In addition, it remains to be determined whether the strong connection between the ability of a host to orient a guest and the magnitude of K_a, apparent from the present work, is a general phenomenon.

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Discrete-Variational-Xα Electronic Structure Studies of the Spherical C_{60} Cluster: Prediction of Ionization Potential and Electronic Transition Energy

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Recent carbon vaporization studies by Smalley and co-workers[1] have provided evidence for the existence of a remarkably stable C_{60} species. It has been proposed that this cluster may be nearly spherical in shape, with a truncated icosahedral structure made up of 12 pentagonal rings and 20 hexagonal rings. The stability of this molecule has been discussed in terms of a simple Hückel model[2] and Herndon–Simpson resonance theory,[3] and the electronic structure has been studied in considerable detail using a three-dimensional Hückel scheme.[4] Very recent MNDO calculations[5] have also investigated the stability of C_{60} and have provided an estimate of the ionization potential of this species.

The present paper describes preliminary results of discrete-variational-Xα (DV–Xα) electronic structure calculations[6] for this soccerball-shaped carbon cluster. This method has been used to study a wide range of molecules, from small hydrocarbons[7] to large aromatic systems,[8] and the accuracy of the Slater transition-state technique[9] in calculating optical transition energies and ionization potentials is well-documented.[7,8]

For the C_{60} molecule, ground-state calculations and transition-state calculations for the lowest allowed optical transition and the first ionization energy were performed. In order to simplify the computations, it was assumed that all carbon–carbon bond lengths are equal. Two cases were considered: (a) C–C bond length of graphite (1.421 Å) and (b) C–C bond length of benzene (1.395 Å). The atomic basis functions were determined from a separate Hartree–Fock–Slater calculation; in this, an effective configuration of $1s^2 2s^2 2p^2 3s^0 3p^0$ was used for carbon. Also, a potential well[7,10] was placed on the C atom to localize the virtual 3s and 3p orbitals, which would otherwise be unreasonably diffuse in the ground-state potential. Finally, for convenience, the calculations were performed under D_3 symmetry rather than under the full I_h symmetry of the molecule.

The results of the ground-state calculation are shown in Figure 1 for the case where the C–C bond distance of graphite was used. The results of the calculation using the shorter C–C bond length of benzene are very similar, with the ground-state orbital energies shifted to higher values by less than 0.10 eV for the occupied orbitals and by less than 0.20 eV for the unoccupied, compared to the diagram in Figure 1. For comparison, the orbital energies from the three-dimensional Hückel studies of Raghavachari and co-workers[4] are also displayed. In that work, the energy of the lowest allowed electronic transition ($h_u \rightarrow t_{1g}$) was found to be equal to $-\beta$. In Figure 1, the value of β was taken from matching the DV–Xα calculation of this transition energy (see Table I and the discussion below). Also, in the schematic energy level diagrams, the energy of the highest occupied molecular orbital of the Hückel study (h_u) was set equal to that found in the DV–Xα work ($22a_1 + 39e + 40e$) in order to allow a straightforward comparison. The DV–Xα results correspond quite well with those of the simple Hückel model. This correspondence is shown in Figure 1 by lines connecting the two energy level schemes. It is clear from the diagrams that the lowest energy allowed electronic transition under D_3 symmetry is $22a_1 + 39e + 40e \rightarrow 20a_2 + 42e$, which corresponds to the $h_u \rightarrow t_{1g}$ transition under the full I_h symmetry of the molecule.

