are listed in Table I and the spectra are shown in Figures 5 and 6.

The optical spectra of all these radical anions but that of pyridine are shown on Figures 7, 8, and 9. The λ_{max} and the respective extinction coefficients are marked on the drawings. There is a striking similarity in the absorption spectra of naphthalene and quinoline and isoquinoline radical ions as well as that of the anthracene and acridine radical ions. However, in both systems the absorption maxima of the aza compounds are shifted to the shorter wavelength when compared with the relevant hydrocarbons; the respective energy gaps are increased by about 4–5 kcal/mol.

Acknowledgment. We thank Dr. Cserhegyi for preparing the deuterated quinoline, and we gratefully acknowledge the financial support of this investigation the National Science Foundation, the United States Air Force, Contract AF33(615)3788, and the Petroleum Research Fund administered by the American Chemical Society.

Intramolecular Energy Transfer between Nonconjugated Chromophores. Effect of Rigid Perpendicular Orientation

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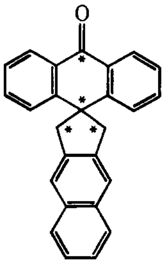
Contribution from the Department of Chemistry, The George Washington University, Washington, D. C. 20006. *Received April 29, 1968*

Abstract: Fluorene and *p*-dimethoxybenzene have been incorporated in the same molecule by attaching them rigidly to an inflexible frame. The lowest excited singlet and triplet states of the two chromophores are of proper energy to allow efficient energy transfer. Although in a random orientation in solution efficient energy transfer takes place between the separated chromophores, when they are held in a rigid perpendicular position even at close distance, no interaction was detected. The results verify the orientation requirements for electric dipole energy transfer.

During the last five years several efforts have been made to verify experimentally the theory developed originally by Förster[2] for the transfer of electronic excitation energy between two nonconjugated chromophores on model compounds in which the two chromophores are connected to the same molecular frame.[3] The two important features in such compounds are the separation distance and the mutual orientation of the donor and acceptor chromophores.

An increase in the number of interposing methylene groups did not lead to known separations because of free rotation in the $-CH_2-$ links.[3a,b] Although the average distance was known more accurately in compounds in which the chromophores were connected to a saturated steroidal frame or to a polyamide helix, their mutual orientation was essentially random due to rotation about the connecting σ bonds.[3c,g]

Apparently, the author in only one recently reported work has prepared model compounds having a distinct donor–acceptor relative orientation. Thus, Keller[3e] presented evidence of triplet–triplet energy transfer between presumably perpendicular anthrone and naphthalene chromophores in compounds I and II.



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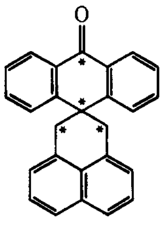
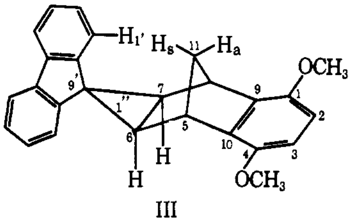


II

Presently we report the results of an energy transfer study on 1,4-dimethoxy-5,8-methano-6,7-*exo*-[fluorene-9′-spiro-1′′-cyclopropane]naphthalene (III).



III

Unlike I and II, the rigid frame between the *p*-dimethoxybenzene (DB) and fluorene (F) chromophores has no flexible connections and the two π systems are in a perfectly perpendicular orientation. It is known that singlet–singlet resonance interaction is effective at distances up to 200 Å[2] whereas triplet energy migration requires either collision or close molecular approach.[4]

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[1] In partial fulfillment of the Ph.D. requirement for J. R. D.

[2] (a) T. Förster, *Z. Elektrochem.*, **64**, 157 (1960); (b) *Discussions Faraday Soc.*, 27, 1 (1959); (c) *Naturwissenschaften*, 33, 1661 (1946); (d) *Ann. Phys.*, 2, 55 (1948); (e) "Fluorezenz Organische Verbindungen," Vandenhoech and Ruprech, Gottingen, 1951, p 83–86.

