

ether, dried over calcium chloride and then fractionated *in vacuo*.

The data given in the literature for *p*-toluidine are reported here for the sake of completeness. These data were plotted and the line treated as an experimental line.

Results

The data obtained for *p*-cymene and cumene in this work give straight lines when plotted as $\log P$ vs. $1/T$. The data of Woringer¹ lie above these lines and give curves. This discrepancy has been reported for other compounds by Kassel² and by Linder.³ The points obtained for these compounds by Linder at about 0° by the dynamic method lie slightly below the extrapolation of our straight line. The data of Kudryavtzev⁹ give points considerably below the $\log P$ vs. $1/T$ line found in this work. For 2-nitro-*p*-cymene, the data of Mann, Montonna and Larian¹⁰ fit exactly on the line from our data. For 2-amino-*p*-cymene their data lie below our line and a line through their points has a slope which differs considerably from ours and which leads to extraordinarily high values at higher pressures. The same thing is true of their values for methyl *p*-tolyl ketone, though their line differs less from ours than with the 2-amino-*p*-cymene. The *p*-nitrotoluene and *p*-toluidine are of importance as Kobe and Doumani^{6,8} showed that in the nitration of *p*-cymene about 8% of the product was *p*-nitrotoluene accompanying the 2-nitro-*p*-cymene. This product could be reduced and the *p*-toluidine separated from the 2-cymidine. Our work on *p*-nitrotoluene substantiates the data of Berliner and May,¹¹

(9) Kudryavtzev, *J. Gen. Chem.* (U. S. S. R.), **4**, 563-566 (1934).

(10) Mann, Montonna and Larian, *Ind. Eng. Chem.*, **28**, 598-601 (1936).

(11) Berliner and May, *THIS JOURNAL*, **48**, 2630 (1926).

which are somewhat higher than those of Kahlbaum¹² and of Mann, Montonna and Larian¹⁰ at low pressures. The data for *p*-toluidine were collated and those of Berliner and May¹³ shown to agree well with Kahlbaum and be somewhat higher than the data of Mann, Montonna and Larian. The $\log P$ vs. $1/T$ plot for menthol shows a downward curvature at low pressures, necessitating a three constant equation. The boiling points, molal latent heats of vaporization, and vapor pressure equation constants are given in Table I.

TABLE I

Compound	B. p., °C., 760 mm.	L_v	Vapor pressure equation, $\log p =$
<i>p</i> -Cymene	176.8	10,670	$-2,332/T + 8.063$
Cumene	152.6	9,950	$-2,175/T + 7.991$
2-Nitro- <i>p</i> -cymene	decomp.	14,100	$-3,075/T + 8.70$
3-Nitro- <i>p</i> -cymene	decomp.	12,900	$-2,820/T + 8.24$
2-Hydroxy- <i>p</i> -cymene	237.3	13,250	$-2,897/T + 8.556$
3-Hydroxy- <i>p</i> -cymene	232.5	12,750	$-2,787/T + 8.394$
2-Chloro- <i>p</i> -cymene	217.6	11,800	$-2,579/T + 8.138$
3-Chloro- <i>p</i> -cymene	217.1	11,270	$-2,463/T + 7.906$
2-Bromo- <i>p</i> -cymene	234.3	12,010	$-2,625/T + 8.053$
3-Bromo- <i>p</i> -cymene	234.1	11,500	$-2,525/T + 7.86$
<i>p</i> -Tolyl methyl ketone	224.4	12,440	$-2,719/T + 8.347$
<i>p</i> -Nitrotoluene	238.2	12,030	$-2,630/T + 8.025$
<i>p</i> -Toluidine	200.3	11,880	$-2,597/T + 8.366$
Carvone	229.0	12,320	$-2,694/T + 8.247$
Fenchone	193.2	10,820	$-2,366/T + 7.954$
Isopulegol	212.0	11,900	$-2,601/T + 8.243$
Menthol	216.5	12,050	$-4,695/T - 10.250$ $\log T + 40.033$

Summary

Vapor pressures have been determined for *p*-cymene, its important derivatives and some closely related compounds. Comparisons are made with the data in the literature.

(12) Kahlbaum, *Z. physik. Chem.*, **26**, 624 (1898).

(13) Berliner and May, *THIS JOURNAL*, **49**, 1007 (1927).

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The Ultraviolet Absorption Spectra of the Monomethylchrysenes

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The effects of substitution and position isomerism on the ultraviolet absorption spectra of similarly constituted aromatic compounds have been studied by several investigators.^{1,2,3,4} Brode⁵ has shown that the substitution of a methyl radical in the ortho position of benzeneazophenol causes a

decrease in the intensity of the absorption band, which can be correlated with the recent work of O'Shaughnessy and Rodebush⁶ indicating a decrease in the intensity of the absorption band when steric hindrance is possible.

