Excited-State Dipole Moments of Azulene and 3,5-Dimethylcyclopenta[*ef*]heptalene

Hiroyuki YAMAGUCHI, Teruki IKEDA,* and Hiroaki MAMETSUKA**

Department of Chemistry, Kumamoto University, Kumamoto 860

(Received November 6, 1975)

The dipole moments of the lower two singlet excited states of azulene (I) and 3,5-dimethyl derivative of cyclopenta[*ef*]heptalene (II) have been determined from the frequency shift of the absorption and emission spectra in various solvents. The direction of the excited-state dipole moments of molecules I and II is opposite to the direction of the ground-state dipole moments. The dipole moments of the two excited states of molecules I and II have been calculated by using the semi-empirical SCF-π-MO CI method. There is a general agreement between the theoretical results and the experimental results. This agreement shows that the polarization effect of the σ-electrons is almost identical in the ground and excited states of both molecules.

Many phenomena occurring in the electronically-excited states of molecules, such as photochemical reactions, are dependent on the changes in the electronic structures. Electronic excitation in molecules usually leads to a new electron density distribution and, consequently, to changes in dipole moments. Pariser[1] has calculated the dipole moments for the singlet excited states of azulene (I) and found that they increase in magnitude and reverse in sign with respect to the ground state. This behavior has been used to interpret the blue shift of the longest absorption band going from a nonpolar solvent to a polar solvent.

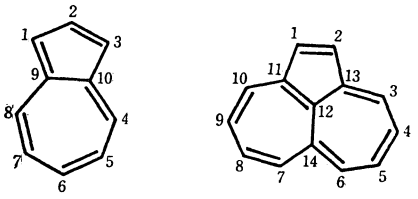

Fig. 1. Numbering of carbon atoms.

The change in dipole moment for the excited state of a polar molecule could be measured by observing the absorption and emission spectra, as suggested by Mataga *et al.*,[2] Lippert,[3] and McRae.[4] By using the equations developed by McRae, Robertson *et al.*[5] have experimentally investigated the values of the change in dipole moment for each of the singlet excited states of I. However, they have not obtained the definitive values of the change in dipole moment for each of the excited states of I.

The electronic structures of cyclopenta[*ef*]heptalene (II) have been of interest since Hafner and Schneider[7] prepared its dimethyl derivative in 1958—59. The electronic spectra of II may be considered to be well understood as a result of the work of Ali and Coulson,[8] Julg and Francois,[9] and others.[10] Recently, Eaton *et al.*[11] have shown that the observed emission in the case of 3,5-dimethylcyclopenta[*ef*]heptalene corresponds to anomalous fluorescence due to a transition from the second excited singlet, as in the case of I.

The purpose of our research was to determine experimentally the dipole moments in the lower two electronic excited states of I and the dimethyl derivative of II and to compare the experimental results with the theoretical results obtained by using the semi-empirical SCF-π-MO CI method.[12,13] It may be possible to use the results of such investigations to deepen our understanding of the electronic properties for excited states of nonbenzenoid aromatic hydrocarbons containing an azulene nucleus.

Experimental

Chemicals. Substance I was purchased from Tokyo Kasei Chemicals Co. The 3,5-dimethyl derivative of II was received from Professor K. Hafner. These Substances were carefully purified by recrystallization from hexane and by subsequent sublimation *in vacuo*. Both compounds were spectroscopically pure, from comparison with published spectra.[11] The solvents used were carefully purified according to the descriptions in Ref. 14. The purity of solvents was established by checking for emission before use.

Measurements. The dielectric constants were determined with a home-made resonance-method apparatus. A dielectric constant measurement cell with cylindrical platinum electrodes was used. The refractive indices were measured by means of a Pulfrich refractometer. The static dielectric constant (ε) and the refractive index (n) at the sodium D line of the solvents agreed with the values cited in Ref. 14. The densities of the solutions were measured by the use of a pycnometer for volatile liquids. The absorption spectra were obtained with a Cary Model 14 recording spectrophotometer equipped with a thermostated cell holder. The fluorescence spectra were taken with a Shimadzu RF-502 recording spectrophotometer equipped with a thermostated cell holder. The wave numbers of the emission-band maxima were determined from the emission spectra, as corrected for the spectral sensitivity of the instrument. The concentration of I and 3,5-dimethyl derivative of II was kept less than 10^{-4} mol/l for all solutions prepared, so that the system was free from any undersired concentration quenching. All measurements were made on deaerated samples at 20 °C.

