BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1919—1921 (1972)

Electronic Spectra and Structures of 3-Substituted 1,2-Diphenylcyclopropenyl Cations

Zen-ichi Yoshida and Hideki Miyahara

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto, 606

(Received September 2, 1971)

The simplest and most strained non-benzenoid aromatic, cyclopropenyl cation($2\pi 3c$) system is expected to have unique electronic properties. Thus, the electron donating σ-inductive effect of an attached n-propyl group is more significant for the stabilization of this carbonium ion than the electron donating π-conjugative effect of an attached phenyl group,[1] in contrast to most other carbonium ions. The ^{13}C–H coupling constant of parent cyclopropenyl cation indicates that the orbital used for bonding with the hydrogens is *sp* hybrid.[2]

Only a few papers[3] have appeared on the electronic spectra and structures of the cyclopropenyl system. This paper deals with the electronic spectra and structures of 3-substituted 1,2-diphenylcyclopropenyl system (Fig. 1) obtained by using the variable integrals method I (VI/I)[4] devised to contain only one arbitrary molecular parameter.

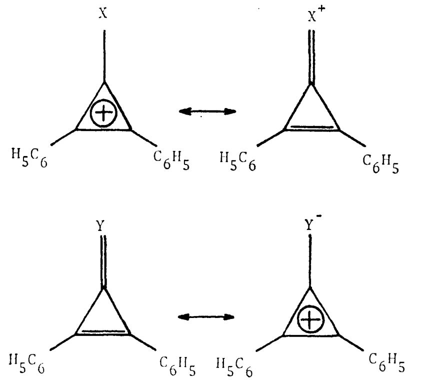

Fig. 1. 3-Substituted-1,2-diphenylcyclopropenyl system taken up in this study.
X: OC_2H_5 (**2**), SC_2H_5 (**4**), $N(CH_3)_2$ (**5**)
Y: O (**1**), S(**3**)

Experimental

Materials. 1,2-Diphenylcyclopropenone[5] (**1**), 1,2-diphenyl-3-ethoxycyclopropenyl tetrafluoroborate[5] (**2**), 1,2-diphenylcyclopropenethione[6] (**3**), and 1,2-diphenyl-3-dimethylaminocyclopropenyl tetrafluoroborate[5] (**5**) were prepared according to literature. 1,2-Diphenyl-3-ethylthiocyclopropenyl tetrafluoroborate (**4**), mp 149—150°C (decomp.) (Anal. Found: C, 60.20; H, 4.54%; Calcd for $C_{17}H_{15}BF_4$: C, 60.37; H, 4.47%) was prepared from **3** and triethyloxonium tetrafluoroborate in 70% yield in a similar manner to that for **2**.

Measurements of Spectra. Ultraviolet spectra were taken on a Hitachi Model ESP-3T spectrometer. Solvents used were of spectrograde from E. Merck & Co.

Method of Calculation

Details of the VI/I method have been described.[4] In order to assume reasonable geometries of the molecules the linear bond order(p) - bond length(l) relationships are used in each iteration step of the SCF procedure.[7] For the three membered ring the reference of the double bond length was taken to be equal to that of cyclopropene[8]:

$$l_{C-C} = 1.477 - 0.177p \qquad (1)$$

The procedure is known to give satisfactory bond lengths for fulvenes *etc.*[7] The molecules were assumed to be planar. Numbering of atoms in the molecules are giving in Fig. 2. The CI calculations were made on the singly excited configurations for which inner orbitals of five occupied and five unoccupied levels are responsible.

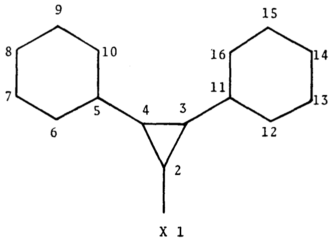

Fig. 2. Numberings of the atoms.

Results and Discussion

The observed electronic spectra of **1** and **3** in cyclohexane and **2**, **4**, and **5** in methylene chloride solutions are given in Table 1 with calculated transition energies. For **1** and **3** the weak least energy bands were obviously assigned to the n-π^* bands which shifted toward higher energy in ethanol.[3a,9] This is not included in our calculation.

We see that the agreement between calculated and observed values is relatively satisfactory and the reasonable assignments of the bands could be made

---

[1] R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

[2] R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).

[3] a) G. Laban, J. Fabian, and R. Mayer, *Z. Chem.*, **8**, 411 (1968). b) A. Watanabe, H. Yamaguchi, Y. Amako, and H. Azumi, This Bulletin, **41**, 2196 (1968).

[4] Z. Yoshida and T. Kobayashi, *Theor. Chem. Acta*, **19**, 377 (1970).

[6] Y. Kitahara and M. Funamizu, This Bulletin, **37**, 1897 (1964).

[7] Z. Yoshida and T. Kobayashi, *ibid.*, **45**, 316 (1972).

[8] P. H. Kasai, R. J. Meyers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

[9] E. Osawa, K. Kitamura, and Z. Yoshida, *J. Amer. Chem. Soc.*, **89**, 3814 (1967).

