# SHORT COMMUNICATIONS

# SPECTRUM OF AZULENE\*

# V.† GEOMETRY OF THE EXCITED STATE OF THE 3500 Å TRANSITION

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The rotational structure of the origin band of the 3500 Å transition  $({}^{1}A_{1}(2) \leftarrow {}^{1}A_{1}(1))$  of azulene has been analysed, yielding the rotational constants A', B', C' of the excited state, and thus the corresponding moments of inertia.<sup>1</sup> Of themselves, rotational constants give little specific information about geometries in large molecules. They may, however, be used to check theoretical predictions.

Such a prediction is now made for the excited state of azulene, along lines which have previously proved encouraging for the ground states of naphthalene,<sup>2</sup> anthracene,<sup>2</sup> and single-ring nitrogen heterocycles,<sup>3</sup> and for an excited state of naphthalene.<sup>4</sup> Bond lengths within the rings are first calculated by conventional molecular orbital methods. The ring angles are then obtained by the heuristic assumption that, but for constraints imposed by non-uniform bond lengths, they would be those of the appropriate regular polygon. The regular polygon angles for azulene are  $108^{\circ}$  and  $128 \cdot 57^{\circ}$  for the five- and seven-membered rings respectively. The calculation of ring angles then requires minimizing the energy needed to deform them to accommodate the actual bond lengths; a suitable potential function has to be assumed (see below). For want of better information the CH bond lengths in the ground state are taken as  $1 \cdot 08$  Å and the CH bonds are assumed to bisect the external CCC angles in all states.

Such an *a priori* calculation was first carried out for the ground state of azulene. The wave function and derived bond orders were those of Pariser,<sup>5</sup> and Coulson's relation<sup>6</sup> gave the bond lengths. The potential function used for the ring angles contained only one adjustable parameter, called k'/k in ref.<sup>5</sup>; k is the diagonal CCC bending force constant, assumed the same for all angles, and k' is an off-diagonal constant connecting adjacent CCC angles in different rings. The value attributed to the constant k' cannot be simply compared with a similar force constant appearing in the more elaborate force-fields used for normal coordinate analyses.

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<sup>5</sup> Pariser, R., J. chem. Phys., 1956, 25, 1112.

<sup>6</sup> Coulson, C. A., Proc. R. Soc. A, 1939, 169, 413.

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In crystalline azulene the molecules are disordered, and the directly determined X-ray structures are susceptible to unusually high errors. Recently, however, the structure of azulene in its sym-trinitrobenzene complex has been determined by Hanson.<sup>7</sup> Since the geometry of anthracene in the corresponding complex<sup>8</sup> is the same as in pure crystalline anthracene, we take Hanson's structure to be the most reliable of the X-ray results. It is given in Table 1. There is also a recent electron diffraction structure, due to Bastiansen and Derissen.<sup>9</sup> The length of the central (9–10) bond is  $1.501 \pm 0.005$  Å, in good agreement with Hanson's figure. The values for the other bonds do not agree so well, but the standard errors are much greater (0.008-0.016 Å). For the angles, agreement is to within  $0.2^{\circ}$ , except for a pair in the seven-membered ring; this disagreement is noted in Table 1.

### TABLE 1

# SKELETAL GEOMETRY OF AZULENE Carbon atoms are numbered as follows: the central bond is 9-10; atom 1 is in the five-membered

ring, next to atom 9; other atoms are numbered 2 to 7 cyclically from atom 1. Bond lengths in Å

Ground State Excited State Ground State Excited State Bond Angle Obs.ª Cale. Calc. Change Obs.ª Calc. Calc. Change  $-1 \cdot 1^{\circ}$  $1 \cdot 409$ +0.0201 - 2 - 3 $110 \cdot 2^{\circ}$  $109 \cdot 7^{\circ}$  $108.6^{\circ}$ 2-3 $1 \cdot 392$ 1.389 $108 \cdot 1^{\circ}$  $-0.3^{\circ}$ 2 - 3 - 10 $108 \cdot 6^{\circ}$  $108.4^{\circ}$ 3 - 10 $1 \cdot 399$  $1 \cdot 399$  $1 \cdot 416$ +0.0174 - 10 $1 \cdot 391$ 1.399 $1 \cdot 416$ +0.0171 - 9 - 10 $106 \cdot 3^{\circ}$  $106 \cdot 7^{\circ}$  $107 \cdot 5^{\circ}$  $+0.8^{\circ}$ 4 - 5 $1 \cdot 397$  $1 \cdot 391$  $1 \cdot 403$ +0.0124 - 10 - 9 $127 \cdot 4^{\circ}$  $127 \cdot 8^{\circ}$  $121 \cdot 1^{\circ}$  $+0.3^{\circ}$ 128.6°b 5 - 6 $1 \cdot 394$  $1 \cdot 392$  $1 \cdot 401$ +0.00910 - 4 - 5 $128.8^{\circ}$  $128 \cdot 2^{\circ}$  $128 \cdot 4^{\circ}$  $+0\cdot 2^{\circ}$ 127·3°b  $129 \cdot 1^{\circ}$  $129 \cdot 1^{\circ}$  $-0.4^{\circ}$ -0.032 $129 \cdot 5^{\circ}$ 9 - 101.498 $1 \cdot 467$  $1 \cdot 435$ 4 - 5 - 65 - 6 - 7 $129.5^{\circ}$  $128 \cdot 9^{\circ}$  $128 \cdot 8^{\circ}$  $-0.1^{\circ}$ 

<sup>6</sup> Hanson, ref. 7. For pairs of equivalent bonds (individually quoted to +0.004 Å) and angles, mean values are quoted here. They have been slightly adjusted to give ring closure in the planar molecule.

