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# Geometrical Structures of Excited States of Conjugated Molecules: Benzene, Naphthalene, Azulene, and Heptalene

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A semiempirical SCF CI MO method used in combination with the variable bond-length technique, which has proved to be quite successful in predicting the ground-state geometrical structures of conjugated molecules, has been applied with modifications suitable to their excited states. The values of the parameters appearing in the expression of the resonance integral were adjusted so as to reproduce both the absorption and fluorescence spectra of benzene. The lower three singlet states (${}^1B_{2u}$, ${}^1B_{1u}$, and ${}^1E_{1u}$) and the lowest triplet state (${}^3B_{1u}$) of benzene, the lower two singlet states (${}^1B_{1u}$ and ${}^1B_{2u}$) of naphthalene, the lower two singlet states (${}^1B_2$ and ${}^1A_1$) of azulene, and the lowest singlet state of heptalene are examined. It is predicted that the ${}^1B_{1u}$ and ${}^3B_{1u}$ states of benzene have the antiquinoidal and quinoidal conformations of the $D_{2h}$ symmetry respectively, and that the symmetry of the lowest singlet state of heptalene is higher than that ($C_{2h}$) of the ground state.

The prediction of the geometrical structures, that is, of the C–C bond distances of conjugated hydrocarbons, has long been one of the major problems in $\pi$-electron theories. For the ground states of benzenoid hydrocarbons, it has been well recognized that the molecular symmetry is always that suggested by superposition with an equal weight of the equivalent Kekulé-type resonance structures, and that the bond orders calculated using molecular orbital methods, assuming the full molecular-symmetry, yield the theoretical C–C bond lengths, which are themselves in good agreement with the experimental values.

On the other hand, it was somewhat amazing to discover that the ground states of certain nonbenzenoid hydrocarbons (*e.g.*, heptalene) and open-shell or charged $\pi$-electron systems (*e.g.*, the cyclopentadienyl radical or the benzene positive ion) do not adopt the fully-symmetrical nuclear arrangement to be expected on the basis of the conventional resonance theory, but, rather, a less symmetrical conformation in which the nuclei have been displaced to a certain degree.[1] These nuclear distortions, accompanied by a molecular-symmetry reduction, have now been well interpreted as due to the Jahn-Teller or pseudo-Jahn-Teller effects.[1,2]

Another interesting case of such bond distortion concerns the electronically-excited states. It has been known, for example, that the ESR line shapes of the lowest triplet state (${}^3B_{1u}$) of benzene are not those which would be expected from a molecule with at least a trigonal symmetry.[3] The geometrical structures of the excited states of a conjugated molecule are, in general, different from that of the ground state, the difference being reflected primarily in the band shapes of the electronic spectrum. For example, the UV spectrum of heptalene shows a very long absorption tail throughout the visible region,[4] which probably indicates that the geometrical structure of the first excited state is greatly different from that of the ground state. Furthermore, information on the geometrical structures of excited states is quite useful in understanding the inducing and accepting modes of the intramolecular radiationless transitions.[5,6]

It is the purpose of this paper to propose, on the basis of the semiempirical SCF LCAO MO theory, a computational method of determining the molecular symmetries and C–C bond distances for the electronically-excited states of conjugated molecules and to examine the geometrical structures of the lower excited states of benzene, naphthalene, azulene, and heptalene.

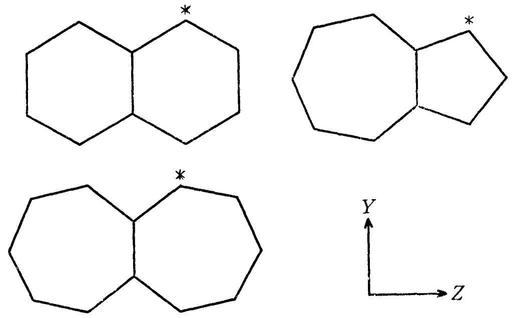

Fig. 1. Numbering of atoms and choice of axes. Carbon atoms are numbered consecutively, starting with the starred atom and proceeding in a clockwise fashion along the periphery.