Determination of Excited-state Dipole Moments. If we ignore any changes in the solute polarizability on excitation, the solvent shifts can be written as follows:[4] for the wave number of the band maxima of absorption spectra (ν_a)

$$\nu_a = K\left[\frac{n^2-1}{2n^2+1}\right] + C\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + \text{Const.}, \quad (1)$$

* Present address: Japan Spectroscopic Co. Ltd., Hachioji, Tokyo 192

** Present address: Research Institute of Industrial Science, Kyushu University, Fukuoka 812

and for the difference ($\Delta\nu_{af}$) between ν_a and the wave number ν_f of the corresponding fluorescence

$$\Delta\nu_{af} = C'\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + \text{Const.} \quad (2)$$

The constants C and C' are given by Eqs. 3 and 4, respectively,

$$C = \frac{2m_0(m_0-m_i)}{a^3hc} \quad (3)$$

$$C' = \frac{2(m_0-m_i)^2}{a^3hc} \quad (4)$$

where a is the cavity radius in Onsager's theory[6] of the reaction field, and m_0 and m_i are the dipole moments of the ground state and the ith excited state of the solute molecule, respectively.

For the hydrocarbon solvents, the second term of Eq. 1 is zero and the constant K is the least-squares slope of the curve of ν_a against $(n^2-1)/(2n^2+1)$. It remains to evaluate the constants C and C' of Eqs. 1 and 2 for the lower two transitions observed in a range of polar solvents. By using the constant K determined from the nonpolar solvents, the constants C and C' are chosen to give the best reproduction of the observed frequency shifts. From the constants C and C', the excited-state dipole moments, m_i, for each transition of I and the 3,5-dimethyl derivative of II can be calculated using Eqs. 3 and 4 and the dipole moments m_0 determined experimentally.

MO Calculation

The method of calculation used for obtaining the energetically most stable structure in a conjugate molecule is the SCF formalism of the Pariser-Parr-Pople semiempirical MO method,[15,16] taken together with the variable bond-length technique. The C–C bond distances and, correspondingly, the resonance and Coulomb repulsion integrals are allowed to vary with bond orders at each iteration until self-consistency is achieved. Bond lengths are correlated with bond orders by the aid of the following formula:[17]

$$r_{\mu\nu}\,(\text{Å}) = 1.520 - 0.186p_{\mu\nu} \quad (5)$$

The Coulomb repulsion integrals are evaluated using the Mataga-Nishimoto formula.[18] The resonance integral is assumed to be of exponential form $\beta=A\exp(-br)$, the value of exponent b being taken as 1.7Å^{-1}.[12]

As the starting geometries for iterative calculation, we take all the possible structures in which bond lengths are distorted so that the set of displacement vectors may form a basis of an irreducible representation of the full symmetry group of a molecule.

In order to discuss the geometrical structures of electronically excited states, the procedure described above is used, except for the use of a different value, 3.3 Å^{-1}, for exponent b in the exponential form of the resonance integral.[13] This value of b was determined so that the predicted fluorescence energy from the lowest singlet excited state ($^1B_{2u}$) in benzene may fit the experimental value.

In discussing the properties of excited states, configuration mixing of all the singly excited states is included.

Results and Discussion

For the hydrocarbon solvents, the constants K for the first electronic transitions of I and the dimethyl derivative of II were obtained from the least-squares slopes of the curves of ν_a against $(n^2-1)/(2n^2+1)$ (see Figs. 2 and 3). By using the constants K, the constants C for these transitions were chosen to reproduce the frequency shifts observed in a range of polar solvents (see Figs. 4 and 5). The observed $\Delta\nu_{af}$ for the second electronic transitions against $[(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)]$ rela-

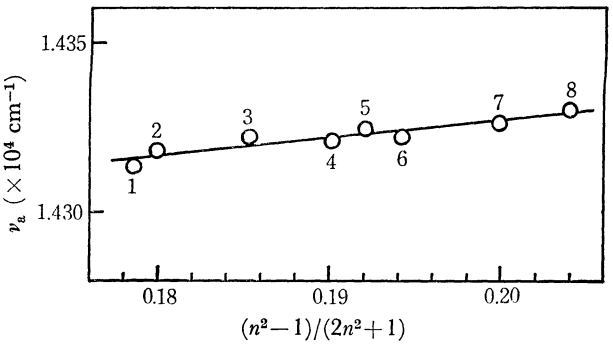

Fig. 2. The plot of ν_a against $(n^2-1)/(2n^2+1)$ for azulene. Here numbers denote the solvents as (1): isopentane, (2): pentane, (3): hexane, (4): heptane, (5): 2,2,4-trimethylpentane, (6): octane, (7): decane, (8): cyclohexane.

