

## Spectral Resemblances of CataCondensed Hydrocarbons

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## Spectral Resemblances of Cata-Condensed Hydrocarbons

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The spectra of naphthalene, anthracene, naphthacene, phenanthrene, 1,2-benzanthrene, chrysene, and acenaphthene in *n*-heptane solution are extended to 1700Å. Electronic energy levels of 17 such cata-condensed hydrocarbons are collected and compared. The lowest five or six excited states shift in a regular way with changes of molecular length and shape. Intensities and vibrational structures of corresponding bands are remarkably alike in the different compounds. The total oscillator strength is almost proportional to the number of  $\pi$ -electrons, but the proportionality constant differs from that in

polyenes. With new identifications, the positions of energy levels in naphthalene, anthracene, and azulene agree remarkably well with previous LCAO molecular orbital calculations.

The lowest singlet state is of one type in benzene, naphthalene, and most non-linear systems; of another type in anthracene and the higher linear polyacenes because of a cross-over. This clears up some controversial questions, such as the relations among the spectra of naphthalene, anthracene, and phenanthrene.

## I. PREVIOUS WORK

THE spectra of condensed ring systems have been investigated in the quartz ultraviolet.<sup>1,2</sup> and Jones<sup>3</sup> has identified conjugation and steric effects, fine-structure changes and red shifts in the spectra resulting from different substitutions. The polarization of certain bands was used by Lewis and co-workers<sup>4,5</sup> and by Scheibe<sup>6,7</sup> in interpreting the effect of substitutions on the spectra of triphenylmethyl ions and dyes. The polarization was assumed to be along mutually perpendicular axes in the main plane of the molecule. In a long, narrow molecule, the longitudinal frequency would be lower than the transverse, just as in the analogous classical vibrations of a flat plate. Mulliken,<sup>8</sup> using LCAO (linear-combination-of-atomic-orbitals) molecular orbitals, showed theoretically that the longest wave-length transition in polyenes and similar compounds must be polarized approximately along the long axis, and shorter wave-length transitions will be polarized, some along the long axis and some along a transverse axis; and he explained intensity changes in *cis-trans*-isomerism. Zechmeister<sup>9</sup> applied these ideas to the changes in spectra accompanying isomerism in carotenoids.

Jones,<sup>10</sup> in a comprehensive review, favored extending the conclusions of Lewis and co-workers to

the condensed ring systems. He showed that the first band of anthracene was probably transversely polarized, the second longitudinally. Coulson,<sup>11</sup> applying the LCAO method to the polyacenes or linear polycyclics, confirmed Jones' assignment. The longest wave-length absorption bands (26,000  $\text{cm}^{-1}$  in anthracene) are from a transition of symmetry  $A_{1g} - B_{2u}$ , polarized across the width of the molecule. Coulson assigns the second band to a transition  $A_{1g} - B_{1u}$ , polarized along the length of the molecule. His intensity predictions were not so successful. Recently, Wheland and Mann<sup>12</sup> in calculating the expected dipole moments for azulene and fulvene, have shown that results based on Coulson's simplifying assumptions are in poor agreement with the experimental dipole moments of these molecules or with the results of more refined calculations. However, dipole moments, like intensities, are more sensitive to the accuracy of the wave-functions than energy levels. We shall show below that Coulson's LCAO computations made including overlap integrals, on the height of the states of polyacenes, and other similar calculations on azulene, an isomer of naphthalene,<sup>13</sup> give quite good agreement with the height of levels determined from the spectra (Fig. 4).

Sponer<sup>14</sup> has compared the HLSP method and the molecular orbital method of calculating levels, and has made calculations for the non-linear condensed ring systems, phenanthrene, 3,4-benzophenanthrene, 1,2-benzanthracene, chrysene, pyrene, and triphenylene, similar to those of Förster<sup>15</sup> on the

<sup>1</sup> See R. N. Jones, Chem. Rev. **32**, 1 (1943) for recent review.

<sup>2</sup> E. Clar, *Aromatische Kohlenwasserstoffe* (Verlag. Julius Springer, Berlin, 1941).

<sup>3</sup> R. N. Jones, J. Am. Chem. Soc. **67**, 2127 (1945).

<sup>4</sup> G. N. Lewis and J. Bigeleisen, J. Am. Chem. Soc. **65**, 520, 2102, 2107 (1943).

<sup>5</sup> G. N. Lewis and M. Calvin, Chem. Rev. **25**, 273 (1939).

<sup>6</sup> G. Scheibe, Kolloid Zeits. **82**, 1 (1938).

<sup>7</sup> G. Scheibe, Zeits. f. angew. Chem. **42**, 631 (1939).

<sup>8</sup> R. S. Mulliken, J. Chem. Phys. **7**, 364 (1939).

<sup>9</sup> L. Zechmeister, Chem. Rev. **34**, 207 (1944).

<sup>10</sup> R. N. Jones, Chem. Rev. **41**, 353 (1947).

<sup>11</sup> C. A. Coulson, Proc. Phys. Soc. **60**, 257 (1948).

<sup>12</sup> G. W. Wheland and D. E. Mann, J. Chem. Phys. **17**, 264 (1949).

<sup>13</sup> D. E. Mann, J. R. Platt, and H. B. Klevens, J. Chem. Phys. **17**, 481 (1949).

<sup>14</sup> H. Sponer and G. Nordheim, "Theoretical Studies on the Electronic Levels of Polynuclear Hydrocarbons," ONR Contract N6ori-107, T.O.1, Annual Report, June 1, 1948.

<sup>15</sup> Th. Förster, Zeits. f. physik. Chemie **B41**, 287 (1938).

lowest electronic singlet levels of the polyacenes. Förster and Sponer both took into account only the unexcited valence-bond structures.

Daudel and Pullman<sup>16</sup> and others of their school have modified the valence-bond method to what they term the "molecular diagram" method and applied it to anthracene and naphthacene by inclusion of polyexcited structures in their calculations.

Craig<sup>17</sup> has made new calculations of the long wave-length absorption bands in aromatic molecules, similar to those of Sklar<sup>18</sup> and Förster,<sup>19</sup> and has discussed assignments and polarizations.

There has been some confusion of assignments and of interpretations by different authors, and ignorance of weak bands and of higher levels. The spectra given here and the systematic correlation of energy levels shown in Figs. 4-7 may help to clear up some of these difficulties. To describe the regularities found here, a new system of naming the levels of many aromatics is proposed. This scheme is

based on the free-electron metallic model used by Pauling,<sup>20</sup> Lonsdale,<sup>21</sup> Schmidt,<sup>22</sup> Bayliss,<sup>23</sup> Kuhn,<sup>24, 24a</sup> and others to interpret the diamagnetism and electronic spectra of various conjugated systems. It enables us to give the same names to corresponding states in different molecules. These names will be used in the present paper. Description of the properties each name connotes and justification of its assignment to a particular observed sequence of states in the different compounds will be found in the following paper (hereafter called II).<sup>25</sup>

A comparison is made in Table I of the names used in this system and those used in previous papers to describe the states and bands of individual molecules. The polarizations listed are those inferred from the free-electron model.

## II. SPECTRA

The spectra of a series of condensed ring compounds, naphthalene, anthracene, naphthacene,

TABLE I. Correspondence between names of states used by different authors.