The recent interest in the carcinogenic activity of certain hydrocarbons has stimulated the development of methods for the synthesis of various types of these compounds, and made available

(1) Baly, *J. Chem. Soc.*, **107**, 1058 (1915).

(2) Purvis, *ibid.*, **103**, 1088 (1913).

(3) Klingstedt, *Compt. rend.*, **175**, 365 (1922).

(4) De Laszlo, *Z. physik. Chem.*, **118**, 369 (1925).

(5) Brode, *THIS JOURNAL*, **51**, 1204 (1929).

(6) O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

all of the monomethylchrysene derivatives. It has been the object of this investigation to determine and compare the ultraviolet absorption spectra of these compounds with the parent, chrysene.

Experimental

A Bausch and Lomb medium quartz spectrograph, with a modified Hilger sectorphotometer attached, was used in conjunction with a tungsten-steel spark. Absorption cells of the type described by Brode⁷ consisting of matched quartz end-plates held over Pyrex tubes of matched length were employed to hold the solution and solvent.

Preliminary work on chrysene, using cells of different thicknesses, seemed to indicate that this compound behaved in accordance with the laws of Lambert and Beer. Therefore, it was assumed that the methylchrysenes obeyed this law; $E_{\text{molar}} = \log_{10} I_0/I \cdot 1/cl$, where E_{molar} is the specific molar extinction, $\log_{10} I_0/I$ is the extinction as read from the photometer, c is the concentration of the solute in moles per liter, and l is the thickness of the cell expressed in centimeters. On the basis of this equation the concentration was so adjusted that the fine structure of the curves would come at the points of maximum sensitivity, or where readings of $\log_{10} I_0/I$ are greater than one. In each case a 0.00094 M solution was prepared by weighing a sample of the compound on a semi-micro balance and dissolving it in absolute ethanol. Solutions of 0.000094 and 0.0000094 M concentrations were made by successive dilution of the original 0.00094 M solution. As a check, a second set of solutions of the same concentrations was prepared.

Two Eastman 33 plates were used with each solution, one with a 1-cm. cell and the other with a 4-cm. cell. Thirteen exposures at $\log_{10} I_0/I = 0.3, 0.4, 0.5, \dots, 1.5$ and three additional exposures with the cells reversed at $\log_{10} I_0/I = 0.5, 1.0, \text{ and } 1.5$ were made on each plate. A slit opening of 0.10 mm. was used and all measurements were made at 20–25°. These plates were developed in Eastman M. Q. developer and spotted visually against an evenly illuminated background. With the aid of a conversion plate the points were read directly in frequency units.

Points on the curve below $\log E = 1.80$ were necessarily obtained (because of the limited

quantity of the compounds available) by recovering the samples from the solutions and making new ones of the concentrations given in the table:

Chrysene	1-Me	2-Me	3-Me	4-Me	5-Me	6-Me
Concn., M	0.0375	0.0121	0.0069	0.0102	0.0049	0.0079	0.0072
Solvent	Pyridine			Absolute alcohol			

One plate using a 4-cm. cell was made with each of these solutions.

The results are plotted with values of $\log_{10} E_{\text{molar}}$ along the ordinate because of the great differences in the value of E_{molar} and with fresnel units along the abscissa to show up any multiple relationships between maxima.

Discussion of Results

Chrysene.—The ultraviolet absorption spectrum of chrysene has been determined previously, and the data of Mayneord and Roe⁸ and of Clar and Lombardi⁹ are compared in Table I with those obtained in this Laboratory. The curve for chrysene is shown in Fig. 1. The data are obviously in good agreement, the only outstanding exception being the observation of a new band at 758 f. in the present work. This band was first detected in a saturated toluene solution of chrysene and later measured using pyridine as the solvent.

TABLE I

POSITIONS AND INTENSITIES OF BANDS IN CHRYSENE			
Band	B. and P.	M. and R.	C. and L.
1	758 (0.96)
2	833 (2.81)	832 (2.80)	833 (3.00)
3	855 (2.57)	854 (2.55)	851 (2.62)
4	875 (2.81)	872 (2.75)	872 (2.76)
5	940 (4.13)	938 (4.10)	944 (4.18)
6	982 (4.13)	981 (4.10)	984 (4.18)
7	1023 (4.09)	1021 (4.06)	1017 (4.12)
8	1064 (4.09)	1063 (4.06)	1064 (4.13)
9	1122 (5.20)	1121 (5.16)	1124 (5.25)
10	1163 (4.96)	1166 (4.90)	1163 (5.00)

