Theoret. chim. Acta (Berl.) 9, 51—56 (1967)

SCF MO CI Calculations on the Electronic Spectra of Fluorenone and Related Compounds

Haruo Kuroda, and Tosiyasu L. Kunii*

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo, Japan

Received July 17, 1967

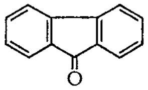
The electronic spectra of fluorenone, 9-iminofluorene and 9-ethylidenefluorene are studied by means of the SCF MO CI calculation. It is shown that the lowest singlet-singlet transition of fluorenone located at 380 mμ can be assigned to a $\pi - \pi^*$ transition (${}^1B_2 \leftarrow {}^1A_1$). The nature and location of the lowest triplet state are also discussed.

Die Elektronenspektren von Fluorenon, 9-Iminofluoren und 9-Äthylidenfluoren werden mit Hilfe der SCF MO CI-Methode studiert. Es wird gezeigt, daß der niedrigste Sigulett-Singulett-Übergang in Fluorenon bei 380 mμ einem $\pi \to \pi^*$-Übergang (${}^1B_2 \to {}^1A_1$) zugeordnet werden kann. Die Natur und Lage des niedrigsten Triplett-Übergangs werden ebenfalls studiert.

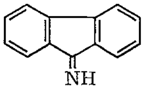
Les spectres électroniques de la fluorénone, du 9 iminofluorène et du 9-éthylidène fluorène sont étudiés à l'aide de calculs SCF-MO-CI. On montre que la plus basse transition singulet-singulet de la fluorénone, située à 380 mμ, peut être attribuée à une transition $\pi \to \pi^*$ (${}^1B_2 \to {}^1A_1$ La nature et la position du plus bas état triplet sont aussi étudiées.

The lowest singlet-singlet transition of fluorenone (I) observed at 380 mμ in its absorption spectrum, has long been believed as an $n - \pi^*$ transition [10]. Recently, however, Kuboyama [7] proposed on the basis of the observations of solvent effect that the 380 mμ band of fluorenone should be assigned to a $\pi - \pi^*$ transition. This assignment was supported later by Yoshihara and Kearns [13]. There has been also a dispute on the nature and location of the lowest triplet state of fluorenone [4, 5, 9, 12]. In view of these situations, it seems of particular interest to make a theoretical study of the π-electron states of fluorenone.

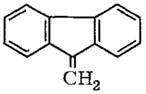
In the present study, we have calculated the SCF MO's of fluorenone by means of the variable-β modification of the Pariser-Parr-Pople method [8], and carried out the configuration interaction calculations. The electronic spectra of 9-iminofluorene (II) and 9-ethylidenefluorene (III) have been also theoretically studied by the same method.



(I)



(II)



(III)

Method

The numbering of atoms is shown in Fig. 1. The exact molecular structure has not been determined for none of the compounds studied here. In the variable-β

---

* Present address: Computer Centre, University of Tokyo, Hango, Tokyo.

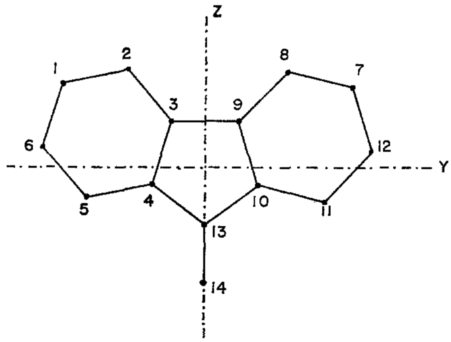


Fig. 1

procedure, however, we need not specify the precise molecular geometry and we can start the calculation assuming an approximate structure. Thus we assumed the initial molecular structures as follows: the molecules possess a planar structure with the symmetry of C_{2v}, all C—C distances within the ring system are 1.395 Å, the C=O bond distance in fluorenone is 1.23 Å, the C=N bond distance in 9-iminofluorene is 1.35 Å and the distance of C(13) – C(14) bond in 9-ethylidenefluorene is 1.34 Å.