Jones (Names of bands)		Coulson		Symmetry species		Proposed	Polarization*	
Anthracene	1,2-benzanthracene	Naphthalene	Anthracene	Benzene	Naphthalene, anthracene		Anthracene	Phenanthrene
		<i>N</i>	<i>N</i>	<sup>1</sup> A <sub>1g</sub>	<sup>1</sup> A <sub>1g</sub>	— <i>f</i> <sup>1</sup>	<sup>1</sup> A	
		<i>P</i> <sub>2</sub> <i>R</i> <sub>2</sub>	<i>Q</i> <sub>2</sub> <i>S</i> <sub>2</sub>	<i>E</i> <sub>1u</sub> {	<i>B</i> <sub>2u</sub>	— <i>f</i> <sup>2</sup> <i>g</i>	<i>B</i> <sub>a</sub>	trans. strong
<i>A</i> — <i>B</i>	<i>A</i> — <i>D</i>	<i>S</i> <sub>1</sub> <i>R</i> <sub>2</sub>	<i>R</i> <sub>2</sub> <i>S</i> <sub>2</sub>		<i>B</i> <sub>1u</sub>		<i>B</i> <sub>b</sub>	long. strong
	<i>J</i> — <i>K</i>	<i>P</i> <sub>2</sub> <i>Q</i> <sub>2</sub>	<i>Q</i> <sub>2</sub> <i>P</i> <sub>3</sub>		<i>B</i> <sub>2u</sub>		<i>L</i> <sub>b</sub>	long. trans. very weak
<i>C</i> — <i>H</i>	<i>F</i> — <i>I'</i>	<i>S</i> <sub>1</sub> <i>Q</i> <sub>2</sub>	<i>R</i> <sub>2</sub> <i>P</i> <sub>3</sub>	<i>B</i> <sub>1u</sub>	<i>B</i> <sub>2u</sub>		<i>L</i> <sub>a</sub>	trans. long. very weak
		<i>Q</i> <sub>1</sub> <i>R</i> <sub>2</sub>	<i>P</i> <sub>2</sub> <i>S</i> <sub>2</sub>			— <i>e</i> <sup>3</sup> <i>f</i> <sup>4</sup> <i>g</i>	<i>C</i> <sub>a</sub>	forb. long. strong
		<i>R</i> <sub>1</sub> <i>R</i> <sub>2</sub>	<i>S</i> <sub>1</sub> <i>S</i> <sub>2</sub>				<i>C</i> <sub>b</sub>	forb. trans. strong
		<i>Q</i> <sub>1</sub> <i>Q</i> <sub>2</sub>	<i>P</i> <sub>2</sub> <i>P</i> <sub>3</sub>		<i>A</i> <sub>1g</sub>		<i>K</i> <sub>b</sub>	forb. long. very weak
		<i>R</i> <sub>1</sub> <i>Q</i> <sub>2</sub>	<i>S</i> <sub>1</sub> <i>P</i> <sub>3</sub>		<i>B</i> <sub>3g</sub>		<i>K</i> <sub>a</sub>	forb. trans. very weak
		<i>P</i> <sub>1</sub> <i>Q</i> <sub>2</sub>	<i>Q</i> <sub>1</sub> <i>P</i> <sub>3</sub>			— <i>d</i> <sup>3</sup> <i>e</i> <sup>4</sup> <i>f</i> <sup>4</sup> <i>g</i>	<i>J</i> <sub>b</sub>	long. trans. very weak
			<i>R</i> <sub>1</sub> <i>P</i> <sub>3</sub>		<i>B</i> <sub>2u</sub>		<i>J</i> <sub>a</sub>	trans. long. very weak

\* trans: transverse is equivalent to along the short axis; long: longitudinal is equivalent to along the long axis; forb: forbidden.

<sup>16</sup> For references to this work, see: P. Daudel and R. Daudel, J. Chem. Phys. 16, 639 (1948).

<sup>17</sup> D. P. Craig, Nature 158, 235 (1946).

<sup>18</sup> A. L. Sklar, J. Chem. Phys. 5, 669 (1937).

<sup>19</sup> Th. Förster, Zeits. f. Elektrochemie 45, 548 (1939).

<sup>20</sup> L. Pauling, J. Chem. Phys. 4, 673 (1936).

<sup>21</sup> K. Lonsdale, Proc. Roy. Soc. (London) 159A, 149 (1937).

<sup>22</sup> O. Schmidt, Zeits. f. physik. Chemie 39B, 59 (1938); 42B, 83 (1939); 44B, 185, 194 (1939); 47B, 1 (1940).

<sup>23</sup> N. S. Bayliss, J. Chem. Phys. 16, 287 (1948).

<sup>24</sup> H. Kuhn, J. Chem. Phys. 16, 840 (1948); Helv. Chim. Acta 31, 1441 (1948).

<sup>24a</sup> W. Kuhn, Helv. Chim. Acta 31, 1780 (1948).

<sup>25</sup> J. R. Platt, J. Chem. Phys. 17, 484 (1949).

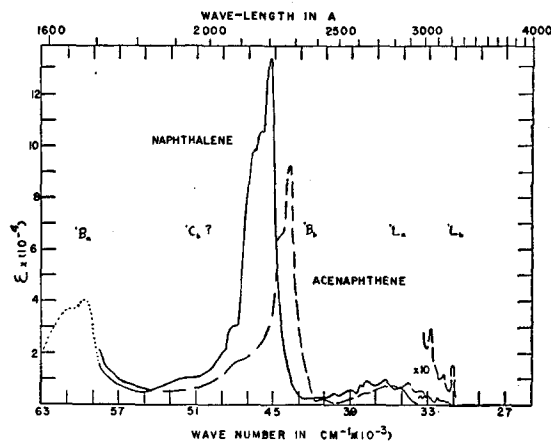


FIG. 1. Spectra of naphthalene and acenaphthene.

phenanthrene, 1,2-benzanthracene, chrysene and acenaphthene, were measured in *n*-heptane solution in an 0.13-mm lithium fluoride cell in the region 1700–2500Å. These are all cata-condensed hydrocarbons, general formula  $C_{4n+2}H_{2n+4}$ , in which no carbon atom is shared by more than two rings. The significance of this in simplifying interpretation of the spectra will be discussed in II. The spectrograph used was a Cario-Schmitt-Ott vacuum fluorite instrument on loan from the University of Michigan. The experimental techniques used were similar to those described previously.<sup>26,27</sup> All the compounds, with the exception of naphthacene, were kindly given to us by Dr. R. N. Jones and had been purified for his studies by chromatographic adsorption. The naphthalene, anthracene, and phenanthrene were the most highly purified. Possible impurities in the other compounds range up to about 1 percent. The naphthacene (tetracene) was obtained from Dr. C.

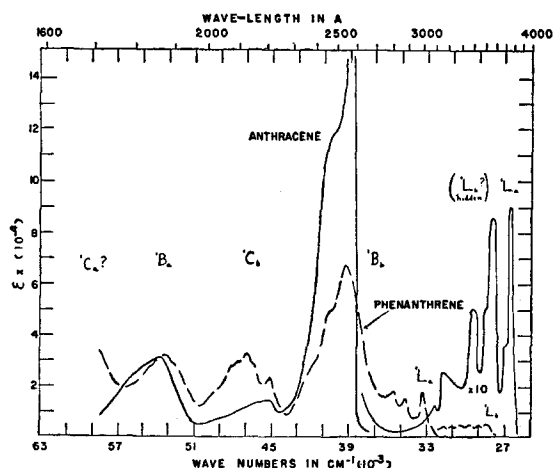


FIG. 2. Spectra of anthracene and phenanthrene.