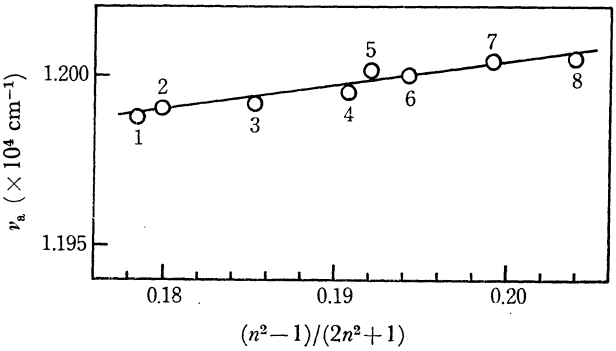

Fig. 3. The plot of ν_a against $(n^2-1)/(2n^2+1)$ for 3,5-dimethylcyclopenta[*ef*]heptalene. The numbers are the same as described in Fig. 2.

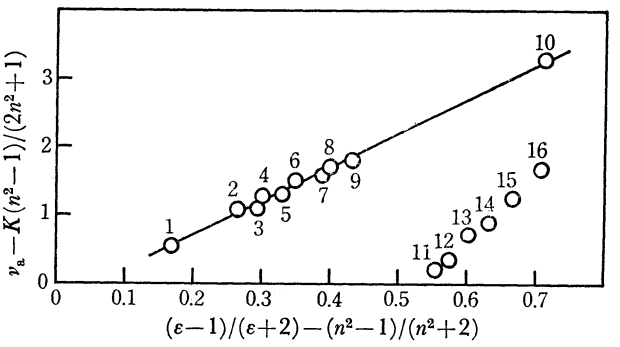

Fig. 4. The plot of $\nu_a - K(n^2-1)/(2n^2+1)$ against $(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)$ for azulene. Here numbers denote the solvents as (1): dibutyl ether, (2): diisopropyl ether, (3): chlorobenzene, (4): diethyl ether, (5): butyl acetate, (6): isobutyl acetate, (7): propyl acetate, (8): ethyl acetate, (9): methyl acetate, (10): acetonitrile, (11): pentyl alcohol, (12): isopentyl alcohol, (13): butyl alcohol, (14): isopropyl alcohol, (15): ethyl alcohol, (16): methyl alcohol.

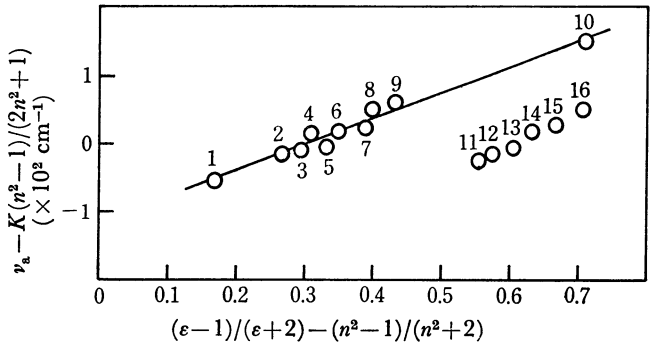

Fig. 5. The plot of $\nu_a - K(n^2-1)/(2n^2+1)$ against $(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)$ for 3,5-dimethylcyclopenta-[*ef*]heptalene. The numbers are the same as described in Fig. 4.