The core resonance integrals, $\beta_{\mu\nu}$, were adjusted at each iteration by assuming the following relations.

$$\beta_{CC} = -0.51\,p - 1.84$$

$$\beta_{CN} = -0.53\,p - 2.02$$

$$\beta_{CO} = -0.56\,p - 2.20\,.$$

The two-center repulsion integrals, $\gamma_{\mu\nu}$, were estimated by using the Nishimoto-Mataga's equation,

$$\gamma_{\mu\nu} = 1.4397/(a_{\mu\nu} + r_{\mu\nu})\,.$$

The values of $a_{\mu\nu}$ assumed in the present study are given in Tab. 1 together with the assumed values of valence-state ionization potential, $W_{\mu\nu}$, and one-center repulsion integral, $\gamma_{\mu\mu}$. These are taken as proposed by NISHIMOTO and FORSTER [8].

A satisfactory self-consistency could be attained after 10 iterations in SCF MO calculation. The configuration interaction calculations were carried out for the singlet excited states as well as for the triplet excited states by taking into account lower 30 configurations among 49 singly-excited configurations. The calculations were made with HITAC 5020E in the Computer Center, University of Tokyo.

Table 1

Atom X	$-W_X$ [eV]	γ_{XX} [eV]	a_{CX}
C	11.16	11.13	1.294
N	14.12	12.34	1.167
O	17.70	15.23	0.945

Results

The bond order and charge density calculated for the ground state from the SCF MO's are summarized respectively in Tab. 2 and Tab. 3.

Table 2. *Bond orders calculated from the* SCF MO's

Bond	Fluorenone	9-Iminofluorene	9-Ethylidenefluorene
1 - 2	0.6540	0.6596	0.6705
2— 3	0.6559	0.6498	0.6377
3— 4	0.5997	0.5993	0.5994
4— 5	0.6577	0.6508	0.6399
5— 6	0.6522	0.6583	0.6690
6— 1	0.6737	0.6683	0.6585
4—13	0.2747	0.2908	0.3091
13—14	0.8534	0.8874	0.8968
3— 9	0.2878	0.2988	0.3194

Table 3. *Charge densities calculated from the* SCF MO's

Atom	Fluorenone	9-Iminofluorene	9-Ethylidenefluorene
1	0.9836	0.9886	1.0022
2	0.9975	0.9966	0.9977
3	0.9926	0.9970	1.0067
4	1.0274	1.0240	1.0131
5	0.9591	0.9737	0.9999
6	0.9987	0.9992	1.0028
13	0.7052	0.8302	0.9979
14	1.3770	1.2116	0.9576

Table 4. *Energies of excited states of fluorenone*

States	Calculation			Experiment [1, 7]
	$E - E_0$ [eV]	f	λ [mμ]	λ (log ε) [mμ]
$^1B_2$	3.46	0.07	358	378(2.43)
$^1B_2$	4.17	0.05	297	328(2.89), 308(3.24), 294(3.62)
$^1A_1$	4.30	0.04	288	
$^1B_2$	5.23	1.27	237	258(4.90)
$^1A_1$	5.33	0.39	233	
$^1A_1$	5.69	0.05	218	
$^1B_2$	5.98	0.12	207	
$^3B_2$	2.28		544	
$^3A_1$	2.80		443	
$^3B_2$	3.41		364	
$^3B_2$	3.49		355	

The energies of excited states, $E - E_0$, and the oscillator strengths (f) and wavelengths (λ) of transitions are given in Tabs. 4—6, together with the experimental values.

Table 5. *Energies of excited states of 9-iminofluorene*

States	Calculation			Experiment [3]
	$E - E_0$ [eV]	f	λ [mμ]	λ (log ε) [mμ]
$^1B_2$	3.51	0.07	353	354(2.45)
$^1A_1$	4.22	0.12	295	309.5(3.03), 297(3.58), 290.5(3.72)
$^1B_2$	4.22	0.04	295	
$^1A_1$	5.15	0.51	241	254(4.86), 245.5(4.72)
$^1B_2$	5.21	1.17	238	
$^1A_1$	5.66	0.007	220	217.5(4.22)
$^1B_2$	5.92	0.21	210	
$^3B_2$	2.34		530	
$^3A_1$	2.37		523	
$^3A_1$	3.41		364	
$^3B_2$	3.43		361	