<sup>26</sup> J. R. Platt and H. B. Klevens, Chem. Rev. 41, 301 (1947).

<sup>27</sup> H. B. Klevens and J. R. Platt, J. Am. Chem. Soc. 69, 3055 (1947).

F. H. Allen and had been purified by repeated crystallization from benzene solution in a nitrogen atmosphere. It was kept in a nitrogen atmosphere while its spectrum was being run. Naphthacene dissolved and run in the presence of air showed strong new bands, which probably represent decomposition products. The intensity measurements are believed to be accurate to our usual figure of about  $\pm 10$  percent, except for naphthacene. Its low solubility caused difficulty in weighing, and the uncertainty in its curve may be  $\pm 50$  percent.

The spectra are shown in Figs. 1–3 and some main features, such as location of main bands and components,  $\epsilon_{\max}$ , and oscillator strength,  $f$ , are summarized in Table II. The curves at longer wavelengths have been taken from various sources. In all cases, the curves in the overlap region, 2250–2500Å, were in agreement within experimental accuracy. The naphthalene and anthracene long wave spectra are from Mayneord and Roe;<sup>28</sup> phenanthrene, 1,2-benzanthracene, chrysene, and acenaphthene from Jones.<sup>10,29</sup> The 3,4-benzanthracene data in Figs. 4–6 are from Mayneord and Roe;<sup>30</sup> triphenylene and the 5-ring data from Clar;<sup>2</sup> and the phosphorescent triplet levels are from Kasha.<sup>31</sup> The curve of naphthalene above 58,000  $\text{cm}^{-1}$  is from visual estimates on an unpublished vapor spectrum plate taken by Dr. W. C. Price in this laboratory. The azulene data (Fig. 4) are from Mann, Platt, and Klevens.<sup>13</sup>

In Figs. 4–6, the excited electronic energy levels from these cata-condensed ring spectra are plotted for comparison with each other. The vibrational structure has been omitted for clearness.

### Naphthalene-Acenaphthene

Acenaphthene is essentially a disubstituted naphthalene and has a spectrum similar to naphthalene (Fig. 1) except for about 1800  $\text{cm}^{-1}$  red shift. The  ${}^1C_b$  transition seems to be weaker or has shifted its relative position in the acenaphthene. [Since the ground state is always the same, we may designate a band after its upper state alone.] If this peak in naphthalene is the forbidden transition it is assumed to be in II, it should be somewhat more allowed in acenaphthene, though the effect of alkyl substitution on forbidden band intensities is often surprisingly small, as the benzene 2600Å bands have shown.

### Anthracene-Phenanthrene

The spectrum of anthracene in Fig. 2 looks much like the spectrum of naphthalene except for a red

<sup>28</sup> W. V. Mayneord and E. M. F. Roe, Proc. Roy. Soc. (London) 152A, 299 (1935).

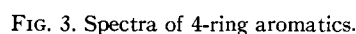
<sup>29</sup> R. N. Jones, J. Am. Chem. Soc. 67, 2127 (1945).

<sup>30</sup> W. V. Mayneord and E. M. F. Roe, Proc. Roy. Soc. (London) 158A, 634 (1937).

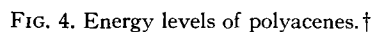
<sup>31</sup> M. Kasha, Chem. Rev. 41, 401 (1947).

The  $^3L_a$  state also moves upward 7000  $\text{cm}^{-1}$  in phenanthrene. This motion parallels that of  $^1L_a$  but not of  $^1L_b$  and is a major reason for believing the phosphorescent state is of  $L_a$  type. The singlet-triplet separation should be roughly constant with changing molecular size or at least should vary in a regular way. From Fig. 4 it is seen that the phosphorescent state is 19,000  $\text{cm}^{-1}$  below  $^1L_a$  in benzene, 14,000  $\text{cm}^{-1}$  in naphthalene, and 12,000  $\text{cm}^{-1}$  in the longer systems. It has no such regular relation to  $^1L_b$ ; so again must be  $^3L_a$ . The symmetry species of

<sup>31a</sup> W. C. Price, Chem. Rev. 41, 257 (1947).



Kasha<sup>31</sup> tabulated the fluorescent-phosphorescent level separation in many compounds, and found strange variations in this separation, which he expected to be the singlet-triplet interval and therefore roughly constant. The explanation of his variations is seen in Fig. 4. The fluorescent level is the lowest singlet; but it is sometimes  $^1L_a$ , the same type as the triplet, as in anthracene; and other times it is  $^1L_b$ , as in phenanthrene, and gives an abnormally small fluorescent phosphorescent interval.\*



\* After the text of the present paper was prepared, M. Kasha and R. V. Nauman kindly let us see a prepublication copy of their manuscript "The Metastability of the Lowest

TABLE II. Main features of spectra of *cata*-condensed hydrocarbons.

	${}^1A \rightarrow {}^1L_b$	${}^1A \rightarrow {}^1L_a$	${}^1A \rightarrow {}^1B_b$	${}^1A \rightarrow {}^1C_b$	${}^1A \rightarrow {}^1B_a$	${}^1A \rightarrow {}^1C_a$	Total <i>f</i> -value
<i>Benzene</i>							
onset of absorption $\text{cm}^{-1}$	38000	48050					
peak			54500				
$\epsilon_{\text{max}}$	220	6900	4600				
<i>f</i> (to cut-off)	0.002 (45300)	0.10 (51200)	0.69 (59000)				0.79
<i>Naphthalene</i>							
onset of absorption $\text{cm}^{-1}$	32000	34600					
peak			45400	52500?	$\sim 59800$		
$\epsilon_{\text{max}}$	280	9300	133000	10000	$\sim 30000$		
<i>f</i> (to cut-off)	0.002 (34000)	0.18? (42500)	1.70 (49500)	0.20 (55000)	$\sim 0.6?$ (63000)		$\sim 2.8$
<i>Acenaphthene</i>							
onset of absorption $\text{cm}^{-1}$	29800	33100			52700		
peak			43800				
$\epsilon_{\text{max}}$	2800	7100	93000		$\sim 35000$		
<i>f</i> (to cut-off)	0.012 (33100)	0.14 (41500)	1.08 (52700)		0.28 (59500)		1.51
<i>Anthracene</i>							
onset of absorption $\text{cm}^{-1}$		26400					
peak			39000	45300	53700		
$\epsilon_{\text{max}}$		9000	180000	14500	32000		
<i>f</i> (to cut-off)		0.10 (35000)	2.28 (44400)	0.28 (50800)	0.65 (59300)		3.31
<i>Naphthacene</i>						unknown transition 55500	
onset of absorption $\text{cm}^{-1}$		21100		43500			
peak			36700		47400	53400	
$\epsilon_{\text{max}}$		12500	180000	17000	44000	16000	40000
(to cut-off)		0.08 (29200)	1.85 (43000)	0.28 (46000)	0.45 (50500)	0.27 (54800)	0.68 (59500)
							3.53

### Four-Ring Systems

The strong bands in the spectra of naphthacene, chrysene, and 1,2-benzanthracene in Fig. 3 are shifted to the red from anthracene by 2000–4000  $\text{cm}^{-1}$ , the largest shifts being for the straight molecule, naphthacene. The  ${}^1L_b$  transition is again masked by  ${}^1L_a$  in the linear, but revealed in the bent, molecules. Generally,  ${}^1L_a$  moves upward with increased number of bends. Thus in 1,2-benzanthra-

cene it is shifted 8500  $\text{cm}^{-1}$  to the blue, in 3,4-benzphenanthrene 9500  $\text{cm}^{-1}$ , in chrysene 10,500  $\text{cm}^{-1}$  and in triphenylene 14,000  $\text{cm}^{-1}$  from its position in naphthacene.

