that (i) manganese(III) is not an intermediate in the process and (ii) the single detectable intermediate contains 1 oxidn equiv referred to overall manganese: at maximum concentration of the intermediate a 1:1 mixture of Mn(IV) and Mn(II) is present.

The kinetic isotope effect and the substituent effect exhibited by the decomposition of the detectable intermediate[1,2] do not contradict Scheme I as manganese(IV) should disappear by oxidizing TCA and/or the organic intermediates, and obviously, both reactions may be subject to the above effects. Soluble manganese(IV) may be involved in permanganate oxidations more extensively than recognized thus far.

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(4) Other forms of soluble manganese(IV) differing in the number of H_2O molecules formally attached to MnO_2 are also conceivable, as are species produced by acid dissociation. However, the intermediate is not colloidal, at least initially.
(5) F. Freeman, C. O. Fuselier, and E. M. Karchefski, *Tetrahedron Lett.*, 2133 (1975).
(6) It should be noted that the spectrum of the intermediate very closely resembles that of the soluble manganese(IV) species formed via disproportionation of manganese(III) during the permanganate oxidation of *cis*-2-butene-1,4-diol.[11]
(7) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).
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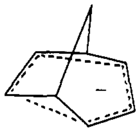
On the Use of Proton Nuclear Magnetic Resonance As a Tool in Determining Long Range π-Interactions in Carbanions

Sir:

A number of reports have appeared in the recent literature describing long range π-interactions between a carbanionic center and a suitably placed carbon–carbon double bond, to produce such species as **1**,[1] **2**,[2] **3**,[3] and others.[4]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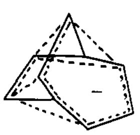
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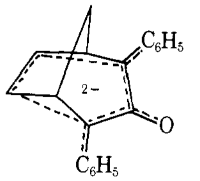

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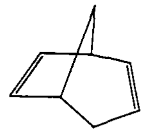
In the majority of cases[2a,3,4a-c] the experimental evidence in support of π-electron participation in these anions was based exclusively on their ^{1}H NMR spectra. Most significantly, sizable upfield shifts (ca. 1–2.5 ppm) in the resonance of the protons directly attached to the remote carbon–carbon double bond have been interpreted as evidence indicating considerable charge delocalization in these species.

However, despite the strong reliance on ^{1}H NMR as a tool for detecting the presence and/or extent of π-participation in carbanions, the effect of the negative charge on the chemical shift of the vinylic and other neighboring protons *in the absence of π-participation* has received very little,[2a] if any, consideration.

Recently, we have reported[5] that replacement of the hydrogens at C(2) and C(4) in the bicyclic systems **4** and **5** by phenyl groups reduces the rate difference of the base-catalyzed hydrogen–deuterium exchange of their allylic hydrogens from $10^{4.5}$ to 3.3, clearly indicating that the stabilization rendered by the phenyl groups to the incipient carbanion **8** has totally eliminated the charge delocalization from the allylic part of the system to the C(6)–C(7) double bond.[6,8]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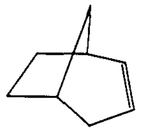
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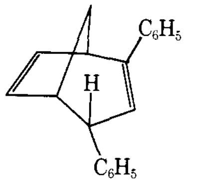
	4	**5**
k_{rel}	$10^{4.5}$	1



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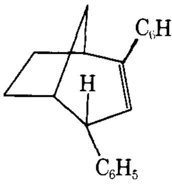

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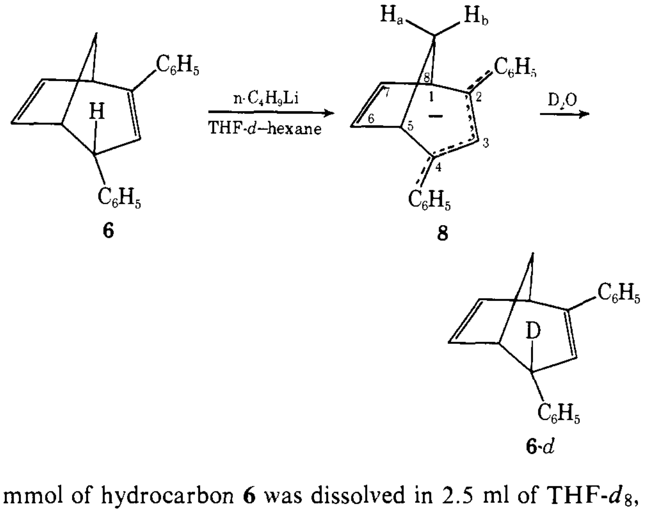
	6	**7**
k_{rel}	3.3	1

It occurred to us that a study of the ^{1}H NMR spectrum of carbanion **8**, and especially a comparison of this spectrum with that of anion **1**, previously reported by Winstein and his co-workers,[1c] would be ideally suited in providing information concerning the effect of the negative charge on the chemical shift of neighboring protons in the absence of long range π-interactions, and more generally in answering questions about the appropriateness of employing proton NMR *alone* as a tool in detecting long range π-interactions and homoaromaticity in carbanions.

