been made that k_2 is the rate determining step, i.e., that $k_2 \gg k_{-1}$. This assumption is well documented for delocalized carbanions.[1b,7]

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(8) The slightly faster rate of diphenylbicyclooctadiene **6** relative to **7** has been attributed to the inductive effect of the C(6,7) carbon–carbon double bond, rather than π participation.[5]

(9) The ^{1}H NMR spectrum of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (**6**) in THF-d_8-hexane, recorded on a Varian A-60 spectrometer using Me$_4$Si as an external reference, displayed the following resonances: δ 1.92 (m, 2 H, H(8a,b)), 2.70 (m, 1 H, H(5)), 2.87 (m, 1 H, H(1)), 3.48 (m, 1 H, H(4)), 4.95 (d of d, 1 H, H(6)), 5.38 (m, 1 H, H(3)), 6.13 (d of d, 1 H H(7)), 6.96 (m, 10 H, aromatic protons).

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(14) It should be pointed out that although the work presented in this communication does not exclude the possibility of a residual long-range π interaction and ring current in carbanion **8**, no explanation of the large chemical shift differences between anion **8** and the starting hydrocarbon **6** is possible without invoking new mechanisms of charge transmittance. Research currently underway in our laboratories is aimed at examining the relationship between ring currents and the extent of stabilization in bicyclic carbanions.

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The Geometry of Bicyclo[5.4.1]dodecapentaenylium Ion

Sir:

The structure of bicyclo[5.4.1]dodecapentaenylium cation synthesized by Vogel and co-workers[1] is a matter of debate. Some authors[2] regard the system as a perturbed [11]annulenium cation (**1**), others[3] describe it as a perturbed benzohomotropenylium ion (**2**), which implies the presence of considerable 1,6 bonding. Recently,[4] Haddon has evaluated by a PMO approach the energy change for the annulene system (**1**) when the effect of a 1,6-transannular interaction is considered. To what extent the molecule avails itself of the resulting extra stabilization, however, cannot be predicted by this treatment. It is evident that the knowledge of the molecular geometry, particularly of the C(1)–C(6) distance, would contribute to elucidate the electronic structure. To this aim, a single-crystal x-ray diffraction analysis of bicyclo[5.4.1]dodecapentaenylium hexafluorophosphate was carried out. Preliminary studies on similar compounds[5] suggested performing the analysis with low temperature data.

1   **2**
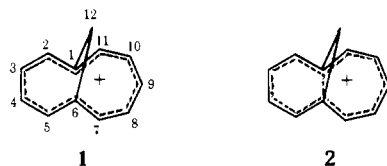
A sample of the substance, kindly supplied by Professor E. Vogel, was recrystallized from ethanol–acetonitrile solution. Crystal data at 110 K were:[6] a = 15.478 (4), b = 6.821 (2), c = 11.373 (3) Å, Z = 4; μ(Mo Kα) = 3.01 cm^{-1}; orthorhombic, space group $Pca2_1$ or $Pcam$ by systematic absences. Intensity data were measured with a Syntex P$\bar{1}$ diffractometer using graphite-monochromated Mo Kα radiation (λ 0.71069 Å). Of the 1449 independent reflections collected within a θ sphere of 27.5°, a total of 1375 reflections with $I > 0$ were judged observed after usual corrections. Standard Patterson, Fourier, and direct methods
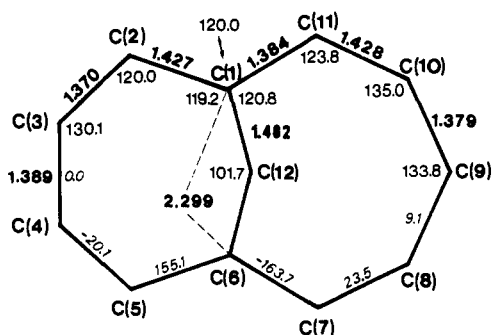

Figure 1. A schematic representation of the cation geometry. Torsion angles (in italics) along the annulene ring, bond lengths, and angles, averaged assuming m-symmetry, are reported.

techniques led to two plausible interpretations of the structure. One of them (space group $Pca2_1$) could be disregarded since the least-squares refinement of the corresponding model failed to converge.[7] The second one assumes the centrosymmetric space group $Pcam$: phosphorus and two fluorine atoms lie on a mirror plane, and the cation is disordered such that the observed electron density is a 1:1 superposition of two annulene systems with their seven- and eight-membered rings interchanged; bridge atoms C(1), C(6), and C(12) are displaced from the mirror plane, all in the same direction, by 0.1–0.3 Å. After a few cycles of least-squares refinement of this model, the structure showed that along the perimeter of the disordered cation the statistical overlap of atoms is not very marked; distances of separation for the various atom pairs are all >0.5 Å. This means that the choice of the correct set of atoms to define the molecule appears unambiguous.[8] However, for a more reliable refinement of the structure, a supplementary set of data was collected; it consisted of all the reflections (719 in number) with $I \geq 3\sigma(I)$ in the range 27.5 < θ < 53° (d_{min} = 0.45 Å) and 230 reflections randomly distributed in the same range, with $I < 3\sigma(I)$. The full-matrix least-squares refinement of the final set of data (2398 reflections, including 120 with $I < 0$), using anisotropic temperature factors for P and F atoms, and isotropic temperature factors for the cation atoms,[9] led to a conventional R index[10] of 0.076 and to a weighted R index[11] of 0.072 for the 2278 observed reflections (R = 0.064 and R_w = 0.065 for the 1375 observed reflections within the Cu sphere). Full details of this structure determination, together with those of parent compounds,[5] will be published elsewhere.