## Method of Calculation

The method used in predicting the energetically most favorable symmetry group and the C nuclear arrangement for an electronically-excited state of a conjugated molecule which is assumed to be planar is a modified version of the semiempirical SCF CI MO method used in combination with the variable bond-length technique, which has proved to be quite successful in predicting the ground-state geometrical

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[1] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," Benjamin, New York (1966).

[2] T. Nakajima, in "The Chemistry of Nonbenzenoid Aromatic Compounds," International Symposium on The Chemistry of Nonbenzenoid Aromatic Compounds, Butterworths, London (1970), in press.

[3] M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963).

[4] H. J. Dauben, Jr. and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4659 (1961).

[5] S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1966).

[6] K. F. Freed and J. Jortner, *ibid.*, **52**, 6272 (1970).

structures of a variety of conjugated molecules.[7,8]

Assuming a certain C nuclear arrangement for a conjugated molecule, we carry out the SCF CI MO calculation in the framework of the Pariser-Parr-Polpe approximation.[9,10] Using the wavefunction for an excited state obtained after the inclusion of the configuration mixing all the singly-excited states, we then calculate the C–C bond length for the excited state by the aid of a suitable bond-order—bond-length relationship (*vide infra*). The new C nuclear arrangement is taken as the geometrical structure for the next SCF MO calculation, and the process is repeated until the convergence of the C–C bond lengths for the excited state is reached. As the starting geometrical structures for the iterative calculation, we take all the possible distorted structures in which C–C bond lengths are distorted so that the set of displacement vectors may form a basis for an irreducible representation of the full symmetry group of the molecule.[11,12]

If the self-consistency of the geometrical structure is achieved at two or more different nuclear arrangements, the total energies should be compared with each other in order to determine which one is the energetically most favorable. The total energy of a conjugated molecule is assumed to be the sum of the $\pi$-electron energy and the $\sigma$-core energy, which may itself be regarded as the sum of the independent contributions from the C–C $\sigma$-bonds. Further, for the reduced distance variation, the individual contribution of the $\sigma$-bonds may safely be approximated by the quadratic function of the bond-distance variation:

$$E_\sigma = \sum_{\mu<\nu} \frac{k}{2}(\Delta r_{\mu\nu})^2 \tag{1}$$

where $k$ is the force constant for an $sp^2$ hybridized C–C $\sigma$-bond. The value of $k$ used in the present calculations is 714 kcal mol$^{-1}$ Å$^{-2}$.[13]

It has now been well established[14] that if the total energy of a conjugated hydrocarbon is written as the sum of the $\pi$-electron energy, as calculated using a Hückel approximation, and the $\sigma$-bond energy, as approximated by Eq. (1), then the minimization of the total energy with respect to the bond-length variations yields a linear relationship between the bond length, $r$, and the bond order, $p$:

$$r_{\mu\nu} = r_0 - ap_{\mu\nu} \tag{2}$$

where $r_0$ is the length for an $sp^2$–$sp^2$ C–C single bond and where $a=2\beta'/k$, $\beta'$ being the first derivative of the resonance integral.

Recently, Julg[15] has shown that the inclusion of electron repulsions in calculating the $\pi$-electron energy by the use of the Pariser-Parr-Pople-type semiempirical SCF MO formalism leads to the following relationship between the bond order and the bond length:

$$r_{\mu\nu} = r_0 - ap_{\mu\nu} + bp^2_{\mu\nu} \tag{3}$$

where $b=\gamma'/2k$ and where $\gamma$ is the Coulomb repulsion integral between neighboring atoms. The $b/a$ ratio being of the order of 0.1 for the bond distance of 1.34 Å, which corresponds to $p=1$, we may safely neglect the $p^2$ term in Eq. (3) for the longer bond distances with the lower $p$ values. Further, by minimizing the excited-state total energy with respect to the bond-distance variations, Julg[15] has demonstrated that the same linear relationship between $p$ and $r$ that is appropriate for the ground state holds approximately even for both singlet and triplet excited states. In this paper, we adopt, as the bond-order—bond-length relationship for use in excited states, Eq. (2) with $r_0=$ 1.520 Å and $a=0.186$,[8] the parameter values giving the ground-state bond lengths, which are in good agreement with the experimental values. Miller and Murrell[16] have proposed the following formula for predicting the excited-state bond lengths of conjugated molecules:

$$\Delta r_{\mu\nu} = -0.228\ \Delta p_{\mu\nu} \tag{4}$$

This formula gives $r_0=1.55$ Å, which seems to be somewhat exaggerated as the length for the $sp^2$–$sp^2$ C–C single bond.

