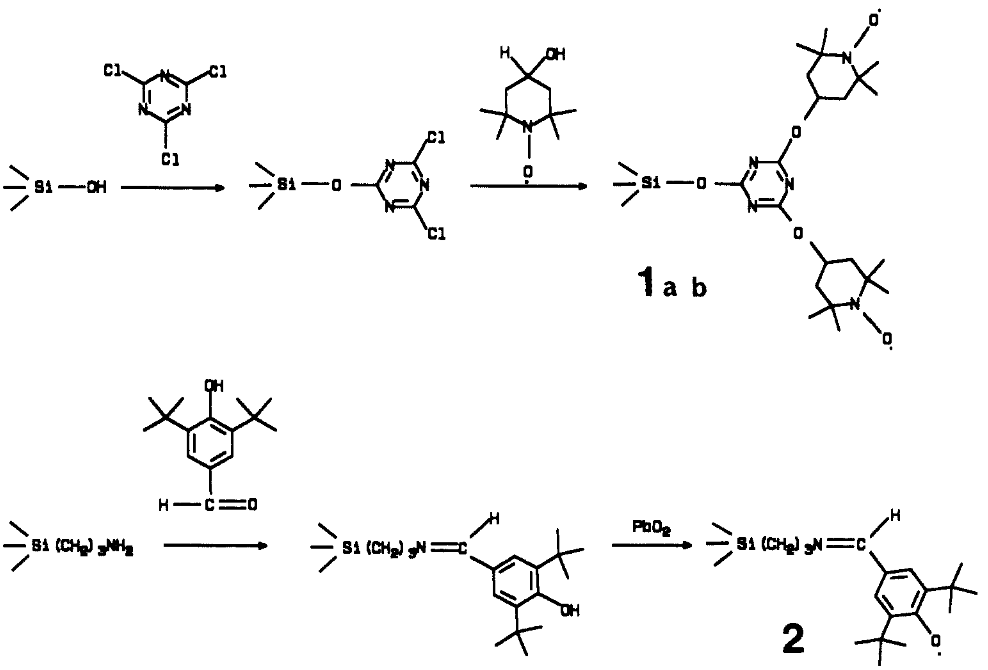
Scheme I



enhancements occur for flow rates above $\sim$0.5 mL/min. In order to ensure that the measured SLIT DNP enhancements were not due to low level leakage of the spin label from the silica gel surface, ^{1}H nuclear relaxation times were measured. The measured *static* ^{1}H nuclear relaxation times ($T_{1\text{no}} \simeq 10.5$ s) were not altered after passage through region A containing the immobilized spin labels in comparison with pure benzene (no immobilized radical in region A).[11] Whereas, in the absence of a microwave field ($B_{1s} = 0$) the monitored NMR magnetization did not decrease even at high flow rates (e.g., 10 mL/min), suggesting the high efficacy of these systems in reducing nuclear relaxation times.[7]

The immobilized nitroxide spin label systems **1a** and **1b** have significantly reduced Overhauser enhancements relative to typical liquid values. In addition, the DNP spectral line shape $(1/T_2)_{\text{DNP}}$ is broader for **1b** and **1c** relative to the liquid–liquid intermolecular case (**1a**). These results and the corresponding EPR spectra[6,7] suggest reduced molecular motion for these immobilized spin label/benzene interactions. Furthermore, *the immobilized phenoxy spin label 2 has a dominant solid-state effect* (enhancements at $\omega_e \pm \omega_n$) which is not only completely antisymmetric but also contains a minor Overhauser contribution.[2] This suggests that the immobilized phenoxy spin label **2** has significant contributions from time independent nuclear–electron interactions.

In conclusion, it is important to note the similarity between the present flow SLIT ^{1}H DNP results and data obtained previously for solid ^{1}H DNP studies. For example, the solid-state effect monitored by the messenger group (flowing benzene) for the immobilized phenoxy free radical **2** system clearly distinguishes the present study from previous liquid DNP studies. Since the reporter group reflects properties of the surface, *the flow SLIT DNP experiment could provide a new method for monitoring liquid or gas/surface intermolecular interactions*. An important characteristic of the flow SLIT DNP experiment is the longer nuclear relaxation times ($T_{1\text{no}}$) for the flowing bolus after polarization transfer. This more readily facilitates experiments where the flowing bolus is polarized in low magnetic fields (region A), but the NMR magnetization is monitored in higher magnetic fields (region C).[12] The latter experiment is similar in some respects to flow CIDNP experiments[13] where the polarization is generated in low magnetic fields but monitored in higher fields. Similar flow SLIT DNP experiments are presently under study in our laboratory.

