four β positions, respectively, are optically as well as chemically equivalent. At the same time it shows that there is a great difference between the alpha and beta position both from an optical and chemical point of view. It should also be noted that the $E\Sigma^{20°}_{D}$ value, and hence the structure of the $\beta_2\beta_3$ compound, is nearer to that for naphthalene than are the α,α bodies. This is borne out by our measurement of the absorption curves.

Melting Point.—Körner was the first to observe that in the case of the di-substitution product of benzene, the para derivatives always had the highest melting point. In 1882 Carnelley[19] made the suggestion that those isomers whose structures were the most compact and symmetrical would have the highest melting points. This rule was based on his knowledge of members of the benzene and aliphatic series but did not include naphthalene derivatives. We have previously noted,[9] that in the case of the mono-substitution products of naphthalene, the β compound melts higher than the α. We find that the ten isomeric dichloro- and dibromonaphthalenes (see Table IV) may be ordered into three groups, namely, $\beta,\beta > \alpha,\alpha > \alpha,\beta$ where the $\beta_2\beta_6$ compounds always have the highest melting point. The latter part of the rule seems also to hold

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[19] Carnelley, *Phil. Mag.*, **13,** 116 (1882).

for $(OH)_2$, $(NH_2)_2$, $(CH_3)_2$, $(CN)_2$ and $(NO_2)_2$ dinaphthalene derivatives, in so far as their isomeric forms have been investigated. We would add that, assuming the conventional plane formula for naphthalene, then the $\beta_2\beta_6$ position possesses a marked degree of symmetry, and at the same time the substituent atoms are as far apart as possible, in a position in fact that is analogous to the para compounds of the benzene series.

On reviewing all the melting points and Figs. 5 and 3, we see that it is possible to place a plane of symmetry (S) through the plane formulas of all the β,β and α,α isomers, which at the same time all show higher melting points than the α,β compounds. The latter exhibit no degree of symmetry.

Thus Carnelley's rule may be applied to members of the naphthalene series.

Summary

A. The investigation of the absorption spectra of the dichloronaphthalenes has shown that any structural formulas which may be evolved for them must conform to three conditions:

(1) Both halves of the molecule are symmetrical in structure.

(2) The four alpha positions are optically equal.

(3) The two pairs of beta positions, $\beta_3\beta_7$ and $\beta_2\beta_6$, are not quite equivalent, the members of each pair, however, being equal to each other.

B. All the isomers show two frequency intervals. The larger approximates closely to that found for naphthalene, and the smaller varies considerably depending on the position of substituent atoms.

C. The melting point of the $\beta_2\beta_6$ compound for a great variety of di-substituted naphthalenes is the highest in any particular set of isomers. The unsymmetrical α,β derivatives have a lower melting point than the symmetrical β,β and α,α compounds.

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