$\cos^2 23^\circ$. An alternative approach would assign a hybridization $\sim sp^{2.6}$ to each carbon atom to minimize σ-bond strain, thus altering the values of the semiempirical integrals. Other considerations such as parameter changes due to variations in bond length, couplings of σ- and π-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[5,6] 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 σ-valences are satisfied (i.e., there are no dangling σ-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 θ^n with $n \geq 2$ for small angular deflections θ 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[1] 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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Registry No. Buckminsterfullerene, 99685-96-8.

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, Ruaudel-Teixier et al.[1] 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.

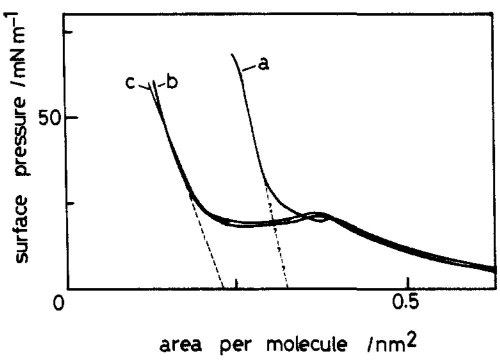

Figure 1. Surface pressure-area isotherms of **1** at different subphase temperatures (4 °C, curve a; 13 °C, curve b; 17 °C, curve c).

Table I. Ratios of Absorbance for HTF and LTF

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

[a] The ratio of absorbance under following conditions: *A*1, incident angle $\theta_i = 45^\circ$ and electric field E parallel to the long axis of the sample; *A*2, $\theta_i = 45^\circ$ and E perpendicular; *A*3, $\theta_i = 90^\circ$ and E parallel; *A*4, $\theta_i = 90^\circ$ and E perpendicular.

Surface pressure-area (Π-*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.[2] Ac conductivity of LB films was measured by using the method of Sugi et al.[3]

By varying the subphase temperature, **1** showed two types of Π-*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° 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.[4]

The polar angle δ of the dipole moment with respect to the *Z* axis normal to the surface is given according to Schmidt and Reich,[5]

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

where β is the refractive angle of the film. Assuming that the refractive index of the film is 1.53 ($\beta = 27.5^\circ$),[2] 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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which is ca. 10% larger than the observed value. This difference suggests the higher ordering involving the interlocking of TCNQ radical anions.

The LB films exhibited higher conductivities in the lateral direction even without the I_2 vapor treatment. The value of conductivity in the film plane of HTF (3×10^{-5} S cm^{-1}) was larger than that of LTF (7×10^{-7} S cm^{-1}), due to the difference in orientation of TCNQ radical anion. No anisotropy of conductivity was observed in the film plane of HTF in spite of the structural anisotropy. The compacted sample of **1** exhibited a conductivity of 6.1×10^{-10} S cm^{-1}.

The relatively large values of conductivity in the lateral direction result from the highly anisotropic layered structure of LB films: the close stacking of charge-transfer layer sandwiched between layers of insulating long alkyl chains. The conductivity of the order of 10^{-14} S cm^{-1} was obtained in the normal direction for HTF.

These results indicate that the conductivity of films can be controlled by the subphase temperature and demonstrate the feasibility of controlling the orientation of donors and acceptors in the charge-transfer complex by means of LB technique.

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Acetal-Initiated Cyclizations of Vinylsilanes. A General Synthesis of Allylically Unsaturated Oxacyclics

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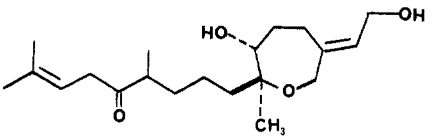
Oxacyclics have been isolated from nearly all sources of natural products,[2] and a number of these contain a single endo- or exocyclic double bond allylic to the oxygen atom.[3] An example of this latter group from plant sources is the unusual diterpene zoapatanol (**1**).[4] A potentially general route to oxacyclics of this type is outlined in eq 1 (X = O). In this vinyl silane-based approach, the silicon substituent[5] is utilized to both assist assembly of the cyclization substrate (**2** → **3**) and control the regiochemistry and stereochemistry of the product double bond.[6] In this paper we outline the successful use of this strategy to prepare five-, six-, and seven-membered unsaturated oxacyclics. We also report the unprecedented control that double-bond stereochemistry can exert on the ring size of the cyclization product.



