

9-Nitroanthracene was obtained *via* the direct nitration of anthracene,³⁴ mp 142–144° (lit.³⁴ mp 145–146°).

9-Ethylanthracene, 9-isopropylanthracene, and 9-phenylanthracene were prepared from the reaction of anthrone with the appropriate Grignard reagent,³⁵ the product of which underwent spontaneous dehydration to yield the desired 9-substituted anthracenes: 9-ethylanthracene, mp 54.5–56.5° (lit.³⁶ mp 59°); 9-isopropylanthracene, mp 76–77° (lit.³⁶ mp 75–76°); 9-phenylanthracene, mp 148.5–151.5° (lit.³⁷ mp 152–153°).

All of the materials used in this investigation had purities in excess of 98% as determined by glpc.

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Procedure for Kinetic Studies. A solution of the substituted anthracene, *trans*-stilbene, *p*-dibromobenzene, bromotrichloromethane, and benzene was prepared in the approximate molar ratio of 1:2:1:50:75. A small amount was reserved for analysis as starting material. The remainder was divided among ampoules containing a small amount of benzoyl peroxide. The ampoules were sealed under a reduced pressure of nitrogen and then placed in a constant-temperature bath at $70.0 \pm 0.2^\circ$ for 77–122 hr during which time 14–73% of the substituted anthracene had been consumed. After completion of the reaction, the ampoules were cooled and opened and analyzed for the disappearance of substituted anthracene and *trans*-stilbene *via* glpc using *p*-dibromobenzene as an internal standard. The relative rates of reaction, $k_{\text{substituted anthracene}}/k_{\text{trans-stilbene}}$, were then determined by standard techniques.³⁸

Acknowledgment. We thank Oregon State University Computer Center for supplying the necessary funds for the calculations.

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Charge-Transfer Spectra of Some Phenyl and Naphthyl Derivatives. Relative Importance of σ - π and n - π Conjugation Involving the π Si-Si System¹

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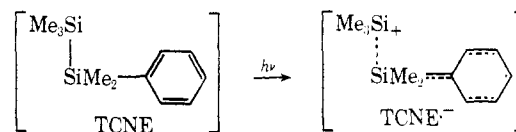
Abstract: The ionization potentials of several α -naphthyl, β -naphthyl, and phenyl derivatives (Ar-X, X = Me₃Si-SiMe₂, Me₃SiCH₂, MeO, and CH₃) have been determined by charge-transfer spectra. These data were used to evaluate the relative efficiencies of σ (or n)- π conjugations by using the first-order perturbation theory. It is shown that a silicon 3p orbital is only one-third as effective as carbon or oxygen 2p orbital to overlap with carbon π systems. The considerable σ - π interaction seen in Si-Si π systems may be attributed to the very high energy of the Si-Si σ orbital.

It has been reported in 1964 that the silicon-silicon bond has conjugating properties with phenyl and vinyl groups.²⁻⁴ These "conjugating properties" have been rationalized at first in terms of "d- π " interaction in the excited state.²⁻⁷ Later, the ground-state interaction between the silicon-silicon σ bond and the π system was recognized as an important factor in addition to d- π^* interactions.

Although inductive polarization of benzene molecular orbitals by the β -trimethylsilyl group has been suggested,⁸ the importance of σ - π conjugation between the Si-Si bond and the benzenoid π system has been indicated recently by reaction,⁹ electronic and charge-

transfer (CT) spectra,^{10,11} stereoelectronic aspects,¹² and photoelectron spectroscopy.¹³

The importance of such a σ - π conjugation has been recognized in general by Traylor and coworkers¹⁴ in a number of chemical and spectroscopic investigations. In terms of σ - π conjugation, the vertical stabilization by the silicon-silicon bond in the charge-transfer complex must involve a silicon-carbon double bond.



In spite of the increasing evidence for the silicon-

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(14) T. G. Traylor, H. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown [*J. Amer. Chem. Soc.*, **93**, 5715 (1971)] summarized the previous works on σ - π conjugation.