The main features of the cation geometry are represented in Figure 1. Most of the individual values which have been averaged in the figure do not differ from the corresponding average value by more than 2σ (the formal esd's are 0.004–0.008 Å for bond lengths, 0.2–0.5° for bond angles, and 0.5–1.4° for torsion angles).

The value of 2.299 Å for the C(1)–C(6) distance proves the minimal nature of the 1,6 overlap; it should be noticed that disorder does not make this value dubious, since both atoms lie on the same side of the mirror plane. The present value can be compared with those of similar transannular distances in other annulene systems: 2.26 Å for C(1)–C(6) in 1,6-methano[10]annulene-2-carboxylic acid;[12] 2.309 Å for C(4)–C(9) in 2-hydroxy-4,9-methano[11]annulenone;[13] and 2.418 Å for C(1)–C(7) in 4,10-dibromo-1,7-methano[12]annulene.[14] In satisfactory agreement with the experimental value of the C(1)–C(6) distance is that (2.35 Å) obtained by a molecular mechanics treatment[15] of the system. These calculations also give torsion angle values which do not differ substantially from the experimental ones, except for C(7)–C(8)–C(9)–C(10) (27.3 vs. 9.1°).

Bond lengths along the annulene ring are consistent with

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.

References and Notes

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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; $\rho_{calcd} = 1.598$, $\rho_{measd} = 1.59$ 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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(15) Procedure and parameters as reported in T. Beringhelli, A. Gavezzotti, and M. Simonetta, *J. Mol. Struct.*, 12, 333 (1972).
(16) Calculated following the method of A. Gavezzotti and M. Simonetta, *Acta Crystallogr., Sect. A*, 31, 645 (1975). Since in this approach only the molecule under investigation is allowed to move, while the surrounding ones are motionless, the calculated potential energy barrier is certainly overestimated.

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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
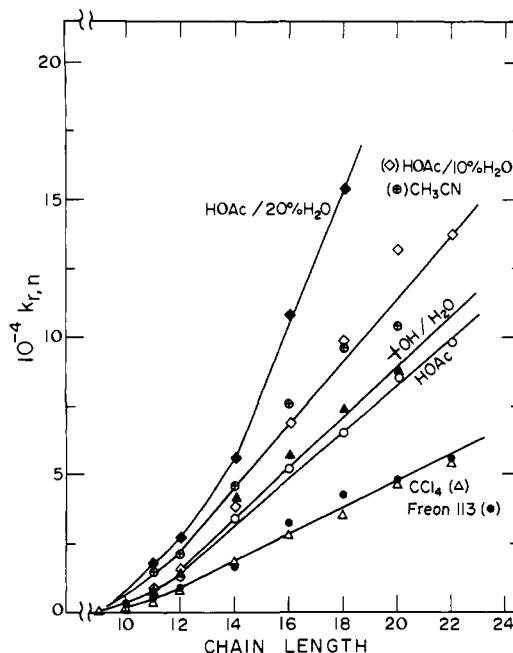

Figure 1. Values of the rate constant $k_{r,n}$ in **1** for intramolecular emission quenching in various solvents: carbon tetrachloride (△); Freon 113 (●); acetic acid (○); 10% water–acetic acid v/v (◇); 20% water–acetic acid v/v (◆); *tert*-butyl alcohol–water azeotrope (▲); acetonitrile (⊕).

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.
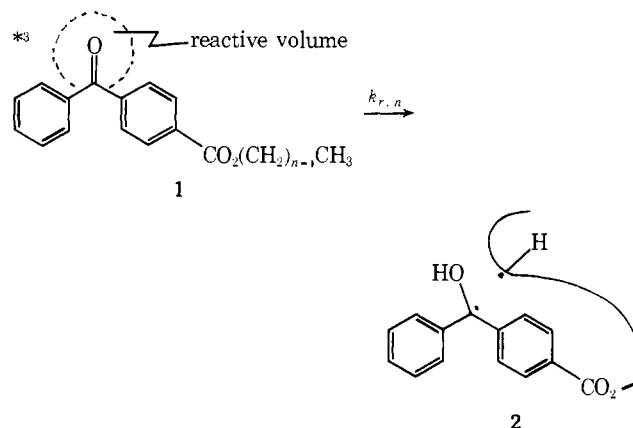
Our probe of hydrocarbon chain conformation is **1**, which phosphoresces in fluid solution at room temperature with a triplet lifetime τ. τ_n is obtained from flash-emission studies. When $n > 9$, **1** can undergo an intramolecular hydrogen abstraction reaction. This quenches the triplet, and for these 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.

$$\frac{1}{\tau_n} - \frac{1}{\tau_1} = k_{r,n} \tag{1}$$

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