[3] (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963); (b) *ibid.*, **87**, 2322 (1965); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965); (d) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); (e) R. A. Keller, *ibid.*, **90**, 1940 (1968); (f) N. Filipescu, S. Bjorklund, N. McAvoy, and C. R. Hurt, *Can. J. Chem.*, **45**, 1714 (1968); (g) L. Stryer and R. P. Haugland, *Proc. Nat. Acad. Sci. U. S.*, **58**, 719 (1967).

[4] (a) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953); (b) V. L. Ermolaev, *Opt. Spectry.*, **6**, 417 (1959); (c) V. L. Ermolaev, *Soviet Phys. Usp.*, **6**, 333 (1963).

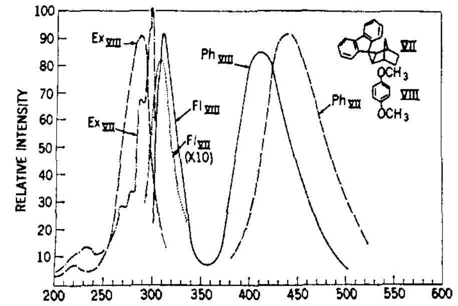


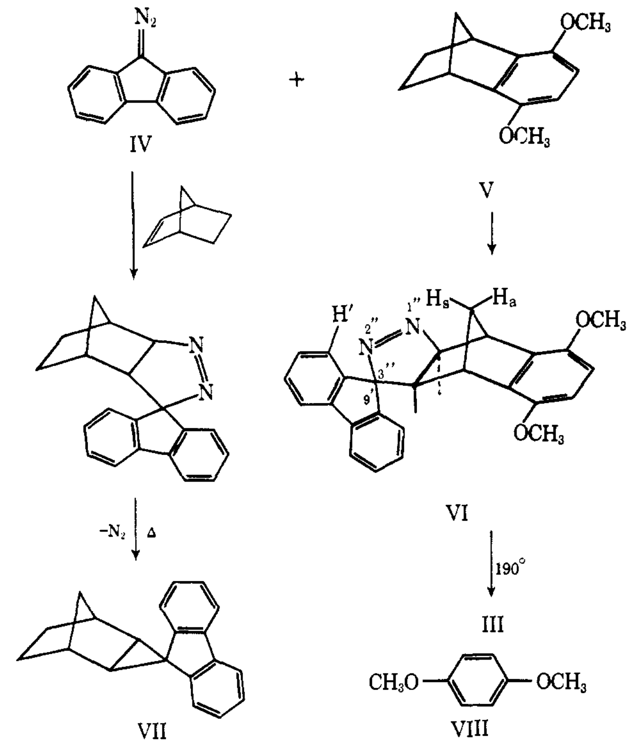
Figure 1. Emission and excitation spectra of separated chromophores $10^{-3}M$ in EPA at 77°K (uncorrected). VII and VIII exhibit both fluorescence (Fl) and phosphorescence (Ph): Ph_{VII} excited at 306 mμ, Fl_{VIII} and Ph_{VIII} excited at 292 mμ, Fl_{VII} excited at 265 mμ; for Ex_{VIII} emission at 412 mμ, for Ex_{VII} emission at 435 mμ.

Therefore, the predicted vanishing of dipole interaction terms for a $\pi/2$ angle between the transition vectors, valid for both types of energy, can probably be verified conveniently in compound III. The small separation distance between DB and F and the fact that the chromophores exhibit both fluorescence and phosphorescence make III particularly suitable. The lowest excited singlet and triplet states of DB and F lend themselves to both S–S and T–T transfer.

Contrary to conclusions in ref 3e, we found that although in a random orientation in solution energy transfer does take place, when the same two chromophores are held in a rigid perpendicular position at close distance no energy transfer can be detected.

Preparation and Structure of Spirocyclopropane III

Thermal decomposition of 1-pyrazoline VI obtained by addition of 9-diazofluorene (IV) to 1,4-methano-5,8-dimethoxynaphthalene (V) yielded III in 37% over-all yield.