### Behavior of Bands

We may comment on some general trends observed with particular types of bands in moving from compound to compound.

#### ${}^1L_b$

The  ${}^1L_b$  state moves the slowest with increasing chain length. It is little affected in position or intensity by rearrangements and substitutions within any family of compounds of the same number of  $\pi$ -electrons. The stability of location of this band in benzene with various substitutions has been repeatedly remarked in the literature. The greatest

Excited Singlet Level of Naphthalene," in which they prove Sponer's suggestion (see reference 14), which we have used here, that the long wave absorption of naphthalene consists of two electronic transitions. It is especially interesting that they report that the fluorescent state has similar properties—a long lifetime, near  $10^{-6}$  second, and a motion upwards in low temperature rigid glass systems—in naphthalene, phenanthrene, and chrysene, where we have called the lowest singlet state  ${}^1L_b$ ; but that it has opposite properties—a short lifetime and a motion downwards in the glass—in anthracene, where this state is  ${}^1L_a$ .

TABLE II.—Continued.

	${}^1A \rightarrow {}^1L_b$	${}^1A \rightarrow {}^1L_a$	${}^1A \rightarrow {}^1B_b$	${}^1A \rightarrow {}^1C_b$	${}^1A \rightarrow {}^1B_a$	${}^1A \rightarrow {}^1C_a$	Total f-value
<i>Pentacene</i>							
onset of absorption $\text{cm}^{-1}$		17100					
peak	24000		32300				
$\epsilon_{\text{max}}$	600	12000	300000				
$f$ (to cut-off)		0.08 (23600)	2.2 (40000)				2.28
<i>Phenanthrene</i>							
onset of absorption $\text{cm}^{-1}$	28300	33000				56400	
peak			39400	47100	53400		
$\epsilon_{\text{max}}$	350	16000	65500	33000	31000		
$f$ (to cut-off)	0.003 (32300)	0.18 (36300)	1.09 (44000)	0.60 (50800)	0.59 (56400)	0.29 (59500)	2.75
<i>Chrysene</i>							
onset of absorption $\text{cm}^{-1}$	27500	30200					
peak			37200	45600	51300	54300	
$\epsilon_{\text{max}}$	650	16000	150000	34500	18500	50000	
$f$ (to cut-off)	0.005 (29500)	0.36 (36700)	1.29 (41300)	0.69 (49300)	0.22 (52600)	0.76 (61000)	3.32
<i>1,2-benzanthracene</i>							
onset of absorption $\text{cm}^{-1}$	25800	27300					
peak			34800	45100	49300	54900	
$\epsilon_{\text{max}}$	1000	8500	113000	33000	21000	23000	
$f$ (to cut-off)	0.003 (27000)	0.13 (33600)	1.67 (42200)	0.53 (47300)	0.42 (52600)	0.54 (61000)	3.29
<i>3,4-benzphenanthrene</i>							
onset of absorption $\text{cm}^{-1}$	26700	30300					
peak			35600	45600			
$\epsilon_{\text{max}}$	400	12000	85000	55000			
$f$ (to cut-off)	0.0056 (28900)	0.12 (34000)	1.57 (42000)	1.38 (51000)			3.08
<i>Triphenylene</i>							
onset of absorption $\text{cm}^{-1}$	29200	33200					
peak			38900				
$\epsilon_{\text{max}}$	900	20000	150000				
$f$ (to cut-off)	0.012 (32300)	0.22 (36500)	2.26 (45000)				2.49

shift of  ${}^1L_b$  in the levels of Figs. 4 to 6 is a red shift of 17,000  $\text{cm}^{-1}$  found in going from the normal ring system naphthalene to its abnormal isomer, azulene, which has one 5-carbon and one 7-carbon ring; the shift accounts for the blue color of azulene. But azulene is quite a special case.

The arguments in II indicate a polarization for  ${}^1L_b$  longitudinal in the polyacenes, but parallel to the symmetry axis in phenanthrene.

#### ${}^1L_a$

This band moves to the red the fastest with increasing length, and its interval from  ${}^1B_b$  increases

at the same time. The interval decreases by more than 50 percent for the first bend in the molecule, but changes little with further bending.

Jones<sup>10</sup> showed that the intensity of the  ${}^1L_a$  band in polyacenes was increased by substitutions which increased the molecular width, and concluded that this band must be transversely polarized. This is supported by Coulson's calculations<sup>11</sup> and by the arguments of II. In phenanthrene it should be polarized perpendicular to the symmetry axis.

Since the position of the  ${}^1L_a$  band is sensitive to bending of the molecule, and since the strong carcinogens are bent, we examined whether the  ${}^1L_a$

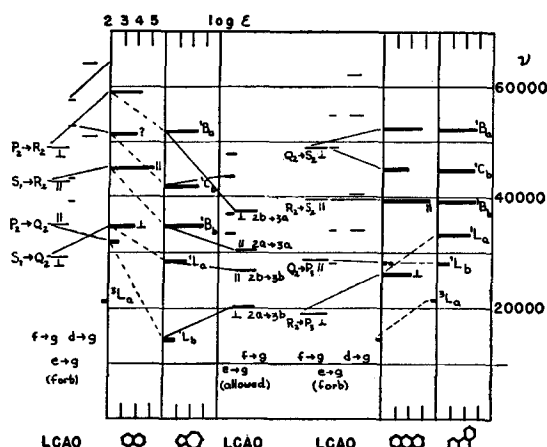


FIG. 5. Energy levels of naphthalene and azulene, anthracene and phenanthrene, with LCAO-predictions of centers-of-gravity of singlets and triplets.<sup>†</sup>

position was better correlated with carcinogenic potency of alkyl-substituted 1,2-benzanthracenes than the position of the  ${}^1B_b$  band used by Jones for such a correlation.<sup>32</sup> We found that the wave-length of the peak  ${}^1L_a$  vibration, which is given by Jones, does change nearly twice as fast with potency as the wave-length of the  ${}^1B_b$  peak. But the exceptions to his correlation which Jones found remain exceptions to the  ${}^1L_a$  correlation. They still remain exceptions when differences between the two bands are used for the correlation. The location of particular peaks of  ${}^1L_a$ , including the first, is not so unambiguous as the location of  ${}^1B_b$ .