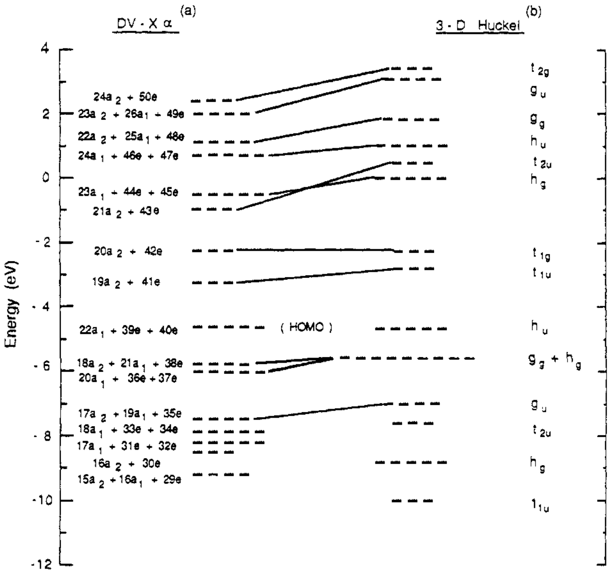

Figure 1. Orbital energy level diagram for the C_{60} cluster: (a) DV–Xα calculations assume D_3 symmetry; the results shown are for a uniform carbon–carbon bond distance of 1.421 Å (graphite). (b) Hückel results are from ref 4. In the diagram, β has been given a value of −2.52 eV.

Table I

	case A[a]	case B[a]
first IP[b]	6.42 eV	6.38 eV
optical transition[c]	2.52 eV	2.65 eV

[a] Case A: C–C bond length = 1.421 Å. Case B: C–C bond length = 1.395 Å. [b] $22a_1 + 39e + 40e$ under D_3 symmetry; h_u under I_h symmetry. [c] $22a_1 + 39e + 40e \rightarrow 20a_2 + 42e$ under D_3 symmetry; $h_u \rightarrow t_{1g}$ under I_h symmetry.

Since Koopmans' theorem is not valid in local density, the transition-state method[9] was used to calculate the first ionization potential and the energy of the first electronic transition. This method is known to take into account electron relaxation effects which occur upon ionization or optical excitation.[7,11] The results of these calculations are listed in Table I. The calculated ionization potential (6.4 eV) differs substantially with the results of previous studies, where values of 7.45–8.41 eV[5] and 8.1–9.1 eV[4] were obtained. It is also interesting to note that this lower value for the ionization potential raises the possibility that a near-resonance ionization process may be an important factor in the production of C_{60}^+ ions when an ArF laser (6.42-eV photon energy) is used as the ionizing source.[12] Finally, it is apparent that changing

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the carbon–carbon distance from that of graphite (case A) to that of benzene (case B) has very little effect on the calculated ionization potential (the difference is less than 1%) and only a moderate effect on the calculated optical transition energy. For both cases, the calculations predict that the lowest energy electronic transition should lie in the visible region of the spectrum; the absorption wavelength is found to be 492 nm for case A and 468 nm for case B.

Thus, the DV–Xα calculations predict that the lowest electronic transition in the soccerball-shaped cluster C_{60} should lie at an experimentally accessible energy. Measurement of this transition would provide valuable evidence as to whether or not the C_{60} species detected by Smalley and co-workers[1] is indeed shaped like a soccerball. The previous success of the DV–Xα method in the calculation of ionization potentials and optical excitations certainly suggests that its use as a predictive tool is warranted, and the results of experimental studies of the optical spectrum of C_{60} are eagerly awaited.

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Structure of Cervinomycin, a Novel Antianaerobic Antibiotic

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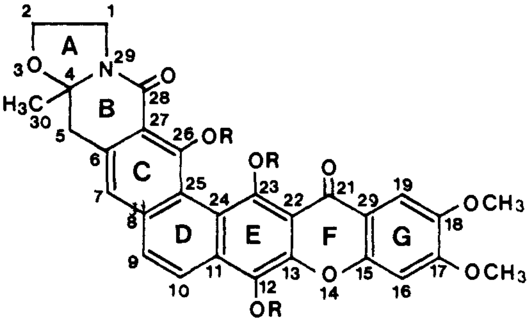
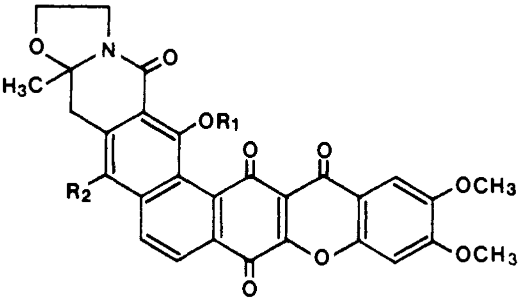
Cervinomycin[1] is an antianaerobic and antimycoplasmal antibiotic produced by *Streptomyces cervinus* sp. nov. The antibiotic consists of two components, A_1 (**1**), $C_{29}H_{23}NO_9$, and A_2 (**2**), $C_{29}H_{21}NO_9$, which are hardly soluble in any solvents. Triacetylcervinomycin A_1 (**3**) [mp 283–285 °C, $[\alpha]^{26}_{D}$ −115° (*c* 0.3, $CHCl_3$); EIMS, *m/z* 655 (M^+), $C_{35}H_{29}NO_{12}$], which was obtained in the course of the structure elucidation of cervinomycins, is developing as a medical drug because of its high solubility and low toxicity in addition to a potent antianaerobic activity against *Clostridium difficile*, *Reptococcus variabillis*, and *Streptococcus mutans*. In this paper we wish to report the structure of cervinomycin by means of 400-MHz NMR spectroscopy.