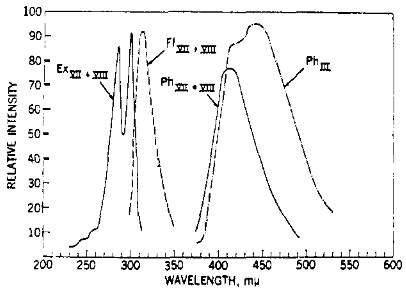


Figure 2. Phosphorescence (Ph), fluorescence (Fl), and excitation (Ex) spectra of a $10^{-3}M$ VII and VIII mixture and the phosphorescence of model compound III (uncorrected). $Ph_{VII+VIII}$ excited at 290–310 mμ, $Fl_{VII+VIII}$ excited at 265 mμ, $Ex_{VII+VIII}$ emission at 410 mμ, Ph_{III} excited at 300 mμ.

The ir spectrum of pyrazoline VI shows a characteristic –N=N– absorption band at 1535 cm^{-1} and the 1 H signal at δ 5.49 in the nmr spectrum is indicative of the HCN=N proton.[5] Actually the nmr spectrum of VI resembles those of other 1-pyrazolines obtained by addition of IV to bicyclic[2.2.1]olefins. We have shown that these adducts have *exo* orientation.[6]

The structure of model compound III was confirmed by both nmr and uv absorption spectra. The nmr resonance line for protons in positions 5, 6, 7, 8, 11s, and 11a are virtually identical with those observed for similar spirocyclopropane compounds in which DB was absent.[6] The only notable difference was some general deshielding brought about by the additional π system. The *exo* positioning of the cyclopropane ring was verified by the extinction coefficient values in the uv absorption spectrum of III; ϵ^{III} was found to be essentially equal to $\epsilon^{VII} + \epsilon^{VIII}$. If the spiro-linked fluorene were attached *endo* to the norbornane frame, the uv absorption would certainly reflect the perturbation caused by extensive spacial overlap of the two π systems suggested by molecular models. The nmr spectrum of III is consistent with its high symmetry, proof of the rigid perpendicularity of the aromatic chromophores.[7]

Spectrophotofluorometry

The uv absorption spectrum of a 10^{-5} *M* solution of III in cyclohexane coincided within 5% with that of a mixed solution 10^{-5} *M* in both VII and VIII. Figure 1 shows the emission and excitation spectra of each chromophore by itself in ether–isopentane–ethanol (EPA) glass at liquid nitrogen temperature. The energy of the 0–0 bands in excitation and fluorescence appearing in the 280–320-mμ region show rather extensive overlap of the DB and F lowest excited singlet states and their vibrational levels. The long-lived phosphorescence (τ_{Ph}^{F} = 3.1 sec, τ_{Ph}^{VIII} = 1.7 sec) of fluorene and VIII corresponds to bands centered at about 440 and 410 mμ, respectively.

The emission and excitation spectra of a 10^{-3} *M* 1:1 mixture of VII and VIII in rigid matrix at 77°K are shown in Figure 2. Practically no F phosphorescence (λ_{max} 440 mμ) could be detected from the

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[5] T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962).

[6] N. Filipescu and J. R. DeMember, *Tetrahedron*, **24**, 5181 (1968).

[7] We found that small distortions in the mirror symmetry caused by replacing the planar fluorene group with the slightly bent xanthene at the spiro linkage were clearly reflected in the nmr spectrum.

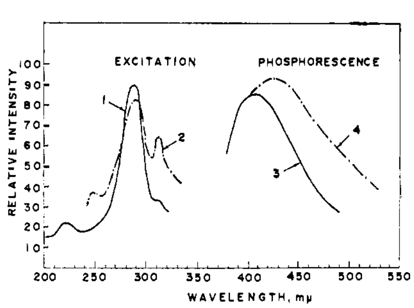

Figure 3. Excitation and emission of a 2.5×10^{-5} M VII and VIII mixture: 1, emission at 410 mμ; 2, emission at 430 mμ; 3, excitation at 292 mμ; 4, excitation 306 mμ.

