The Similarity between the π,π^* Absorption Spectra of 1-Indenone and 1,2-Naphthoquinone

Akira KUBOYAMA* and Hitoshi MATSUMOTO†

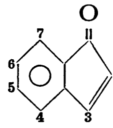
National Chemical Laboratory for Industry, Shibuya-ku, Tokyo 151

†*School of Pharmacy, Tokushima University of Arts and Science, Yamashiro-cho, Tokushima 770*

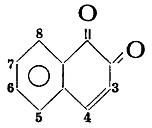
(Received October 6, 1978)

The π,π^* absorption spectrum and its solvent effect of 2-methyl-1-indenone have been found to be similar to those of 1,2-naphthoquinone. This fact is discussed on the basis of the results calculated using the P-P-P method. The similarity of the calculated π-electronic structures in the low-energy π,π^* singlet states between 1-indenone and 1,2-naphthoquinone is not so good as that between fluorenone and 9,10-phenanthrenequinone.

Recently, we have found a similarity between the π,π^* absorption spectra of fluorenone and 9,10-phenanthrenequinone.[1] This similarity is thought to be due to a similarity between the π-electronic systems of the two compounds, on the assumption that the carbonyl group of fluorenone and the α-dicarbonyl group of phenanthrenequinone are equivalent. According to this idea, the above similarity has been reasonably explained on the basis of the results calculated using the P-P-P method. Such a similarity may be expected to exist between 1-indenone and 1,2-naphthoquinone. Heretofore, scarcely nothing has been known about the π,π^* absorption spectra of 1-indenone and its alkyl derivatives.[2] In this work, we have obtained the π,π^* absorption spectra of relatively stable 2-methyl-1-indenone in solutions and have studied the similarity between the π,π^* absorption spectra of 2-methyl-1-indenone and 1,2-naphthoquinone.[3,4]



1-Indenone



1,2-Naphthoquinone

Experimental

Measurements. The absorption spectra of 2-methyl-1-indenone and 1,2-naphthoquinone were measured with a Hitachi 200-20 and a Cary 14 spectrophotometer respectively. Hexane, heptane, benzene, and methanol were used as the solvents.

Materials. According to an earlier article,[5] 2-methyl-1-indenone was synthesized from *trans*-α-methylcinnamic acid by UV inside irradiation (Hg 253.7 nm line) in the ethanol solution,[6,7] and then by a ring-closure reaction in sulfuric acid. The product thus obtained was purified by vacuum distillation and then by recrystallization from a diluted aqueous solution of ethanol (mp 46.5—47.0 °C). It began to decompose four days after its preparation. The 1,2-naphthoquinone was the same as that used in a previous work.[4] The solvents used were of a commercially available spectrograde.

Results. The absorption spectra obtained and the numerical data about them are shown in Fig. 1 and Table 1 respectively.

Calculations

Method. In the calculations using the P-P-P method for 1-indenone, the values of the core and electronic repulsion integrals were the same as those used for 1,2-naphthoquinone in the previous work.[4] As for the effect of alkyl-group substitution, the core Coulomb integral of the substituted carbon atoms was taken as −9.00 eV, considering only the inductive effect, as in the previous work. In the calculations, all the singly-excited configurations were included. The molecular dimensions[8] of 1-indenone assumed are shown in Fig. 2.

Results. The calculated results are shown in Tables 2 and 3 and in Fig. 3. In Table 2, the first column

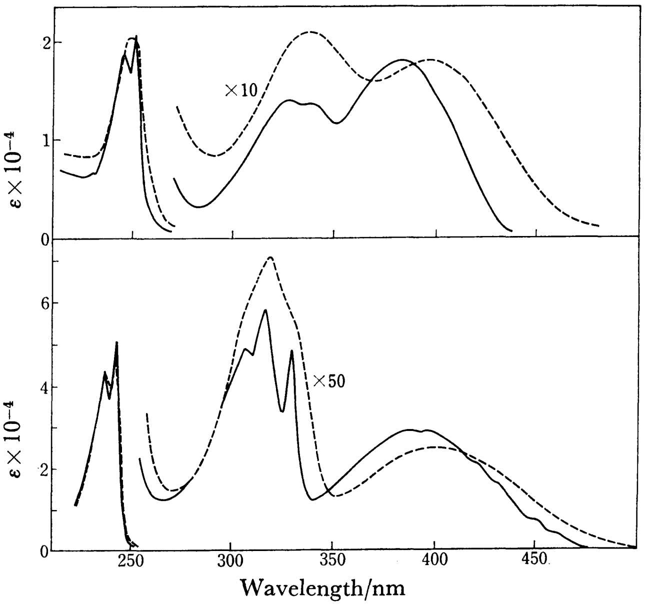


Fig. 1. Absorption spectra of 2-methyl-1-indenone and 1,2-naphthoquinone in solutions.
Lower curves: 2-methyl-1-indenone (——: hexane, ----: methanol). Upper curves: 1,2-naphthoquinone (——: heptane, ----: methanol). ε denotes molar absorption coefficient/10^{-3} mol cm^{-2}. In the heptane solution of 1,2-naphthoquinine, the scale of the ordinate is arbitrary.