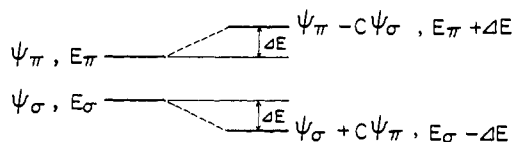


Figure 1. Before and after σ - π interaction diagram.

carbon double bond,¹³ π overlap between silicon and carbon would be expected to be less effective than that between carbon and C, N, or O. Therefore, the extent of $\sigma(\text{Si-Si})$ - π conjugation relative to $\sigma(\text{C-metal})$ - π or n - π conjugation is interesting and is the matter to be ascertained.

We have prepared 1- and 2-pentamethyldisilyl and trimethylsilylmethyl derivatives of naphthalene and observed their charge-transfer spectra with tetracyanoethylene (TCNE) as an acceptor. These results together with other pertinent data will serve to elucidate the nature of $\sigma(\text{Si-Si})$ - π conjugation.

After the present work was finished, we received a report on the similar work by Pitt, *et al.*¹⁶ However, their work has not been extended beyond the 1-naphthyl derivatives. In the present paper, we report our own results with some quantitative evaluation of the relative importance of these conjugations.

Results and Discussion

Tables I and II list the frequencies of charge-transfer

Table I. CT Band Maxima of Complexes of Naphthalene Derivatives ($\text{X-C}_{10}\text{H}_7$) with TCNE in CH_2Cl_2 (cm^{-1}) and Estimated Ionization Potentials (eV)

X	CT-I, cm^{-1}	CT-II, cm^{-1}
H	18,100 (8.03) ^a	23,100 (8.78) ^a
α - CH_3	17,000 (7.86)	22,800 (8.73)
β - CH_3	17,400 (7.92)	21,700 (8.57)
α - CH_2SiMe_3	15,800 (7.68)	22,700 (8.72)
β - CH_2SiMe_3	16,400 (7.77)	20,600 (8.40)
α - Si_2Me_3	16,900 (7.85)	22,900 (8.75)
β - Si_2Me_3	17,200 (7.89)	20,700 (8.42)

^a Values of 8.11 and 8.79 eV by photoelectron spectroscopy (PE) have been reported: M. J. S. Dewar, E. Haselbach, and S. D. Worley, *Proc. Roy. Soc., Ser. A*, **315**, 431 (1970).

Table II. CT Band Maxima of Complexes of Benzene Derivatives ($\text{X-C}_6\text{H}_5$) with TCNE in CH_2Cl_2 (cm^{-1}) and Estimated Ionization Potentials (eV)

X	CT-I, cm^{-1}
H	25,600 (9.15) ^a
CH_3	23,000 (8.76) ^b
CH_2SiMe_3	20,100 (8.33) ^c
Si_2Me_3	20,400 (8.37) ^d

^a 9.245 eV by photoionization method (PI) has been reported: K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). ^b 8.82 eV by PI (see ref in footnote a, Table II). ^c 8.35 eV by PE.¹³ ^d 8.35 eV by PE.¹³

bands of several monosubstituted benzenes and naphthalenes, including the ionization energies estimated by using the $h\nu_{\text{CT}}$ -IP correlation of Voigt and Reid.^{17,18}

(15) (a) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968), and references cited therein.

(16) C. G. Pitt, R. N. Carey, and E. C. Toren, Jr., *J. Amer. Chem. Soc.*, **94**, 3806 (1972).

$$h\nu_{\text{CT}} = 0.83\text{IP} - 4.42 \quad (1)$$

$$\Delta E(\text{IP}) = \Delta E(\text{CT})/0.83 \quad (2)$$

The two well-separated CT bands of naphthalene-TCNE complexes were attributed to the transitions from the highest (ψ_5) and the penultimate occupied (ψ_4) molecular orbitals of the donor to the lowest unfilled orbital of the acceptor, respectively.²⁰

