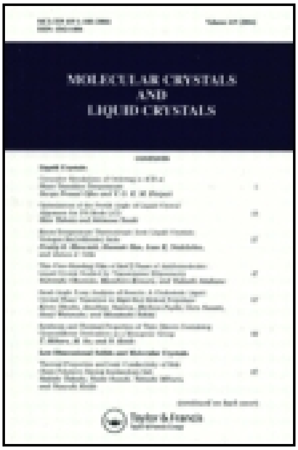

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Theoretical Studies of Hydronaphthyl Radicals Embedded in Naphthalene Single Crystal

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Optical transition energies of the 1- and 2-hydronaphthyl radicals have been calculated using the semi-empirical self-consistent-field method including the configuration interaction and the result has been used for the comparison of the ionization energy of the 1- and 2-hydronaphthyl radicals. It is found that transition energies calculated using the variable β method yield results which agree with experiments, not only for the first transition but also for the second and third transitions of the radicals and for the first transition of the radical ions. The calculation of the ionization potential is made using the Hush and Pople's relation and it was shown that the 1-hydronaphthyl radical has an ionization potential higher by 0.1 $\sim$ 0.2 eV than the 2-hydronaphthyl radical. The charge transfer energy from the radicals to the host molecules in naphthalene crystal is discussed.

I INTRODUCTION

Considerable attention has been paid to the cyclohexadieny-type radicals as an intermediate for the reaction products of aromatic hydrocarbon molecules. Recent studies of EPR,[1] ENDOR,[2,3] optical absorption[4–7] and luminescence[8] have revealed a number of interesting properties of these radicals embedded in the host molecular crystals. Among them we note in particular the experimental results (1) that the radicals substitute for the host molecule with little misorientation,[2] (2) the optical transition energies of 1- and 2-hydronaphthyl radicals in naphthalene and 9-cyclohexadienyl radical in anthracene have been determined and (3) that the optical absorption lines associated with the lowest electronic transition comprises both the

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vibrational progression and the lines whose transition dipole moment is oriented differently from that of the vibrational progression. These lines have been ascribed to charge transfer transition between the host molecules and the radicals.[4]

The charge transfer transition in pure aromatic crystals has been discussed by several authors even though direct experimental evidence has not yet been presented.[9] Nevertheless it appears certain that charge transfer transition plays an important role in the electronic processes of the elementary molecular solids. Since the cyclohexadienyl radicals provide charge transfer transitions for a few guests in the same host molecule, they appear to be interesting systems which may give further insight into charge transfer transitions in general. Thus it is of interest to study the properties of the molecular orbitals relevant to the charge transfer transition. Furthermore, the detrapping current of electrons from hydronaphthyl negative ions has been observed in naphthalene single crystal.[10, 11] For the detailed analysis of the origin of the electronic transition involved in the detrapping current, it is of interest to calculate the transition energy of hydronaphthyl positive and negative ions.

Semiempirical molecular orbital calculation has been developed first by Pariser and Parr[12] and by Pople.[13] Subsequently Nishimoto and Forster[14] and Kunii and Kuroda[15] have determined the parameters in the Hamiltonian for the closed shell system so that the optical transition energies agree with experimental results. It is useful to determine the parameters which can be used for the calculation of transition energies in hydrogen-add radicals to alternant hydrocarbon molecules. Calculation based on the Pariser-Parr-Pople method (PPP method) has been carried out by Shida and Hanazaki,[16] who obtained values of the transition energy and the oscillator strength of the 1- and 2-hydronaphthyl radicals, which agreed with the experimental results.[17,18] Yet the agreement for the higher energy transitions was relatively poor.

Useful information concerning the charge transfer transitions between the radical and host molecules is the ionization energy and the electron affinity of the radical. There is no unambiguous way of deriving these quantities out of the results of the MO calculation. A great deal of discussion, however, has been presented on the relation of the ionization energy and the electron affinities to the energies of the molecular orbitals. For the closed shell system, Koopmans[19, 20] has shown that the orbital energy of the highest occupied level can be equated to the negative of the ionization potential. This theorem has been extended by Hush and Pople[21] for the electron affinity: the orbital energy of the lowest occupied level may be equated to the negative of the electron affinity. Further extension of the approximation to the odd alternant hydrocarbon system has been made by these authors. They used the relation that the ionization potential of the radical is equal to the electron affinity of the positive ion and that the electron affinity of the radical is equal to the ionization potential of the negative ion. Using these relations Hush and Pople have shown that the summation of the ionization potential and the electron affinity should have the same value for even and odd alternant hydrocarbons, irrespective of the number of π-orbitals. Some semiempirical correction is necessary to derive the ionization potential and the electron affinity from the orbital energy.[14,22,23] Another approach to obtain the ionization potential and the electron affinity has been developed by Dewar and coworkers.[24] They calculated the difference in the total energy of a molecule and that of the ionized molecule. The parameters optimized for such calculations do not necessarily yield appropriate transition energies.