<sup>b</sup> Bastiansen and Derissen, ref. 9. Errors quoted are +0.6 and  $\pm 1.3^{\circ}$  respectively.

The calculated structure of the ground state is given in Table 1, the sole adjusted parameter being k'/k, which was taken as +1. In previous work<sup>2</sup> it was  $-1 \cdot 5$ . Had this value been used the calculated angles would have been changed by only  $0 \cdot 2^{\circ}$  or less. They are rather insensitive to this quantity, in both azulene and naphthalene (but not in anthracene), provided its value is between +3 and -3. Agreement with Hanson's figures is good, except for an expected discrepancy with the central bond (see below).

The rotational constants can then be calculated from all three structures. The experimental values are  $A \ 0.0948$ ,  $B \ 0.0419$ , and C (not independent) 0.0290 cm<sup>-1</sup>. For B the calculated constants all come out to be slightly high ( $0.0001 \text{ cm}^{-1}$ ),

<sup>7</sup> Hanson, A. W., Acta crystallogr., 1965, 19, 19.

<sup>8</sup> Mason, R., Acta crystallogr., 1964, 17, 547.

<sup>9</sup> Bastiansen, O., and Derissen, J. L., Acta chem. scand., 1966, 20, 1319.

which is acceptable in the context of parameters determined from the electronic spectrum. In A the X-ray, electron-diffraction, and theoretical structures give errors of +0.0006, -0.0006, and +0.0016 cm<sup>-1</sup> respectively. The difference between the first two is almost wholly due to the distance from the long molecular axis attributed to the CH group at position 4. As the most distant group, the value of A is particularly sensitive to its position. In terms of the structural parameters of Table 1, the position of the group depends especially on the 9–10 bond length, and on the value of the angle 9–10–4. Since the experimental structures agree on the former, the actual value of the latter is probably about halfway between the two independent determinations. The calculated value of this angle is then satisfactory, but the 9–10 bond length is too short, and this is thus the chief cause of the high value of A so obtained.

As foreshadowed above, molecular orbital theory has a systematic difficulty in dealing with the exceptionally long 9–10 bond, a feature which valence bond theory takes in its stride since the central bond participates in no Kekulé structure. For this reason, we propose that in extending the calculations to excited states, the theoretical values are best used to predict *changes* in moments of inertia, rather than their absolute values.

For the excited state of the 3500 Å transition the changes in the rotational constants are then predicted to be as follows (units of  $10^{-4}$ cm<sup>-1</sup>):<sup>†</sup>

In these units the observed changes<sup>1</sup> are 0.0, -8.4, -4.0, and 0.0, -7.2, -3.3 respectively.

To see this comparison in proper perspective it is desirable to have some feeling for the limits within which the inertial constants are likely to change in other excited states. Similar calculations have therefore been carried out for the seven other  $\pi^* \leftarrow \pi$ singlet states and the six lowest triplets for which Pariser gives the wave functions. In azulene- $d_0$  the extreme range of variation of  $\Delta A$  is from  $+8\cdot1$  to  $-26\cdot2$ , of  $\Delta B$ from  $-6\cdot6$  to  $-16\cdot8$ , and of  $\Delta C$  from  $-3\cdot9$  to  $-9\cdot2$ . One may thus say that for the excited state of the present study the error in the calculated value of  $\Delta A$  is 4% of the range within which  $\Delta A$  could fall if the computed values were no more than random numbers of roughly the right order of magnitude; for  $\Delta B$  the discrepancy, similarly defined, is 6%; and for  $\Delta C$  it is negligible. For azulene- $d_8$  the comparison is equally good.

We are of the opinion that this still speculative method of calculation requires some further tests. However, in the light of previous successful applications and the reasonable agreement obtained in the present case, we feel justified in proposing the derived changes in bond lengths and angles, given in columns 5 and 10 of Table 1, as highly probable estimates of the geometrical shifts associated with the electronic excitation  ${}^{1}A_{1}(2) \leftarrow {}^{1}A_{1}(1)$  in azulene.

<sup>†</sup> The CH bonds were assumed to contract by 0.01 Å as happens in the first excited singlet state of benzene. If there were no contraction at all,  $\Delta A$  would be decreased by 1.5,  $\Delta B$  by 0.3, and  $\Delta C$  by 0.2 (for azulene- $d_0$ ) and by twice these numbers for azulene- $d_s$ . These changes are marginal.