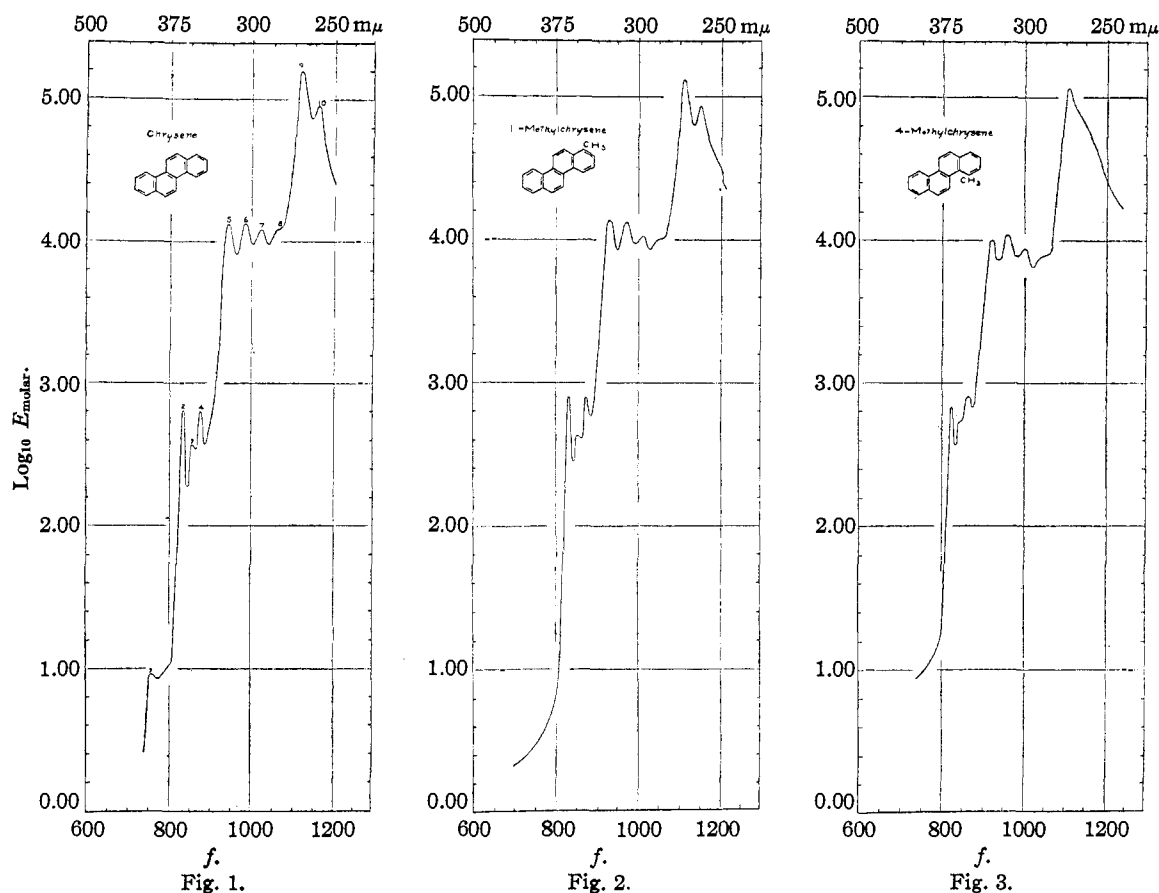
Monomethylchrysene Derivatives.—The ultraviolet absorption curves of the monomethyl derivatives of chrysene are, in general, very similar to that of chrysene. The positions of the maxima in fresnels and the intensities of the bands in terms of $\log_{10} E_{\text{molar}}$ are summarized in Table II, the bands being numbered as in the case of chrysene (Fig. 1).

These derivatives are similar to those studied by Klingstedt³ with respect to the benzene nucleus and those studied by de Laszlo⁴ with respect

(7) Brode, "Chemical Spectroscopy," John Wiley and Sons, New York, N. Y., 1939, pp. 179–180.

(8) Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A152**, 299 (1935).

(9) Clar and Lombardi, *Ber.*, **65**, 1411 (1932).



Figs. 1-3.—Absorption spectra of chrysene and methylchrysenes.

to the naphthalene nucleus in that the added weight of the methyl group produces a bathochromic shift. They are also in keeping with the

TABLE II
POSITIONS AND INTENSITIES OF BANDS IN THE MONO-METHYL DERIVATIVES OF CHRYSENE

Source ¹⁰	Chry. a	1-Me b	2-Me b	3-Me b	4-Me b	5-Me c	6-Me c
M. p., °C.	251	249.5-	224.5-	190.0-	149.0-	117.2-	161.0-
Band	250.0	225.5	190.5	149.5	117.8	161.4	
1	758	742	..
	0.96					1.04	
2	833	829	831	829	820	817	828
	2.81	2.91	2.41	2.94	2.84	2.94	3.03
3	855	850	852	850	843	..	849
	2.57	2.63	2.49	2.53	2.73		2.63
4	875	870	872	872	862	860	868
	2.81	2.91	2.64	2.94	2.91	2.97	3.03
5	940	928	936	936	918	924	928
	4.13	4.15	4.05	4.13	4.00	4.01	4.13
6	982	969	976	976	956	961	968
	4.13	4.13	4.12	4.12	4.05	4.01	4.15