The one-center repulsion integral for carbon, given as $I_c$–$A_c$, is taken to be 11.16−0.03 eV. The two-center repulsion integrals are calculated using the Mataga-Nishimoto formula.[17] The resonance integrals, $\beta_{\mu\nu}$ (in units of eV), are evaluated using the following formula:

$$\beta_{\mu\nu} = -2.38 \exp\left[(1.397-r_{\mu\nu})/A\right] \tag{5}$$

where the pre-exponential factor has been determined so as to reproduce the experimental excitation energies of benzene. On the other hand, the value of $A$, on which depend sensitively the geometrical structures of conjugated molecules, cannot be determined by reference to the excitation energies of benzene. In this paper, the value of $A$ is adjusted so as to reproduce the emission energy of the fluorescence from the lowest singlet excited state ($^1B_{2u}$) in benzene. Using the experimental emission energy, 4.44 eV[18] we thus obtain $A=0.30$ Å.

## Results and Discussion

*Benzene.* The geometrical structures of the lower three singlet excited states, $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$, and the lowest triplet state, $^3B_{1u}$, are examined. As the starting bond distortions for iterative calculation, we adopt carbon-stretching symmetry coordinates

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[7] M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, **21**, 3423 (1965).

[8] H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, **12**, 349 (1968).

[9] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 446, 767 (1953).

[10] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[11] T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).

[12] A. Toyota and T. Nakajima, *ibid.*, **6**, 144 (1970).

[13] L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

[14] G. Binsch and E. Heilbronner, "Structural Chemistry and Molecular Biology," ed. by A. Rich and N. Davidson, Freeman, San Francisco (1968), p. 815.

[15] A. Julg, *J. Chim. Phys.*, **65**, 541 (1968).

[16] K. Miller and J. N. Murrell, *Theor. Chim. Acta*, **3**, 231 (1965).

[17] N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (Leipzig), **13**, 140 (1957).

[18] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York (1965), p. 42.

Table 1. Carbon-stretching symmetry coordinates for benzene

| Mode | Symmetry coordinate[a)] |
|---|---|
| $a_{1g}$ | $S_1=\frac{1}{\sqrt{6}}(\varDelta r_{12}+\varDelta r_{23}+\varDelta r_{34}+\varDelta r_{45}+\varDelta r_{56}+\varDelta r_{61})$ |
| $b_{2u}$ | $S_{14}=\frac{1}{\sqrt{6}}(\varDelta r_{12}-\varDelta r_{23}+\varDelta r_{34}-\varDelta r_{45}+\varDelta r_{56}-\varDelta r_{61})$ |
| $e_{2g}$ | $S_{8a}=\frac{1}{\sqrt{12}}(\varDelta r_{12}-2\varDelta r_{23}+\varDelta r_{34}+\varDelta r_{45}-2\varDelta r_{56}+\varDelta r_{61})$ |
|  | $S_{8b}=\frac{1}{\sqrt{2}}(\varDelta r_{12}-\varDelta r_{34}+\varDelta r_{45}-\varDelta r_{61})$ |
| $e_{1u}$ | $S_{19a}=\frac{1}{\sqrt{2}}(\varDelta r_{12}-\varDelta r_{34}-\varDelta r_{45}+\varDelta r_{61})$ |
|  | $S_{19b}=\frac{1}{\sqrt{12}}(\varDelta r_{12}+2\varDelta r_{23}+\varDelta r_{34}-\varDelta r_{45}-2\varDelta r_{56}-\varDelta r_{61})$ |

a) The plus and minus signs indicate the bond shortening and lengthening, respectively. For the numbering of symmetry coordinates, see E. B. Wilson, *Phys. Rev.*, **45**, 706 (1934).