One of suggested requirements for strong σ - π interaction in a π AB system is good overlap between the p orbitals of A and π .¹⁴ However, strong interaction occurs even with poor overlap provided that the σ orbital is of sufficiently high energy as observed in the case of phenylpentamethyldisilane. This may be understood in terms of perturbation theory, which represents explicitly the effect of relative energy levels between interaction orbitals.²¹ Conjugation of a π orbital and a σ orbital, both of which have the same symmetry, can be described schematically in before-after interaction diagrams (Figure 1). According to the second-order perturbation, we can estimate the extent of the stabilization energy by a neighboring σ bond as ΔE (eq 3) for a radical or a cation radical, and $2\Delta E$ for a cation.

$$\Delta E = \frac{(\int \psi_\sigma \mathbf{P} \psi_\pi d\tau)^2}{|E_\sigma - E_\pi|} \quad (3)$$

This second-order perturbation energy can be changed to

$$\Delta E(\text{IP}) = \frac{c_i^2 \beta'^2}{|E_\sigma - E_\pi|} \quad (4)$$

where c_i is the coefficient of the atomic orbital at the point of substituent group attachment in the pertinent π orbitals of benzene or naphthalene and $\beta' = \int \chi_\sigma \cdot \mathbf{P} \psi_\sigma d\tau$ is a measure of the extent of the interaction. The values of E_π can be estimated from eq 1²² and E_σ from the reliable ionization potential measured by other direct methods. Thus, for C-H σ bond, ionization potential of CH_4 , 12.99 eV,²³ for C-Si σ bond, 10.5 eV of Me_4Si ,¹³ for Si-Si σ bond, 8.69 eV of Me_8Si_2 ,¹³ and for O-Me n level, 10.85 eV²³ of MeOH were taken, respectively. Relative energy levels of necessary π and σ orbitals are shown in Figure 2.

Charge-transfer bands of methyl-substituted benzene and naphthalenes have been treated by using Coulomb perturbation by Lepley,²⁰ in which $\beta\text{-Me} = 0.21\beta_{\text{AH}}$ for the first charge-transfer band and $\beta\text{-Me} = 0.26\beta_{\text{AH}}$ for the second were derived. This difference was considered within experimental error. Alternatively it can be due to the difference of $|E_\sigma - E_\pi|$ values. Because the values of $|E_\sigma - E_\pi|$ do not seriously change

(17) E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3930 (1964).

(18) Similar CT frequencies have been reported for phenyl derivatives.¹⁹

(19) (a) H. Bock and H. Alt, *J. Amer. Chem. Soc.*, **92**, 1569 (1970); (b) *J. Organometal. Chem.*, **13**, 103 (1968); (c) *Chem. Ber.*, **102**, 1534 (1969).

(20) (a) A. R. Lepley, *J. Amer. Chem. Soc.*, **86**, 2545 (1964); (b) *Tetrahedron Lett.*, 2833 (1964).

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(22) Probably, these values should be taken from the more direct measurement such as photoelectron spectroscopy, but the differences are so small that the following discussion is not affected.

(23) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

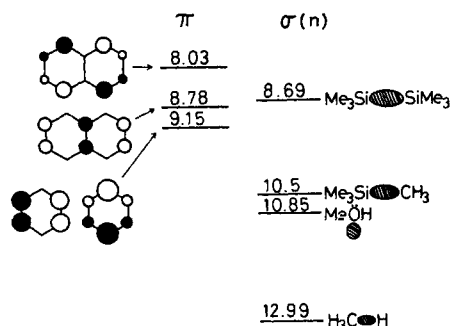


Figure 2. Relative energy levels (eV) of naphthalene and benzene π orbitals and pertinent σ orbitals.

in this series, ΔE may be regarded as the function of c_i^2 in both Coulomb and conjugation perturbation terms. However, including the term $1/|E_\sigma - E_\pi|$ we can obtain a meaningful β' .

