

mechanism. The preassociative stepwise mechanism only remains tenable if one assumes that the lifetime of the putative intermediate  $[H_2O \cdot PO_3^- \cdot AMP]$  complex is so short that it always collapses back to starting material faster than rotation about the  $O_3P-O$  bond of AMP can occur within the complex.

Positional isotope exchange of  $[\beta\text{-}^{18}O_4]ADP$  in acetonitrile is consistent with the preassociative stepwise mechanism, the  $[CH_3CN \cdot PO_3^- \cdot AMP]$  complex collapsing back to the  $CH_3CN \cdot ADP$  encounter complex faster than acetonitrile can diffuse from it. The possibility that the product  $[CH_3CN^+ \cdot PO_3^{2-} \cdot AMP]$  complex (which would be the same for both the concerted and stepwise mechanism) is responsible for allowing positional isotope exchange to occur thereby introducing mechanistic ambiguity is, however, difficult to rigorously exclude although the control experiment suggests that the lifetime of the  $[CH_3CN^+ \cdot PO_3^{2-} \cdot AMP]$  is too short for phosphoryl transfer to the phosphate group of AMP to occur.

The above observations suggest that when water or an alcohol preassociates with ADP (and presumably other monosubstituted phosphates) a concerted transfer of the phosphoryl group is likely leading to inversion of configuration, although the possibility of a stepwise mechanism occurring especially if the leaving group has an exceptionally low  $pK_a$  cannot be excluded. If, however, preassociation occurs with a weak nucleophile such as acetonitrile, ethers, etc. which cannot form a stable phosphorylated product, the extent to which it can compete with the ultimate acceptor will determine the degree of racemization observed in stereochemical experiments. As reported in the preceding paper, incubation of adenosine  $5'$ - $[\beta\text{-}^{16}O, ^{17}O, ^{18}O]$ - $(S)$ -diphosphate as its trianion in acetonitrile with 2-*O*-benzyl- $(S)$ -propane-1,2-diol as the ultimate acceptor leads to almost complete racemization with a small degree of retention.<sup>10</sup> This observation suggests that the ultimate product is formed by way of  $CH_3CN^+ \cdot [^{16}O, ^{17}O, ^{18}O]PO_3^{2-}$  and that the  $[^{16}O, ^{17}O, ^{18}O]PO_3^-$  moiety is usually transferred to other acetonitrile molecules before it is captured by the ultimate acceptor, but it is also possible that the  $(CH_3CN \cdot [^{16}O, ^{17}O, ^{18}O]PO_3^- \cdot AMP)$  complex on the stepwise pathway has a lifetime long enough for the  $[^{16}O, ^{17}O, ^{18}O]PO_3^-$  moiety to tumble and contribute to racemization.

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## Resonance in $C_{60}$ , Buckminsterfullerene<sup>†</sup>

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Recently Kroto et al.<sup>1</sup> have found that laser vaporization of graphite in a high-pressure supersonic nozzle produces a remarkably stable  $C_{60}$  molecule in high yield. It was argued that this new species takes the form of a truncated icosahedron with C atoms at each of the vertices and  $\sigma$ -bonds along each edge, and in recognition of Buckminster Fuller's studies of such (geodesic-dome-like) structures the name buckminsterfullerene was suggested. The remaining  $\pi$ -bonds delocalized through resonance were presumed to account for the indicated high stability. Here we report energy calculations for this soccerball-like structure via quantitative resonance theories and make comparisons to simple Hückel MO results.

The proposed structure has icosahedral symmetry including inversion,  $I_h = I \times C_i$  so that the Hückel molecular orbitals are

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Table I. Orbital Energies and Symmetries<sup>a</sup>

	+	-
A	-3.000	
F <sub>1</sub>	+0.382	-2.757, +0.139
F <sub>2</sub>	+2.618	-1.820, +1.438
G	-1.000, +2.000	-1.562, +2.562
H	-2.303, -1.000, +1.303	-0.618, +1.618

<sup>a</sup> In units of  $|\beta|$ , with  $\alpha = 0$ .

Table II. Various Resonance Energies for Several Species

	Hückel MO, $\beta$	Kekulé count, <sup>a</sup> J	conjugated circuit, <sup>b</sup> eV
$C_{60}$			
uncorrected	0.553	-0.178	-0.120
corrected	0.509	-0.150	-0.101
benzene	0.333	-0.131	-0.140
pentacene	0.388	-0.092	-0.084
coronene	0.440	-0.141	-0.146
graphite	0.575	-0.183	-0.168

<sup>a</sup> Calculated from eq 4, ref 3b, as corrected: *Chem. Phys. Lett.* **1985**, *118*, 1101. <sup>b</sup> Calculated from eq 1, truncated after 10 cycles,  $R_1 = -0.841$  eV,  $R_2 = -0.336$  eV.

labeled by irreducible representations of  $I$  and  $C_i$ . The orbital energies of these various symmetries appear in Table I. The A, F<sub>1</sub>, F<sub>2</sub>, G, and H representations of  $I$  yield 1-, 3-, 3-, 4-, and 5-fold degeneracies of the associated levels (so that overall there are 30 antibonding and 30 bonding  $\pi$ -MO's). The + and - labels identify the  $C_i$  symmetry.