### ${}^1B_b$

The  ${}^1B_b$  band increases in intensity almost linearly with increase in length, like the corre-

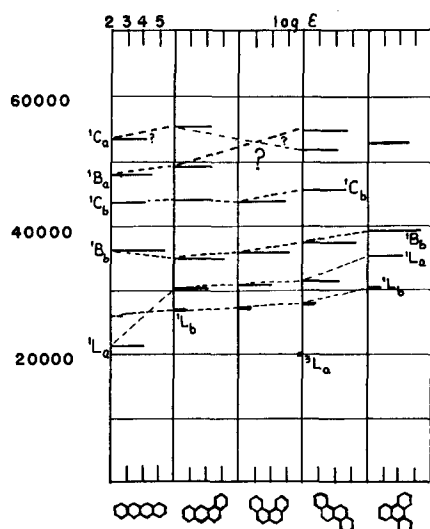


FIG. 6. Energy levels of 4-ring aromatics.<sup>†</sup>

<sup>32</sup> R. N. Jones, J. Am. Chem. Soc. 62, 148 (1940).

sponding strong transition in the polyenes. This band must then be longitudinally polarized. Jones' work<sup>10</sup> confirms this. Coulson concluded this was the lowest longitudinal transition in anthracene and applied his calculations to it; but as we have seen above, the hidden  ${}^1L_b$  band, if it is longitudinally polarized in polyacenes, as we suppose, must be the lowest of this type; and  ${}^1B_b$  must be the second longitudinal band.

### ${}^1C_b$

The  ${}^1C_b$  band which appears weakly in the polyacenes may be forbidden in them, according to II. It always increases in strength with destruction of central symmetry of the conjugated system. However, according to this argument, one would expect it to be stronger than it seems to be in acenaphthene, and weaker than it appears in chrysene, which is centrally symmetric again. Some of the discrepancy might be due to experimental error; or possibly the  ${}^1C_b$  band has shifted in acenaphthene, or it may be misidentified in chrysene.

### ${}^1B_a$

The  ${}^1B_a$  band has almost constant intensity in polyacenes, and is taken to be due to an allowed transition polarized transverse to the long axis of the molecule. The intensity increases in some bent systems, presumably because the molecule is wider and the effective transverse dipole length has increased.

The  ${}^1B_a$  and  ${}^1B_b$  states should form a degenerate pair in benzene if they have the properties postulated in II and if they have been correctly identified in the spectra. Only one band is observed. The same should be true in any molecule with  $D_{3h}$  symmetry or higher. Triphenylene is such a molecule. A band has been observed in its spectrum at about 1900Å<sup>33</sup> but this may be a  ${}^1C$  band.

## III. INDIVIDUALITY OF LEVELS

The preceding discussion has imputed distinct properties to levels of a given type, which they retain from compound to compound and which make possible unambiguous identification according to type. That states in compounds so diverse as benzene and benzantracene should have so much in common seems to be a novel idea. To date, theory has offered no prediction of such a result, and indeed has sometimes denied the likelihood of it. We should therefore state this doctrine of types explicitly and summarize the evidence for it.

1. *Levels of a given type have unambiguous identifying characteristics*, which do not change from compound to compound. The most useful characteristics

<sup>33</sup> H. Mohler and J. Sorge, Helv. Chim. Acta 22, 229 (1939).



are intensity and vibrational sharpness of the transition from the ground state to the level in question.

The intensities of the  ${}^1L_b$ ,  ${}^1L_a$ , and  ${}^1B_b$  bands are shown in Fig. 8 for all the cata-condensed systems of four rings or less. There is no mixing or confusion of properties. The  ${}^1B_b$  bands vary in oscillator strength by a factor of two; but they are separated by a factor of ten from the  ${}^1L_a$  oscillator strengths. In these compounds and among the longer wave-length bands there are no bands with oscillator strengths between these two groups. Similarly the  ${}^1L_a$  bands vary in strength by a factor of four; but are two orders of magnitude stronger than  ${}^1L_b$ , and there are no bands of intermediate strength. The  ${}^1L_b$  strengths vary over a factor of ten, but there is no ambiguity as to type. The variability of intensities, increasing with increasing molecular size, shows that these rules are only first approximations; with seven- or eight-ring systems, the ranges of variability will begin to overlap as shown by the trends in Fig. 8, and doubtful assignments may occur. As might be expected, the variability produced by mixing affects the relative intensity of the weak bands more than that of the strong ones.

The case is the same with vibrational structure.

The  ${}^1L_b$  bands have sharp vibrational structure, with individual vibrational peaks about  $300\text{ cm}^{-1}$  in half-width. There are 5 or 6 visible peaks when not overlapped, the strongest one commonly the first or third.

The  ${}^1L_a$  bands have more diffuse vibrational structure, with peaks about  $500\text{ cm}^{-1}$  in half-width, but still with distinct maxima and minima. There are usually 5 or 6 visible peaks, the first, second or third the strongest. It is most remarkable that these same  ${}^1L_b$ ,  ${}^1L_a$  distinctions are found in benzene<sup>26</sup> whose high symmetry is usually supposed to make it a special case.

The  ${}^1B_b$  band is the strongest in each spectrum. The vibrational structure is still more diffuse so that often no clear minima can be seen, but only step-outs. After naphthalene, the first peak is narrow and much the strongest, and only two or three others can be seen.

The second strongest band is  ${}^1B_a$ . It is broad and almost symmetrical and shows little structure.

These rules become less accurate for the larger and more unsymmetrical systems.

2. Levels of a given type move in a systematic way from compound to compound. Except for the  ${}^1L_a$ — ${}^1L_b$  crossover near anthracene, and the  ${}^1C_b$ — ${}^1B_a$  crossover which seems to occur near pentacene, the levels preserve their sequence in each compound. They all lie on smooth curves as a function of length, except for  ${}^1L_a$  in bent systems. They generally lie near the same energy in isomers. Except for  ${}^1L_a$  and except for the special case of azulene, levels of a

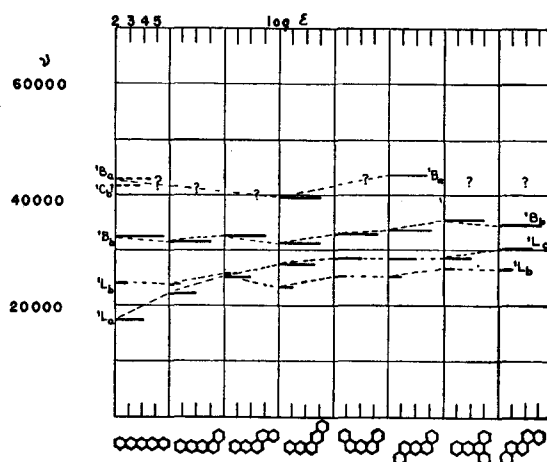


FIG. 7. Energy levels of 5-ring aromatics.†

given type in isomers all lie in a region only about  $4000\text{ cm}^{-1}$  wide.

The  ${}^1L_a$  position is variable, but in a regular way. It moves upward with increased bending of the molecule. The  ${}^1L_a$ — ${}^3L_a$  separation changes smoothly with length, and is not changed in bent isomers even when both levels move far.

3. (a) Each type, as determined from appearance and intensity alone, occurs once and only once in each compound.

(b) The number of lower levels remains constant from compound to compound up to any particular upper level to which the spectra have been carried. There are a few reasonable exceptions, where degeneracies occur, or where a weak band is expected to be overlapped by a stronger and its upper state cannot be located accurately.

