

Figure 1. Absorbance spectra observed upon photolysis of tetracyanoanthracene (TCA) in acetonitrile in the presence of *meso*-1,2-diphenyl-1,2-diaminoethane showing the formation of $\text{TCA}^{\bullet-}$ and the disappearance of TCA.

formation is greatly enhanced by the addition of water (10% by volume). The maximum yield noted was 91%. These results indicate that with additional stabilization of the radical anion the Ohashi reaction no longer takes place.

A similar result was obtained for TCA with triethylamine but without added salt. Thus irradiation of an acetonitrile solution of TCA (5×10^{-5} M) and triethylamine (1×10^{-3} M) leads to the disappearance of TCA with the concurrent appearance of an intense blue color and complex absorption spectrum with a clean isosbestic point. Although the quantum efficiency is low, irradiation can be continued until all the TCA has been converted. Admitting oxygen regenerates the TCA without detectable loss.²⁶ The radical anion was identified by its ESR spectrum. It can also be prepared electrochemically with the same characteristic absorption spectrum. The TCA radical anion is completely stable under these conditions for weeks. It is also stable under conditions of added water (up to 50% v/v) and in the presence of acetic anhydride. In the case with acetic anhydride, diethylacetamide is identified through GC-MS, which again suggests that the triethylamine is converted to diethylamine, which is then trapped by the anhydride. $\text{TCA}^{\bullet-}$ is apparently not a strong base nor a good nucleophile under these circumstances. The reaction appears to be quite general for amines.²⁵ When *meso*-1,2-diphenyl-1,2-diaminoethane (*meso*-DPED) is irradiated with TCA under similar conditions, $\text{TCA}^{\bullet-}$ is formed (Figure 1), along with benzaldehyde, a product of a fragmentation reaction characteristic of 1,2-diamines.²⁷ If the reaction is carried out in the presence of oxygen, the TCA is not consumed and acts as a true "sensitizer" for the oxidative fragmentation reaction.

Additional information can be obtained from transient absorption spectroscopy. Pulsed laser excitation of acetonitrile solutions of DCA or TCA in the presence of 0.05 M triethylamine, with 0.15 M biphenyl as a cosensitizer,²⁴ results in rapid (<20 ns) production of $\text{DCA}^{\bullet-}$ or $\text{TCA}^{\bullet-}$ absorbance, followed by a slower growth of an absorbance that is equal to that formed rapidly, on a microsecond time scale. The rapid formation is evidently the result of the initial electron transfer between biphenyl and cyanoaromatic. The slower formation is attributed to reduction of a second ground-state cyanoaromatic by the iminium radical formed by oxidation of TEA ($\text{TEA} + \text{Bp}^+ \rightarrow \text{TEA}^{\bullet+} + \text{Bp}$) and deprotonation of the so-formed $\text{TEA}^{\bullet+}$.²⁸ Similar two-stage redox reactions have been noted in other systems.²⁹ The

(26) The regeneration reaction is presumably electron transfer from $\text{TCA}^{\bullet-}$ to oxygen to form $\text{O}_2^{\bullet-}$. This process is endothermic by ca. 0.4 eV but may occur on a time scale of seconds.

(27) Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 2314.

(28) The second stage of the redox reaction (eq 4) is favorable by ca. 0.7 eV. The iminium radical oxidation potential is -1.12 V while the reduction potential of the ground-state TCA is -0.45 V. Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(29) Monserrat, K.; Foreman, T. K.; Grätzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

cyananthracene radical anions are not observed to undergo any decay even on a time scale of milliseconds.

