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GEOMETRICAL STRUCTURES AND SPECTRA OF CORANNULENE AND ICOSAHEDRAL C_{60}

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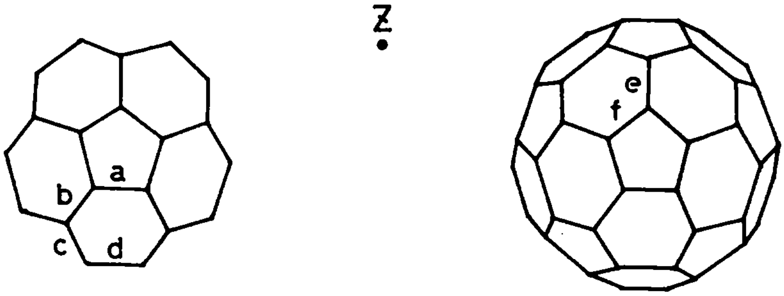
Abstract - On the basis of the second-order Jahn-Teller theory and the semiempirical SCF MO method, the ground states of both corannulene and icosahedral C_{60} are predicted not to undergo any bond distortions accompanied with molecular-symmetry reductions. The π-type electronic spectra for corannulene calculated by using the energetically most favorable geometrical structures obtained by the SCF MO method are in good agreement with experimental data.

Recently, Kroto et al.[1] have obtained a remarkably stable cluster consisting of 60 carbon atoms, and have suggested an icosahedral (I_h) structure for this molecule. Using the Hückel molecular orbital (HMO) method, Haymet[2] has predicted a large π-electronic delocalization energy for the I_h C_{60}. Using the HMO theory for non-planar conjugated organic molecules,[3] Haddon et al.[4] have examined the electronic structure and properties of the proposed icosahedral geometry of C_{60}. On the basis of the double-bond fixation theory[5] based on the second-order Jahn-Teller (SOJT) effect,[6] they have further shown that the I_h C_{60} will not undergo a distortion to a less symmetrical structure. Disch and Schulman,[7] however, have questioned the stability of the icosahedral structure with respect to non-totally symmetric distortions because the energy gap between the HOMO and LUMO of the I_h C_{60} calculated by using the STO-3G basis set is not greater than those found in other symmetric, neutral clusters such as a truncated tetrahedral C_{12}, which has been considered to suffer a molecular-symmetry reduction.[7] In the present paper, we report the theoretical studies on the geometrical structures and electronic spectra of corannulene and C_{60} (Figure 1). It is of interest to examine corannulene because this molecule has a bowllike structure[8] regarded as a fragment of C_{60}.

We first examine the stability of the most symmetrical structures of these



1 2

Figure 1. Carbon skeletons of the C_{5v} corannulene 1 (planar projection) and the I_h C_{60} 2 (a hemisphere).

molecules by using the SOJT theory. Nakajima *et al.*[9] have applied this theory to the prediction of the ground-state geometries of conjugated hydrocarbons, and have proposed the rule that if the first excitation energy is calculated to be smaller than about 1.2 eV, a bond distortion usually accompanied with a molecular-symmetry reduction will occur in the ground state of a molecule.

We calculate the first excitation energies of corannulene (C_{5v}) and C_{60} (I_h), using the semiempirical SCF MO CI method with the variable bond length technique.[9] The non-planar form of the π-type electronic system decreases the effective π-overlap and, consequently, the magnitude of the core-resonance integral β_c. Following Haddon,[4] we assume a reduced core-resonance integral for corannulene and C_{60} to be 0.877 β_c.

RESULTS AND DISCUSSION

Geometrical Structures

The calculated first excitation energies and the symmetries of the first excited singlet state are, respectively, 3.28 eV and E_2 for the C_{5v} corannulene and are 2.69 eV and T_{1g} for the I_h C_{60}. These values are much larger than the critical value for bond distortions, about 1.2 eV.[9] It is predicted therefore that these molecules do not undergo any ground-state bond distortions accompanied with molecular-symmetry reductions. In fact, X-ray experiment of corannulene[8] shows that this molecule belongs to C_{5v}.

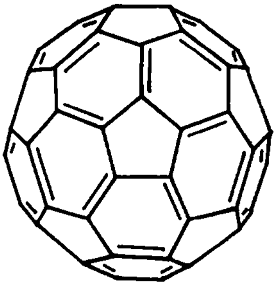
In Table 1 we show the calculated C-C bond lengths for the C_{5v} corannulene and the I_h C_{60}. The obtained bond lengths of corannulene is in good agreement with those calculated by Gleicher,[10] who first predicted the non-planar structure of corannulene. The predicted lengths of bonds a, b, and c are in good agreement with the X-ray data, but the predicted length of bond d is fairly small as compared with the experimental one. In calculating the bond lengths of corannulene, we have assumed the same CCC bond angles as those in the I_h C_{60}, and the discrepancy between theory and experiment is most likely attributable to the steric strain which is due to the assumed bond angles and

Table 1. Bond lengths (Å) of corannulene (C_{5v}) and C_{60} (I_h).