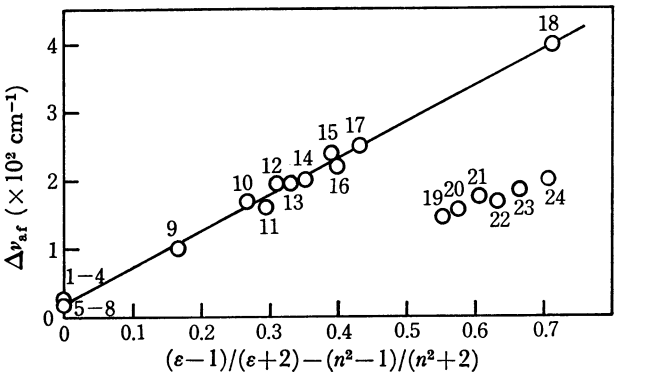

Fig. 6. The plot of $\Delta\nu_{af}$ against $(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)$ for azulene. Here numbers denote the solvents as (1): isopentane, (2): pentane, (3): hexane, (4): pentane, (5): 2,2,4-trimethylpentane, (6): octane, (7): decane, (8): cyclohexane, (9): dibutyl ether, (10): diisopropyl ether, (11): chlorobenzene, (12): diethyl ether, (13): butyl acetate, (14): isobutyl acetate, (15): propyl acetate, (16): ethyl acetate, (17): methyl acetate, (18): acetonitrile, (19): pentyl alcohol, (20): isopentyl alcohol, (21): butyl alcohol, (22): isopropyl alcohol, (23): ethyl alcohol, (24): methyl alcohol.

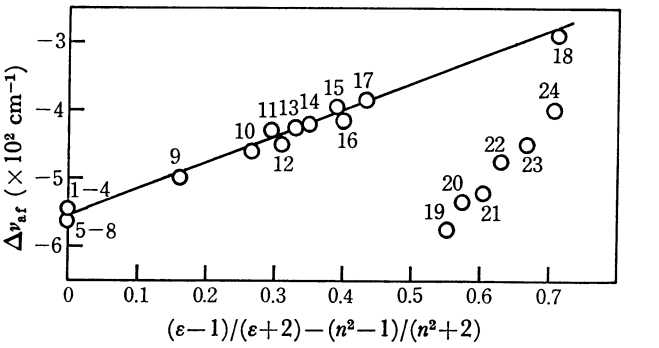

Fig. 7. The plot of $\Delta\nu_{af}$ against $(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)$ for 3,5-dimethylcyclopenta[*ef*]heptalene. The numbers are the same as described in Fig. 6.

tions are shown in Figs. 6 and 7. The straight lines in the figures were obtained by the least-squares method. The C' values for both molecules were determined by using the slopes of these lines. It was evident that the alcohol solvents had to be separated from the other polar solvents for Eqs. 1 and 2 to represent the frequency

Table 1. Constants of frequency shifts

Molecule	a (Å)[a]	Excited state	K (cm^{-1})	C (cm^{-1})	C' (cm^{-1})
I	3.65[b]	S_1	499	476	
		S_2			530
II	4.29[b]	S_1	509	399	
		S_2			351

a) Estimated from the apparent molal volume ϕ_v. The ϕ_v is defined by the relation: $\phi_v = 1000(d_2-d_1)/(m_1 d_2 d_{12}) + M_1/d_{12}$, where d_2 and d_{12} are the densities of the solvent and the solution of molality m_1 of the solute having molecular weight M_1, respectively.
b) Measured in cyclohexane.

Table 2. Excited-state dipole moments

Molecule	Dipole moment (D)[a]	
	S_1	S_2
I	−1.30	−0.60
II	−1.13	−0.37

a) The negative sign represents the fact that the direction of the dipole moment is opposite to that of the ground-state dipole moment.

shifts successfully. These different results in the alcohol solvents are attributed to hydrogen bonding and to the resulting erroneous value of the local field expressed in terms of the solvent dielectric constant and refractive index in Eqs. 1 and 2. Thus, the constants C and C' were determined from frequency shifts observed in nonalcoholic solvents; these values are listed in Table 1. From Eqs. 3 and 4, the excited-state dipole moments, m_i, for each transition were obtained by using the constants C and C', the experimentally-determined m_0, and the value of a estimated from the apparent molal volume. The results are given in Table 2. Using $a=3$ Å and $a=4$ Å, Robertson *et al.*[5] have obtained the dipole moments for each transition of I. The agreement with the present results in the case of $a=4$ Å is satisfactory, but in the case of $a=3$ Å is less satisfactory.