The number of Kekulé structures for this molecular species provides another indication of its stability. We have carried out this enumeration via a recently implemented transfer matrix technique<sup>2</sup> and find that there are (exactly)  $K = 12500$  Kekulé structures. The logarithm of such a count has been argued<sup>3</sup> to be proportional to the resonance energy. Pauling bond orders<sup>4</sup> may be obtained by taking the ratio of the number of Kekulé structures with a double bond between a particular pair of atoms to  $K$ . This leads to bond orders of 7/25 for edges separating pentagonal and hexagonal faces and 11/25 for edges separating two hexagonal faces.

We also apply the Herndon-Simpson resonance theory<sup>5</sup> (with an underlying valence-bond rationale) or the conjugated-circuit method<sup>6</sup> (with an empiric rationale related to Clar's<sup>7</sup> ideas). In these methods the resonance energy is given as a ratio  $H/K$ , with

$$H = \sum_{n \geq 1} \{ \#^{2n+2} R_n + \#^{2n} Q_n \} \quad (1)$$

where the  $R_n$  and  $Q_n$  are (exchange matrix element) parameters and  $\#^{2m}$  is the sum over the number of conjugated  $2m$  circuits in the various Kekulé structures. (Here a conjugated  $2m$  circuit in a Kekulé structure is a length  $2m$  cycle with alternating single and double bonds.) Again utilizing the transfer matrix approach<sup>2</sup> we obtain  $\#^6 = 83\,160$ ,  $\#^8 = 0$ ,  $\#^{10} = 59\,760$ ,  $\#^{12} = 50\,880$ , and  $\#^{14} = 44\,760$ .

Computation of explicit resonance energy estimates requires consideration of the effects of the molecule's nonplanarity upon the model parameters. The angle between nearest-neighbor sites (and hence the twist angle between  $\pi$ -orbitals oriented normal to the "sphere" surface) as measured from the center of the cage is  $\cong 23^\circ$  if all the bond lengths are similar. Thence the overlap and one-electron resonance integrals should be reduced from their ordinary planar values by a factor  $\cong \cos 23^\circ \cong 0.92$ . Likewise two-electron exchange integrals should be reduced by a factor  $\cong$

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$\cos^2 23^\circ$ . An alternative approach would assign a hybridization  $\sim sp^{2.6}$  to each carbon atom to minimize  $\sigma$ -bond strain, thus altering the values of the semiempirical integrals. Other considerations such as parameter changes due to variations in bond length, couplings of  $\sigma$ - and  $\pi$ -networks, and further effects of electron correlation are possible as well. Here we shall simply reduce the ordinary Hückel MO and resonance-theory parameters by factors of 0.92 and 0.84, respectively.

In Table II we report our computed resonance energies for buckminsterfullerene and compare them to a few other representative species. The Hückel-MO and Kekulé-structure-enumeration methods agree with one another that the  $C_{60}$  structure is highly aromatic, even taking into account the nonplanarity. The presumably more reliable<sup>5,6</sup> Herndon-Simpson-type resonance theory, however, predicts the species to be slightly less aromatic. The stability indicated from the Kekulé count is larger because, though there are many Kekulé structures, they infrequently differ from one another in a simple local manner so that they interact among one another less strongly than is typical.

Nevertheless, in comparison to other 60-atom clusters (with no H atoms) the present structure is likely to be highly stable. First, all  $\sigma$ -valences are satisfied (i.e., there are no dangling  $\sigma$ -bonds), a feature that is certainly crucial to the structure's relative stability. Second, granted a two-dimensional network bent to close on itself in three dimensions, the effect of the attenuation of the interaction parameters due to nonplanarity seems to be minimized. To see this note that because these parameters vary as  $\theta^n$  with  $n \geq 2$  for small angular deflections  $\theta$  from planarity, the maximum local deflection should be minimized; this occurs for a structure approximating a spherical surface with as much similarity as possible from one point on the surface to another (thereby smearing out the strain and deviation from nonplanarity). But this seems likely to be achieved by the proposed<sup>1</sup>  $C_{60}$  structure, as indicated by its high symmetry. Finally, as established here, the structure does exhibit a fecundity of Kekulé structures and a sizable resonance energy (for a nonplanar structure).

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### Structure-Dependent Electrical Conductivity of Alkylpyridinium Tetracyanoquinodimethane Langmuir-Blodgett Films

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The orientation of donors and acceptors has a significant influence on the conductivity of a charge-transfer complex. The control of the orientation, however, is difficult by application of usual preparation methods of a single crystal, including a diffusion method and an electrocrystallization.