The present report describes our findings with regard to the formation, ^{1}H NMR spectrum, and deuteration of carbanion **8**.

2,4-Diphenylbicyclo[3.2.1]octadienyl anion **8** was obtained from the corresponding hydrocarbon[5] **6** in practically quantitative yield by treatment of **6** with *n*-butyllithium in THF-d_8-hexane (Scheme I). In a typical experiment, 1.9 mmol of hydrocarbon **6** was dissolved in 2.5 ml of THF-d_8, the solution was cooled to −5°, and 1.13 ml (2.5 mmol) of a 2.2 M solution of *n*-butyllithium in hexane was added. The reaction mixture was stirred at 0–5° for 30 min and at room

Scheme I



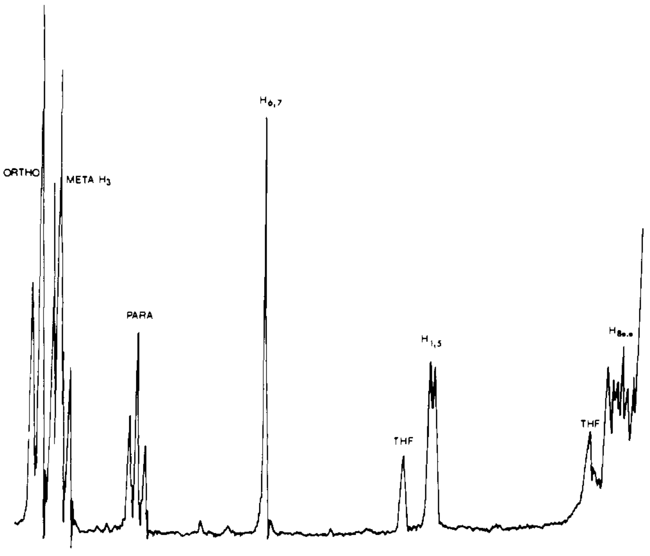


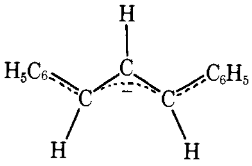
Figure 1. ^{1}H NMR spectrum of 2,4-diphenylbicyclooctadiene anion **8** in THF-d_8–hexane recorded on a Varian XL-100 spectrometer using Me_4Si as an external reference.

temperature for 1.5 h to produce a dark red solution of the anion **8**.

The presence of monoanion **8** was ascertained by direct examination of the reaction mixture by NMR, and by quenching the anion solution with deuterium oxide to give the deuterated hydrocarbon **6**-*d* in 72% yield (Scheme I).

The ^{1}H NMR spectrum of **8** in THF-d_8–hexane was recorded on a Varian XL-100 instrument using tetramethylsilane (Me_4Si) as an external reference and is displayed in Figure 1. The multiplet centered at δ 1.30, and partly overlapped by the signals due to the hexane protons and the residual β-protons of the THF, was attributed to protons H(8a,b) and it arises from geminal coupling between H(8a) and H(8b) as well as from coupling between H(8a) and H(1,5). The doublet (J = 4.5 Hz) appearing at δ 3.02 was assigned to protons H(1,5) and it arises from coupling with H(8a). Irradiation at the H(8a,b) frequency reduced the doublet to a sharp singlet. The singlet at δ 4.52 integrating for two protons was assigned to the vinylic hydrogens H(6) and H(7). Irradiation at H(1,5) sharpened the singlet at δ 4.52. The para protons of the phenyl rings at C(2,4) appeared as a triplet at δ 5.66. Finally, the multiplet centered at δ 6.48 integrated for nine protons and was assigned to the four ortho and four meta protons of the aromatic rings and to the H(3) proton of the bicyclic ring.