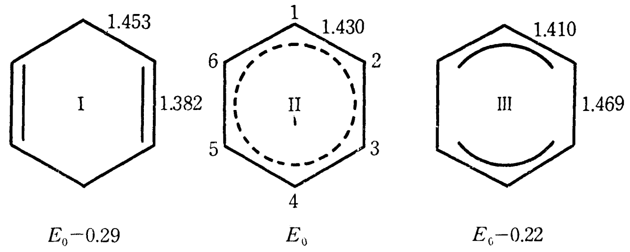

Fig. 2. Predicted equilibrium configurations for the lowest $^3B_{1u}$ excited state of benzene (bond lengths in Å and energies in eV).

belonging to $a_{1g}$, $b_{2u}$, $e_{2g}$, and $e_{1u}$ irreducible representations of the $D_{6h}$ point group (Table 1). Further, if a certain carbon-stretching symmetry coordinate and its countertype, in which the bond-length variations are reversed, are not equivalent (*e.g.*, $S_{8a}$), these two bond distortions should be differentiated as the starting geometry.

As for the lowest singlet excited state ($^1B_{2u}$), it turned out that all the starting bond distortions converge into a unique hexagonal nuclear arrangement with the C–C bond length longer by 0.031 Å than that in the ground state. By applying the Franck-Condon principle to the experimental intensity distribution in the 2600 Å band system of benzene, Craig[19)] has found the value of 0.037 Å for the increase in the C–C distance associated with the lowest singlet transition, $^1B_{2u}\leftarrow{}^1A_{1g}$. The predicted increase in bond length is in fairly good agreement with this experimentally-estimated value. The $^1B_{2u}$ state should, in principle, suffer pseudo-Jahn-Teller distortions upon coupling with the closely-spaced $^1B_{1u}$ *via* the $a_{2g}$ vibration and upon coupling with the $^1E_{1u}$ state *via* the skeletal bending modes corresponding to the symmetry coordinate, $S_6$, of the $e_{2g}$ symmetry.[20)] However, the $a_{2g}$ vibration has no influence on the C skeletal arrangement, and the bending displacements, $S_6$, should cause a change in the small $\beta_{\mu\nu}$ value (zero in the P–P–P approximation) between non-neighboring C atoms.

In case of the lowest triplet state ($^3B_{1u}$), the starting nuclear displacements belonging to $a_{1g}$ and $b_{2u}$ representations converge into a hexagonal conformation with the C–C bond length equal to 1.430 Å, while those belonging to the $e_{2g}$ and $e_{1u}$ representations lead to two $D_{2h}$ conformations; one of these is the quinoidal form (I), and the other, the antiquinoidal form (III) (Fig. 2). As for the symmetry displacements of the $e_{2g}$ symmetry, $S_{8a}$ and its countertype bring about the antiquinoidal and quinoidal forms respectively, while $S_{8b}$ and its countertype lead to the other two equivalent quinoidal forms. In Fig. 2 are shown the bond lengths of these equilibrium conformations, together with their relative total energies. The quinoidal form is more stable than the antiquinoidal form by 0.07 eV, the latter being the metastable quilibrium conformation corresponding to the saddle point of the energy surface. The passage from one of the quinoidal conformations, by way of the antiquinoidal saddle points, to the other two equivalent quinoidal conformations may be caused by the $e_{2g}$ vibration.[1,3,21)]

In recent years various kinds of experimental studies of the geometry of the $^3B_{1u}$ state of benzene have been attempted. Electron spin resonance experiments by de Groot and van der Waals[3)] have indicated that, in solid matrices, the electron-spin distribution in the $^3B_{1u}$ state is far from hexagonal. The study of the phosphorescence spectra of various partly-deuterated benzenes in a $C_6D_6$ host crystal at 4.2°K by Nieman and Tinti[22)] led to the conclusion that the symmetry of the $^3B_{1u}$ state is lower than $D_{3h}$. The $^3B_{1u}\leftarrow{}^1A_{1g}$ absorption spectrum in benzene vapor mixed with oxygen was studied by King and Pinnington,[23)] who concluded that the upper state is of the $D_{2h}$ symmetry. Recently Goncalves and Hutchison[24)] studied the electron nuclear double-resonance spectrum of benzene in $C_6D_6$ single host crystals and suggested that the $^3B_{1u}$ state has an antiquinoidal structure rather than a quinoidal one. It should be noted, however, that, in the experiments in the crystalline or glassy matrix, the degradation of the local $D_{6h}$ symmetry might be due to an environmental effect.