One of the most important of the many factors that control the reactivity of photochemical SET generated ion radicals is solvent polarity. A closely coupled question is whether the primary intermediate is a solvent-separated radical ion pair (SSRIP) or a contact radical ion (CRIP). The SSRIP are more stable than CRIP in polar solvents ($\epsilon > 7$),³⁰ and in these solvents the highly solvated ion radicals can separate to form free radical ions. Thus under these conditions the anion radicals are potentially less reactive with the radical cations (as bases and nucleophiles) than in nonpolar solvents, in which the CRIP are more important. For the CRIP the lower solvation and close proximity of the ion radicals can result in higher reactivity, especially toward each other. Thus we find that irradiation of DCA (1×10^{-4} M) in acetonitrile with the amino ketone 3-methyl-3-(4-morpholinyl)-2-butanone (0.025 M) and tetra-*n*-butylammonium phosphate (7×10^{-3} M) yields $\text{DCA}^{\bullet-}$ as a stable (in the absence of O_2) product (80% yield) and very little 4-acetylmorpholine, the major product from radical cation-radical anion reaction. In contrast, irradiation in benzene, where 4-acetylmorpholine is produced in >80% yield, leads to no detectable stable anion radical, even on prolonged photolysis.³¹ Similarly, irradiation of TCA in benzene with various diamines leads only to fragmentation and disappearance of TCA (presumably to TCAH_2) but not to stable $\text{TCA}^{\bullet-}$, in contrast to the results described above for acetonitrile. These results reinforce that the reactivity of ion radicals generated by photoinduced electron transfer can be strongly altered by the choice of solvent and/or added solutes; while the present results focus on attenuation of anion radical reactivity, it seems clear that similar modification of cation radical reactivity can be readily obtained for other donor-acceptor combinations.

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(30) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93.

(31) No salt was present in the product studies. Addition of salt to benzene solutions does not lead to detection of $\text{TCA}^{\bullet-}$.

Stereochemical Studies on the Atomic Inversion of Divalent Oxygen: The Use of Dinaphtho[*a*,*j*]anthracenes To Restrict Rotational Motion¹

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The barrier to atomic inversion ("linearity barrier") at ether oxygen³ is not known; the rotational barrier about the C–O bond, in contrast, is well documented.⁴ According to the calculations

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(3) One may distinguish between the following types of ether oxygen: $\text{C}_{sp^3}\text{-O-C}_{sp^3}$, $\text{C}_{sp^3}\text{-O-C}_{sp^2}$, and $\text{C}_{sp^2}\text{-O-C}_{sp^2}$.

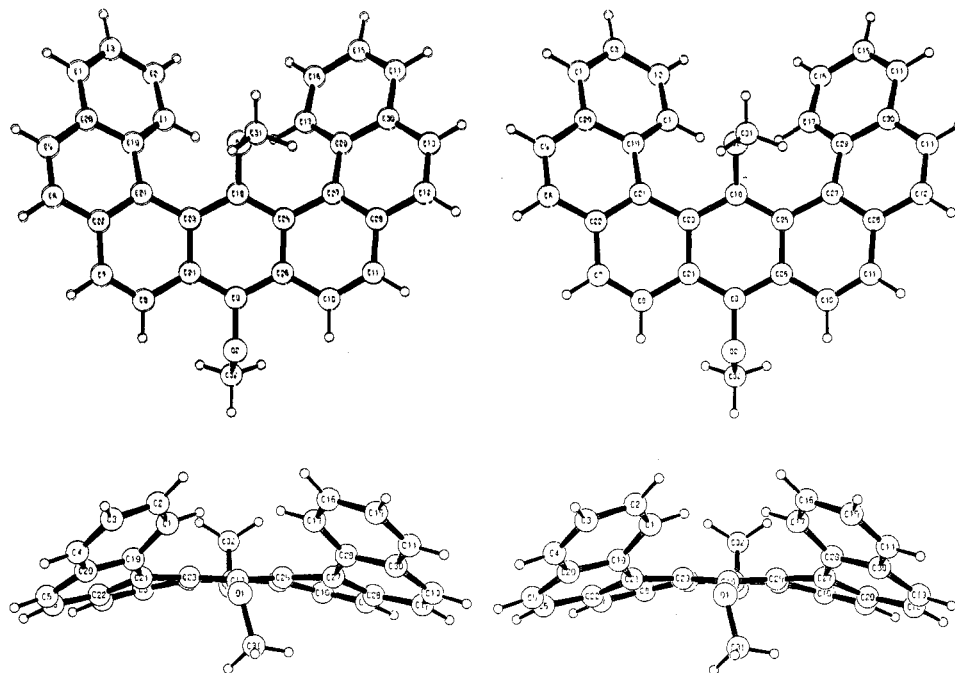
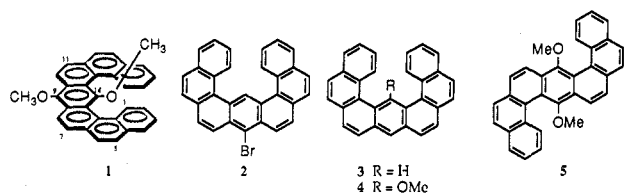