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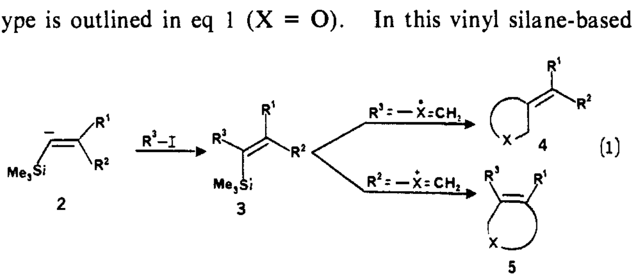
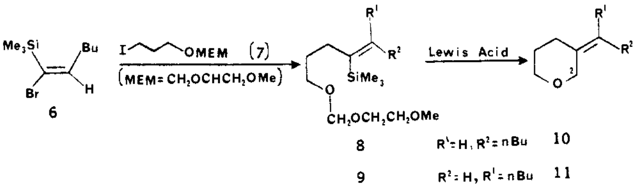


(1)

Although cations derived from acetals have been employed for years to initiate cyclizations to form carbocyclic products,[7] it is only recently that Kocienski, Itoh, and others[8] have demonstrated the utility of related cyclization reactions for the synthesis of oxacyclic products. Our initial studies employed (methoxyethoxy)methyl (MEM) ethers,[10] since these mixed acetals had been shown[8a,c,e] to be useful cyclization initiators. Alkylation of the lithium reagent derived from readily available bromide **6**[11] with iodide **7** afforded vinylsilane acetal **8** (80% yield, >99% *Z*[12]), which could be isomerized[13] to provide the more stable (*E*)-vinylsilane **9** (53% yield, 99% *E*).[12] A variety[14] of Lewis acids promote the desired cyclization reactions of **8** and **9**. Yields were best with $SnCl_4$ (2–8 equiv, CH_2Cl_2, −20 °C; quench at −70 °C with aqueous NaOH) which gave the 3-(*Z*)-pentylidenetetrahydropyran (**10**)[12] and the (*E*)-pentylidene isomer **11**[12] in 89% and 92% yields from **8** and **9**, respectively.[15,16] Quantitative capillary GC analysis demonstrated that the conversions of **8** → **10** and **9** → **11** were both *>99.5% stereospecific.*



The preparation of a representative group of oxacyclics by similar cyclizations is summarized in Table I. In all cases only a single C–C double bond positional isomer was obtained. Both 3-alkylidenetetrahydrofurans and 3-alkylideneoxepanes can be prepared also in this way. Entries 1 and 2 represent, to our knowledge, the first examples of vinylsilane cyclizations that form seven-membered ring products. The clean formation[17] of the (*E*)-3-alkylideneoxepane **12** (entry 2) is particularly significant since it supports the potential viability of an oxacyclization approach for the synthesis of zoapatanol (**1**) and congeners. The

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(1) (a) COSNET-SEP Mexico Graduate Fellow, 1982–1985. (b) NIH NRSA Postdoctoral Fellow (GM09444), 1984–1986.

(2) See, e.g.: Katritzky, A., Rees, C. W., Eds. "Comprehensive Heterocyclic Chemistry"; Pergamon Press: Oxford, 1984; Vol. 1–6.

(3) Marine organisms are a rich source of unsaturated oxacyclics, see: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, 251.

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(7) (a) For a review of the pioneering efforts of W. S. Johnson and his colleagues, as well as other literature in this area, see: Bartlett, P. A. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 5. (b) Acetal-initiated cyclizations of vinylsilanes that occur in the exocyclic mode to form cyclohexene products have been described by Fleming: see: Chow, H.-F.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1815. See also: Tius, M. A. *Tetrahedron Lett.* **1981**, *22*, 3335.

(8) For examples of acetal-initiated cyclizations that occur in an endocyclic mode[9] with respect to the initiator and thus yield oxacyclic products, see: (a) Nishiyama, H.; Itoh, K. *J. Org. Chem.* **1982**, *47*, 2496. (b) Nishiyama, H.; Narimatsu, S.; Sakuta, K.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1982**, 459. (c) Cockerill, G. S.; Kocienski, P. *J. Chem. Soc., Chem. Commun.* **1983**, 705. (d) Kay, I. T.; Williams, E. G. *Tetrahedron Lett.* **1983**, *24*, 5915. (e) Bunnelle, W. H.; Seamon, D. W.; Mohler, D. L.; Ball, T. F.; Thompson, D. W. *Tetrahedron Lett.* **1984**, *25*, 2653. (f) Melany, M. L.; Lock, G. A.; Thompson, D. W. *J. Org. Chem.* **1985**, *50*, 3925. (g) Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2093.

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(12) (a) Yields refer to pure (>98%) material isolated by chromatography (silica gel) or distillation. (b) Isomer ratios and product purities were determined by capillary GC analysis.

(13) Zweifel, G.; On, H.-P. *Synthesis* **1980**, 803.

(14) The most effective are $TiCl_4$, $TiCl_3O$-*i*-Pr, $EtAlCl_2$, $SnCl_4$, and $ZnBr_2$.

(15) Stereochemical assignments for the 3-alkylidene products followed directly from the diagnostic[16] ^{13}C NMR shifts of C-2: e.g., 67.1 ppm for **10** and 75.0 ppm for **11**.

(16) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 112–118.

(17) Cyclization of analogues of the substrates described in Table I entries 1 and 2 but lacking the *gem*-dimethyl substituent are more complex.

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