Langmuir-Blodgett (LB) technique has become of interest as an effective means of molecular arrangement. Recently, Ruau-del-Teixier et al.<sup>1</sup> prepared a conducting LB film of *N*-docosylpyridinium tetracyanoquinodimethane (TCNQ) (1). After having been treated with iodine vapor, the film exhibited a conductivity of  $10^{-1}$  S  $cm^{-1}$ . The studies of the orientation control of a charge-transfer complex, however, have not yet come to our knowledge. We show herein an example of controlling the conductivity through the orientation of 1 by use of LB technique.

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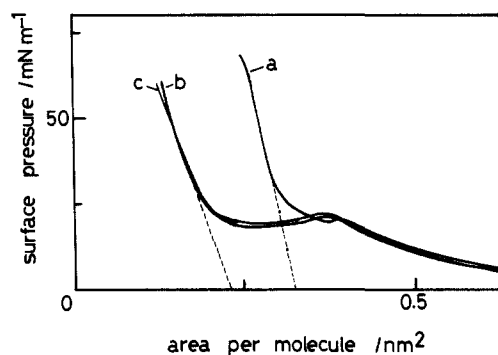


Figure 1. Surface pressure-area isotherms of 1 at different subphase temperatures (4 °C, curve a; 13 °C, curve b; 17 °C, curve c).

Table I. Ratios of Absorbance for HTF and LTF

	$r_{45^\circ} = A1/A2^a$	$r_{90^\circ} = A3/A4^a$
HTF	$1.25 \pm 0.02$	$1.15 \pm 0.01$
LTF	$1.33 \pm 0.02$	$1.05 \pm 0.03$

<sup>a</sup>The ratio of absorbance under following conditions: A1, incident angle  $\theta_i = 45^\circ$  and electric field E parallel to the long axis of the sample; A2,  $\theta_i = 45^\circ$  and E perpendicular; A3,  $\theta_i = 90^\circ$  and E parallel; A4,  $\theta_i = 90^\circ$  and E perpendicular.

Surface pressure-area ( $\Pi$ -A) isotherms were measured on pure water by use of a Lauda Filmwaage. Benzene-acetonitrile (1:1) was used as a spreading solvent. Electronic spectra were obtained by differential spectroscopy according to Kuhn et al.<sup>2</sup> Ac conductivity of LB films was measured by using the method of Sugi et al.<sup>3</sup>

By varying the subphase temperature, 1 showed two types of  $\Pi$ -A isotherms (Figure 1). The extrapolated areas per molecule of 1 at zero pressure were 0.23 and 0.32  $nm^2$  when the subphase temperatures were 13-17 and 4 °C, respectively. The monolayers of 1 were deposited as Y-type films at 3-5 and 17 °C (abbreviated as LTF and HTF, respectively), on a glass slide coated with three monolayers of cadmium eicosanoate.

Both LTF and HTF exhibited the peaks at  $2\theta = 1.80^\circ$  in the X-ray small-angle scattering patterns. This value is reduced to the bilayer  $d$  spacing of 9.8 nm assuming that each peak is the second-order reflection.

The structures of these films were confirmed by the electronic spectra, using polarized light with the incident plane normal to the dipping direction. The incident angles  $\theta_i = 90^\circ$  and  $45^\circ$  to the film surface were chosen, and the electric fields of polarized light were parallel and perpendicular to the incident plane. The ratios of maximum absorbance are shown in Table I for the broad band at 655-665 nm which is assigned to the locally excited transition in a TCNQ radical anion, polarized to the long axis of the radical anion.<sup>4</sup>

The polar angle  $\delta$  of the dipole moment with respect to the Z axis normal to the surface is given according to Schmidt and Reich,<sup>5</sup>

$$\cos^2 \delta = \frac{(1/r_{45^\circ} - \cos^2 \beta / r_{90^\circ}) / \sin^2 \beta}{1/r_{90^\circ} + 1 + (1/r_{45^\circ} - \cos^2 \beta / r_{90^\circ}) / \sin^2 \beta} \quad (1)$$

where  $\beta$  is the refractive angle of the film. Assuming that the refractive index of the film is 1.53 ( $\beta = 27.5^\circ$ ),<sup>2</sup> we obtain the rough estimates  $\delta = 90^\circ$  for LTF and  $\delta = 60^\circ$  for HTF. For  $\delta = 90^\circ$ , the molecular model indicates that the cross-sectional area of a TCNQ radical anion is 0.30  $nm^2$  when the short axis is normal to the surface. This value is almost identical with the observed cross-sectional area of 1 upon an air-water interface at 4 °C. In case of HTF,  $\delta = 60^\circ$  leads to a cross-sectional area of 0.26  $nm^2$ ,

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