

## Spectral Resemblances in Azulene and Naphthalene

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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>

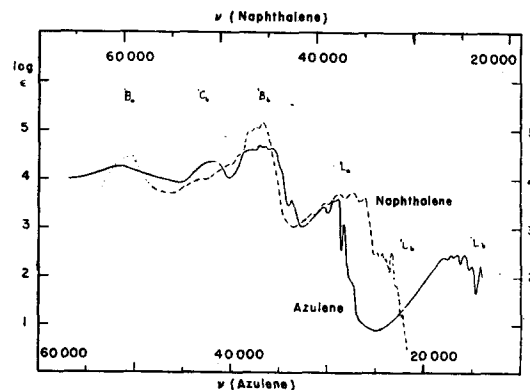


FIG. 1. Spectra of azulene and naphthalene.

<sup>6</sup> 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).

TABLE I. Main features of spectra.

	${}^1A \rightarrow {}^1L_b$	${}^1A \rightarrow {}^1L_a$	${}^1A \rightarrow {}^1B_b$	${}^1A \rightarrow {}^1C_b$	${}^1A \rightarrow {}^1B_a$
Onset of Absorption ( $\text{cm}^{-1}$ )	31300	35000	4300	—	58000
Peaks of Component Bands ( $\text{cm}^{-1}$ )	31300 31600 31900 32350 32750 32900 33200 33550	35000 36300 37800 38200 39000 40300	45250 46000 48000 48900	53000?	59700 60900
Maximum Molar Extinction ( $E_{\text{max}}$ )	370	9500	133000	10000	~40000?
Oscillator		0.18	1.68	0.21	~0.8?
Strength, $f$ (to cut-off)	(34000)	(42500)	(51000)	(55000)	(61000)
Azulene					
Onset of Absorption ( $\text{cm}^{-1}$ )	14400	25000	32700	40300	45000
Peaks of Component Bands ( $\text{cm}^{-1}$ )	14400 15200 15900 16700 17300 17900 18600 19400 20100 20900	27500 28300 28800 29300 30500	33800 35700 36600 37100 38000	42300	51800
Maximum Molar Extinction ( $E_{\text{max}}$ )	300	4000	47000	22000	18000
Oscillator	0.009	0.08	1.10	0.38	0.65
Strength ( $f$ ) (to cut-off)	(25000)	(32700)	(40300)	(45000)	(58000)

who computed the dipole moment by the linear-combination-of-atomic orbitals (LCAO) molecular orbital method for comparison with their measured values.

In the present work, azulene was prepared by the method of Plattner and Wyss.<sup>8</sup> The portion of the spectrum between 2340 and 7000Å was obtained by the measurement of *n*-heptane solutions of azulene with a Beckman Model DU Quartz Spectrophotometer. Our results are in essential agreement with those of the Swiss workers.<sup>1-4</sup> The portion of the spectrum below 2340Å was obtained by the use of techniques described previously.<sup>9</sup> The data for naphthalene above 58,000  $\text{cm}^{-1}$  are estimated from unpublished vapor spectra taken by Dr. W. C. Price in this laboratory. The data for

TABLE II. Predicted levels in azulene.

Configura- tion*	One-electron Jump (see Fig. 3)	Name*	Polarization	Excitation Energy (in units of $\beta$ )
$f^3g$	$2a \rightarrow 3b$	$L_b$	trans	0.8713
	$2b \rightarrow 3b$	$L_a$	long	1.1709
	$2a \rightarrow 3a$	$B_b$	long	1.3307
	$2b \rightarrow 3a$	$B_a$	trans	1.6303
$e^2f^4g$	$1a \rightarrow 3b$	$K_b$	trans	1.4574
	$1b \rightarrow 3b$	$K_a$	long	1.6138
	$1a \rightarrow 3a$	$C_b$	long	1.9169
	$1b \rightarrow 3a$	$C_a$	trans	2.0733

\* See reference 12.

<sup>8</sup> Joachim Wyss, *Synthesen Einfacher Azulene* (University of Zürich Press, Zürich, Switzerland, 1941), p. 27ff.