Figure 1. X-ray crystal structure of 9,18-dimethoxydinaphtho[*a,j*]anthracene (**1**).

of Diab and Simons⁵ the linearity barrier of H₂O is 27.5 kcal/mol.; ab initio calculations for the same barrier yielded the values of 21.6,⁶ >34,⁷ and 37.2 kcal/mol⁸ (MP2/6-31G*). For methanol, the calculated barrier is 32.5 kcal/mol⁹ (HF/DZ, Hartree-Fock/double- ζ basis). The C–O–C linearity barrier for dimethyl ether, on the other hand, has recently been calculated to be 36.3 kcal/mol (6-31G(d)).¹⁰ In 1970, Gordon and Gallagher¹¹ reported the linearity barrier in doubly bridged diphenyl ethers to be 20 kcal/mol. Cremer and co-workers¹² calculated (HF/STO-3G, HF/4-31G, MP2/STO-3G, MNDO, and correlation-corrected MNDO) the barrier of inversion in 1,6:8,13-bisoxido-[14-annulene] to be 32–34 kcal/mol; further, they determined the barrier for the chiral 2,9-dibromo derivative to be 32 kcal/mol. We report on our experimental studies on the linearity barrier of oxygen in a novel molecular framework designed to restrict the rotational motion about the C–O bond; we reach the important conclusion that the minimum barrier to linear inversion in aryl methyl ethers is about 18 kcal/mol.

It was our working hypothesis that 9,18-dimethoxydinaphtho[*a,j*]anthracene (**1**) constitutes a suitable molecular



(4) The following rotational barriers about the C–O bond have been reported: anisole-*d*₃, 4.08 kcal/mol; anisole-*d*₅, 3.6 kcal/mol (cf.: Owen, N. L.; Hester, R. E. *Spectrochim. Acta* **1969**, *25A*, 343); thioanisole, 0.7 kcal/mol (cf.: Schweig, A.; Thon, N. *Chem. Phys. Lett.* **1976**, *38*, 482); dimethyl ether, 2.720 kcal/mol (cf.: Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1959**, *30*, 1096); dimethyl sulfide, 2.1 kcal/mol (cf.: Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479).

(5) Diab, S.; Simons, G. *Chem. Phys. Lett.* **1975**, *34*, 311.

(6) Takahata, Y.; Parr, R. G. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1380.

(7) Gordon, A. J.; Sanders, W. A., unpublished results.

(8) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. (b) Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435.

(9) Tel, L. M.; Wolfe, S.; Csizmadia, I. G. *J. Chem. Phys.* **1973**, *59*, 4047.

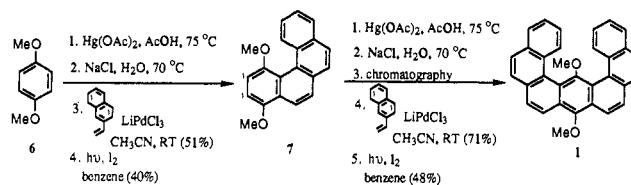
(10) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697. These authors also report the corresponding value for C–O–Si to be 6.8 kcal/mol.