For molecules I and II, the starting bond distortions belonging to the irreducible representation, a_1 and b_2, of the full symmetry group, C_{2v}, are taken as the starting bond distortions for iterative calculation. It turns out that, in the ground state (S_0) and the two lower excited states (S_1 and S_2) of both molecules, all the starting bond distortions converge into a unique self-consistent set of electronic structures corresponding to C_{2v}. The dipole moments for S_0, S_1, and S_2 states of both molecules are calculated by using the theoretical electron densities and bond lengths. The calculated dipole moments for S_0, S_1, and S_2 of I are 2.82, −3.55, and −2.65 D, respectively, and those of II are 3.08, −3.27, and −1.30 D, respectively. The calculated dipole moment for S_0 of I is somewhat larger than the experimental value 1.0 D.[19] A similar difficulty has been met with in case of II: the calculated value is somewhat larger than the observed value 1.29 D for its 3,5-dimethyl-derivative.[20] Pariser[1] has shown that the disagreement between the theoretical and experimental values is attributable to the polarization effect of the σ-electrons. If the calculated dipole moment for S_0 of II is multiplied

by the correction factor, 1.0/2.82, which is derived from the fact that the calculated dipole moment for S_0 of I must agree with the experimental value, the dipole moment for II is predicted to be 1.09 D, in agreement with the experimental value. If the same procedure is carried out for the dipole moments of the excited states, the dipole moments for S_1 and S_2 states of molecules I and II become −1.26 and −0.94 and −1.16 and −0.46 D, respectively. Such obtained-theoretical values are in general agreement with the experimental values, except that the theoretical values of S_2 for I and II are slightly larger than the observed values. This discrepancy between the experimental moments and the theoretical moments indicates that the σ core is much more polarized in the second excited state than in the first. The methyl groups would not play any decisive role in the equilibrium structures of molecule II.[8]

Since the direction of the dipole moments of the excited states of I and II is opposite to the direction of the dipole moments of the ground states, it may be expected that in the excited states of both molecules the nucleophilic substitution occurs on the five-membered ring and the electrophilic substitution occurs on the seven-membered ring. Recently, Vink *et al.*[21] have shown that with molecule I a reaction starting from the excited state with a nucleophile leads to substitution at the same positions as an electrophilic substitution in the ground state.

One of the present authors (H. Y.) especially wishes to thank Professor T. Nakajima of Tohoku University for his fruitful discussions and to thank Professor K. Hafner of Technische Hochschule Darmstadt for the supply of 3,5-dimethylcyclopenta[*ef*]heptalene. The investigation was supported in part by a Scientific Research Grant from the Ministry of Education.

References

1) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).
2) N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **28**, 690 (1955).
3) E. Lippert, *Z. Naturforsch.*, **A10**, 541 (1955).
4) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).
5) W. W. Robertson, A. D. King, Jr., and O. E. Weigang, Jr., *J. Chem. Phys.*, **35**, 464 (1961).
6) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
7) K. Hafner and J. Schneider, *Angew. Chem.*, **70**, 702 (1958); *Justus Liebigs Ann. Chem.*, **624**, 37 (1959).
8) M. A. Ali and C. A. Coulson, *Mol. Phys.*, **4**, 65 (1961).
9) A. Julg and P. Francois, *Theor. Chim. Acta (Berl.)*, **7**, 101 (1966).
10) H. Yamaguchi, T. Terasaka, and T. Nakajima, *Theor. Chim. Acta (Berl.)*, **18**, 255 (1970).
11) D. F. Eaton, T. R. Evans, and P. A. Leermarkers, *Mol. Photochem.*, **1**, 347 (1969).
12) H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta (Berl.)*, **12**, 349 (1968).
13) Y. Fujimura, H. Yamaguchi, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **45**, 384 (1972).
14) J. A. Riddick and W. B. Bunger, "Organic Solvent," Vol. II, ed. by A. Weissberger, John Wiley & Sons, New York (1970).
15) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 446, 767 (1953).
16) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
17) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).
18) N. Mataga and K. Nishimoto, *Z. Phys. Chem.*, **13**, 140 (1957).
19) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).
20) K. Hafner and G. Schneider, *Justus Liebigs Ann. Chem.*, **672**, 194 (1964).
21) J. A. J. Vink, C. M. Lok, J. Cornelisse, and E. Havinga, *J. Chem. Soc., Chem. Commun.*, **1972**, 710.