the expected dispersal of charge density. No localization of the negative charge was noticed in the $[PF_6]^-$ anion, where slight deviations from ideal octahedral symmetry are within experimental errors. The P–F bond distances range between 1.595 and 1.606 Å (weighted average 1.599 Å).

The disorder in the crystal structure does not lead to any unusual approach distances between ions; the closest F. . .C contact is 3.12 Å, well above the sum of the van der Waals radii, 3.00 Å. The lack of strong packing interactions is reflected in the rather low potential energy barrier (<20 kcal)[16] that separates the two minima of potential energy corresponding to the observed orientations of the cation at the same site.

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(5) Prior to this investigation, two other derivatives were studied, namely the $[BF_4]^-$ and $[SbF_6]^-$ salts. In the first structure extensive disorder affecting both the anion and the cation prevented a reliable refinement of the structural parameters. In the second one, the anion atoms could be located unambiguously, but disordering of the cation still thwarted our efforts to obtain accurate dimensions.

(6) Crystal data at room temperature were: a = 15.794 (4), b = 6.904 (1), c = 11.444 (3) Å; ρ_{calcd} = 1.598, ρ_{measd} = 1.59 g cm^{-3}.

(7) Several correlation coefficients greater than 0.7, anomalously long (1.60 Å) and short (1.10 Å) C–C bond lengths in the cation, and peaks of residual electron density (2–3 eÅ^{-3}) along the annulene perimeter indicated that the model was incorrect.

(8) In the final model only two atoms, C(12) and its mirror image C(12′), approach each other (statistically) closer than the resolution of the measurements. An alternative description would place this atom exactly on the mirror plane; the consequent slight modifications in bond lengths and angles involving C(12), however, would not alter the substantial features of the molecule.

(9) Most of the hydrogen sites were clearly indicated by a difference Fourier synthesis, yet we preferred to introduce H atoms at calculated positions assessing their temperature factors by difference maps calculated after each cycle of least-squares refinement.

(10) $R = \sum \| F_o| - |F_c \| / \sum |F_o|$.

(11) $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$.

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Phosphorescence of Substituted Benzophenones in Solution. Probes for the Conformation of Hydrocarbon Chains in Polar and Protic Solvents

Sir:

It is well known that many systems of contemporary concern—micelles, biological membranes, other phospholipid systems—derive their interesting properties from the flexibility of their component hydrocarbon chains. There have been experiments with model systems interpreted in terms of chain shape, but our knowledge of the conformation of these relatively short chains remains meager.[1,2] This stands in strong contrast to polymer chemistry. For sufficiently long chains, one can use light scattering to see that in good solvents polymer chains swell, and in poor solvents, they coil into compact configurations which minimize solvent-solute contacts.[3] In this paper, we present results which take us one or two steps closer to achieving an equally vivid picture of how solvents affect the shape of hydrocarbon chains in dilute solution.

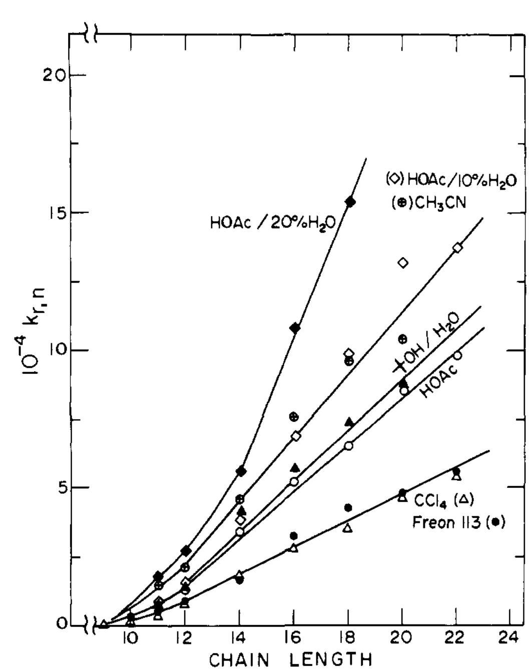
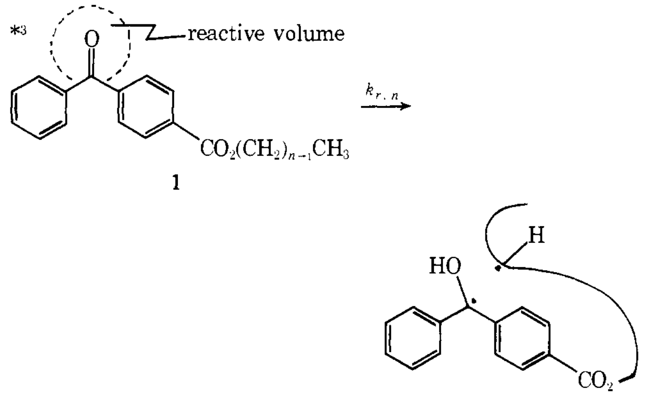


Figure 1. Values of the rate constant $k_{r,n}$ in **1** for intramolecular emission quenching in various solvents: carbon tetrachloride (△); Freon 113 (●); acetic acid (○); 10% water-acetic acid v/v (◇); 20% water-acetic acid v/v (◆); *tert*-butyl alcohol-water azeotrope (▲); acetonitrile (⊕).