These rules should pretty well remove fears which have been expressed in the past that these spectra

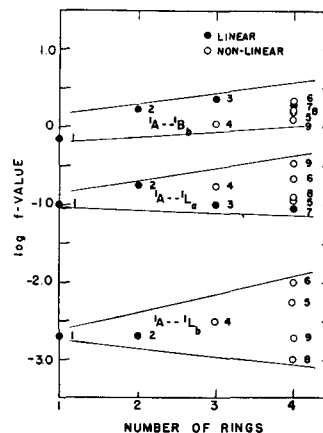


FIG. 8. Constancy of intensities in different band types.

Compounds:

1. benzene
2. naphthalene
3. anthracene
4. phenanthrene
5. 3,4-benzphenanthrene
6. triphenylene
7. naphthacene
8. 1,2-benzanthracene
9. chrysene

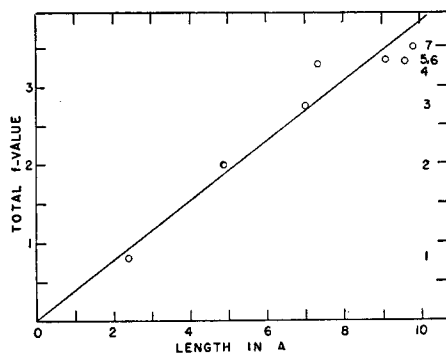


FIG. 9. Integrated intensity to 1700Å as function of molecular length.

Compounds:

- |                 |                       |
|-----------------|-----------------------|
| 1. benzene      | 4. anthracene         |
| 2. naphthalene  | 5. chrysene           |
| 3. phenanthrene | 6. 1,2-benzanthracene |
|                 | 7. tetracene          |

might never be understood because of their complexity, the breadth of the peaks and bands, and the numerous weak transitions which might be hidden by stronger transitions and never located. When the vibrational structure is ignored, only 4 to 6 electronic bands are found, as far as the spectra have been carried. Though they are broad, they are usually well separated. The three or four other singlet bands which might lie in this region are expected to be weak and therefore hidden, but their positions can be estimated from LCAO theory as seen below.

#### IV. OTHER REGULARITIES

Some other regularities discovered in the data are shown in Figs. 9 and 10 and in Table III. Figure 9 shows that the total oscillator strength,  $f$ , summed over all the bands up to the highest limits so far reached, is closely proportional to the greatest length of the conjugated system. Reasons are given

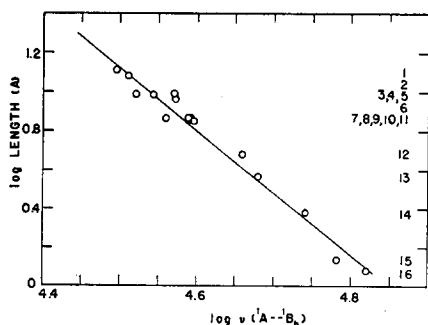


FIG. 10. Location of  ${}^1B_b$  bands in chains, ring-chains and condensed rings as a function of greatest molecular length.

Compounds:

- |                       |                  |
|-----------------------|------------------|
| 1. decapentaene       | 9. hexatriene    |
| 2. pentacene          | 10. phenanthrene |
| 3. octatetraene       | 11. triphenylene |
| 4. 1,2-benzanthracene | 12. naphthalene  |
| 5. tetracene          | 13. butadiene    |
| 6. chrysene           | 14. benzene      |
| 7. 3,4-benzanthracene | 15. ethylene     |
| 8. anthracene         | 16. acetylene    |

in II for believing that very little additional oscillator strength in  $\pi$ -electron transitions will lie at shorter wave-lengths. The molecular lengths were determined from scale drawings, using hexagonal rings, with 1.40Å as the C—C distance. Some shorter "effective length" would be more suitable for the comparison, but it would not be so simple to determine its proper value in bent systems.

That total  $f$  is proportional to length in these compounds is not greatly different from saying that it is proportional to number of rings, or, what is the same thing, proportional to number of  $\pi$ -electrons. The mean contribution to  $f$  per  $\pi$ -electron is tabulated in Table III. It is seen to be nearly constant, between 0.19 and 0.23, for two-, three-, and four-ring systems. The benzene value is low. In polyene chains, the  $f$ -value per unit length is about  $\frac{1}{4}$  that in condensed rings. The  $f$ -value per  $\pi$ -electron is between 0.11 and 0.14, which is about  $\frac{1}{2}$  of its value in rings. The value for ethylene is higher, but is uncertain by  $\pm 50$  percent. Systems containing both rings and chains seem to have intermediate values of the contribution per  $\pi$ -electron, in proportion to the relative lengths of the chain and ring sections. The data in Table III is obtained in part from spectra reported here and from some unpublished data<sup>34</sup> except for the symmetric cyanine data which has been calculated from spectra reported by Brooker.<sup>35</sup> The spectra of the chains and ring-chains need to be extended to shorter wave-lengths before making a final comparison of the intensity contributions per  $\pi$ -electron.

The linear relation between the height and  $f$ -value of the first strong peak,  $N-V_1$  (in our notation,  ${}^1A-{}^1B_b$ ), in polyenes and the molecular length was found by Hausser, Smakula and co-workers,<sup>36-38</sup> and is in agreement with theoretical calculations of Mulliken.<sup>39,40</sup> Coulson<sup>11</sup> expected the longitudinal transitions in polyacenes, our  ${}^1A-{}^1L_b$  and  ${}^1A-{}^1B_b$ , to have intensities proportional to the length. This result is approximately confirmed experimentally for  ${}^1A-{}^1B_b$ . Since these strong transitions in the straight polyenes and polyacenes have most of the oscillator strength, the total strength summed over all bands will also vary in much the same way with length. This result should then apply also to bent systems, for the strength which the strongest transition loses in these cases is gained by others, so that the total remains about constant. Actually, the total  $f$ -value is more accurately linear with length than

<sup>34</sup> Unpublished work of the authors.

<sup>35</sup> L. G. Brooker, Rev. Mod. Phys. **14**, 275 (1942).

<sup>36</sup> K. W. Hausser, Zeits. f. tech. Physik **15**, 10 (1934).

<sup>37</sup> A. Smakula, Zeits. f. angew. Chemie **47**, 657 (1934).

<sup>38</sup> K. W. Hausser, R. Kuhn and others, Zeits. f. physik. Chemie **29B**, 364 (1935).

<sup>39</sup> R. S. Mulliken, J. Chem. Phys. **7**, 364, 570 (1939).

<sup>40</sup> R. S. Mulliken and C. A. Rieke, Rep. Prog. Phys. **8**, 231 (1941).

the  $f$ -value of the  ${}^1A - {}^1B_u$  transition alone even for the straight polyacenes. The longitudinal  ${}^1A - {}^1L_u$  transition intensity seems to show no special dependence on length, but in the longer molecules our observation of it is restricted to bent systems, where interaction may alter intensities in an irregular way.

Figure 10 shows the dependence of the frequency of the first strong allowed longitudinal transition,  ${}^1A - {}^1B_u$ , on the greatest length of the conjugated system. Both polyenes and ring systems are included. The frequency is seen to vary approximately as the inverse 0.3 power of the length. The correspondence principle would indicate that this frequency should be a function of the length alone, but varying as the inverse first power, as in a macroscopic dipole antenna. The LCAO molecular orbital theory of polyenes also predicts too fast a variation,<sup>39</sup> as do the free-electron theories.<sup>23, 25</sup> Kuhn<sup>24</sup> has suggested that introduction of a suitable periodic potential in the latter theories will improve the agreement. It would be extremely interesting to have spectra of "metallic" molecules in the little known range of lengths between 50Å and a few microns, to see whether this kind of transition goes over asymptotically into the classical dipole frequency, and if so, what the law of dependence of frequency on length will be in this range.