It has been reported that the photochemical reaction of benzene derivatives to Dewar benzene occurs through the $^3B_{1u}$ state.[25–27)] To determine the most favorable conformation for the photochemical isomerization, we

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19) D. P. Craig, *J. Chem. Soc.*, **1950**, 2146.

20) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

21) J. H. van der Waals, A. M. D. Berghuis, and M. S. de Groot, *Mol. Phys.*, **13**, 301 (1967).

22) G. C. Nieman and D. S. Tinti, *J. Chem. Phys.*, **46**, 1432 (1967).

23) G. W. King and E. H. Pinnington, *J. Mol. Spectrosc.* **15**, 394 (1965).

24) A. M. Ponte Goncalves and C. A. Hutchison, *J. Chem. Phys.*, **49**, 4235 (1968).

25) E. E. van Tamlem and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

26) A. W. Burgstahlen and P. L. Chien, *ibid.*, **86**, 2940 (1964).

27) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commum.*, 593 (1966).

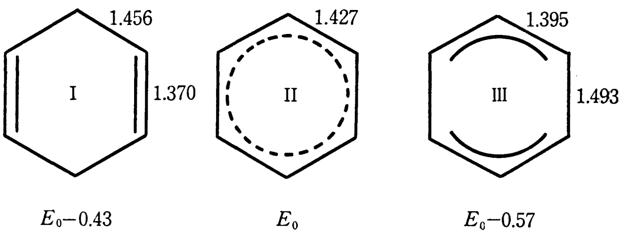

Fig. 3. Predicted equilibrium configurations for the lowest $^1B_{1u}$ excited state of benzene (bond lengths in Å and energies in eV).

examined the nonneighbor 1—4 and 2—5 bond orders of the three conformations, I, II, and III. The predicted 1—4 and 2—5 bond orders of I and III are 0.155 and −0.299, and −0.193 and 0.028, respectively. The predicted 1—4 bond orders of II is −0.057. From the above results, it can be concluded that the most favorable conformation for the reaction in the $^3B_{1u}$ state is I.

For the second singlet state ($^1B_{1u}$), three equilibrium conformations, hexagonal, quinoidal, and antiquinoidal, are obtained. The situation is similar to that predicted for the $^3B_{1u}$ state, except that the relative energies of I and III are interchanged and that the bond length of the unstable hexagonal structure is slightly shorter than that for the $^3B_{1u}$ state (Fig. 3). In the third excited state ($^1E_{1u}$), all the starting distortions lead to the same hexagonal structure, that obtained for the lowest singlet-excited state.

It is well known that the $^1B_{1u}$ state is subjected to the pseudo-Jahn-Teller interaction with the $^1E_{1u}$ state through vibrations of the $e_{2g}$ symmetry[1,21,28] and that the $^1B_{1u}\leftarrow{}^1A_{1g}$ transition is vibronically induced by these vibrations.[29,30] On the other hand, no Jahn-Teller coupling effects are expected to be exhibited at the lowest vibronic level of the $^1E_{1u}\pi^*\leftarrow\pi$ excited state.[31] The results of a recent experimental study by Katz *et al.*[31] of the absorption spectra of benzene and deuterated benzenes in solid rare-gas matrices are in agreement with these predictions. It seems that our results are all consistent with these findings.

*Naphthalene.* Since the energy difference between the first ($^1B_{1u}$) and second singlets ($^1B_{2u}$) is comparatively small, it may be expected from the symmetry rule[32-34] that the two states will interact strongly with each other through the normal displacement of the $b_{3g}$ symmetry and will suffer a symmetry reduction. Thus, the symmetry groups and the bond lengths for the energetically most favorable nuclear arrangements of the two states were examined. For the two states, the starting bond distortions belonging to the irreducible representations, $a_g$, $b_{3g}$, $b_{1u}$, and $b_{2u}$, of the full symmetry group, $D_{2h}$, are taken as the starting bond distortions for iterative calculation. It turns out that, in the two states, all the starting bond distortions converge into a unique self-consistent set of bond lengths corresponding to $D_{2h}$. The calculated bond lengths of both the states are listed in Table 2 and compared with the experimental values of the ground state.