1

2

Our probe of hydrocarbon chain conformation is **1**, which phosphoresces in fluid solution at room temperature with a triplet lifetime τ. τ_n is obtained from flash-emission studies. When $n > 9$, **1** can undergo an intramolecular hydrogen abstraction reaction. This quenches the triplet, and for these compounds τ_n is smaller than τ_1, the lifetime of the corresponding methyl ester. τ_n is observed to decrease with increasing chain length n, for $n > 9$. The rate constant $k_{r,n}$ is proportional to P_n, the probability that any CH_2 group from the chain occupies the reactive volume about the ketone carbonyl oxygen in **1**. Values of $k_{r,n}$ are obtained from eq 1. These values, as a function of n, provide an insight into the chain length dependence of the cyclization probability P_n.

$$\frac{1}{\tau_n} - \frac{1}{\tau_1} = k_{r,n} \qquad (1)$$

The experimental techniques used to measure τ and the derivation of eq 1 have been reported previously.[4] Here we

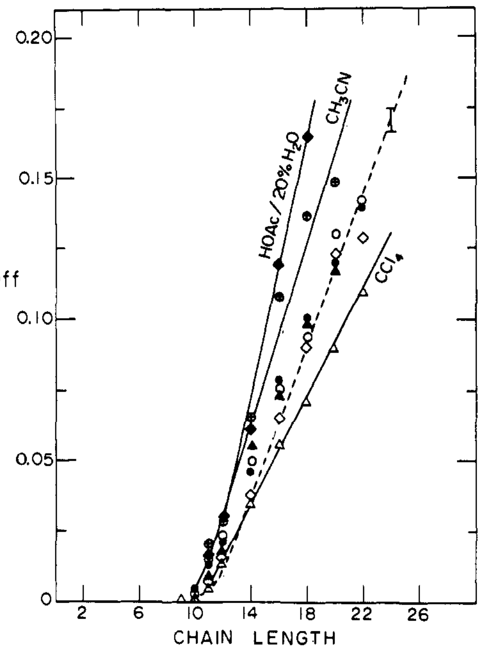


Figure 2. Values of the effective concentration $k_{r,n}/k_2$ for the same solvents as in Figure 1. The dashed line represents the results of theoretical calculations reported in ref 4b, with the error bar representing one standard deviation.

are concerned with the solvent dependence[5] of $k_{r,n}$. These values are presented in Figure 1; $k_{r,n}$ increases both with chain length and with solvent polarity.

The solvent effect on $k_{r,n}$ may have two sources: a solvent effect on chain shape, and a solvent effect on the reactivity of the triplet state of **1**. To separate these effects, we chose as a model the bimolecular quenching by *n*-hexane of methyl ester (**1**-1) phosphorescence in the various solvents. We obtained this bimolecular rate constant k_2 from eq 2. If this reaction is a good model for the reactivity of the triplet state of **1** toward unactivated hydrocarbon chains, then solvent effects on the ratio ($k_{r,n}/k_2 = C_{eff}$) must be due to solvent effects on the cyclization probability[6] in **1**. These data are plotted in Figure 2.

$$\frac{1}{\tau_1} = \frac{1}{\tau_1{}^{\circ}} + k_2[\text{hexane}] \qquad (2)$$

Many of the differences between solvents in Figure 1 have disappeared in Figure 2, indicating a large solvent effect on triplet reactivity. Remaining differences are still substantial. Solvent effects fall into three classes. Four solvents (Freon 113, acetic acid, 10% H_2O-acetic acid, and 11% H_2O-*tert*-butyl alcohol) have indistinguishable differences in $k_{r,n}/k_2$ ratios. We arbitrarily call these solvents "normal". For carbon tetrachloride, the consistently lower ratio implies a somewhat lower cyclization probability in this good solvent. In acetonitrile and 20% H_2O-acetic acid there is a marked increase in cyclization probability.

The source of the solvent effect on chain shape is not obvious. The cyclization probability correlates better with the indices of refraction of the media than with molecular polarizability or bulk dielectric constant. Bulk solvent properties may not be meaningful in mixed solvents. We favor an explanation based upon specific local interactions between the solvent and solute.