Molecule	Bond	PPP-type[a]	X-ray[b]	HMO[c]	STO-3G[d]	this work
corannulene	a	1.430	1.413			1.437
	b	1.408	1.391			1.403
	c	1.430	1.440			1.434
	d	1.374	1.402			1.370
C_{60}	e			1.418	1.376	1.396
	f			1.436	1.465	1.443

[a] Ref.10, [b] Ref.8, [c] Ref.4, [d] Ref.7

can be relaxed most effectively by the elongation of bond d. For the I_h C_{60}, the two different structures have been proposed; a π-type delocalized structure obtained by using the three-dimensional HMO theory[4] and the Kekulé-type structure **2b** provided by the STO-3G calculation.[7] The predicted geometrical structure, which is between the above two structures, still retains a fairly amount of the π-type electronic delocalization.



2b

Electronic Spectra

In calculating electronic spectra, we use the bond lengths obtained above. The computational method employed is the Pariser-Parr-Pople-type SCF MO CI method[9] with the reduced core-resonance integrals. All singly excited configurations are included for corannulene, and 60 singly excited configurations are included for C_{60}. These 60 single excitations arise from one-electron jumps from the HOMO (h_u) and the next HOMO (h_g) to the LUMO (t_{1u}) and the next LUMO (t_{1g}).

In Table 2 we summarize the calculated electronic spectra of corannulene (C_{5v}) and C_{60} (I_h). Table 2 shows that the predicted excitation energies and intensities of corannulene agree well with the observed values.[11] The observed tail of 3.5-4.0 eV is probably assigned to the first three forbidden excitations (E_2, A_2, and E_2). The observed peak of 4.3 eV is most likely

Table 2. Singlet transition energies and intensities of the C_{5v} corannulene and the I_h C_{60} with the most stable geometrical structures

Molecule	Transition symmetry	E_{cal}/eV	f(cgs)	E_{obs}/eV (log ε)[a]
corannulene	E_2	3.28	forb.	long tail of 3.5-4.0
	A_2	3.42	forb.	3.87(shoulder)
	E_2	3.70	forb.	
	A_1	4.26	0.109	4.30 (4.52)
	E_1	4.32	0.657	
	E_1	4.82	0.508	4.90, 4.98, 5.04
				(4.96, 4.73, 4.78, progression)
	E_2	5.22	forb.	
	E_1	5.39	0.000	
	E_1	5.55	0.516	
	A_1	5.62	0.115	
	E_2	5.64	forb.	
	E_1	5.71	0.142	broad absorption of 5.2-6.2
	A_2	5.73	forb.	
	E_2	5.86	forb.	
	E_2	5.97	forb.	
	E_1	6.06	0.000	
	E_1	6.26	1.051	
C_{60}	T_{1g}	2.69	forb.	
	T_{2g}	2.79	forb.	
	G_g	2.79	forb.	
	T_{2u}	3.18	forb.	
	H_g	3.19	forb.	
	G_u	3.35	forb.	
	H_u	3.39	forb.	
	H_u	3.81	forb.	
	G_u	3.96	forb.	
	T_{1u}	4.01	0.215	
	T_{2u}	4.07	forb.	
	T_{2g}	4.37	forb.	
	G_g	4.40	forb.	
	T_{1g}	4.45	forb.	
	T_{1u}	4.64	4.283	
	H_g	4.65	forb.	

[a] Ref.11

assigned to the allowed excitations to the A_1 and E_1 states. The progression of about 5.0 eV probably corresponds to the allowed E_1 state. The broad absorption of the observed spectra in the region of 5.2-6.2 eV includes the allowed excitations to a single A_1 and the five E_1 states. On the other hand, the electronic spectra of C_{60} turn out to be fairly simpler than those of corannulene; the calculated electronic spectra of 2.7-4.6 eV comprise many forbidden excitations, only two T_{1u} excitations being allowed. The simplicity of the electronic spectra is due to the highly symmetrical structure of the molecule.[4] The two allowed excitations can be represented as linear combinations of the two excitations: the HOMO (h_u) → the next LUMO (t_{1g}) and the next HOMO (h_g) → the LUMO (t_{1u}). The lower T_{1u} state is produced mainly by the $h_u \rightarrow t_{1g}$ excitation and the higher T_{1u} state is produced mainly by the $h_g \rightarrow t_{1u}$ excitation. The first $A_g \rightarrow T_{1u}$ transition is relatively weak and the second $A_g \rightarrow T_{1u}$ transition is considerably strong, as was predicted by Haddon _et_ _al_.[4]

CONCLUDING REMARKS

In the present study we have examined the geometrical structures and electronic spectra of corannulene (C_{5v}) and C_{60} (I_h), using semiempirical SCF CI MO method. The calculated bond lengths and spectra for corannulene are in agreement with the observed values. The ground state of the I_h C_{60} turn out not to undergo any bond distortions and any molecular-symmetry reductions and to have a π-electronic delocalized structure. It is hoped that the calculated geometrical data and excitation energies in the present paper will be useful for understanding the properties of the I_h C_{60}.

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