It is well known that a change in symmetry manifests itself on electronic excitation itself by the appearance of progressions in vibrations which, with respect to the covering symmetry of the ground state, are non-totally symmetrical.

Craig *et al.*[35] have studied the $^1B_{1u}\leftarrow{}^1A_g$ absorption spectrum in naphthalene vapor and shown that such progressions are not found in this absorption band. They have concluded that naphthalene belongs to the $D_{2h}$ symmetry group in the $^1B_{1u}$ electronic state as in the ground state, and that its dimensions are little changed on excitation. The results of Craig *et al.*[35] are in good agreement with the present results.

TABLE 2. GEOMETRICAL STRUCTURES FOR VARIOUS STATES OF AROMATIC HYDROCARBONS

| Molecule | State | Bond length (Å) | | | | | |
|---|---|---|---|---|---|---|---|
| Napthalene | | 1—2 | 1—10 | 2—3 | 5—10 | | |
| | $^1B_{1u}$ | 1.399 | 1.421 | 1.430 | 1.457 | | |
| | $^1B_{2u}$ | 1.427 | 1.417 | 1.382 | 1.427 | | |
| | $^1A_g$[a] | 1.364 | 1.421 | 1.415 | 1.418 | | |
| Azulene | | 1—2 | 1—10 | 4—5 | 4—10 | 5—6 | 6—7 |
| | $^1B_2$ (1) | 1.394 | 1.438 | 1.439 | 1.416 | 1.385 | 1.416 |
| | $^1A_1$ (2) | 1.437 | 1.381 | 1.458 | 1.467 | 1.376 | 1.426 |
| | $^1A_1$ (1)[b] | 1.398 | 1.399 | 1.406 | 1.469 | 1.398 | 1.400 |
| Heptalene | | 1—2 | 1—12 | 2—3 | 6—12 | | |
| | $^1B_{3g}$ | 1.402 | 1.412 | 1.405 | 1.463 | | |

a) D. W. J. Cruikshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960).
b) A. W. Hanson, *Acta Crystallogr.*, **19**, 19 (1965).

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28) A. D. Lieher, *Z. Naturforsch.*, **A16**, 641 (1961).
29) J. N. Murrell and J. A. Pople, *Proc. Phys. Soc.*, **69A**, 245 (1956).
30) A. C. Albrecht, *J. Chem. Phys.*, **33**, 169 (1959).
31) B. Katz, M. Brith, B. Sharf, and J. Jortner, *ibid.*, **52**, 88 (1970).
32) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 1252, 4947 (1969).
33) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1969).
34) R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970).
35) D. P. Craig, J. M. Hollas, M. F. Redies, and S. C. Wait Jr., *Phil. Trans. Roy. Soc.*, **253**, 543 (1961).

The bond-length changes for excitation to the $^1B_{2u}$ state are calculated by Miller and Murrell,[16] who used Eq. (4) in the framework of the ASMO CI method. The results of these authors are in good agreement with the present ones. By using the predicted bond length changes, they have calculated the intensity of a vibrational progression, which gives a good agreement with the experimental results.

We can draw an important conclusion from the considerations stated above that, on excitation to both the states, there is no change in the symmetry of the molecule.

*Azulene.* It has been confirmed that azulene does not fluorescence from the lowest singlet ($^1B_2(1)$) state, but instead emits from the second excited singlet ($^1A_1(2)$).[36,37] From this fact, it can be expected that the geometry of the $^1B_2$ (1) state may be considerably deformed compared with that of the ground state ($^1A_1$ (1)). It seemed that it would be interesting to apply the present method to both the excited states.