(10) Sources: (a) Fraenkel and Landau, Germany. (b) Kindly supplied by Bachmann and Struve, see, *J. Org. Chem.*, **4**, 456 (1939), and **5**, 416 (1940). (c) Kindly supplied by Newman, see *THIS JOURNAL*, **60**, 2947 (1938), and **62**, 870 (1940).

7	1023	1010	1017	1016	995	1000	1012
	4.09	4.03	4.12	4.09	3.95	3.93	4.08
8	1064	1053	1060	1058	1038	1042	1053
	4.09	4.00	4.16	4.13	3.89	3.91	4.02
9	1122	1114	1114	1114	1107	1116	1114
	5.20	5.13	5.18	5.13	5.08	5.08	5.18
10	1163	1152	1154	1156	1154
	4.96	4.94	4.88	4.87			4.90

theoretical work recently done by Sklar¹¹ in which he points out that the substitution of a methyl group on an aromatic nucleus produces a comparatively small change in the electronic resonance of the parent substance and consequently little change in the intensities of the bands.

The monomethylchrysene derivatives may be divided into two groups according to the nature of their ultraviolet absorption curves. In the first group there would appear the 1-, 2-, 3- and 6-methyl derivatives, the curves of which show two maxima in the most intense section as shown in Fig. 2. It should be noticed, however, that an exception might be made in the case of 2-methyl-

(11) Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

chrysene, for although the bands fall at approximately the same frequency, the intensities in the two lower sections of the spectrum progressively increase rather than decrease in passing to higher frequencies.

In the second group are found the remaining 4- and 5-methyl compounds, which are exemplified by the absorption curve in Fig. 3. These compounds exhibit a bathochromic and hypochromic shift which is greater than that noticed in the other monomethylchrysenes. However, the ninth band of 5-methylchrysene does not show a shift to a lower frequency that is in keeping with that seen in the rest of this curve, and it is also different in that it exhibits, like chrysene, a maximum at 737 f. Both of these effects may possibly be attributed to the nature of the component curves and the shifts produced on their addition.¹² To the nature of the component curves might also be attributed the appearance of a mere inflection in place of the tenth band of the two derivatives in this group.

A study of the stereochemistry of these compounds effectively accounts for the division of these derivatives into the aforementioned groups. Fig. 4 shows a diagram, modified from one given by O'Shaughnessy and Rodebush,⁶ that indicates the possibilities of steric hindrance and distortion of the planar nature of the molecule. This is only possible if substitution occurs in the 4- or 5-position, and it is these derivatives that have ultraviolet absorption spectra that are the least like that of chrysene. Therefore, this classification of the derivatives into two groups serves to separate the compounds on the basis of the effect that substitution of the methyl group in a

(12) Brode, *Proc. Roy. Soc. (London)*, **A118**, 286 (1928).

given position has on the electronic resonance of the parent molecule.

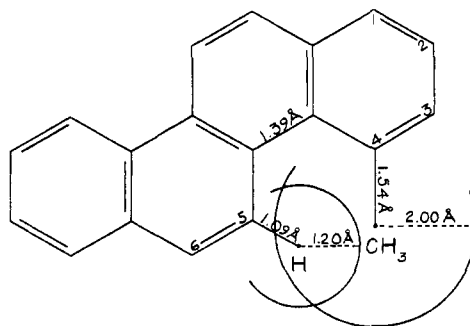


Fig. 4.—Diagram showing the possibility of steric hindrance in 4- or 5-methylchrysene.

Although there is sufficient difference in the ultraviolet absorption spectra of the monomethylchrysene derivatives to characterize them in the pure state, any attempt to determine the constituents of a mixture of these compounds would be unsuccessful.

Summary

The ultraviolet absorption spectra of chrysene and the six monomethyl derivatives have been determined. Concentrated solutions of chrysene in pyridine were found to give a band of 758 f. While the absorption curves of the monomethyl derivatives are very similar to that of chrysene, steric hindrance effects in the case of 4- and 5-methylchrysene were found to produce greater bathochromic and hypochromic shifts in these derivatives.¹³

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(13) Since the completion of this work, Jones, *THIS JOURNAL*, **63**, 313 (1941), has published data for 5-methylchrysene. His results have been compared with those reported in this paper and were found to be in excellent agreement.