The purpose of the present paper is to make MO calculations of the 1- and 2-hydronaphthyl radicals and their positive and negative ions. The parameters of the Fock matrix for the hydronaphthyl radicals were chosen so that the calculated values of the transition energy agree with the experimental values. The calculated values of the orbital energies were used to discuss the ionization potential and the electron affinity. The energy of the charge transfer transition is also discussed.

II MO CALCULATION OF THE TRANSITION ENERGIES

1 Method of calculation

Calculation was made using the variable-β method developed by Nishimoto and Forster.[14] In this method the value of the bond energy is adjusted according to the bond orders at each step of the SCF process. The relation between the bond energy $\beta_{\mu\nu}$ and the bond order $P_{\mu\nu}$ is given by

$$\beta_{\mu\nu} = A_0 + A_1 p_{\mu\nu}, \tag{1}$$

where A_0 and A_1 are parameters given semi-empirically. The one-center repulsion integrals $\gamma_{\mu\mu}$ have been evaluated to be 11.13 eV. The evaluation of $\gamma_{\mu\nu}$ was made using the method employed by Mataga and Nishimoto,[25] with the bond length of 1.395 Å. The value of A_0, 1.9 eV, obtained by Nishimoto and Forster, was used for the calculation of the naphthalene molecule and its ions. For the 1-hydronaphthyl radical the values of A_0 was optimized to yield the transition energies in good agreement with experimental data. The value of A_1 optimized for naphthalene was used also for the radicals. The core energy of the carbon $2p\pi$ orbital was assumed to be -11.16 eV.

In order to take hyperconjugation into consideration, we used two models. In the first model (referred to as model A), it was assumed that the hyperconjugated H_2^- forms a pseudo-π orbital. The core energy and the one center coulomb integral of the pseudo-π orbital was taken to be -9.42 eV and 10.12 eV, respectively, according to Hanazaki and Nagakura.[26] The bond energy between the carbon $2p\pi$ orbital and the pseudo-π orbital has been also evaluated to be 5.9 eV.

In the other model (referred to as model B) for the hydronaphthyl radical, it was simply assumed that the hyperconjugated carbon $2p\pi$ orbital is missing.[27] Namely the hydronaphthyl radicals were assumed to be composed of 9 carbon $2p\pi$ orbitals. It turns out that the transition energies calculated with the two methods do not differ appreciably. Moreover, as far as the 9 carbon $2p\pi$ orbitals which are included in two models are concerned, the bond orders and the elements of the Fock matrix have nearly the same value.

The calculation was made for both the neutral radicals and hydronaphthyl ions. In order to confirm that the parameters optimized for the molecule can be used for the ions, the calculation for naphthalene molecules and ions were also made. After getting the SCF eigenvalues and matrices, the transition energies were calculated by taking the configuration interaction into account. The methods of CI calculation for the closed shell developed by Pople[13] and for the open shell developed by Longuet-Higgins and Pople[28] were used. The details of the CI calculation for the open shell have been described by Wasilewski.[29]

2 Results of the calculation

The transition energies of naphthalene and its positive and negative ions were calculated. The results are compared with experimental values[30,31] in Table I. Good agreement between the theory and experiments was obtained for the naphthalene molecule. The calculated result for the naphthalene ion is slightly smaller, but the agreement can be regarded as reasonable.

A calculation was made for the radical with the same parameters employed for the calculation of the naphthalene molecule. The result disagrees with the experimental values. The lowest transition energy of the 1-hydronaphthyl radical calculated using these parameters was 1.64 eV and 1.67 eV for models A and B, respectively, whereas the experimental value is 2.31 eV.[17] The β-parameter was modified so that the calculated result yields values close to the experimental data. In order to avoid the complexity introduced by adjusting many parameters, we changed only the parameter A_0. It turns out that an increase of A_0 to 2.55 eV gives almost satisfactory results for most of the optical absorption transition energies for 1- and 2-hydronaphthyl radicals (abbreviated as HNR, hereafter) as shown in Table II.