The NMR spectrum of anion **8** contains a number of interesting and in many respects unexpected features that merit further discussion. Perhaps the most outstanding of these is the close similarity of this spectrum to that of the bicyclooctadienyl anion **1**. Thus, just as in the case of **1**, the vinylic protons H(6,7) in **8** have experienced a substantial upfield shift (1.04 ppm; 45% as large as that observed in **1**) relative to the starting hydrocarbon[9] **6**. Similarly, the protons at C(8) have undergone a 0.62 ppm upfield shift (60% as large as that observed in **1**), while the proton at C(3) moved 1.10 ppm downfield. On the basis of these observations and in the absence of other evidence to the contrary, it may be concluded that the diphenyloctadienyl carbanion **8** is also a completely delocalized, homoaromatic species. Since this anion was shown earlier to display *no* charge delocalization from C(2,3,4) to the C(6,7) double bond,[5] it is now evident that anisotropic effects due to charge delocalization at C(2,3,4) must play a much more important role in influencing changes in the chemical shifts of carbanions such as **1**, **8**, and probably many others, than previously anticipated. Thus, the upfield shift of the vinylic protons H(6,7) and that of the protons at C(8) in anion **8** is almost certainly the result of an anisotropic shielding effect due to charge delocalization over C(2,3,4). On the other hand, the unusually large downfield shift of proton H(3) is quite reminiscent of that experienced by H(2) in the 1,3-diphenylallyl anion[8] **9**, and can be similarly attributed to deshielding anisotropic effects of the charge at C(2,3,4), and to the diamagnetic deshielding effect of the phenyl rings.[8,9] That the anisotropic deshielding effect of the negative charge at C(2,3,4) contributes significantly to the downfield shift of protons H(3) and H(2) in carbanions **8** and **9**, respectively, is strongly supported by the fact that a sizable downfield shift is also experienced by the H(2) proton in the allyl anion[12,13] **10**.



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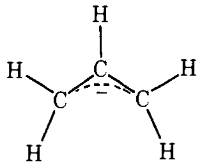
$\Delta\delta_{H_2} = 0.90$ ppm



10

$\Delta\delta_{H_2} = 0.63$ ppm

A final point of interest in connection with carbanion **8** is that, unlike **1**, its H(1,5) protons underwent a small *downfield* shift (ca. 0.25 ppm), most likely due to the deshielding influence of the phenyl rings, which is apparently sufficiently strong to offset the shielding effect of the neighboring negative charge.

In conclusion, the above results serve to indicate that while proton NMR spectroscopy is certainly a powerful tool in detecting the presence and extent of the effect of the negative charge on the chemical shift of neighboring protons in a carbanionic system, the exact mechanism by which the charge is transmitted cannot be accurately predicted. For this reason, conclusions regarding long range π interactions, homoaromaticity, and homoaromatic ring current effects are best and most safely arrived at by examining not only the ^{1}H NMR spectrum of the anion under consideration but also its stability relative to a suitably chosen reference system.[14]

Acknowledgment. The authors wish to thank Dr. George Slomp of the Upjohn Company, Kalamazoo, Mich., for a number of interesting and stimulating discussions. Thanks are also extended to Mr. Stephen A. Mizsak and Mr. T. A. Scahill, also of the Upjohn Company, for their invaluable help in obtaining the 100-MHz NMR spectra.

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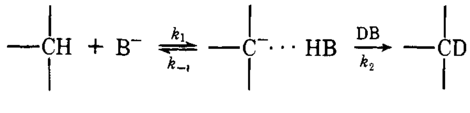
(6) In using kinetic acidities to draw conclusions on the relative stabilities of the carbanion intermediates formed during the base-catalyzed hydrogen–deuterium exchange of hydrocarbons **6** and **7**, the assumption has



$$-\overset{|}{\underset{|}{C}}H + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} -\overset{|}{\underset{|}{C}}{}^-\cdots HB \underset{k_2}{\xrightarrow{DB}} -\overset{|}{\underset{|}{C}}D$$

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]

(7) (a) J. R. Jones, "The Ionization of Carbon Acids", Academic Press, New York, N.Y., 1973, pp 39–40; (b) A. Streitwieser, Jr., and J. H. Hammons, *Prog. Phys. Org. Chem.*, **3**, 41 (1965); (c) A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1, 155 (1963); (d) A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

(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_4Si 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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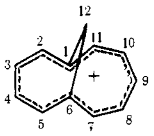
The Geometry of Bicyclo[5.4.1]dodecapentaenylium Ion

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.



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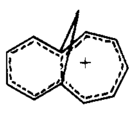

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A sample of the substance, kindly supplied by Professor E. Vogel, was recrystallized from ethanol–acetonitrile solution. Crystal data at 110 K were:[6] a = 15.478 (4), b = 6.821 (2), c = 11.373 (3) Å, Z = 4; μ(Mo Kα) = 3.01 cm^{-1}; orthorhombic, space 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 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 $27.5 < \theta < 53°$ ($d_{\min}$ = 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.

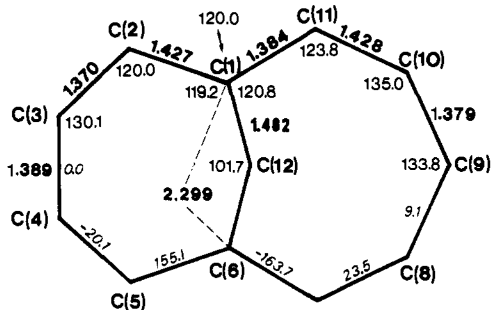

Figure 1. A schematic representation of the cation geometry. Torsion angles (in italics) along the annulene ring, bond lengths, and angles, averaged assuming *m*-symmetry, are reported.

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