<sup>9</sup> J. R. Platt and H. B. Klevens, Chem. Rev. **41**, 301 (1947).

the long wave polyacene spectra are from Clar,<sup>10</sup> and for the shorter wave-lengths are from Klevens and Platt.<sup>11</sup>

## DISCUSSION

In Fig. 1 the spectrum of azulene is compared with that of naphthalene, the spectrum of the latter having been shifted about 9000  $\text{cm}^{-1}$  to lower frequencies for easier comparison. There appear to be five distinct band systems in the azulene spectrum. These are labeled  ${}^1B_a$ ,  ${}^1C_b$ ,  ${}^1B_b$ ,  ${}^1L_a$ , and  ${}^1L_b$ . These labels are derived from a scheme of systematic nomenclature for condensed hydrocarbons which is described elsewhere.<sup>12</sup> It is seen that these bands resemble the similarly labeled bands in the naphthalene spectrum with respect to (a) intensity, (b) vibrational structure, and (c) position and separation, except for the lowest frequency band,  ${}^1L_b$ . In peak intensity, the two sets of bands agree within a factor of about two. (See Table I summarizing the main features of the spectra.) In integrated intensity over the important  ${}^1B_b$  band and over the whole spectrum, the agreement is still better. In position, on Fig. 1, the agreement is within about 2000  $\text{cm}^{-1}$  for corresponding bands in the two compounds except for the  ${}^1L_b$  set. The essential difference between the two spectra is then the following. With respect to the higher states (the  ${}^1B$ 's and  ${}^1C_b$ ) two states have moved: the ground state,  ${}^1A$ , has moved upward by about 9000  $\text{cm}^{-1}$ ; and the  ${}^1L_b$  state has moved downward by about 8000  $\text{cm}^{-1}$ . The blue color of azulene is due to the resulting 17,000  $\text{cm}^{-1}$  shift of the  ${}^1L_b$  band.

In Fig. 2 and Table I the known singlet electronic states of azulene are compared with those of the naphthalene-pentacene series.<sup>11</sup> In Fig. 2 the vibra-

TABLE III. Computed and observed energies for lowest states.

	Computed	Observed States	Center of Gravity
<i>Naphthalene</i>			
Lowest transverse ( $N-V_1$ )	$1.267\gamma^* = 28,200 \text{ cm}^{-1a}$	${}^1L_a$ 35,000 $\text{cm}^{-1}$ ${}^3L_a$ 21,300 $\text{cm}^{-1b*}$ ${}^1L_b$ 32,300	28,200
Lowest longitudinal ( $N-V_2$ )	$1.532\gamma = 34,100^a$	${}^1L_b$ (36,000) <sup>c</sup>	34,100
<i>Azulene</i>			
Lowest transverse	$.871\beta = 19,400^a = 16,100^b$	${}^1L_b$ 14,400 ${}^3L_b$ (18,200?) <sup>d</sup> ${}^1L_a$ 28,300	16,300
Lowest longitudinal	$1.171\beta = 26,100^a = 21,600^b$	${}^3L_a$ (14,600?) <sup>d</sup>	21,500

<sup>a</sup>  $\beta = \gamma = 22,200 \text{ cm}^{-1}$ ; <sup>b</sup>  $\beta = 18,500 \text{ cm}^{-1}$ ; <sup>c</sup> estimated from benzene (see references 12, 16); <sup>d</sup> singlet-triplet separation assumed to be the same as in naphthalene.

\* See reference 14.

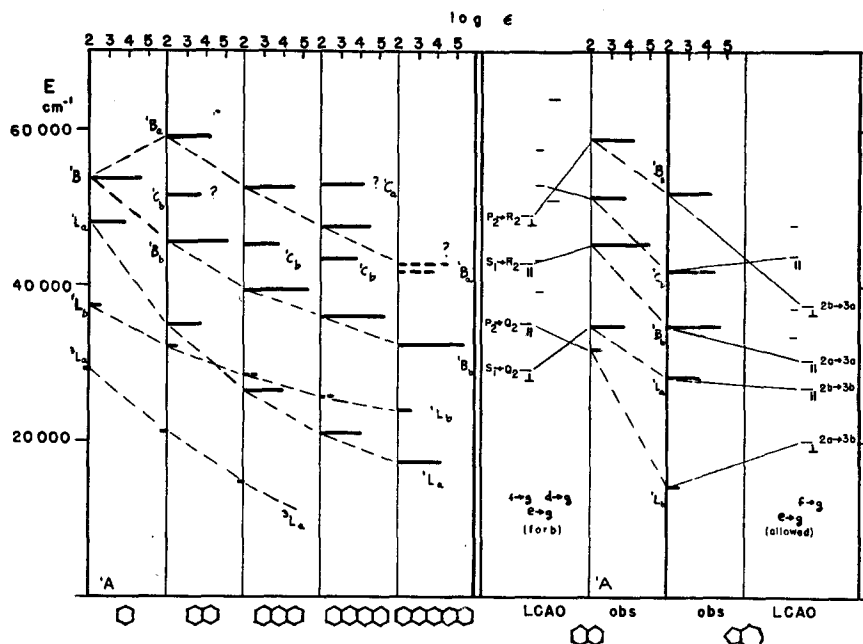
\*\* M. Kasha, Chem. Rev. **41**, 401 (1947).