The starting C-C bond distortions, which are assumed to be inplane, belonging to two irreducible representations, $a_1$ and $b_2$, of the full symmetry group, $C_{2v}$, are taken as the starting ones. Table 2 lists the calculated structures of the $^1B_2$ (1) and $^1A_1$ (2) states, along with the experimental structure of the ground state. For the $^1B_2$ (1) state, the predicted geometrical structure has the $C_{2v}$ symmetry. An analysis of the absorption spectra in the 7000 Å band indicated that azulene retains the $C_{2v}$ symmetry in the $^1B_2$ (1) state.[38] The central bond in the $^1B_2$ (1) state becomes drastically shorter than that in the ground state. In naphthalene, the changes in the bond lengths upon the $^1B_{1u} \leftarrow {}^1A_g$ excitation of naphthalene are comparatively small, so that vibrational frequencies of the upper state can be correlated with those of the ground state. However, a drastic change in the central bond-length of the $^1B_2$ (1) state in azulene would lead to a large variation in the vibrational frequencies of this state. In fact, Hunt and Ross[38] have reported that it is difficult to correlate the vibrational frequencies of the $^1B_2$ (1) state with those of the ground state.

For the $^1A_1$ (2) state, the predicted geometrical structure has the $C_{2v}$ molecular symmetry. McHugh and Ross[39] calculated the structure of the state based on Hückel molecular orbitals with configuration interaction. There are considerable differences between their results and ours in the bond length of the periphery of the molecule. While the C-C bond lengths in the periphery of the molecule are smoothed out in their results, there is a moderate double-bond fixation in the periphery in our results.

From a consideration of the above geometrical structures and the large electronic energy gap[40] between the $^1B_2$ (1) and $^1A_1$ (2) states, it is possible to give a qualitative explanation of the anomalous emission of azulene. The drastic geometrical change in the central bond between the ground and the $^1B_2(1)$ states will lead their two potential surfaces to intersect in the vicinity of the equilibrium point of the $^1B_2$ (1) state. As a result of the intersection, a direct relaxation to the ground state may be the dominant process in the electronic relaxation from the $^1B_2$ (1) state. On the other hand, the bond-length changes in the $^1A_1$ (2) state are moderate, so that the potential surface of the $^1A_1$ (2) state will not intersect with the other potential surfaces ($^1B_2$ (1), $^1A_1$ (1)) in the vicinity of the equilibrium point of the $^1A_1$ (2) state. The large energy gap between the $^1B_2$ (1) and $^1A_1$ (2) states (that is, the small Franck-Condon factors) will cause the nonradiative transition to the lower $^1B_2$ (1) state to be negligibly small. From the above considerations, it can be thought that azulene is emitted from the $^1A_1$ (2) state.

*Heptalene.* The SCF calculations show that the starting bond distortion, belonging to the $b_{3g}$ representation (that is, alternation), which converges into the geometry of the symmetry group, $C_{2h}$, in the ground state does not give rise to a symmetry reduction in the lowest excited state; that is, the lowest excited state exhibits no bond alternation. Furthermore, our calculations predict that bond distoritions belonging to $b_{1u}$ and $b_{2u}$ representations do not result in a symmetry reduction, either all the possible starting distortions produce a unique set of bond lengths belonging to the point group $D_{2h}$. The predicted bond lengths are summarized in Table 2.

The above results may easily be explained on the basis of the symmetry rule[32-34] from the energy-level arrangement in the heptalene molecule with the $D_{2h}$ symmetry. The excitation energies from the ground state to the $^1B_{3g}$, $^1B_{1u}$, and $^1B_{2u}$ states are 0.26, 2.68, and 3.37 eV respectively, and the $E_2$—$E_1$ and $E_3$—$E_1$ energy gaps are too large to give rise to pseudo-Jahn-Teller distortions in the lowest excited state.

The geometrical structure of the lowest excited state predicted above perhaps gives one of the reasons for the appearance of a long absorption tail in the long-wave length side of the first absorption band in heptalene.[4]

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[36] H. C. Longuet-Higgins and M. Beer, *J. Chem. Phys.*, **23**, 1390 (1955).

[37] G. Viswanath and M. Kasha, *ibid.*, **24**, 574 (1956).

[38] G. R. Hunt and I. G. Ross, *J. Mol. Spectrosc.*, **9**, 50 (1962).

[39] A. J. McHugh and I. G. Ross, *Aust. J. Chem.*, **21**, 3055 (1968).

[40] R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).