The composition of water-containing solvents is listed in Table I. Anhydrous acetic acid exists in solution as a dimer. A small amount of water in the acetic acid does not disrupt the preferential solvation of the chain by the polarizable and nonpolar acetic acid dimer We infer from Figure 2 that when the mole fraction of water in acetic acid approaches 0.5, hydrogen bonding between water and acetic acid makes the dimer structure unfavorable. The chains are forced to interact with water or the polar acetic acid monomer. Under these circumstances, the chains have an enhanced probability of folding back onto the benzophenone in **1**. We were surprised to see that acetonitrile also perturbs chain shape. The unfavorable interaction here could be due to disruption by the chain of the dipole-dipole interactions between solvent molecules.

Table I. Mole Fraction Water in the Aqueous Solvents

Solvent	Mole fraction water
20% water-acetic acid (v/v)	0.44
10% water-acetic acid (v/v)	0.26
tert-butyl alcohol-water azeotrope (11% water w/w)[a]	0.34

[a] "Handbook of Chemistry and Physics", 52d ed, The Chemical Rubber Company, Cleveland, Ohio, 1974, p D-1 ff.

The ratio $k_{r,n}/k_2$ (= C_{eff}) has units of molarity.[6] It represents the concentration of chain elements in the reactive volume in **1**, and serves as a quantitative measure of P_n. Further insight into the conformation of the hydrocarbon chains of **1** in the various solvents would require theoretical calculations of P_n based upon models of chain shape. Using a diamond lattice model developed in our laboratory[7] and Monte Carlo methods, we have calculated the cyclization probability P_n in **1**. The model assumes flexible chains, randomly oriented within the limitations of tetrahedral bond angles. It rigorously accounts for steric interactions with the benzophenonecarboxylate group as well as chain-chain interactions. From P_n we can calculate the effective concentration of chain elements in the reactive volume if the size of that volume is known.[4] For simplicity we take the reactive volume to be spherical, with radius r (eq 3). While r is in effect a variable parameter, chemically meaningful values of r should lie in the range 1.5-2.5 Å.[4]

$$C_{eff} = \frac{397P_n}{r^3} \qquad (3)$$

In Figure 2, the dashed line represents values of C_{eff} obtained from the Monte Carlo calculations[4] and eq 3 with r = 1.9 Å. The success of the calculations in describing C_{eff} supports the validity of using *n*-hexane as model for the chain in separating solvent effects on triplet reactivity from solvent effects on chain shape. It serves also as a rigorous test of our theoretical model, and gives us confidence that we have focused on the key features of the chemistry of **1** in designing our rather simple diamond lattice model.

One should note that the differences between carbon tetrachloride and the four "normal" solvents are sufficiently small that choosing a reactive radius of 2.0 Å instead of 1.9 Å shifts the theoretical curve in Figure 2 to pass approximately through the points representing C_{eff} in carbon tetrachloride.

The theoretical calculations do make it clear that in the four solvents and in carbon tetrachloride the chains are behaving as though they are flexible and randomly oriented, with conformations dictated almost exclusively by the internal rotational and steric interactions of the chains.

Acknowledgment. The authors with to express their appreciation to the Research Corporation and the National Research Council of Canada for financial assistance.

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Exciplex Substitution (S_{ex}). A New Photophysical Process

Sir:

The role of singlet exciplexes in 2 + 2 photocycloadditions to the phenanthrene chromophore has been conclusively proven[1] by an exciplex quenching method. We have established the charge-transfer nature of the quenching mechanism[1b,2] but the fate of the three components of the interaction remains unknown. We now report that one mode of interaction of an exciplex with a quencher is an exchange of partners, which we term exciplex substitution, S_{ex}, recognizing the formal analogy to ground state nucleophilic (S_N) and electrophilic (S_E) substitutions.

$$M^* + Q_1 \rightleftharpoons (MQ_1)^* \quad (1)$$

$$(MQ_1)^* + Q_2 \rightarrow (MQ_2)^* + Q_1 \quad S_{ex} \quad (2)$$

Quenching of the 3,10-dicyanophenanthrene (3,10-$(CN)_2P$)-*trans*-anethole (t-An) exciplex[3] (MQ_1^*, λ_{max} = 466 nm, τ = 37.5 ns) by diethylaniline ($PhNEt_2$) is accompanied by the formation of a new species with emission properties very similar to those of the 3,10-$(CN)_2P$-$PhNEt_2$ exciplex (MQ_2^*, λ_{max} 535 nm, τ = 100 ns), and the observation of an isoemissive point at 519 nm (Figure 1).

