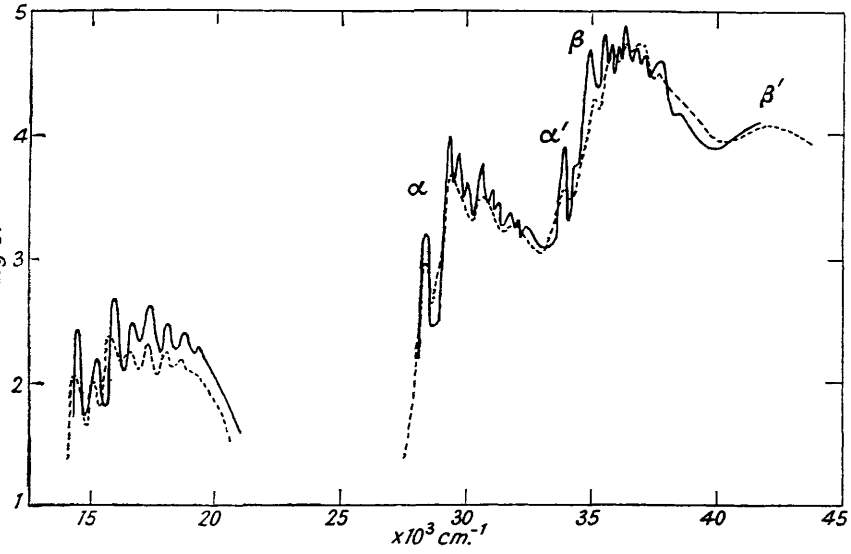
368. *Aromatic Hydrocarbons. Part LVIII. The Structure of Azulene.*

By E. Clar.

Comparison of the visible and the ultra-violet absorption spectrum at room temperature and at −170° gives the characterisation and classification of the different band groups. The results thus obtained correlate the aromatic state of azulene with the ultra-violet part of the spectrum, whilst the visible part is correlated with a non-aromatic metastable state.

The anellation principle provides a simple relation between the absorption spectrum and the number of π-electrons in an aromatic hydrocarbon (Clar, *Chem. Ber.*, 1949, **82**, 495). Thus the first group of bands (α-bands) in benzene at 2600 A. shows a steady shift to the red with increasing number of π-electrons in passing to naphthalene, phenanthrene, and the higher phenes (angular aromatic hydrocarbons).

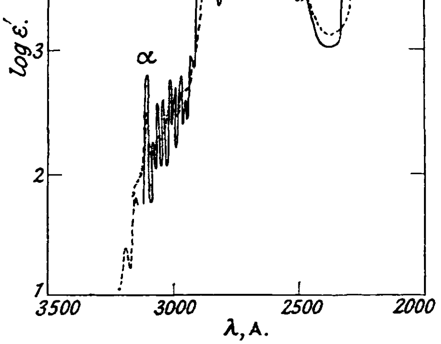
FIG. 1.



- - - - - *Absorption spectrum of azulene at* +18°.
——— ,, ,, ,, −170°.

This rule would require a similar group of α-bands for azulene and naphthalene. If allowance is made for the fact that the average angle in uniplanar azulene is greater than the 120° of the benzenoid hydrocarbons, a small shift might be expected. This is indeed the case. The first ultra-violet group of bands lies between that of naphthalene and phenanthrene. Investigation at low temperature has shown beyond any doubt that these are α-bands. This class of bands is characterised by a very small (or no) ultra-violet shift at low temperature. (For the classification of bands, see Clar, *J. Chem. Physics*, 1949, **17**, 741; *Spectrochim. Acta*, 1950, in the press.)

FIG. 2.



- - - - - *Absorption spectrum of naphthalene at* +18°.
——— *Absorption spectrum of naphthalene at* −170°.