mixture regardless of the excitation wavelength. On the other hand DB phosphorescence (λ_{max} 410 mμ) was excited by light absorbed by either chromophore as shown by the excitation spectrum $Ex_{VII\ +\ VIII}$ in Figure 2. At much lower concentrations (2.5×10^{-5} M in both VII and VIII, Figure 3) the individual F and DB phosphorescences were excited and observed separately. Within the limitations of F and DB fluorescence spectral overlap, the only fluorescence detected in the 10^{-3} M mixture of VII and VIII regardless of the excitation wavelength was that of DB ($Fl_{VII\ +\ VIII}$ in Figure 2; λ_{max} 315 mμ). Figure 2 also includes the phosphorescence spectrum of model compound III in frozen EPA. Each of the two chromophores in III exhibited $T_1 \rightarrow S_0$ emission. The phosphorescence excitation spectrum varied with detection wavelength on the emission monochromator in the 400–500-mμ range and approached the excitation spectrum of VIII and VII at the two ends, respectively. Both phosphorescence and excitation spectra show DB and F in III to be noninteracting entities and closely resemble those of the very dilute mixture of VII and VIII. The fluorescence emission of the two chromophores was not included in the diagram because the $S_1 \rightarrow S_0$ emission of DB is more than ten times more intense and overlaps that of F. The emission and excitation spectra in Figures 1–3 have not been corrected for the uneven spectral output of the xenon excitation source or for photomultiplier response.

Discussion

The frozen EPA solution containing 10^{-3} M each of VII and VIII has the F and DB chromophores separated on the average by distances well in excess of their molecular diameters.[8] However, the phosphorescence and excitation spectra in Figure 2 show that efficient energy transfer from F to the DB chromophore has taken place. The only known type of transfer operative at such separation distances in rigid solution is the singlet–singlet resonance transfer. The donor emission and acceptor absorption overlap is satisfied, the energetic location of the two singlets is proper, and the average separation distance is well within the interaction range.[2,3] At very large separation distances (low concentration) no interaction between F and DB was observed.

When the same two chromophores were held at distances of less than 10 Å by an inflexible saturated frame in III in a mutually perpendicular orientation, no $S_F \rightarrow S_{DB}$ or reverse $T_{DB} \rightarrow T_F$ transfer of energy could be detected. The transition vector for the first excited singlet state in DB was determined from polarized absorption measurements to lie in the molecular plane along the directions of the two *para* substituents.[9] It is also accepted that the analogous transition vector in F lies in the plane of the molecule[9a,10] but its direction has not been established with certainty. However by anology with biphenyl[10] and from the wavelength of the fluoresence, this vector is probably along the direction crossing both benzene nuclei in fluórene. All these directions are within about ±15° of a 90° angle (Dreiding) with the line connecting the centers of the two chromophores in III. Connsequently, in the absence of vibronic interaction of the first excited singlets with other excited states the dipole–dipole coupling between the two chromophores in III should be very small or vanish.

Our results seem to contradict conclusions reached by Keller in his measurements on compounds I and II. It seems to us that the assertion of perpendicularity between naphthalene and anthrone chromophores in I and II is inconclusive. Scale molecular models (Dreiding) of the two compounds suggest that because of rotations along the bonds marked by asterisks, at least two conformers of both I and II are possible. Interconversions between these stereoisomers require practically no activation energy.[11] In addition, the assumption that n,π* lowest triplet energy in anthrone is localized exclusively in the carbonyl group is only a simplifying approximation for a conjugated C=O chromophore.

We believe that compound III does not present these structural ambiguities. In our opinion, the absence of interaction between the two nonconjugated and mutually perpendicular chromophores which are held at close distance in III tends to verify the orientation requirements for electric dipole energy tansfer. It also suggests an orientation dependence for T–T transfer since the two chromophores are only 7 Å apart, well within the 15–20-Å distances reported for exchange interactions.[4]

Experimental Section

General. Ir and uv spectra were determined in double beam Beckman Model IR5A and Cary Model 15 spectrophotometers, respectively. Nmr spectra were recorded on a Varian Model A-60 spectrometer with TMS as internal standard. Elemental analysis were performed in our laboratory with an Aminco C & H Analyzer. Molecular weights were determined with a Mechrolab vapor pressure osmometer, Model 301A. Excitation and emission spectra were recorded on an Aminco–Bowman spectrophotofluorometer. The 10^{-3} to 10^{-4} EPA slutions in the 3-mm OD quartz tube were lowered in the coldfinger dewar in liquid nitrogen. Phosphorescence decay times were measured using the time-base recorder.