Table 6. *Energies of excited states of 9-ethylidenefluorene*

States	Calculation			Experiment [11]
	$E - E_0$ [eV]	f	λ [mμ]	λ (log ε) [mμ]
$^1B_2$	3.82	0.11	325	340(2.6, shoulder)
$^1A_1$	4.13	0.20	301	312(3.93), 298(3.97), 282(4.11), 273(4.08)
$^1B_2$	4.39	0.0008	282	
$^1A_1$	5.01	0.47	248	257(4.55), 247.5(4.38)
$^1B_2$	5.25	0.80	236	
$^1B_2$	5.65	0.89	219	229.5(4.73)
$^1A_1$	5.70	0.32	218	
$^1A_1$	5.86	0.12	212	
$^3A_1$	2.02		615	
$^3B_2$	2.50		496	
$^3A_1$	3.35		370	
$^3B_2$	3.51		353	

Discussions

The bond order is nearly same for the C—C bonds in the hexagonal rings, but is considerably small for C(3)—C(9), C(4)—C(13) and C(10)—C(13). If we estimate the C—C bond distances in fluorenone from the bond orders by assuming the following relation [8],

$$r_{\mathrm{C-C}} = 1.517 - 0.180\,p\ \text{Å}\ ,$$

the values given in Tab. 7 are obtained, which are quite similar to the corresponding bond distances in fluorene determined by the crystal structure analysis [2].

The ultra-violet and visible absorption spectrum of fluorenone observed for the n-heptane solution is reproduced in Fig. 2. The spectrum can be devided into three bands: "band A" in the 330 – 420 mμ region, "band B" in the 250 – 330 mμ region, and "band C" in the 200 – 260 mμ region. Band A has been assigned to an $n - \pi^*$ transition by the earlier workers. Recently KUBOYAMA [7] has shown

Table 7. *Bond lengths of fluorenone estimated from* SCF MO's

Bond	Fluorenone [Å]	Fluorene [Å]	
	cal.	obs.	calc.[a]
(1)— (2)	1.399	1.402	1.396
(2)— (3)	1.399	1.407	1.403
(3)— (4)	1.409	1.410	1.403
(4)— (5)	1.399	1.434	1.396
(5)— (6)	1.400	1.390	1.398
(6)— (1)	1.396	1.383	1.397
(3)— (9)	1.465	1.482	1.462
(4)—(13)	1.468	1.465	

[a] Theoretically estimated by the same method as that used for fluorenone.

that this absorption band is shifted to longer wavelength in a polar solvent whereas a band associated with an $n - \pi^*$ transition is usually shifted to shorter wavelength, and proposed to assign it to a $\pi - \pi^*$ transition. YOSHIHARA and KEARNS [13] have pointed out that an absorption band possibly corresponding to band A of fluorenone can be found in the spectrum of fluorenone oxime as well as in the spectrum of 9-ethylidenefluorene where we can exclude the possibility of an $n - \pi^*$ transition. A similar absorption band appears also in the spectrum of 9-iminofluorene. As shown in Tab. 4, our calculation predicts that fluorenone possesses a ${}^1B_2 \leftarrow {}^1A_1$ transition ($\pi - \pi^*$) located at 358 mμ with an oscillator strength of 0.07, and the corresponding transition is at 353 and 325 mμ respectively for 9-iminofluorene and 9-ethylidenefluorene. These predictions are in good agreement with the observation if we consider that band A of fluorenone is a $\pi - \pi^*$ band. Therefore we shall assigne band A of fluorenone to the ${}^1B_2 \leftarrow {}^1A_1$ transition, not to an $n - \pi^*$ transition. Probably an $n - \pi^*$ band is hidden under the $\pi - \pi^*$ band mentioned above.