Five sets of values of $\Delta E(\text{IP})$ and $c_i^2/|E_\sigma - E_\pi|$ can be calculated from the HMO coefficients of naphthalene and benzene molecular orbitals and the data (Tables I and II) for a particular σ (or n) bond; four sets from CT-I and CT-II bands of α - and β -naphthyl derivatives, respectively, and one from benzene derivatives. As expected from the fact the α carbons are in the nodal plane of the ψ_4 molecular orbital of naphthalene, CT-II bands of α -naphthyl derivatives were little affected by substitution. These data should give straight lines which yield the β' values as square roots of the gradients.

Calculated data are shown in Table III and good linear relationships between $\Delta E(\text{IP})$ and $c_i^2/|E_\sigma - E_\pi|$ were obtained for combinations of π orbitals and each σ (or n) orbitals as shown in Figure 3.²⁴ Meaningless constants (intercepts on ordinate) are nearly zero in all cases. The values of β' for π -C-H and π -C-Si hyperconjugation, and for C- $\ddot{\text{O}}\text{CH}_3$ n - π conjugation, are in the range of 1.7–2.1 eV, while a much lower value, 0.54 eV, is calculated for π Si-Si σ - π conjugation (Table III).

These observations are in accord with Dewar's statement that any resonance effects should be largely independent of the groups R_1 , R_2 , and R_3 attached to the saturated carbon atom, in other words, there is no theoretical justification for Baker and Nathan's postulate that only C-H hyperconjugation is important: C-C hyperconjugation should be quite comparable.¹⁹ Furthermore, it is indicated that the apparent exaltation of σ - π conjugation by carbon-metal bonds, or perhaps by strained σ bonds, is due to the high ionization potential of the concerned σ bonds.

Recently, we have indicated the importance of σ - π conjugation of the Si-Si σ bond with the π orbital on the electronic spectra of phenylpentamethyldisilanes mainly from the stereoelectronic aspects.¹² Pitt and Bock assigned the highest occupied MO of phenylpentamethyldisilane to a linear combination of π (C_6H_5) and $\sigma(\text{SiSi})$ orbitals from the photoelectron spectrum.¹³ However, they suggested also that the smaller values of the overlap and resonance integrals between a silicon atom and a π system could reduce the

(24) Equation 3 can be applied only to the nondegenerate system. Therefore, for the pentamethyldisilyl case interaction between $\sigma(\text{SiSi})$ and ψ_4 (naphthalene) is excluded from the calculation.

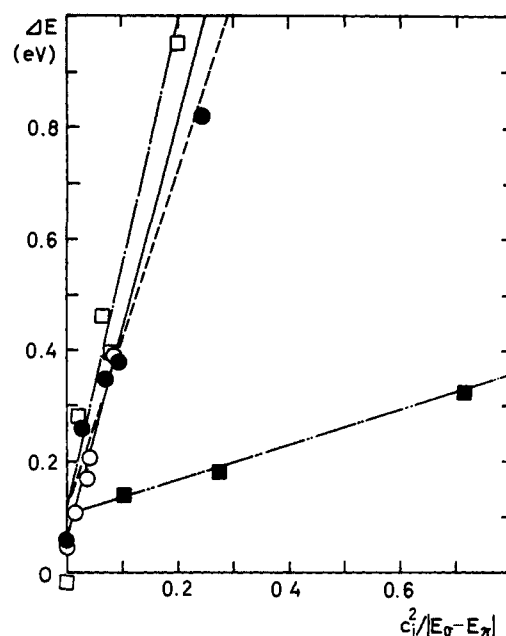


Figure 3. Relationship between $\Delta E(\text{IP})$ and $c_i^2/|E_\sigma - E_\pi|$: (---□---) π -OCH₃; (---○---) π -CH₃; (---●---) π -CH₂SiMe₃; (---■---) π -SiMe₂SiMe₃.