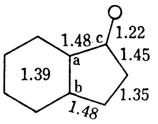


Fig. 2. Molecular dimension of 1-indenone (A).
a: 108.5°, b: 108.5°, c: 127.5°.

Table 1. Wavelengths (λ) and molar absorption coefficients (ε) of the absorption maxima and the oscillator strengths (f) of the absorption bands

Solvent	λ / nm	ε / 10^{-3} mol cm^{-2}	f	Band
(1) 2-Methyl-1-indenone				
Hexane	396	565	0.013	I
	387.5	574		
	329.5	975	0.020	II
	316	1100		
	306	1000		
	242	50300	0.56	III
	236	43800		
Benzene	397	558		I
	331	929		II
	319	1265		
Methanol	401.5	492	0.012	I
	318.5	1385	0.027	II
	242	47400	0.56	III
	237	42700		
(2) 1,2-Naphthoquinone				
Heptane	382			I
	337.5			II
	326			
	251			III
	245			
Methanol	396	1710	0.034	I
	337	1990	0.050	II
	249	19200	0.36	III

Table 2. Calculated results

No.	1-Indenone		1,2-Naphthoquinone[4]		Band
	E / eV	f	E / eV	f	
1	4.16	0.043	4.32	0.077	I
2	4.39	0.023	4.49	0.091	II
3	5.45	0.655	5.29	0.587	III

Table 3. Calculated results for the configurational mixings[a)]

(1) 1-Indenone				
State	(5→6)	(4→6)	(5→7)	(4→7)
No. 1	0.872	0.013	0.029	0.044
No. 2	0.003	0.603	0.150	0.085
No. 3	0.083	0.337	0.143	0.239
(2) 1,2-Naphthoquinone				
State	(6→7)	(5→7)	(6→8)	(5→8)
No. 1	0.481	0.175	0.169	0.030
No. 2	0.464	0.277	0.133	0.000
No. 3	0.015	0.488	0.247	0.108

a) (i→j) denotes the electron configuration due to the one-electron promotion of i-MO→j-MO. Each configuration of 1-indenone in the table corresponds to that of 1,2-naphthoquinone directly below it.

denotes the numbering of the states in the order of increasing excitation energies (calculated).

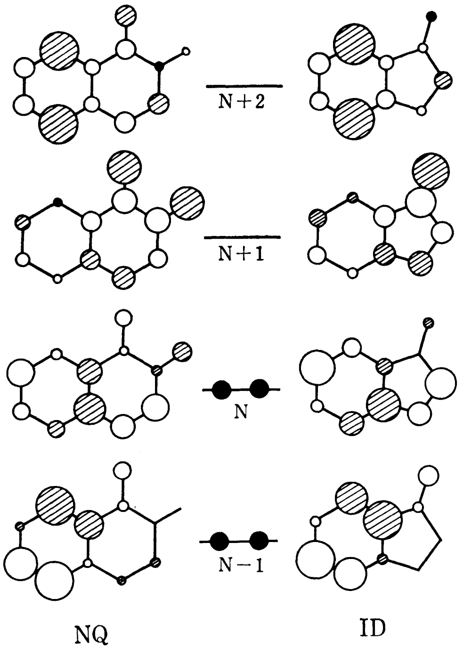


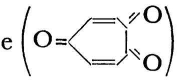
Fig. 3. π-Molecular orbitals of 1-indenone and 1,2-naphthoquinone. The N and N+1 MO energy levels denote the highest occupied and lowest vacant levels respectively. The figures on both sides denote the π-electron distributions and the signs of coefficients of the 2pπ AO's in the corresponding MO's.

Discussion

As may be seen in Fig. 2, both 2-methyl-1-indenone and 1,2-naphthoquinone have two weak π,π^* bands at the longer wavelengths and a strong π,π^* band at the shorter wavelengths. These π,π^* bands are denoted as Bands I—III, as is shown in Table 1. Bands I—III of 2-methyl-1-indenone[9)] are located close to the corresponding bands of 1,2-naphthoquinone. In the hexane solution of 2-methyl-1-indenone, Band II has a far sharper structure than Band I. On the other hand, in the heptane solution of 1,2-naphthoquinone, while Band II has a structure, Band I has no structure at all. In the solvent effects of Bands I—III, the following two similarities are found between the two compounds. First, Band I in the methanol solutions, where the hydrogen bond may be formed between the solute and solvent molecules, lies at longer wavelengths than that in the cyclohexane solutions, while Bands II and III lie at almost the same position in both solutions. Second, the intensity ratio of Band I to Band II in the methanol solutions is similar than that in the cyclohexane solutions. The π,π^* absorption spectrum and its solvent effect of 1-indenone are thought to be similar to those of 2-methyl-1-indenone. Therefore, the above discussion may also equally hold good between the π,π^* absorption spectra of 1-indenone and 1,2-naphthoquinone.