<sup>10</sup> E. Clar, *Aromatische Kohlenwasserstoffe* (Springer-Verlag, Berlin, 1941).

<sup>11</sup> H. B. Klevens and J. R. Platt, "Spectra of cata-condensed hydrocarbons," J. Chem. Phys. **17**, 470 (1949).

<sup>12</sup> J. R. Platt, "Classification of States of cata-condensed hydrocarbons," J. Chem. Phys. **17**, 484 (1949).

FIG. 2. Left: Energy levels of polyacenes. Observed values, see reference 11; Right: Comparison of energy levels of naphthalene and azulene. Observed values, and LCAO-predicted values of centers-of-gravity of singlets and triplets.



Note to Fig. 2.—In the observed spectra, only the lowest vibrational level is shown. Remaining structure of each electronic band omitted for clearness. Length of horizontal lines indicates  $\log \epsilon_{\max}$  of transition from ground state on scale at top of figures. Lines for triplets drawn to left to indicate  $\log \epsilon_{\max}$  is less than 2.

The symbols  $^3L_a$ ,  $^1L_b$ , etc., are generic designations for states of similar properties in the different compounds (reference 12). The symbols  $S_1 \rightarrow Q_2$ , etc., to the left of the LCAO-predicted

levels in naphthalene are from Coulson (see reference 13). The symbols  $2a \rightarrow 3b$ , etc., to the right of the LCAO-predicted levels in azulene are from the present paper (see Table II and Fig. 3). The symbols  $f \rightarrow g$ , etc., below the excited levels on the right half of the figure represent one-electron configuration changes, in the notation of reference 12. The  $e \rightarrow g$  type of transitions are supposed to be parity-forbidden in naphthalene, but allowed in azulene.

tional structure is omitted for simplicity, and the lengths of the horizontal lines indicate  $\log \epsilon_{\max}$  for absorption from the ground state. In the polyacene series (left half of Fig. 2), the  $^1B_b - ^1L_a$  separation increases with number of rings to a value of about 15,000  $\text{cm}^{-1}$ . The  $^1B_b - ^1L_b$  separation decreases until in anthracene and naphthalene the  $^1L_b$  band is concealed by the stronger  $^1L_a$ , and reappears above it in pentacene. In the polyacene series, therefore, it is the  $^1L_a$  band which is principally responsible for the visible color while in azulene (right half of Fig. 2) it is the  $^1L_b$  band, some 20 times less intense, which is responsible.<sup>13</sup>

Coulson<sup>14</sup> has used LCAO molecular orbital theory, including overlap integrals, to compute the energy levels of naphthalene and other polyacenes. One of us (D.E.M.) has computed the energy levels of azulene by the same method (Figs. 2 and 3, and Table II). The reducible representation whose basis is the set of atomic orbitals on the carbon atoms in azulene has the irreducible components  $6A_1$  and  $4B_2$ . The four lowest roots of the secular equation derived from the  $6 \times 6$  symmetric ( $A_1$ ) block are given in terms of  $\gamma$  (where  $\gamma$  is an

abbreviation for  $(\alpha - E')/\gamma_0$ ,  $\alpha$  is the coulomb integral for a carbon atom in benzene,  $E'$  is the appropriate variational approximation to the correct eigenvalue, and  $\gamma_0$  is the resonance or bond integral for benzene) on the left of Fig. 3; the three lowest roots of the  $4 \times 4$  antisymmetric ( $B_2$ ) block are given on the right side. The energy levels for azulene have been calculated from these roots, with the assumption that the overlap integral  $S$  has the rounded-off value 0.25, by the method of Wheland.<sup>15</sup> These results are given in Table II. The polarizations given in Table II are called transverse (or perpendicular) when the transition is between levels which belong to different symmetry classes, and longitudinal (or parallel) when the transition is between levels which belong to the

	6th order (symmetric)		4th order (antisymmetric)
Unfilled	3b +0.4004	—	3a +0.7376
Filled			
2b	-0.8869	—	2a -0.4772
1b	-1.6515	—	1a -1.3556
0	-2.3103	—	

FIG. 3. Roots of secular equations for azulene.

<sup>15</sup> G. W. Wheland, J. Am. Chem. Soc. **63**, 2026 (1941).

<sup>13</sup> See G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944), pp. 159-160, for a bibliography, discussion, and criticism of theoretical studies on the long wave spectra of these and related compounds.