Table III. The Extent of σ - π Conjugation, β' (eV)

Substituent	System ^a	$\Delta E(\text{IP})$, eV	$c_i^2/ E_\sigma - E_\pi ^b$	β' (correl coeff)
CH ₃	A	0.39	0.087	1.97 (0.996)
	B	0.17	0.036	
	C	0.11	0.014	
	D	0.05	0.0	
	E	0.21	0.040	
CH ₂ SiMe ₃	A	0.82	0.247	1.69 (0.987)
	B	0.35	0.073	
	C	0.26	0.028	
	D	0.06	0.0	
	E	0.38	0.097	
Si ₂ Me ₅	A	0.32	0.725	0.54 (0.999)
	B	0.18	0.274	
	C	0.14	0.105	
	D	0.06	<i>c</i>	
	E	0.27	<i>c</i>	
OMe ^d	A	0.95	0.204	2.08 (0.968)
	B	0.46	0.065	
	C	0.28	0.025	
	D	-0.02	0.0	
	E	0.39	0.082	

^a A for phenyl CT-I, B for α -naphthyl CT-I, C for β -naphthyl CT-I, D for α -naphthyl CT-II, and E for β -naphthyl CT-II are used as indices. ^b The $c_i^2/|E_\sigma - E_\pi|$ should be taken for OMe. ^c These are excluded because the energy difference between E_σ and E_π is too small to treat with the perturbation method in nondegenerate system; see Discussion. ^d Calculated from the data of Bock and Alt.^{19c}

magnitude of $\sigma(\text{Si})$ - π interaction relative to the case where carbon was adjacent to a benzene ring. Traylor and coworkers have also pointed out that hyperconjugation will be much less effective if A is a second or higher row element, where the delocalizable σ bond is AB σ bond in π AB system.¹⁴

Our observation that silicon has lower conjugating properties than carbon and oxygen is in good accord with these ideas. Data for Me₃SiCH₂, CH₃O, and HCH₂ derivatives in Figure 3 can be treated as a whole and gave a linear relation from which β' can be calculated

as 1.82 eV ($r = 0.937$). Therefore, silicon ($\beta' = 0.54$ eV) is only one-third as effective as carbon and oxygen in σ - π or n - π conjugation where these atoms are involved to form a double bond to carbon. However, the silicon-silicon bond with a considerably lower ionization potential can interact with benzene or naphthalene π orbitals rather effectively. Large shifts of the second ionization energy of β -naphthylpentamethyldisilane (0.27 eV), which has been excluded from the arguments above,²⁴ can be understood only by the perturbation theory in the degenerated system of σ - π conjugation model. Inductive effect models ($\Delta E = c_i^2 \Delta\alpha$) only predict that the shift should be smaller than that of the first ionization energy of α -pentamethyldisilanyl naphthalene. However, from the perturbation treatment by using the first term with $\beta' = 0.54$ eV, the shift of the second ionization energy of β -naphthylpentamethyldisilane is calculated to be 0.32 eV, very close to the experimental value.

In above discussion, the role of Si 3d orbital is neglected for simplicity, although a number of problems in organometalloid chemistry are interpreted by the idea of $(p-d)\pi$ bonding. Probably such a $(p-d)\pi$ bonding may become more important for interactions with antibonding π orbitals.¹²

Experimental Section

Materials. α - and β -Pentamethyldisilanyl naphthalenes were prepared from the corresponding bromonaphthalene, magnesium, and chloropentamethyldisilane by *in situ* Grignard reaction in the mixed solvent consisting of benzene, ether, and THF (17:11:6). After work-up, α - and β -pentamethyldisilanyl naphthalene were

obtained in 58 and 68% yields, respectively, and were purified by preparative glc: α -C₁₀H₇SiMe₂SiMe₃,¹⁶ nmr (CCl₄, δ) 0.07 (s, 9 H), 0.51 (s, 6 H), 7.22-8.04 (m, 7 H); mass spectrum (70 eV) M⁺ (*m/e*, 258, 15.7%), M⁺ - 15 (5.4%), M⁺ - 73 (100%); β -C₁₀H₇SiMe₂SiMe₃, nmr (CCl₄, δ) 0.08 (s, 9 H), 0.41 (s, 6 H), 7.36-7.93 (m, 7 H); mass spectrum (70 eV) M⁺ (*m/e* 258, 15.1%), M⁺ - 15 (5.7%), M⁺ - 73 (100%).