Acknowledgment. We gratefully acknowledge helpful discussions with C. S. Yannoni (IBM) and R. A. Wind (CSU) during the early phases of this study. We also gratefully appreciate partial financial support for this work from DOW Chemical Company, Mobil Research Foundation, and the U.S. Army (Ft. Belvoir).

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[11] The nuclear spin lattice relaxation times (T_1's) were measured by using a standard (180°-τ-90°-T) sequence. The T_1's were measured after flowing benzene (degassed and recycled) over the immobilized radical for several minutes and then stopping the flow for the static measurement. The T_1 values were within experimental error of the values obtained for a pure static benzene sample (i.e., 10.5 s).

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Dependence of the Lifetime of the Twisted Excited Singlet State of Tetraphenylethylene on Solvent Polarity

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Studies on the cis–trans isomerization of olefins have demonstrated the existence of an intermediate (^{1}p*) on the energy surface of the lowest excited singlet state which corresponds to a geometry in which the p-orbitals of the original π-bond are mutually perpendicular.[1] For a symmetrically substituted olefin, this twisted excited singlet state is described by theory in terms of a highly polarizable species whose electronic character is derived from the mixing of zwitterionic structures I and II. On the excited-state surface, ^{1}p* resides approximately vertically above the transition state (^{1}p) on the ground-state surface for the thermal cis–trans isomerization of the alkene. The electronic nature of ^{1}p is described

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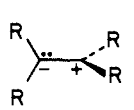
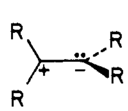
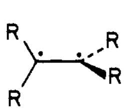


I



II



III

theoretically in terms of biradical III. Although considerations of $^1p^*$ of alkenes and polyenes have long been a focus of theoretical studies,[1] a relatively small amount of experimental evidence[2] exists for the zwitterionic nature of these electronic states. Here we report that the lifetime of $^1p^*$ of tetraphenylethylene depends upon the polarity of the solvent. This dependence is consistent with the theoretically prescribed zwitterionic description of $^1p^*$.

When tetraphenylethylene (**1**) in hexane was excited at 305 nm with a 0.5-ps laser pulse, Greene[3] reported that absorption bands at 423 and 630 nm appeared within the time duration of the excitation laser pulse. The 630-nm band decayed with a time constant of 5 ± 1 ps while the 423-nm band shifted to 417 nm on this time scale. Subsequently, the 417-nm band decayed with a time constant of 3.0 ± 0.5 ns. Greene assigned the 630-nm band to an electronic transition from the vertical excited singlet state (^{1}**1v***) and the 420-nm band to a transition from the nonfluorescent twisted excited singlet state (^{1}**1p***).

Greene's assignments of the two absorption bands are consistent with the results of the time-resolved emission experiments on **1** reported by Barbara, Rand, and Rentzepis.[4] The quantum yields measured for other photoinduced phenomena associated with **1** also support these assignments. Leigh and Arnold[5] reported the quantum yields of the light-induced cis–trans isomerization of several substituted tetraphenylethylenes in benzene. On the basis of their work, the degenerate cis–trans isomerization of **1** should account for >95% of the excited states generated upon electronic excitation. Each of several other deactivation processes, such as fluorescence[6] from ^{1}**1v***, intersystem crossing,[6a] and photocyclization of **1** to give 4a,4b-dihydro-9,10-diphenylphenanthrene,[7] occurs with a quantum yield of <0.025.

We monitored the lifetime of ^{1}**1p*** in several solvents at room temperature by means of picosecond absorption spectroscopy.[8] In each of these experiments, a 0.5–3.0 mM solution of **1** was excited at 266 or 355 nm with a 30-ps laser pulse that was approximately 1 mm in diameter at the sample. A 30-ps white-light pulse which passed through the sample at selected times as long as 18 ns after the excitation pulse was used to probe the sample over a range of wavelengths from 400 to 780 nm for cyclohexane and methylene chloride solutions of **1** and from 400 to 650 nm for tetrahydrofuran, acetonitrile, and methanol solutions of **1**.