<sup>14</sup> C. A. Coulson, Proc. Phys. Soc. **60**, 257 (1948).

same symmetry class. Each computed level properly refers to the center of gravity of a singlet and triplet of the same kind. The energies are expressed in units of  $\beta$  (Coulson's  $\gamma$ ), where  $\beta$ , the resonance or bond integral *corrected for overlap*, must be determined empirically. For accurate comparison with experiment, we must know the triplet levels. In naphthalene, one of these,  $^3L_a$ , is known (Fig. 2), and the other,  $^3L_b$ , can be estimated from the estimated singlet-triplet separation in benzene<sup>16</sup> and from the position of  $^1L_b$ . In azulene, it seems not unreasonable to assume the same singlet-triplet separations as for the corresponding levels in naphthalene.

The computed values for the two lowest states are compared with the observed values in Table III. With  $\beta = 22,200 \text{ cm}^{-1}$  in naphthalene, both centers of gravity are predicted within  $100 \text{ cm}^{-1}$ . With the same value of  $\beta$  in azulene, errors of  $4500 \text{ cm}^{-1}$  are found, but a lower value of  $\beta$ ,  $18,500 \text{ cm}^{-1}$ , will fit the data within  $200 \text{ cm}^{-1}$ .

The comparison of the computations on the upper states is quite crude since only the upper singlets are known in either molecule. The computed centers of gravity are on Fig. 2, using a  $\beta$  of about  $23,000 \text{ cm}^{-1}$  for both molecules. (This figure is taken from reference 12, where this value of  $\beta$  was used in another comparison.) For each state, the deviations of computed levels from observed singlets are in the same direction and of about the same size in both molecules, if the assignments given are correct. The method of making these assignments

is discussed in detail elsewhere.<sup>12</sup> This qualitative agreement tends to support them. No intensity computations were made here.

It should be noted that the values for  $\beta$  for azulene and naphthalene obtained from these spectroscopic considerations are not in agreement with the corresponding  $\beta$ 's obtained from thermochemical (e.g., heats of combustion) measurements of resonance energies. For example, the  $\beta_{\text{spect}}$ 's for azulene, benzene, naphthalene, and anthracene are respectively  $18,500 \text{ cm}^{-1}$ ,  $20,600 \text{ cm}^{-1}$ ,  $22,200 \text{ cm}^{-1}$ , and  $24,300 \text{ cm}^{-1}$ . The corresponding  $\beta$ 's, calculated from heat-of-combustion resonance energies,<sup>15</sup> are ( $10,000 \text{ cm}^{-1}$ ?),  $13,400 \text{ cm}^{-1}$ ,  $14,000 \text{ cm}^{-1}$ , and  $14,000 \text{ cm}^{-1}$ . No explanation of these discrepancies is offered, and their investigation is desirable.

Here we have not compared the observed energy levels in azulene with the HLSP computations of Sklar.<sup>5,13</sup> Although his predicted frequencies for the lowest singlet-singlet transitions for a number of compounds agree well with the observed position of the first absorption bands, the spread in his excited electronic levels is much too large in azulene as well as in benzene and other molecules, and the sequence of his predicted levels is wrong, for example, in benzene. He attributes the unduly large spread to his neglect of ionic structures, which are known to be essential for describing excited states by the HLSP method.<sup>13</sup> The LCAO description which Mayer and Sklar applied later to benzene<sup>17</sup> is much more satisfactory in predicting excited states,<sup>16</sup> and a modification of the latter approach has been used here for that reason.

<sup>16</sup> C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).

<sup>17</sup> M. G. Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

## Classification of Spectra of Cata-Condensed Hydrocarbons

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(Received November 1, 1948)

The classification of  $\pi$ -orbitals in a cata-condensed aromatic system is like that of the orbitals of a free electron traveling in a one-dimensional loop of constant potential around the perimeter. To take into account electron interaction, certain quantities corresponding to angular momenta may be added or subtracted. Introduction of the cross-links in the molecule removes the degeneracy. The first excited configuration in such systems gives two low frequency singlet weak absorption bands and two higher singlet strong dipole absorption bands. Selection and polarization rules are given. The levels are identified from the spectra and some of their properties are determined. An explanation is given of the regularities found by Kleven and Platt. A systematic nomenclature is given. The results agree qualitatively with LCAO theory, can be applied easily to unsymmetrical molecules, and can possibly be extended to other types of ring systems.

### I. THE FREE-ELECTRON MODEL

THE aromatic spectra which were extended into the vacuum ultraviolet in the preceding paper<sup>1</sup> (hereafter called I) show many empirical

resemblances and regularities. In benzene, the LCAO (linear-combination-of-atomic-orbitals) mo-

<sup>1</sup> H. B. Kleven and J. R. Platt, J. Chem. Phys. 17, 470 (1949).