α - and β -Trimethylsilylmethyl naphthalenes^{19c} were prepared from the corresponding chloromethyl naphthalene, magnesium, and trimethylchlorosilane by *in situ* Grignard reaction in ether. After work-up α - and β -trimethylsilylmethyl naphthalene were obtained in 83 and 53% yields, respectively: α -C₁₀H₇CH₂Si(CH₃)₃, bp 110-112° (4 mm) [lit.^{19c} bp 143° (11 mm)]; nmr (CCl₄, δ ppm) 0.10 (s, 9 H), 2.59 (s, 2 H), 7.2-8.0 (m, 7 H); β -C₁₀H₇CH₂Si(CH₃)₃, mp 60-61° [lit.^{19c} mp 61°]; nmr (CCl₄, δ ppm), 0.03 (s, 9 H), 2.25 (s, 2 H), 7.0-7.0 (m, 7 H).

α -Methylnaphthalene was prepared in the most pure state by hydrolysis of α -naphthylmethylmagnesium chloride in ether in 62% yield, bp 74° (3 mm). β -Methylnaphthalene and naphthalene were used as supplied. Other materials appeared in this paper were reported elsewhere. All materials were purified before use by preparative glc, distillation, or recrystallization. Satisfactory elemental analyses of all new compounds were obtained by combustion analysis.

Charge-Transfer Spectra. The solutions of the TCNE complexes were prepared by mixing the components dissolved in methylene dichloride, which was purified according to the literature.²⁵ Their spectra were recorded at room temperature using a Hitachi EPS-3 recording spectrophotometer.

The spectra of trimethylsilylmethyl-, methyl-, and pentamethyldisilanylbenzene were separated to two bands, respectively, by using the method of Voigt.¹⁷

Acknowledgment. We thank Professor T. G. Traylor for helpful discussions during his stay in Tohoku University. Thanks are also due to Toshiba Silicone Co., Ltd. for gifts of chlorosilanes.

(25) M. Pestemer, *Angew. Chem.*, **63**, 121 (1951).

Hindered Internal Rotation of the Methyl Group in α -Substituted Ethyl Radicals. Effect of Fluorine

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Abstract: Hindered internal rotation of a methyl group is examined in solution at various temperatures by the selective line broadening in the esr spectra of the ethyl radical with α -fluoro, α,α -difluoro, α,α -dichloro, and α,α -di-*tert*-butyl substitution. Only the spectrum of CH₃CF₂ shows selective alternation of line widths in the CH₃ quartets due to modulation of the hyperfine splitting of the three methyl protons resulting from hindered rotation about the C $_{\alpha}$ -C $_{\beta}$ bond. Line-shape analysis using the modified Bloch equation affords a barrier of 2.2 kcal mol⁻¹, which is largely associated with the pyramidal configuration induced by two fluorines at the radical center. The latter is also responsible for the unusually small value of the proton hfs (13.99 G) of the α -CH₃ group in this radical. The fitting of the experimental esr spectrum to a calculated one is based on a model involving exchange among three equivalent conformations and includes dipolar line broadening due to the α -fluorine anisotropy. Inversion of the configuration at the radical site is too slow on the esr time scale to contribute to line broadening.

In contrast to the large number of barriers to hindered internal rotation examined for stable molecules,¹ there have been only a few studies of transient species such as charged species² and free radicals.³ Further-

(1) (a) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959); (b) J. Dale, *Tetrahedron*, **22**, 3373 (1966); (c) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).

(2) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, **7**, 253 (1973).

(3) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147

more, there is no experimental observation in solution of hindered rotation of the methyl group.^{3a} The barrier

(1963); (b) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1570 (1964); (c) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, **No. 24**, 147 (1970); (d) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (e) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); (f) K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 7036 (1973).

(3g) NOTE ADDED IN PROOF: We inadvertently missed an earlier reference to hindered rotation of a methylvinyl radical by Fessenden and Schuler.^{3a}