(11) Gordon, A. J.; Gallagher, J. P. *Tetrahedron Lett.* **1970**, 2541.

(12) Cremer, D.; Kraka, E.; Gauss, J.; Bock, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 4768.

framework in which rotational motion about the aryl–C–oxygen bond would be disallowed, whereas linear inversion would be allowed; in this model free rotation about the C–18–oxygen bond is extremely unlikely, whereas atomic inversion at C–18 oxygen may occur through a narrow congested slot; the methoxyl at C–9 acts as a reference group.¹³ At the inception of our work, there was only one report in the literature¹⁴ with the proposed skeletal framework, viz. 9-bromodinaphtho[*a,j*]anthracene (**2**). Subsequently, a synthesis of the parent hydrocarbon (**3**) also appeared.¹⁵

The desired 9,18-dimethoxy derivative **1** was synthesized from commercial 1,4-dimethoxybenzene (**6**) by sequential mercuration,



Heck coupling reaction with 2-vinylnaphthalene, and Mallory photocyclization¹⁶ to give **7**. Subsequent mercuration of **7** led to a mixture of isomeric C-3- and C-2-mercured compounds, which were separated by adsorption chromatography on silica gel; each, in turn, was subjected to further coupling with 2-vinylnaphthalene followed by Mallory cyclization to give compounds **1** and **5**, respectively. The proton NMR of the desired isomer, **1**, revealed two methoxy singlets—at 2.10 and 4.20 ppm (CDCl₃); the isomeric compound **5** exhibited a single MeO signal at 3.00 ppm (CDCl₃). Furthermore, the single-crystal X-ray structure¹⁷ of **1** revealed

(13) The presence of the C-9 OMe group also simplifies the synthesis of the model. However, it cannot be considered as a totally unreactive blocking group, since in the photochemical cyclization, it can be eliminated as MeOH (cf.: Giles, R. F. G.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2447).

(14) Wilcox, C. F.; Lahti, P. M.; Rocca, J. R.; Halpern, M. B.; Meinwald, J. *Tetrahedron Lett.* **1978**, 1893.

(15) Mallory, F. B.; Mallory, C. W.; Sen Loeb, S. E. *Tetrahedron Lett.* **1985**, 3773.

(16) A comprehensive review of this versatile reaction by Mallory and Mallory has appeared in: *Org. React. (N.Y.)* **1984**, *30*, 1–456.