#### V. NEW ASSIGNMENTS: COMPARISON WITH LCAO THEORY

For polyacenes, Coulson<sup>11</sup> computed the location of the centers of gravity of the lowest transverse singlet and triplet, which he called  $N - V_1$ , and of the lowest longitudinal pair, which he called  $N - V_2$ . (A comparison of Coulson's notation with that used here is given in Table I.) He included overlap integrals in his LCAO computations. Since our lowest longitudinal assignment, which we call  ${}^1A - {}^1L_u$ , differs from his, which would be our  ${}^1A - {}^1B_u$ , a new comparison between observation and prediction needs to be made. The results are shown in Fig. 11, and in Table IV. The  $(N - V_2)/(N - V_1)$  energy ratio agrees with the computed ratio within 7 percent, where on Coulson's assignment, which involved unjustified assumptions about the location of the triplet states, the agreement was within 15 percent. The change of the  $N - V_1$  band with length also agrees better with his calculation, by the present assignment.

The computed and observed centers of gravity of these two pairs of states are shown in Fig. 11, under the assumption that the factor  $\beta$ , the LCAO bond integral (Coulson's  $\gamma$ ), is 23,000  $\text{cm}^{-1}$ . Actually, since his prediction of the ratios of the centers is better than the absolute prediction with constant  $\beta$ , we can use the observed centers to determine the best value of  $\beta$ , or  $\beta_{\text{spect.}}$ , for each molecule. The results are in the sixth column of Table IV;  $\beta$  increases

TABLE III.<sup>a</sup>

Compound	Number of $\pi$ electrons	Total $f$	$f$ / $\pi$ electrons
C=C	2	.30	.15
C=C—C=C	4	.55	.14
C=C—C=C—C=C	6	( $\sim 0.7$ )	.11
C=C—C=C—C=C—C=C	8	( $\sim 0.9$ )	.11
Vitamin A	10	1.05+	.11
Carotene	22	2.5–2.7	.12
Fulvene	6	( $\sim 1.2$ )	.20
Benzene	6	0.79	.13
Styrene	8	( $\sim 1.7$ )	.21
Naphthalene	10	2.1–2.8	.22
Diphenyl	12	2.36+	.20
Anthracene	14	3.3	.23
Phenanthrene	14	2.8	.20
Tetracene	18	3.5	.20
1,2-Benzanthracene	18	3.3	.19
Chrysene	18	3.3	.19
Symmetric cyanine	6	1.2*	.20
Symmetric cyanine	8	1.2*	.15
Symmetric cyanine	10	1.6*	.16
Symmetric cyanine	12	1.9*	.15

<sup>a</sup> These data will be discussed and correlated with physical properties in a forthcoming publication.

\* Calculated from experimental data of Brooker (see reference 35).

regularly from benzene to pentacene. With this increasing  $\beta$ , i.e., with essentially two empirically determined parameters, the nine centers can be predicted with a maximum deviation of less than 1000  $\text{cm}^{-1}$  which is little larger than the variation of band locations from one solvent to another.

Similar computations on azulene<sup>13</sup> give about as good results. The  $\beta_{\text{spect.}}$  must now be decreased about 20 percent from its value in naphthalene. The polarizations of the low states must be interchanged, in order to agree with the computed energies. This result is also predicted by the free-electron model.

For the upper states in these molecules the triplets are not known and the center-of-gravity calculations must be compared with the singlets, as shown in Fig. 5. They fit these about as well as they fit the low singlets. The centers are below the singlets, as they should be if the triplets are low; and the deviations for each type of state are about equal and in the same direction for all the compounds, including azulene. The  ${}^1C_u$  transition has been tentatively

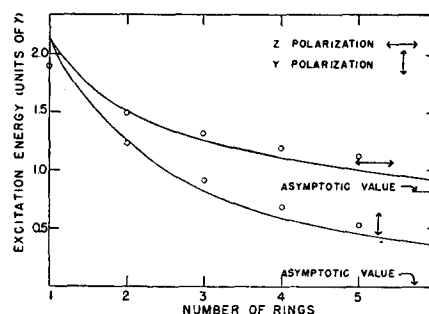


FIG. 11. Observed and predicted centers of gravity of lowest transverse and lowest longitudinal singlet-triplet pairs in polyacenes.  $\beta = 23,000 \text{ cm}^{-1}$ .

TABLE IV. Computed and observed energies for lowest states.

Type		In $\beta$ units	Computed With $\beta = 23,000$	With best $\beta$	Best $\beta_{\text{spect.}}$	Observed (solution)	
			Benzene			States	c. of grav.
Trans. } Long. }	${}^1A_{1g} - {}^1E_{1u}$	2.13 <sup>c</sup>	49,000	(43,000)	20,200	$\begin{cases} {}^1L_a & 48,000^a \\ {}^3L_a & 29,300^d \\ {}^1L_b & 38,200 \\ {}^3L_b & 43,800_{\text{est.}}^b \\ {}^1B & 53,000^a \\ {}^3B & 39,500_{\text{est.}}^b \end{cases}$	43,000 <sup>b</sup>
			Naphthalene				
Trans.	$N \rightarrow V_1$	1.267	29,000	28,200		$\begin{cases} {}^1L_a & 35,000 \\ {}^3L_a & 21,300^d \\ {}^1L_b & 32,200 \\ {}^3L_b & (36,200)_{\text{est.}}^b \end{cases}$	28,200
Long.	$N \rightarrow V_2$	1.532	35,000	34,200	22,300		34,200
			Anthracene				
Trans.	$N \rightarrow V_1$	0.836	19,000	20,200		$\begin{cases} {}^1L_a & 26,700 \\ {}^3L_a & 14,700^d \\ {}^1L_b & (28,000)_{\text{est.}}^b \\ {}^3L_b & (32,000)_{\text{est.}}^b \end{cases}$	20,700
Long.	$N \rightarrow V_2$	1.261	29,000	30,500	24,100		30,000
			Naphthacene				
Trans.	$N \rightarrow V_1$	0.600 <sup>c</sup>	14,000	14,900		$\begin{cases} {}^1L_a & 21,000 \\ {}^3L_a & (10,000)_{\text{est.}}^d \\ {}^1L_b & (25,500)_{\text{est.}}^b \\ {}^3L_b & (29,500)_{\text{est.}}^b \end{cases}$	15,500
Long.	$N \rightarrow V_2$	1.135 <sup>c</sup>	26,000	28,200	24,800		27,500
			Pentacene				
Trans.	$N \rightarrow V_1$	0.443 <sup>c</sup>	10,000	11,400		$\begin{cases} {}^1L_a & 17,300 \\ {}^3L_a & 6,300_{\text{est.}}^d \\ {}^1L_b & 24,000 \\ {}^3L_b & (28,000)_{\text{est.}}^b \end{cases}$	11,800
Long.	$N \rightarrow V_2$	1.035 <sup>c</sup>	24,000	26,600	25,700		26,000
			Azulene				
Trans.	$2a-3b$	0.871 <sup>f</sup>	20,000	16,100		$\begin{cases} {}^1L_b & 14,400 \\ {}^3L_b & (18,400)_{\text{est.}}^e \\ {}^1L_a & 28,300 \\ {}^3L_a & (14,600)_{\text{est.}}^e \end{cases}$	16,400
Long.	$2b-3b$	1.171 <sup>f</sup>	27,000	21,700	18,500		21,500