In our experiments, the absorption bands near 425 and 630 nm appeared within the excitation laser pulse (Figure 1). The 630-nm absorption band appeared very weak because of its rapid decay. Our resolution of ca. 20 ps did not permit the measurement of the decay kinetics of the 630-nm band. The absorption maximum of the band near 425 nm shifted several nanometers during the time duration of the excitation pulse. We observed a lifetime of 1.4 ± 0.2 ns for ^{1}**1p*** in C_6H_{12} when the 355-nm pulse energy was 92 μJ, an energy which lies in the regime over which there is a linear response of signal intensity as a function of excitation pulse energy. When higher pulse energies were used to excite **1** in C_6H_{12}, the 425-nm band decayed with time constants in the range of 3 ns. When monitored at the absorption maximum, the absorption band near 425 nm decayed with a solvent-dependent first-order rate constant k (Table I). Considerations of various solvent parameters[9] for C_6H_{12}, THF, CH_2Cl_2, and CH_3CN revealed a direct linear relationship between log k and the solvent polarity parameter E_T.[9a,10] For C_6H_{12}, CH_2Cl_2, and CH_3CN, the decay kinetics associated with the 425-nm band were measured after 266-nm excitation and after 355-nm excitation of **1** and, within experimental error, were the same.

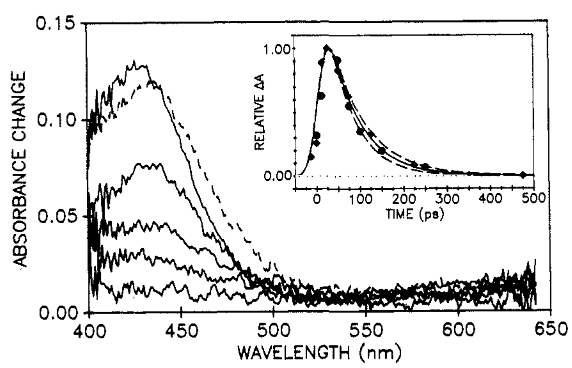


Figure 1. Difference absorption spectra recorded at 23 °C at 25, 50, 75, 100, 150, and 250 ps after 266-nm excitation (average energy = 65 μJ) of a 0.49 mM solution of **1** in CH_2Cl_2. The spectra recorded at 25 and 250 ps are the most and least intense, respectively, near 430 nm. The sample was pumped through a 2-mm optical flow cell. Inset: A plot of relative absorbance change versus time. The data points (●) and (◆) are absorbance changes at band maxima normalized with respect to 266- and 355-nm excitation pulse energies, respectively. The lines are calculated for first-order decay times (τ) that take into account the 30-ps pump and probe pulse widths. The solid line (τ = 70 ps) is bounded by dashed lines which represent τ = 60 and 80 ps.

Table I. The First-Order Rate Constants (k) for the Decay of the Absorption Band Exhibited by ^{1}**1p*** in Several Solvents[a]

solvent	k (s^{-1})	E_T (kcal/mol)
cyclohexane	$(7.3 \pm 1.0) \times 10^8$	31.2
tetrahydrofuran	$(9.1 \pm 1.0) \times 10^9$	37.4
methylene chloride	$(1.4 \pm 0.2) \times 10^{10}$	41.1
acetonitrile	$(6.7 \pm 3.3) \times 10^{10}$	46.0
methanol	$>5.0 \times 10^{10}$	55.5

[a] For each solvent, the value of the empirical solvent polarity parameter E_T[b] is provided. [b] References 9a and 10.

On the basis of the data reported for the photoinduced behavior of **1**,[3-7] the following scenario is proposed to account for our time-resolved spectroscopic data. As the polarity of the solvent increases, ^{1}**1p*** is stabilized relative to ^{1}**1p**. The reduction of the energy gap between the two states for this nuclear geometry increases the coupling of the states resulting in an increased rate of depopulation of ^{1}**1p*** via the radiationless transition to the ground state. An extreme case of solvent interaction leading to addition across the double bond may be possible for several of the solvents studied.[11] For photolyses of **1** in CH_3CN and CH_3OH which were performed with 254-nm light from low-

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pressure mercury lamps, no products resulting from the addition of solvent to **1** were evident.

Interesting spectroscopic parallels evolve if one considers that the absorption band for $^{1}\mathbf{1}\mathrm{p}^{*}$ appears in a region where the diphenylmethyl (DPM) cation and anion exhibit strong absorption bands.[12] In contrast, DPM$^{\bullet}$ exhibits a weak absorption band at 520 nm and a strong band at 330 nm.[13] If the similarities among the spectra of $^{1}\mathbf{1}\mathrm{p}^{*}$, DPM^{+}, and DPM^{-} are manifestations of the zwitterionic nature of $^{1}\mathbf{1}\mathrm{p}^{*}$, $^{1}\mathrm{p}^{*}$ of stilbene, for example, should exhibit an absorption maximum near 360 nm where the benzyl cation and anion[14] absorb light rather than near 320 nm where the benzyl radical[15] absorbs light. This trend is consistent with the absorption spectra of $^{3}\mathrm{p}^{*}$ of **1**,[6a] 1,1-diphenylethylene,[6a] and stilbene,[16] states best described in terms of a biradical. The absorption maximum for each of these triplet states is at a wavelength less than 350 nm. While lifetimes of 3 ± 2 and 10 ± 3 ps have been reported for $^{1}\mathrm{p}^{*}$ of stilbene[17] and 1,1′-biindanylidene,[18] respectively, in hexane, no information about the wavelengths of the absorption maxima is, to our knowledge, available.