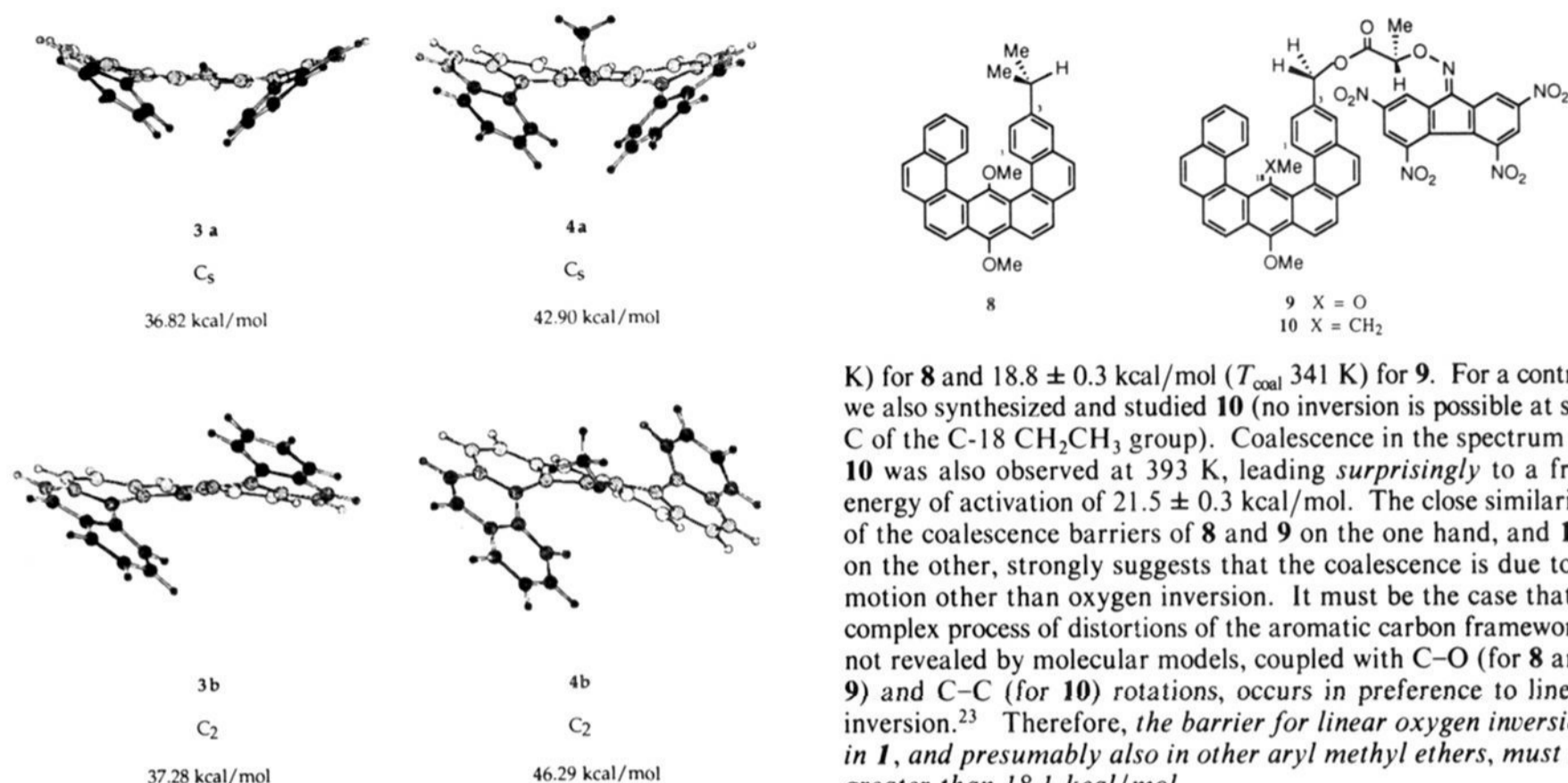


Figure 2. Calculated conformations and corresponding energies of dinaphtho[*a,j*]anthracene (**3a**, **3b**) and 18-methoxydinaphtho[*a,j*]anthracene (**4a**, **4b**).

the C_s (in contradistinction to C_2)¹⁸ symmetry of the dinaphthoanthracene framework (Figure 1).

Interestingly, molecular mechanics calculations¹⁹ show the energies (Figure 2; the calculated globally minimized energies are given under each structure) of the butterfly (C_s) and the helical (C_2) conformations to favor slightly (0.46 kcal/mol) the C_s state **3a** of the parent system, but more so (3.39 kcal/mol) the C_s state **4a** of the C-18 methoxy derivative.²⁰

Interconversion of two such (pseudoenantiomeric) homomeric C_s states of **1**, by a hoped-for linear inversion at C-18 methoxy oxygen, or by some other process, would, on a time-averaged basis, yield a planar molecule of effective C_{2v} symmetry. Such an interconversion could be monitored through the coalescence of either diastereotopic CH₃ groups (enantiomerization) in 3-isopropyl-9,18-dimethoxydinaphtho[*a,j*]anthracene (**8**) or diastereotopic benzylic hydrogens (diastereomerization) in ester **9** derived from (-)-TAPA and 3-hydroxymethyl-9,18-dimethoxydinaphtho[*a,j*]anthracene:²¹