From the solvent shift observed for the vibrational peaks in band B of fluorenone, KUBOYAMA [7] considered that two $\pi - \pi^*$ transitions, probably located at

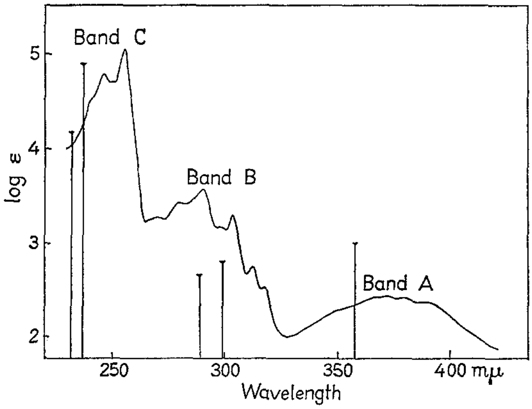


Fig. 2. The absorption spectrum of fluorenone. The calculated transitions are shown by vertical bars, the lengths of which correspond to log f

about 310 and 290 mμ, are involved in the absorption in this region. In agreement with this view, our calculation predicts the presence of two transitions in the region corresponding to band B: a $^1B_2 \leftarrow {}^1A_1$ transition at 297 mμ and a $^1A_1 \leftarrow {}^1A_1$ transition at 288 mμ. Recently INOUE and TANIZAKI [6] have experimentally shown that band B of fluorenone consists of a long-axis polarized band located at a longer wavelength and a short-axis polarized band located at a shorter wavelength. This observation agrees with our theoretical prediction. As can be seen in Tab. 5 and Tab. 6 our calculations well predict also the locations of the corresponding bands in the spectra of 9-iminofluorene and 9-ethylidenefluorene.

There have been conflicting reports regarding the nature and location of the lowest triplet state of fluorenone. HAMMOND et al. [5] observed long-lived emission with a 0 – 0 band at 535 mμ from a rigid-glass solution of fluorenone at 77 °K, and considered it as the phosphorescence. YANG [12] has reported the observation of phosphorescence at 565 mμ. On the other hand, HELLER and WASSERMAN [4] observed a long-lived emission with maxima at 457 and 483 mμ by exciting with 325 mμ light, which was regarded as the phosphorescence. Recently YOSHIHARA and KEARNS [13] suggested that the lowest triplet state could be a $\pi - \pi^*$ state and probably located at 550 – 580 mμ. Our calculation supports their opinion and predict the lowest $\pi - \pi^*$ triplet state at 544 mμ with the symmetry of $^3B_2$.

References

1. BERGMANN, E. D., Y. HIRSHBERG, D. LAVIE, Y. SPRINZAK, et J. SZMVSZKOVICZ: Bull. Soc. chim. France **1952**, 703.
2. BURNS, D. M., and J. IBALL: Proc. Roy. Soc. **A227**, 200 (1955).
3. EABORN, C., and R. A. SHAW: J. chem. Soc. **1955**, 1420.
4. HELLER, A., and E. WASSERMAN: J. chem. Physics **42**, 949 (1965).
5. HERKSTROETER, W. G., A. A. LAMOLA, and G. S. HAMMOND: J. Amer. chem. Soc. **86**, 4537 (1964).
6. INOUE, H., and Y. TANIZAKI: Preprints of the Annual Meeting of Chem. Soc. Japan (Tokyo, 1966) 1ZE228.
7. KUBOYAMA, A.: Bull. chem. Soc. Japan **37**, 1540 (1964).
8. NISHIMOTO, K., u. L. S. FORSTER: Theoret. chim. Acta **4**, 155 (1966).
9. PESTEIL, P., A. ZMERLI et M. BARBARON: C. R. hebd. Séances Acad. Sci. **239**, 255 (1954).
10. PLATT, J.: J. chem. Physics **19**, 101 (1951).
11. PULLMAN, A., B. PULLMAN, E. D. BERGMANN, G. BERTHIER, Y. HIRSHBERG et Y. SPRINZAK: Bull. Soc. chim. France **1951**, 702.
12. YANG, N. C.: Pure appl. Chem. **9**, 591 (1964).
13. YOSHIHARA, K., and D. R. KEARNS: J. chem. Physics **45**, 1991 (1966).

Dr. H. KURODA
Department of Chemistry
Faculty of Science
The University of Tokyo
Tokyo, Japan