Table 1. Calculated singlet-singlet transition energies E (eV) and oscillator strength f [a)]

Compound	E calcd, eV	f	Dominating configurations	E exp., eV[b)] (log ε)
1 E_0				4.13 (3.30) n-π^*
E_1	4.299	0.570	8—9, 0.953	4.20 (4.35)
E_2	4.743	0.005	7—9, 0.596	
E_3	4.744	0.007	8—11, 0.597	4.68 (4.00)sh
E_4	5.507	0.076	5—9, 0.792	
E_5	5.570	0.062	6—12, 0.701	5.64 (4.25)
2 E_0				
E_1	4.307	0.831	8—9, 0.907	4.13 (4.52)
E_2	4·510	0.040	7—9, 0.779	
E_3	4.531	0.140	6—9, 0.766	
E_4	5.240	0.212	5—9, 0.674 8—10, 0.541	5.38 (4.20)
3 E_0				2.69 (2.36) n-π^*
E_1	3.455	0.245	8—9, 0.996	3.44 (3.98)
E_2	4.348	0.697	8—10, 0.813 8—13, 0.517	4.34 (4.28)
E_3	4.787	0.015	5—9, 0.632	
E_4	4.790	0.020	6—9, 0.630	
E_5	5.184	0.422	7—9, 0.880	5.06 (4.52)
E_6	5.751	0.011	4—9, 0.608 5—11, 0.672	5.25 (4.32)
4 E_0				
E_1	4.395	0.626	8—9, 0.842	3.96 (4.40)
E_2	4.506	0.020	7—9, 0.689	
E_3	4.516	0.282	6—9, 0.667	
E_4	4.840	0.577	5—9, 0.311 4—10, −0.452 8—10, 0.793	4.40 (4.30)
E_5	5.719	0.081	5—9, 0.678	
5 E_0				
E_1	4.323	0.776	8—9, 0.887	3.96 (4.30)
E_2	4.516	0.097	7—9, 0.760	
E_3	4.521	0.124	6—9, 0.755	
E_4	5.064	0.346	5—9, −0.564 8—10, 0.764	4.85 (4.50)
E_5	5.790	0.075	5—9, 0.653	

a) E_j denotes the energy of the state Φ_j relative to the energy $E_0=0$ of the ground state Φ_0. The number beside the dominating configuration $i-k(\Phi_i{}^{-1}\Phi_k)$ is the CI coefficient in the linear combination Φ_j. The assumed geometries of the compounds are shown.

b) The solvent is cyclohexane for **1** and **3** and methylene dichloride for **2**, **4**, and **5** (room temperature).

Table 2. Calculated formal π-charges and π-dipole moments, μ

Atoms	Compounds				
	1	**2**	**3**	**4**	**5**
1	−0.667	0.096	−0.636	0.131	0.176
2	0.339	0.235	0.261	0.235	0.230
3, 4	0.140	0.221	0.151	0.213	0.196
5, 11	−0.050	−0.133	−0.060	−0.125	−0.123
6, 10, 12, 16	0.034	0.037	0.038	0.031	0.027
7, 9, 13, 15	0.012	0.035	0.013	0.035	0.034
8, 14	0.027	0.098	0.033	0.092	0.092
μ_{Debye}	6.63	6.55	8.27	5.67	5.35

using the forms of the CI wave functions. The least energy $^1\pi$-$^1\pi^*$ bands for **1**—**4** have a characteristic of the stilbene chromophore[10] with fine structurs due to vibrational levels, though the corresponding band for **5** appears broad. The second allowed lower energy $^1\pi$-$^1\pi^*$ bands in **3**, **4** and **5** are interesting. The strong band in **3** observed near 4.3 eV might be due to the intramolecular charge-transfer transition from ring to sulfur. The 4.40 eV band observed in **4** and 4.85 eV band observed in **5** could also be assigned to the intramolecular charge-transfer transition from heteroatom to ring. In **1** and **2**, however, no intramolecular charge-transfer transitions as above were observed being in line with the prediction from calculations that the bands in question would be shifted toward relatively higher energy. This trend of the substituents at 3-position in these systems for the interaction with the diphenylcyclopropenyl ring is similar to that found in monosubstituted benzenes, in which thiol and amino groups interact strongly with the benzene ring, in contrast to weakly interacting hydroxyl group.[11] The observed $^1\pi$-$^1\pi^*$ bands of **1** show essentially no solvent shift, in ethanol. However, those of ethanol solution of **3** are noticeably shifted to higher energy, and those of **2**, **4**, and **5** in ethanol containing sulfuric acid exhibited slight blue shifts. The spectral features toward solvent polarity can be explained by large polarization in the ground state of these molecules. This can be understood by the calculated formal charges and dipole moments shown in Table 2. It seems that the geometries of these molecules are nearly planar in their dominant conformation in solution.[12]

Financial support (in part) of the present work by a Grant for Scientific Research from the Ministry of Education is gratefully acknowledged.

---

[10] D. L. Beverige and H. H. Jaffé, *ibid.*, **87**, 5340 (1965).

[11] S. Nagagura and K. Kimura, *Nippon Kagaku Zasshi*, **86**, 1 (1965).

[12] For general discussions of this problem see R. Hoffmann, R. Bissell, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969).