<sup>a</sup> Reference 26.<sup>b</sup> C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948), estimated the triplet states and the center of gravity in benzene. They estimated  ${}^1L_b$  was about 5000 cm<sup>-1</sup> above  ${}^1L_a$  in benzene. We take this interval as decreasing to about 4000 cm<sup>-1</sup> in longer molecules, since the  ${}^3L_a - {}^1L_a$  separation decreases from 19,000 to about 13,000 cm<sup>-1</sup>. We have reduced their center of gravity 1500 cm<sup>-1</sup> to correspond to solution measurements.<sup>c</sup> Estimated from Coulson's Fig. 4 and tables.<sup>d</sup> Reference 31; naphthacene and pentacene  ${}^3L_a - {}^1L_a$  separation assumed about 11,000 cm<sup>-1</sup>.<sup>e</sup> Assuming singlet-triplet separations in azulene the same as in naphthalene.<sup>f</sup> Reference 13.

identified as the third forbidden transition of LCAO theory and the good agreement between calculated and observed positions for it is also shown in Fig. 5.

Coulson also made intensity predictions on the two lowest bands. His comparison of theory and experiment for the transverse band is not altered by the present assignments; but his intensity predictions for the longitudinal band are several hundred times larger than those observed in  ${}^1A - {}^1L_b$ . This would suffice to throw serious doubt on the new assignments, except that electron interaction has been neglected in his treatment. Such a treatment of benzene would lead to a fourfold degenerate strongly allowed transition for the lowest frequency band. It is electron interaction which partially removes the degeneracy and makes the two lowest of the resulting bands forbidden. In view of the strong resemblances found in the present paper between

the longest-wave-length bands in benzene and the polyacenes, perhaps the same sort of thing will happen in the latter when electron interaction is introduced. The free-electron model leads to a simple treatment of this interaction and predicts this general weakness for the low frequency bands.

This work was assisted by the Office of Naval Research Contract N6ori-20, T.O. IX, with the University of Chicago. We are very grateful to Dorothy Iker Lossy and to Howard Carter for assistance in the determination of these spectra.

*Note added in proof:*—Recently, the free-electron model has been applied by W. T. Simpson [J. Chem. Phys. 16, 1124 (1948)] to polyenes and to benzene, following unpublished results of K. S. Pitzer. Also the model has now been used by F. O. Rice and E. Teller in their book *The Structure of Matter* [(John Wiley & Sons, Inc., New York, 1949), pp. 107–11] to give a qualitative description of the ground

states of condensed-ring systems like that given here and in II. Kuhn's paper (reference 24) is announced as the first of a series applying the model to polyenes, cyanine dyes, and porphyrin bodies.

Additional triplet ( $^3L_a$  ?) states have now been located in some of the compounds of Figs. 1-7 by D. M. McClure [Ph.D. thesis, University of California, 1948; (also J. Chem. Phys., in press)] acenaphthene, 20,800  $\text{cm}^{-1}$ ; triphenylene, 23,800  $\text{cm}^{-1}$ ; 1,2-benzanthracene, 16,500  $\text{cm}^{-1}$ ; dibenzanthracene, 18,300  $\text{cm}^{-1}$ . These new states have the usual 14,000-11,000  $\text{cm}^{-1}$  separation from the  $^1L_a$  states in these compounds as expected from the regularities found above.

Some of the 1,2-benzanthracene levels of Fig. 6 are in error. The two high states should have been omitted and the  $^1L_a$  state should be lowered about 2000  $\text{cm}^{-1}$ .

M. Kasha has called my attention to a calculation of the lowest excited levels of the naphthalene molecule by A. S. Davydov [J. Exper. Theor. Phys. (U.S.S.R.) 17, 1106 (1947), translated by M. Kasha, Department of Chemistry, University of California]. The results appear to be identical with Coulson's LCAO results on naphthalene, though the identification with the observed bands is slightly different, and the triplets have been ignored in making the comparison with experiment.

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## Spectral Resemblances in Azulene and Naphthalene

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The spectrum of the odd-ring compound azulene,  $\text{C}_{10}\text{H}_8$ , from 1730Å to 7000Å, is compared with that of its regular isomer naphthalene from 1600Å to 3500Å. The 5 band systems found in azulene seem to correspond, with respect to vibrational structure, intensity, and sequence to the 5 found in naphthalene, except that the former are all shifted to lower frequencies. The lowest band is shifted the most, about 17,000  $\text{cm}^{-1}$ , and its absorption gives azulene its blue color. This band has quite different properties from those of the lowest band in the blue compound pentacene. The observed energy levels are compared with LCAO predictions of the lowest states in naphthalene (Coulson) and azulene. The qualitative agreement is good.

THE purpose of this note is to present some new data for the spectrum of azulene, and to draw attention to some resemblances between this spectrum and the spectra of naphthalene and other polyacenes. The spectrum of azulene from 2200 to 3700Å was reported by Heilbronner and Wieland.<sup>1</sup> The visible spectrum has been reported several times by Plattner and his co-workers.<sup>2-4</sup> In this note the complete spectrum of azulene from 1730 to 7000Å (58,000 to 14,000  $\text{cm}^{-1}$ ) is given (Fig. 1).

Theoretical studies of the azulene problem have been made by Sklar,<sup>5</sup> who computed the energy states by the Heitler-London-Slater-Pauling

(HLSP) method; by Coulson and Longuet-Higgins,<sup>6</sup> who computed mobile bond order, free valence, and electron density; and by Wheland and Mann,<sup>7</sup>

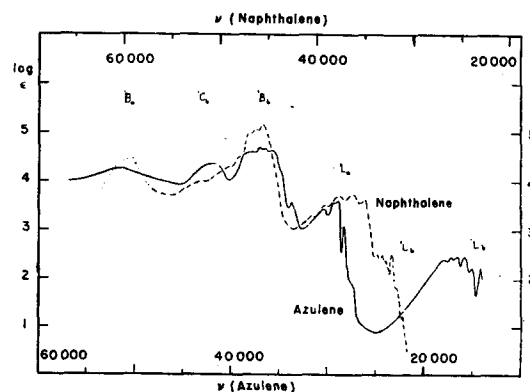


FIG. 1. Spectra of azulene and naphthalene.

\* C. A. Coulson and H. C. Longuet-Higgins, *La Revue Scientifique* 15, 929 (1947).

<sup>7</sup> G. W. Wheland and D. E. Mann, *J. Chem. Phys.* 17, 264 (1949).

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<sup>1</sup> E. Heilbronner and K. Wieland, *Helv. Chim. Acta* 30, 947 (1947).

<sup>2</sup> B. Susz, A. S. St. Pfau, and P. A. Plattner, *ibid.* 20, 469 (1937).

<sup>3</sup> P. A. Plattner, *ibid.* 24, 290/E (1941).

<sup>4</sup> P. A. Plattner and E. Heilbronner, *ibid.* 30, 910 (1947).

<sup>5</sup> A. L. Sklar, *J. Chem. Phys.* 5, 669 (1937).