Additional investigations are underway which probe solvent effects on electronically excited aryl-substituted alkenes.

Acknowledgment. We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grants CHE-8605560 and CHE-8602678) for support of this work.

Registry No. $Ph_2C{=}CPh_2$, 632-51-9.

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Ab Initio Calculations of the Effects of Substituents on the Stabilization of Silyl Radicals versus Methyl Radicals

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The ability of substituents to stabilize carbon-centered radicals has been demonstrated by both experimental and computational investigations.[1] In contrast, Walsh's experimental studies have shown that aryl and alkyl substituents provide little or no stabilization for silyl-centered radicals.[2] However, Walsh did find that an SiH_3 substituent reduces the Si–H bond dissociation energy (BDE) from 90.3 kcal/mol in SiH_4 to 86.3 kcal/mol in H_3SiSiH_3. Subsequently, Griller and co-workers have shown that the effect of silyl substituents on the Si–H BDE is approximately additive; the three trimethylsilyl substituents on silicon in $[(CH_3)_3Si]_3SiH$ reduce the BDE to 79.0 kcal/mol.[3] Nevertheless, despite the fact that silyl substituents are substantially better than alkyl substituents at stabilizing silyl-centered radicals, Walsh found that silyl substituents are only marginally more effective than alkyl substituents at stabilizing carbon-centered radicals.[2]

Table I. MP4SDTQ/6-31G* Energies of the Reaction in Eq 1 and of the Radicals Involved[a]

	ΔE for eq 1[b] (kcal/mol)		$-E$ of X–$AH_2^{\bullet}$ (hartrees)	
X	A = C	A = Si	A = C	A = Si
H	0	0	39.6891	290.6957
Li	9.4	12.0	46.5326	297.5804
BeH	9.0	8.0	54.3612	305.3689
BH_2	12.4	12.2	65.0355	316.0356
BH_2[c]	2.7	0.8	65.0200	316.0175
CH_3	3.3	−0.8	78.8720	329.8878
NH_2	12.2	0.9	94.8915	345.9258
NH_2[c]	3.7	−2.5	94.8780	345.9204
OH	8.6	−0.8	114.7214	365.7776
F	4.4	−3.5	138.7018	389.7816
SiH_3	4.4	2.9	329.8663	580.8773

[a] See footnote 8. [b] ΔE is positive when the BDE of X–AH_3 is smaller than the BDE of AH_4. [c] Twisted 90° about the X–A bond from the equilibrium geometry.

In order to understand the difference between carbon- and silicon-centered radicals in their response to substituents, we have performed ab initio calculations of the energy of the reaction in eq 1. Equation 1 measures the effect of a substituent, X, on

$$\text{X-AH}_2^{\bullet} + \text{AH}_4 \rightarrow \text{X-AH}_3 + \text{AH}_3^{\bullet} \qquad (1)$$

altering the A–H BDE from that in methane (A = C)[1,4] or in silane (A = Si), and it permits cancellation of errors in the absolute A–H BDEs that are computed.

Geometries of the radicals were optimized with the 6-31G* basis set[5] and UHF wave functions.[6] Energies, with electron correlation included at the MP4SDTQ[7] level, were computed at the UHF optimized geometries and are given in Table I, along with the energies derived[8] for the reaction in eq 1. Calculations were performed with the GAUSSIAN 82 package of programs.[9]

The results in Table I show that electropositive substituents with low-lying empty orbitals (Li, BeH, and BH_2) are radical stabilizing for both carbon- and silicon-centered radicals, as evidenced by the fact that these substituents, X, cause the BDE for X–AH_3 to be less than that for AH_4. The calculations with the empty orbital on the BH_2 group twisted 90° from conjugation with the singly occupied orbital on AH_2 indicate that delocalization of the odd electron into the empty p orbital on boron has a stabilizing effect in both carbon- and silicon-centered radicals. From the energy differences between the two geometries, this type of electron delocalization is found to be responsible for stabilizing $H_2B\text{–}CH_2^{\bullet}$ by 9.7 kcal/mol and $H_2B\text{–}SiH_2^{\bullet}$ by 11.3 kcal/mol.

Despite the fact that π bonds to silicon are usually weaker than π bonds to carbon[10] and that silyl radicals are more pyramidalized

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