1,4-Dimethoxy-1,8-methano-6,7-*exo*-[fluorene-9′-spiro-3′′-1-pyrazoline]naphthalene (VI). Four grams (21.7 mmmol) of IV was added to a solution of 2.5 g (16.3 mmol) of V in 20 ml of C_6H_6 (dry). The solution was heated at reflux for 2 hr, allowed to cool,

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[8] After taking into account the solvent contraction at 77°K, the calculated average separation distance is 79 Å.

[9] (a) S. F. Mason, *Quart. Rev.* (London), 15, 335 (1961); (b) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, 23, 1480 (1955).

[10] F. Dörr and H. Gropper, *Ber. Bundsenges. Physik. Chem.*, 67, 193 (1963).

[11] The two benzene rings in anthrone are actually about 23° out of the plane perpendicular to naphthalene. Although flip-flop motions in the center ring of anthrone seem to keep the C=O group in a plane 90° with respect to naphthalene, distortions in the cyclopentane ring of I or the cyclohexane ring of II do not.

and filtered by suction. Crude VI (4.88 g, 12.4 mmol, 85%) was obtained as a yellow powder. Recrystallization from acetone yielded colorless prisms of pyrazoline VI, mp 180° dec; ν^{KBr}: 3030, 2940, 2820, 1535, 1485, 1422, 1284, 1245, 1049, 1019, and 749 cm^{-1}; nmr (CDCl$_3$): δ 6.62–7.91 (8 H, $H_{1'-8'}$) complex, 6.58 (2 H, $H_{2,3}$) AB multiplet, 5.50 (1 H, H_7) doublet (triplet), J = 6.3 (1) cps, 4.49 (1 H, H_8) broad singlet, 3.85 (3 H, OCH$_3$) sharp singlet, 3.58 (3 H, OCH$_3$) sharp singlet, 3.52 (1 H, H_5) broad singlet, 2.32 (1 H, H_6) doublet (doublet), J = 6.3 (2) cps, 1.72 (2 H, $H_{11s,11a}$) AB multiplet; uv (dioxane) $\lambda_{\max}$ mμ (ϵ): 271 (26,990), 258 (23,200), 281 (24,720), 293 (13,280), and 299 (9520).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10; O, 8.11; mol wt, 394. Found: C, 79.32; H, 5.65; N, 7.42; O, 7.61; mol wt, 382.

Preparation of III. VI (0.72 g, 1.83 mmol) was heated in a 100-ml round-bottomed flask at 190° for 15 min in the presence of 20 ml of *trans*-decalin. The solvent was removed by rotary-vacuum evaporation, and 35 ml of hot EtOH was added to the residue. Crystallization afforded 0.35 g (0.96 mmol, 52%) of yellow needles. Recrystallization from 95% EtOH yielded white needles, mp 151–152°; $\nu^{\mathrm{CCl_4}}$: 3030, 2980, 2920, 2830, 1600, 1490, 1440, 1252, 1178, 1075, 1055, 1015, and 745 cm^{-1}; nmr: δ 6.72–8.00 (8 H, $H_{1'-8'}$) complex, 6.69 (2 H, $H_{2,3}$) singlet, 4.10 (2 H, $H_{6,7}$) broad singlet, 3.84 (6 H; OCH$_3$) sharp singlet, 2.96 (1 H, H_{11s}) doublet, J = 9.6 cps, 2.21 (2 H, $H_{5,8}$) broad singlet, 1.70 (1 H, H_{11a}) doublet, J = 9.6 cps; uv (cyclohexane) $\lambda_{\max}$ mμ (ϵ): 277 (17,400), 293 (17,100), and 304 (14,400).