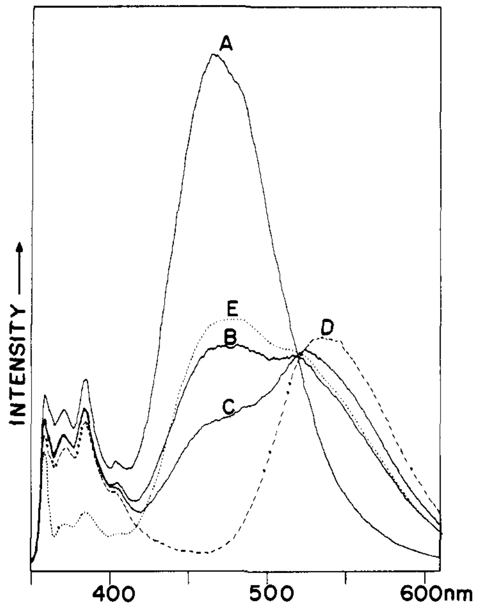

Figure 1. Uncorrected emission spectra in outgassed benzene, [3,10-$(CN)_2P$] = 1.1×10^{-3} M: (A) [t-An] = 8.1×10^{-2} M; (B) [t-An] = 8.1×10^{-2} M, [$PhNEt_2$] = 4.6×10^{-3} M; (C) [t-An] = 8.1×10^{-2} M, [$PhNEt_2$] = 10^{-2} M; (D) [$PhNEt_2$] = 5×10^{-2} M; (E) [t-An] = 2.25×10^{-1} M, [$PhNEt_2$] = 4.6×10^{-3} M.

The intensity of the new emission is always much greater than predicted from the Stern-Volmer slopes for competitive quenching of M* by t-An (265 M^{-1}) and $PhNEt_2$ (420 M^{-1}) and the concentrations of t-An and $PhNEt_2$. Thus at [t-An] = 8.1×10^{-2} M and [$PhNEt_2$] = 4.6×10^{-3} M (Figure 1, B) 58% of the MQ_1 emission (Figure 1, A) is quenched and the MQ_2^* emission is 57% as intense as when [$PhNEt_2$] = 5×10^{-2} M (Figure 1, D) in the absence of t-An. The fraction of M* quenched by $PhNEt_2$ directly in this experiment is not 57% but only 9%. If the [t-An] is increased to 0.225 M but the [$PhNEt_2$] is maintained at 5×10^{-3} M, small *increases* in the emission intensities of *both* exciplexes are observed (Figure 1, E) together with a marked decrease in monomer emission intensity. Steady-state analysis leads to the prediction that the ratio of MQ_2 to monomer emission intensity should be independent of [t-An] if quenching of M* by $PhNEt_2$ is the only route to MQ_2. Our observations show that *quenching of one exciplex can lead to the formation of another exciplex.*

More direct evidence for S_{ex} has been obtained by nanosecond flash emission spectroscopy.[4] Excitation of 3,9-dicyanophenanthrene,[5] 3,9-$(CN)_2P$ (10^{-3} M), in the presence of t-An (0.22 M) and $PhNEt_2$ (4.0×10^{-3} M) in outgassed benzene using the 337-nm pulse from a nitrogen laser produced the fluorescence of 3,9-$(CN)_2P$ (M), the 3,9-

Table I. Thermodynamic and Kinetic Parameters for Exciplex Exchange[a] (S_{ex})

MQ_1	[b]$\lambda_{max}^{MQ_1}$, nm	Q_2	[c]IP(Q_2), eV	MQ_2	[b]$\lambda_{max}^{MQ_2}$, nm	[d]ΔE, kcal mol^{-1}	[e]$k_Q\tau$, l. mol^{-1}
3,10-$(CN)_2P$-t-An	484	$PhNEt_2$	(6.94)[f]	3,10-$(CN)_2P$-$PhNEt_2$	566	8.6	240
3,9-$(CN)_2P$-t-An	496	$PhNEt_2$	(6.94)[f]	3,9-$(CN)_2P$-PhN-Et_2	590	9.1	267
9-CNP-t-An	450	Ph_3N	6.86	9-CNP-Ph_3N	470	2.7	140
9-CNP-t-An	450	$PhNEt_2$	(6.94)[f]	9-CNP-$PhNEt_2$	508	6.8	31.5
9-CNP-t-An	450	Et_3N	7.50	9-CNP-Et_3N[g]	530[h]	9.6	0.4

[a] In benzene. [b] Corrected, precision ±2 nm. [c] Adiabatic values from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26,** (1969). [d] $\Delta E = h\nu_{MQ_1} - h\nu_{MQ_2}$. [e] Outgassed or under N_2, precision ±5%. [f] Estimated from the IP of $PhNMe_2$ (7.14 eV)[c] and the effect of *N*-ethyl substituents expected from published data for aliphatic amines. [g] Very weak emission ($\phi_F{}^c \approx 2 \times 10^{-3}$). [h] Precision ±5 nm.