There is another band of the α-type, marked α' in Fig. 1. This band corresponds to the α'-band in the absorption spectrum of naphthalene at −170°; it is superposed on a group of p-bands (Fig. 2). If the α-bands are the result of a resonating system of 10 π-electrons, the anellation principle would require 6 π-electrons for the α'-bands in naphthalene and azulene. This means that 4 π-electrons would be localised in each ring, whilst 2 π-electrons could move from one ring into the other. However, this idea requires the support of more experimental material, which is forthcoming in the higher acenes (linear aromatic hydrocarbons).

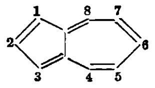
Owing to the non-benzenoid character of azulene no trace of a group of *para*-bands, corresponding to the group beginning in naphthalene at 2885 A., can be found in the spectrum of azulene. The anellation principle correlates the p-bands with the transition from the ground state to a Dewar or *para*-form in the excited state. These bands which become the most prominent in the higher acenes are characterised by a red shift of about 300 cm.$^{-1}$ at low temperature (Clar, *Spectrochim. Acta*, 1950, in the press).

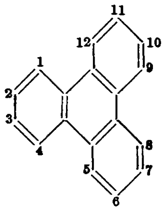
There is an extended group of β-bands in the spectrum of azulene between frequencies of 35,000 and 40,000 cm.$^{-1}$ (Fig. 1). These, which are usually the most intense bands in the absorption spectrum of an aromatic hydrocarbon, are characterised by a considerable red shift at low temperature (cf. Fig. 2 for naphthalene).

Recently (Clar, *Chem. Ber.*, 1949, **82**, 495) it has been found that the difference in frequencies between the first α- and the first β-band is equal to the difference in resonance energy between consecutive members in the anellation series, *i.e.*, the difference in resonance energy between an aromatic hydrocarbon and its preceding member in the phene series with one ring less. The application of this rule in the spectrum of azulene gives 6600 cm.$^{-1}$ or 19 kcals. for one ring. If this value is multiplied by the ratio of resonance energies of (naphthalene–benzene) : naphthalene, a resonance energy of about 40 kcals. for the whole azulene ring system is obtained. This value is also obtained by another method, as seen below.

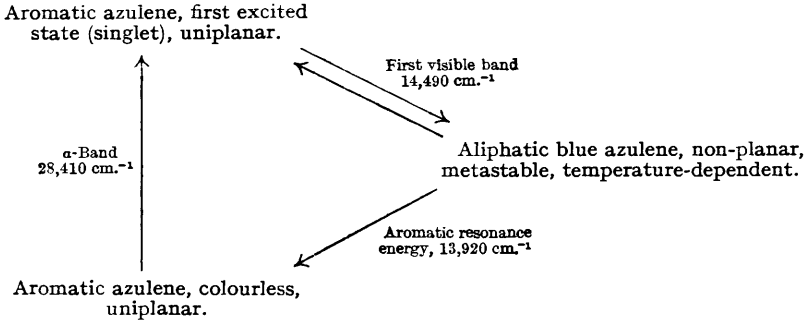
The most striking feature of azulene is its blue colour. Investigation of the group of bands in the visible part of the spectrum shows that it has nothing in common with the other types of bands in aromatic hydrocarbons. It shifts to the ultra-violet about 120 cm.$^{-1}$ at $-170°$. The unusual behaviour of these bands is also shown by the strong ultra-violet shift consequent upon alkyl substitution in positions 2, 4, and 6 (see I) (Heilbronner and Wieland, *Helv. Chim. Acta*, 1947, **30**, 947). A corresponding feature is not observed in the benzenoid aromatic hydrocarbons. The intensity of these bands is doubled at $-170°$. The blue colour of azulene fades reversibly to a considerable degree, in high-boiling solvents such as methylnaphthalene or liquid paraffin. This shows that the blue colour of azulene originates from a metastable state, whose stability decreases with rising temperature. Corresponding metastable states are known to be formed by irradiation of aromatic hydrocarbons at low temperature in solid solution (Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100; Kasha and Nauman, *J. Chem. Physics*, 1949, **17**, 516). They have life-times of several seconds. The longest life-time (about 3 minutes) was observed with triphenylene in the course of this work. It is long enough for the absorption spectrum of the yellow metastable state of the colourless triphenylene to be photographed. It shows absorption bands at 4300 and 4080 A. It is very likely that this long life-time is connected with a non-planar propeller-like state, caused by the overlapping of hydrogen atoms in the positions 1 : 4 : 5 : 8 : 9 : 12 in triphenylene (II) in solution. The blue state of azulene is, therefore, probably non-planar and might be called aliphatic azulene. In that case the aromatic resonance should have disappeared. This view is supported by the fact that the difference between the first band in the visible and the first α-band in the ultra-violet amounts to 28,410—14,490 = 13,920 cm.$^{-1}$ = 40 kcals., *i.e.*, the same value as above. The relation between the different states is therefore as follows :