Methylation of **2** with CH_3I in the presence of Ag_2O in $CHCl_3$/MeOH afforded two methyl derivatives, *O*-methylcervinomycin A_2 (**4**) [mp >300 °C dec, $[\alpha]^{27}_{D}$ −499° (*c* 0.5, $CHCl_3$); EIMS, *m/z* 541 (M^+), $C_{30}H_{23}NO_9$; UV $\lambda_{max}^{CHCl_3}$ 248.0 nm (ϵ 42 700), 317.3 (27 300)] and *C,O*-dimethylcervinomycin A_2 (**5**) [mp >255 °C dec, $[\alpha]^{27}_{D}$ −459° (*c* 0.2, $CHCl_3$); EIMS, *m/z* 555 (M^+), $C_{31}H_{25}NO_9$; UV $\lambda_{max}^{CHCl_3}$ 252.2 nm (ϵ 35 000), 327.2 (21 500). The ^{13}C NMR spectrum (in $CDCl_3$) of **4** indicates the presence of a methyl (δ 23.3), two methylenes (δ 42.2 and 43.5), three methoxyls (δ 56.4, 56.7, and 63.2), an oxymethylene (δ 64.4), and a quaternary carbon (δ 92.1) bonded to an oxygen and a nitrogen atom. Compound **4** contains further 13 olefinic carbons in the region at 100–140 ppm, an amide group and five olefinic oxycarbons in 149–160 ppm, a doubly α,β-unsaturated carbonyl (δ 172.4), and two quinone carbonyls (δ 178.2 and 183.2). The location of two isolated olefinic protons (δ 7.13 and 7.64) was assigned from the structure of 3,4-dimethoxy-6-hydroxybenzoic acid, obtained by degradation of **2** (or **1**) with 0.5 N KOH in dioxane, which suggests the presence of partial structure (I) in cervinomycins.



1 R = H
3 R = COCH3



2 R1, R2 = H
4 R1 = CH3, R2 = H
5 R1 = CH3, R2 = CH3
6 R1 = COCH3, R2 = H

For the connectivity of each functional group, a long-range ^1H and ^{13}C shift-correlated 2D NMR[2] and LSPD (^1H and ^{13}C long-range spin decoupling) experiment[3] were carried out for **4**. The existence of neighboring two methylene groups (C-1, δ 43.5; H-1a,1b δ 3.67 1 H m, 4.18 1 H m; C-2, δ 64.4 H-2a, 2b; δ 4.19 2 H t) placed between a nitrogen and an oxygen atom was confirmed from the proton coupling pattern. The observation of the ^1H and ^{13}C long-range couplings between H-1 and an amide carbon (C-28, δ 160.1) and between H-2 and a quarternary carbon (C-4, δ 92.1) indicated the existence of a five-membered ring including a nitrogen atom of an amide group and an oxygen atom. Long-range couplings were observed between a methyl proton (δ 1.43) and C-4 and between methylenic protons (H-5a,5b, δ 3.21, 3.29) and two sp^2 carbons (C-7, δ 121.3, and C-27, δ 118.5) and C-4. In the A, B type protons H-9 and H-10, appearing at δ 7.93 and 8.18, respectively, the former ($^3J_{CH}$ = 4.0 Hz) couples with C-7 and the later ($^3J_{CH}$ = 3.6 Hz), with C-12 (δ 178.2). These NMR evidences deduced the existence of a partial structure II consisting of conjugated five rings including a 1,4-benzoquinone moiety for **4**, as shown in Scheme I. The validity of structure II was also confirmed from the observation of the NOE effects

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