Dynamic studies²² on **8** and **9**, in DMSO-*d*₆, yielded the following free energies of activation: 18.1 ± 0.2 kcal/mol (T_{coal} 330

K) for **8** and 18.8 ± 0.3 kcal/mol (T_{coal} 341 K) for **9**. For a control we also synthesized and studied **10** (no inversion is possible at sp³ C of the C-18 CH₂CH₃ group). Coalescence in the spectrum of **10** was also observed at 393 K, leading *surprisingly* to a free energy of activation of 21.5 ± 0.3 kcal/mol. The close similarity of the coalescence barriers of **8** and **9** on the one hand, and **10**, on the other, strongly suggests that the coalescence is due to a motion other than oxygen inversion. It must be the case that a complex process of distortions of the aromatic carbon framework, not revealed by molecular models, coupled with C–O (for **8** and **9**) and C–C (for **10**) rotations, occurs in preference to linear inversion.²³ Therefore, *the barrier for linear oxygen inversion in **1**, and presumably also in other aryl methyl ethers, must be greater than 18.1 kcal/mol.*

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Supplementary Material Available: Listing of final atomic parameters, anisotropic thermal parameters, bond lengths, bond angles, and least-squares planes through rings A–G for **1** (10 pages). Ordering information is given on any current masthead page.

(23) This motion involving extreme distortion of the dinaphthoanthracene framework would take place in compound **4** as well.

A Stable Crystalline Carbene

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We report the synthesis, structure, and characterization of the first crystalline carbene. Carbene **1**, 1,3-di-1-adamantylimidazol-2-ylidene, forms colorless crystals with sufficient kinetic and thermodynamic stability to be easily isolated and characterized. The deprotonation of 1,3-di-1-adamantylimidazolium chloride (**2**) in THF at room temperature with catalytic dimethyl anion (⁻CH₂S(O)CH₃) in the presence of 1 equiv of sodium hydride produces carbene **1** (eq 1). This deprotonation can also be accomplished with potassium *tert*-butoxide in THF to give a 96% yield of **1**.

Carbene **1** is stable in the absence of oxygen and moisture. Recrystallization of **1** from toluene affords clear, colorless rectangular prisms with a melting point of 240–241 °C. A sample of **1** that had been melted could be remelted without depression of the melting point. A previously melted sample of **1** showed

(17) The crystals were monoclinic, space group *I*2/*a*, with $a \approx 39.035$ (4), $b = 7.157$ (1), $c = 35.497$ (3) Å; $\beta = 113.91$ (1)°; and $d_{\text{calcd}} = 1.285$ g cm⁻³ for $Z = 16$ (C₃₂H₂₂O₂, $M_r = 438.53$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu K α radiation, θ -2 θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.40 × 0.65 mm. A total of 6126 independent reflections were measured for $\theta < 57^\circ$, of which 4412 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368) and was refined by block-diagonal least-squares procedures in which the matrix was partitioned into two blocks. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indexes are $R = 0.048$ and $R_w = 0.049$ for the 4412 observed reflections. The final difference map has no peaks greater than ±0.2 e Å⁻³.

(18) The C_s symmetry conformation has been dubbed the *butterfly* conformation; whereas the C_2 symmetry conformation is termed the *helical* conformation.

(19) The molecular mechanics calculations were done with MacroModel version 2.5 using MM2 parameters on a microVAX II.

(20) See: Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. J. *Am. Chem. Soc.* **1986**, *108*, 5652.

(21) The rotations about the Ar-*i*-Pr and 9-MeO-Ar bonds are assumed to be substantially faster.

(22) Details of the syntheses, analogous to that outlined for **1**, will be given in the full paper.