(I.)





(II.)



From the ratio of the intensities of the bands it can be concluded that the concentration of the blue azulene amounts to a few per cent. only. Heilbronner and Wieland (*loc. cit.*) report a resonance energy of 46 kcals. for azulene. The difference of 6 kcals. can be explained by application of the Franck–Condon principle.

Recently Klevens and Platt (*J. Chem. Physics*, 1949, **17**, 470,484; cf. Clar, *J. Chem. Physics*, 1949, **17**, 741) used the classification of bands provided by the anellation principle for a quantum-mechanical treatment. Their classification in the case of azulene (Mann, Platt, and Klevens, *J. Chem. Physics*, 1949, **17**, 481) has now been shown to be erroneous. They consider the visible group of bands as strongly shifted α-bands in comparison with the α-bands in naphthalene (in their terminology L_b-bands). The first ultra-violet group of bands is classified as belonging to the *p*-type (L_a-type), whilst the classification of the β-bands (B_b) is the same as in this paper. As shown above the absorption spectrum of the first two groups at low temperature contradicts this view.

There is another band (β') of the β-type at 42,200 cm.$^{-1}$, which is probably connected with the α'-band in the same way as the β-band is with the α-band.

The technique for the low temperature-absorption was that already described (Clar, *Spectrochim. Acta*, 1950, in the press). The solvent was a mixture of 1 part of methyl alcohol and 4 parts of ethyl alcohol. The details of the absorption curve for room temperature are in good agreement with data previously recorded (Susz, St. Pfau, and Plattner, *Helv. Chim. Acta*, 1937, **20**, 469; Plattner, *ibid.*, 1941, **24**, 290; Plattner and Heilbronner, *ibid.*, 1947, **30**, 910; Heilbronner and Wieland, and Mann, Platt, and Klevens, *locc. cit.*).

Azulene (units, cm.$^{-1}$)

	at +18°.	at −170°.
Meta-stable bands	14,370	14,490
	15,130	15,270
	15,850	15,970
	16,610	16,720
	17,300	17,420
	18,050	18,120
	18,690	18,830
		19,420
α-Bands	28,410	28,410
	29,410	29,370
		29,720
		30,030
	30,680	30,680
		31,060
		31,350
	31,950	31,800
		32,150
		32,570

	at +18°.	at −170°.
α'-Bands	33,840	33,890
β-Bands	35,090	34,970
	35,710	35,460
		35,780
	36,360	36,100
		36,360
	36,970	36,770
		37,180
	37,740	37,670
		38,310
β'-Band	42,200	42,000

Naphthalene (units, cm.$^{-1}$)

	at +18°.	at −170°.
Temperature dependent α-bands	31,350	—
	31,850	31,850
α-Bands	32,150	32,240
		32,500
		32,680
		32,910
	33,220	33,190
		33,410
	33,670	33,690
		33,920
		34,190
		34,420
p-Bands	35,090	34,660
		35,150
α'-Bands	36,360	36,100
		36,630
	37,590	37,450
		38,100
	38,910	38,820
	40,320	40,160
β-Band	45,250	

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