TABLE I

Electronic transition energies in naphthalene molecule and naphthalene negative ion. The symmetry of the transition is shown in parenthesis

Substance	Transition energy (eV)	
	calculated	experimental[a]
naphthalene	3.90 ($^1B_{3u}$)	3.97
	4.40 ($^1B_{2u}$)	4.51
	5.46 ($^1A_{1g}$)	—
	5.53 ($^1B_{3u}$)	5.63
Naphthalene mononegative ion	0.76 ($^2B_{3g}$)	0.97
	1.46 ($^2B_{1u}$)	1.52
	1.94 (^2A_u)	—
	2.72 ($^2B_{2u}$)	2.67
	3.01 ($^2B_{3u}$)	3.39
	3.84 ($^2B_{1u}$)	3.83

[a] The results for naphthalene were taken from J. N. Murrel (Ref. 30) and those for naphthalene mononegative ion from P. Bulk, S. Brujin and G. Hoijtink (Ref. 31).

TABLE II

Electronic transition energies in 1- and 2-hydronaphthyl radicals

Substance	Transition energy (eV)		
	calculated		
	present work[a]	Shida and Hanazaki[b]	Experimental[c]
1-Hydronaphthyl radical	2.32 (2.39)	2.40	2.31
	3.19 (3.54)	2.98	3.26
	3.35 (3.72)	3.68	3.68
2-Hydronaphthyl radical	1.95 (2.20)	2.09	1.96
	2.91 (3.06)	3.13	—
	3.51 (3.71)	3.35	3.54

[a] Numbers in parentheses are calculated using the 9-2$p\pi$-orbital model (see text).

[b] T. Shida and I. Hanazaki (Ref. 16).

[c] T. Okubo, N. Itoh, and T. Suita (Ref. 17).

In Table II, the results obtained using model B are shown in parentheses. Results by Hanazaki are also shown. It is of interest to note that the results calculated using model B agree with those calculated using model A. It follows that the π-electron is essentially confined out of the CH_2 group. Since this 9–$2p\pi$-orbitals model is free from a certain degree of uncertainty introduced by using the pseudo-π-orbital, this model was also used in the further calculation.

A few comments are made on the effect of changing other parameters than A. The β-parameter between the pseudo-π and the carbon $2p\pi$-orbitals has larger influence on the higher transition energy. It turns out that the value adopted in the present calculation is most appropriate. The γ values between carbon $2p$-orbitals were also changed. These values are found to cause similar effects as the β values but are less sensitive to the transition energies than the β values. No modification was made of the core energy, which was discussed by Wasilewski.[32] This perhaps yields an effect similar to changing β. It is not very appropriate to give any physical significance to the best-fit parameters for the radical. It appears that the improved parameter compromises the change in the correlation effect and in the core energy of the carbon $2p\pi$-orbital upon the addition of a pseudo-π-orbital to the naphthalene ring.

The electronic transition energies in the radical ions are also calculated. The results are compared with experiments[27] in Table III. The result of the calculation of the higher energy transition is significantly larger than the experimental results, perhaps because of the choice of too large β-parameters. The agreement for the lowest transition may be regarded as reasonable.

III CALCULATION OF THE IONIZATION ENERGY AND ELECTRON AFFINITY

1 Method of calculation

According to Hush and Pople,[21] within the framework of the assumption that the molecular orbitals of electrons in the molecule are unaltered when an electron is removed or added, the summation of the ionization potential I and the electron affinity A is given by

$$I + A = -(U + \tfrac{1}{2}\gamma_{11}), \tag{2}$$

where U and γ_{11} are the core energy and the one center coulomb integral of the carbon $2p\pi$ orbital. Relation (2) holds for both even and odd alternant hydrocarbon molecules. For the odd alternant hydrocarbon molecule Hush

TABLE III

Electronic transition energies in 1- and 2-hydronaphthyl ions

Substance	Transition energy (eV)		
	calculated		
	present work[a]	Hanazaki and Nagakura[b]	experimental[c]
1-Hydronaphthyl positive ion	3.14 (3.17) 3.69 (3.61) 5.64 (5.40)	3.17 3.45 5.18	3.02 3.18 4.43
1-Hydronaphthyl negative ion	3.01 (3.17) 3.49 (3.61) 5.49 (5.40)	— — —	— — —
2-Hydronaphthyl positive ion	2.73 (2.54) 4.48 (4.43) 4.77 (4.67)	— — —	— — —
2-Hydronaphthyl negative ion	2.42 (2.54) 4.40 (4.43) 4.49 (4.67)	— — —	— — —

[a] Numbers in parentheses are calculated using the 9-$2p\pi$-orbital model (see text).

[b] I. Hanazaki and S. Nagakura (Ref. 26).