On the other hand, in Table 2, the calculated results for the low-energy π,π^* singlet states of 1-indenone and 1,2-naphthoquinone are similar and Bands I—III are favorably assigned on the basis of them. The assignment of Band I of 1,2-naphthoquinone in Table 2 was supported by the consistency between the experimental and calculated results for the energy shift of Band I through alkyl-group substitutions in the previous work.[4] As may be seen in Fig. 3, the corresponding highest occupied and lowest vacant π-MO's of the two compounds are similar if we assume that the carbonyl group of 1-indenone and the α-dicarbonyl group of 1,2-naphthoquinone are equivalent, as in the case of the pair of fluorenone and 9,10-phenanthrenequinone. However, the similarity between the π-MO's of 1-indenone and 1,2-naphthoquinone is less than that between the above pair. This may be due to the poor molecular symmetry of 1-indenone and 1,2-naphthoquinone. In a previous work,[1] a close similarity of the configurational mixings in the low-energy π,π^* singlet states was found between fluorenone and 9,10-phenanthrenequinone. On the other hand, in Table 3, although the configurational mixings in 1-indenone and 1,2-naphthoquinone are similar in the No. 3 state, those in the Nos. 1 and 2 states are not so similar. Therefore, the similarity between the π,π^* absorption spectra of 1-indenone and 1,2-naphthoquinone can not be so clearly explained as that between fluorenone and 9,10-phenanthrenequinone. The above-mentioned dissimilarity between the configurational mixings in the two compounds is puzzling in view of the similarity between their π-MO's.

As for the change in the calculated excitation energy of the No. 1 state of 1-indenone through an alkyl-group substitution, it is found that the energy decrease ($\Delta E = -0.094$ eV) for the 2-position is the largest and that there is an energy increase ($\Delta E = 0.014$ eV) for the 5-position. The 2- and 5-positions in 1-indenone are the positions α and para to the carbonyl group respectively. In 1,2-naphthoquinone, similar calculated results have been obtained in a previous work.[4] Therefore, these findings may support the assignment of Band I of 1-indenone to the transition, the No. 1 state←ground state, in Table 2. After all, it may be concluded that the similarity between the calculated π-electronic structures in the low-energy π,π^* singlet states of 1-indenone and 1,2-naphthoquinone is not so good as that between fluorenone and 9,10-phenanthrenequinone.

Recently, data about the π,π^* absorption spectrum of p-tropoquinone  have been obtained by Ito *et al.*[11] which are similar to those of p-benzoquinone.[12] This similarity can be clearly explained, on the basis of the calculated results, much as that between fluorenone and 9,10-phenanthrenequinone.

The authors are grateful to Drs. Hideaki Tanaka and Koichi Honda of this laboratory for their helpful advice about the photochemical *trans*→*cis* isomerization of α-methylcinnamic acid in the preparation of 2-methyl-1-indenone.

References

1) A. Kuboyama, *Chem. Phys. Lett.*, **41**, 544 (1976); *Tokyo Kogyo Shikensho Hokoku*, **73**, 348 (1978).

2) E. D. Bergmann, A. Heller, and H. Weiler-Feilchenfeld, *Bull. Soc. Chim. Fr.*, **1959**, 635.

3) S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954); *Nippon Kagaku Zasshi*, **74**, 97 (1953).

4) A. Kuboyama and H. Arano, *Bull. Chem. Soc. Jpn.*, **49**, 1401 (1976); *Tokyo Kogyo Shikensho Hokoku*, **72**, 170 (1977).

5) R. Stoermer and G. Voht, *Justus Liebigs Ann. Chem.*, **409**, 55 (1915).

6) H. Tanaka and K. Honda, private communication.

7) Y. Urushibara and M. Hirota, *Nippon Kagaku Zasshi*, **82**, 354 (1961).

8) H. R. Luss and D. L. Smith, *Acta Crystallogr., Sect. B*, **28**, 884 (1872).

9) In 2-methyl-1-indenone, the n,π^* band may be hidden under Band I, as in the case of fluorenone.[10] In Fig. 1, the fine structures on Band I in the cyclohexane solution may be partly due to this n,π^* band.

10) A. Kuboyama, *Bull. Chem. Soc. Jpn.*, **37**, 1540 (1964).

11) S. Ito, Y. Shoji, H. Takeshita, M. Hirama, and K. Takahashi, *Tetrahedron Lett.*, **1975**, 1075.

12) W. Flaig, J.-C. Salfeld, and E. Baume, *Justus Liebigs Ann. Chem.*, **618**, 117 (1958); A. Kuboyama, S. Matsuzaki, M. Takagi, and H. Arano, *Bull. Chem. Soc. Jpn.*, **47**, 1604 (1974); *Tokyo Kogyo Shikensho Hokoku*, **71**, 180 (1976).