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05; O, 8.74; mol wt, 366. Found: C, 85.38; H, 6.30; O, 8.32; mol wt, 359.

Acknowledgment. This work has been supported in part by the National Aeronautics and Space Administration on Grant NsG-603.

Nuclear Magnetic Resonance Spectroscopy. Conformational Equilibria and Equilibration of 4,4-Difluoropiperidine. Measurement of the N–H Inversion Rate in a Six-Membered Ring[1]

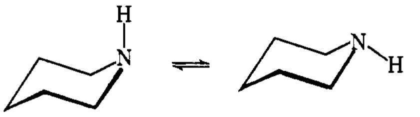
Garib Allah Yousif[2] and John D. Roberts

Contribution No. 3627 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Received March 9, 1968

Abstract: Fluorine magnetic resonance spectroscopy has been used to measure the rates of inversion of 4,4-difluoropiperidine. The activation energy (E_a) was found to be 13.9 and 13.5 kcal/mol in methanol and chloroform, respectively. In acetone, N–H nitrogen inversion was found to be slow on the nmr time scale with an E_a of about 10 kcal/mol. The free-energy difference between the forms with the N–H hydrogen axial and equatorial appears to be 0.42 kcal/mol with uncertain sign.

The conformations assumed by piperidine and N-substituted piperidine rings are of substantial chemical and biochemical interest. A number of X-ray studies have indicated that the chair form is favored for the piperidine ring.[3] The degree of preference for equatorial *vs.* axial positioning of the N–H hydrogen in piperidine is a matter of considerable controversy and of special significance, involving as it does what can be taken as a judgment of the relative steric sizes of hydrogen or a lone pair of electrons. Kerr constant measurements have been interpreted to indicate that the form with the N–H hydrogen *axial* predominates to the extent of 80% or more,[4,5] although recent dipole moment measurements have been taken to indicate a preference for the equatorial location of the N–H hydrogen to the extent of 0.46 kcal/mol.[6] A convincing reversal of the latter assignment has been proposed recently on the basis of nuclear magnetic resonance and infrared evidence.[7]



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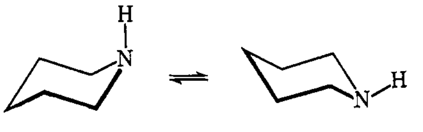

(2)

An important and interesting question with piperidine and piperidine derivatives is the rate of inversion of the nitrogen (eq 1) relative to the rate of inversion of the ring (eq 2). A study of the temperature dependence of the ^{19}F resonances of N-fluoroperfluoropiperidine[8] indicates that either inversion of the N-fluoro nitrogen is fast on the nmr time scale even at −115°, at which temperature ring inversion is quite slow, or else nitrogen inversion is at least somewhat faster than ring inversion

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[1] Supported by the National Science Foundation.

[2] Participant in the Northwestern–Khartoum Universities Exchange Program for 1966–1967.

[3] See E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 245.

[4] M. Aroney and R. J. W. Le Fèvre, *J. Chem. Soc.*, 3002 (1958); M. J. Aroney, C.-Y. Chen, R. J. W. Le Fèvre, and J. D. Saxby, *ibid.*, 4269 (1964).

[5] M. Hanack, "Conformational Theory," Academic Press Inc., New York, N. Y., 1965, p 303; see also D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 73 (1956).

[6] N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *Tetrahedron Lett.*, 3345 (1964); *J. Amer. Chem. Soc.*, **87**, 1232 (1965). See also N. L. Allinger and J. C. Tai, *ibid.*, **87**, 1227 (1965).

[7] (a) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967); J. B. Lambert, *ibid.*, **89**, 1836 (1967); (b) see also commentary by N. L. Allinger, J. A. Hirsch, and M. A. Miller, *Tetrahedron Lett.*, 3729 (1967).

[8] L. W. Reeves and E. J. Wells, *Discussions Faraday Soc.*, **34**, 177 (1962); J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, **63**, 16 (1967).