[c] G. Dallinga, A. E. L. Mackor and A. A. Verrijinstuart (Ref. 34).

and Pople have obtained the relation:

$$I - A = \frac{1}{2} \sum_{\mu\nu} c_{N\mu}^2 c_{N\nu}^2 \gamma_{\mu\nu}, \tag{3}$$

where $c_{N\mu}$'s are the components of the eigen vector for the half-occupied orbital.

It has been pointed out that the absolute value of $I + A$ calculated using Eq. (2) is an overestimation. This difficulty has been avoided using the semi-empirical relation[23] that

$$I + A \approx 8.18 \text{ eV}. \tag{4}$$

Thus Eqs. (3) and (4) were used to derive the ionization potential and electron affinity of the hydronaphthyl radicals. The presence of hyperconjugation does not assure the validity of Eq. (4) for the hydronaphthyl radicals. In view of the good agreement between the transition energies calculated using models A and B, however, the use of Eqs. (3) and (4) for estimating the ionization potential and the electron affinity of the hydronaphthyl radical may be appropriate for a discussion of the qualitative features of these quantities, such as the dependence of the ionization potential on the position of the hyperconjugation.

Youkin *et al.*[23] have obtained another empirical relation concerning the ionization potential and the electron affinity. They correlated these quantities with the lowest allowed transition energy $\hbar\omega$ as follows:

$$A = -0.8\hbar\omega + 3.43 \text{ eV}, \tag{5}$$

and

$$I = +0.48\hbar\omega + 4.75 \text{ eV}. \tag{6}$$

These relations were also used for the hydronaphthyl radical.

2 Results of the calculation

The results of the calculation of the ionization potential and the electron affinity for the 1- and 2-HNR are shown in Table IV. As described in the last section, the quantitative accuracy of the results is not adequate. It is to be noted, however, that the ionization energy of the 1-HNR is larger than that of the 2-HNR by 0.1 eV–0.2 eV. This difference arises from the difference in the electron-interaction energy in the 1- and 2-HNR.

TABLE IV

Calculated ionization potential and electron affinity of the hydronaphthyl radicals. Numbers in the parentheses were obtained from the empirical relation of the ionization potential and the electron affinity with the lowest electronic transition energy obtained by Younkin, *et al.*[23] (Eqs. (5) and (6)).

Radical	Ionization potential (eV)	Electron affinity
1-Hydronaphthyl radical	6.3 (5.9)	1.9 (2.3)
2-Hydronaphthyl radical	6.2 (5.7)	2.0 (2.5)

IV DISCUSSION

The results of the present calculation give a reasonable account of the transition energies in the 1- and 2-HNR. It is shown that the lowest electronic transition consists of mainly the transition of an electron at the half-occupied MO to the lowest unoccupied MO and the transition of an electron at the highest occupied MO to the half-filled MO. The sign of the configuration interactions is such that the two transitions are cancelled. Since the experimental results of the transition energy to the higher excited states of the 1-HNR have been determined by means of excitation spectroscopy of the luminescence line, the results may be regarded as competent to the theoretical analysis. In view of the good agreement between the transition energies obtained from absorption and luminescence measurements for the 1-HNR, the transition energies of 2-HNR, which have been obtained only through optical absorption measurements, may be as accurate as those of the 1-HNR. Thus the good agreement between the theoretical and experimental results assure the accuracy of the results of the calculation of the MO energy levels.

The agreement between the experimental and theoretical transition energies especially for the higher transitions for the hydronaphthyl ions is poor. It has been already pointed out that the MO parameters which yield good results for a molecule do not give necessarily appropriate MO orbital energies for the ions.[32] This is perhaps because of the effect of the change in correlation energy due to the addition or the removal of an electron. Thus the usage of the parameters suggested in the present work should be limited only for radicals and for the lowest transition energy of their ions.

The difference between the calculated values of the ionization energies and the electron affinities of the 1- and 2-HNR arises from the difference in the electron interaction energy and can be qualitatively expected in view of the difference in the electron distributions in the 1- and 2-HNR. In this connection it is of interest to discuss the difference in the energetics of the charge transfer transitions involving the 1- and 2-HNR. Nakagawa and Itoh[45] have shown that the charge transfer transition energies E are related to the distance of the charge transfer:

$$E = E_{\infty} - \frac{e^2}{\varepsilon r}, \tag{7}$$

where e is the electronic charge and ε is the dielectric constant. E_{∞} may be deduced in terms of the ionization potential I and of the electron affinity A of the host molecule and the radical:

$$E_{\infty}^{1} = I_H - A_R + E_P^1, \tag{8}$$

for the charge transfer transition from the host to the radical, and

$$E_{\infty}^{2} = I_R - A_H + E_P^2, \tag{9}$$

for the charge transfer transition from the radical to the host, where suffix H and R denote the host molecule and the radical, respectively, and the E_P's are the polarization energies. According to the relation,

$$I_H + A_H = I_R + A_R,$$

and assuming that $E_P^1 = E_P^2$, we obtain

$$E_{\infty}^{1} = E_{\infty}^{2} \equiv E_{\infty}. \tag{10}$$

TABLE V

Derivation of the ionization potential and the electron affinity of the hydronaphthyl radicals from the results of the charge transfer transition between the radicals and the host molecules

Radical	Charge transfer energy (eV)	Electron affinity (eV) of naphthalene molecules[a]	Polarization energy[b](eV)	Ionization energy (eV) of radical	Electron affinity of radical
	E_∞	A_H	E_P	I_R	A_R
1-Hydronaphthyl radical	2.73	-0.06	-2.86	5.53	2.65
2-Hydronaphthyl radical	2.32			5.12	3.06

[a] R. S. Becker and E. Chen (Ref. 22).
[b] D. M. Hanson (Ref. 9).

Therefore the values of E_∞ obtained from the experiments may be analyzed using either Eq. (8) or (9). The result of the analysis is shown in Table V.

It is worthwhile to discuss the value of E_P. The value of the polarization energy induced by putting an electron in the lattice has been considered to be equal to the difference between the molecular ionization potential and the crystal photoemission threshold.[9] Using the experimental values for the molecular ionization potential[22] and the photoemission threshold of the naphthalene crystal, the polarization energy induced by a negative charge has been obtained to be -1.43 eV.[33] The radical-to-molecule charge transfer transition at infinite separation may induce both an ionized radical and a negatively charged molecule. If the polarization energy induced by a positive unit charge in a radical is assumed to be the same as that induced by a unit negative charge, E_P^2 becomes -2.86 eV. Similarly, E_P^1 may be assumed to be -2.86 eV. These values were used to derive I_R and A_R from the values of E_∞ for 1- and 2-hydronaphthyl radicals as shown in Table V.

According to Eq. (8) or (9), the difference in E_∞ for the 1- and 2-HNR should be ascribed to the difference in I_R for the 1- and 2-HNR if the polarization energy for 1- and 2-HNR is the same. The difference in I_R obtained from E_∞ is 0.4 eV, while the difference in calculated ionization energies is only 0.1 eV or 0.2 eV, depending on the method of calculation. Because of the several unjustified assumptions used in the calculation, the result of the calculation should be understood to be of qualitative implication. The calculated values of I_R differ from the values of I_R estimated from E_∞ by about 15%. A part of the cause of this discrepancy may be that the absolute value of the polarization energy for the radical is underestimated. It is also interesting to note that $E_{\infty}^{1} \approx E_{\infty}^{2}$ as shown in Eq. (10). This relation suggests that the charge transfer transitions from the valence band to the half-occupied MO and from the half-occupied MO to the conduction band have nearly the same energy. It has been already suggested that the coincidence of two transition energies causes the configurational mixing of two transitions and makes the lattice coupling small.[4]

It is also of interest to see whether an electron or a hole trapped by the radical is stable. Experimentally the detrapping photocurrent of an electron trapped by the 1-HNR has been observed.[10] It has been shown that the detrapping current forms a broad peak ranging from 1.0 eV to 2.4 eV. The broad peak has been suggested to be due to the transition of the electron trapped by the radical to the vibronic states of the conduction band. According to this suggestion the energy difference between the bottom of the conduction band and the highest occupied orbital of the 1-hydronaphthyl negative ion is 1.0 eV. This energy difference may be E_{∞} minus the electron affinity of the 1-HNR. The energy difference can be estimated to be 0.8 eV using the calculated value of the electron affinity and to be 0.1 eV using the value of the electron affinity derived from experimental E_{∞}. Thus it appears again that the absolute value of the polarization energy for the radical may be larger than 1.43 eV.

As described above, the molecular orbital calculation can account for the experimental results of not only the electronic transition in the radical but also the correlation between the radical states and the host states. It is hoped that the 1-HNR provides a rather simple example of a deep trap (like an F center in alkali halides) in molecular crystals. The location of the half-occupied level at the middle of the forbidden gap appears to offer several interesting characters. The molecular orbital calculation for a cluster of molecules including a radical may provide further information on the charge transfer transition.

The calculation was made using FACOM in the Computation Center of Nagoya University.

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