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(19) Other structural features which tend to stabilize the diradical but not the carbonyl excited state could similarly serve to promote α cleavage to the linear form. It may, for example, be a factor in the photochemistry of β,γ unsaturated carbonyl compounds (see, e.g., H. Schuh, E. J. Hamilton, H. Paul, and H. Fischer, *Helv. Chim. Acta*, **57,** 2011 (1974); E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Am. Chem. Soc.*, **92,** 4906 (1970), and references therein).
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Received June 21, 1976

The Solvation of Diphenylmethyl Carbanions Using Variable Temperature Carbon-13 Magnetic Resonance

Sir:

Smid was the first to extensively investigate the thermodynamics of the equilibria between contact ion pairs and solvent separated ion pairs for fluorenyl carbanions using ultraviolet absorption spectroscopy.[1,2] UV has been extended to relatively few other carbanion systems because it requires absorptions well enough separated to be assigned to the contact ion and to the solvent separated ion.[3-7] Proton magnetic resonance has also been used to study the solvation of fluorenyl,[8,9] triphenylmethyl,[8] indenyl,[8] and diphenylallyl[10] carbanions. However, proton chemical shift changes are quite small and the most solvation-sensitive carbon may not have an attached proton. Further, proton shifts are frequently affected by other factors such as ring current and a sensitive site may be obscured by solvent resonances.

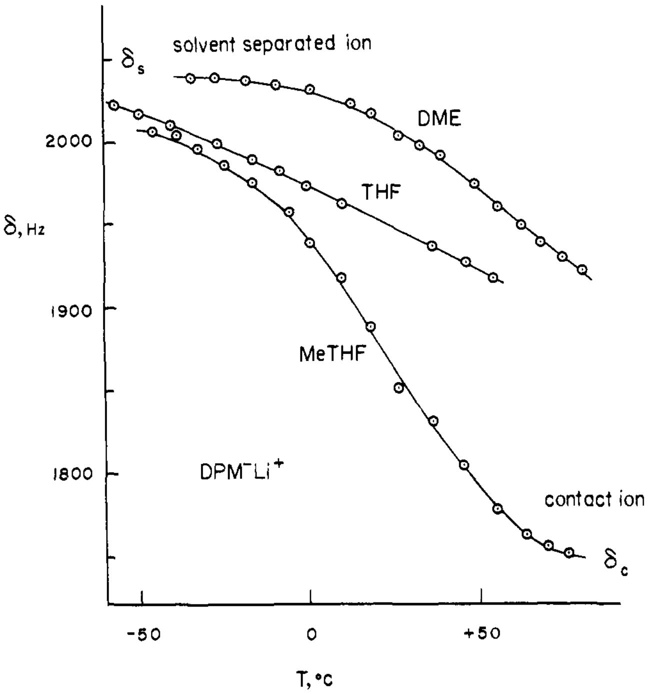

Figure 1. The α-carbon chemical shifts for diphenylmethyllithium.

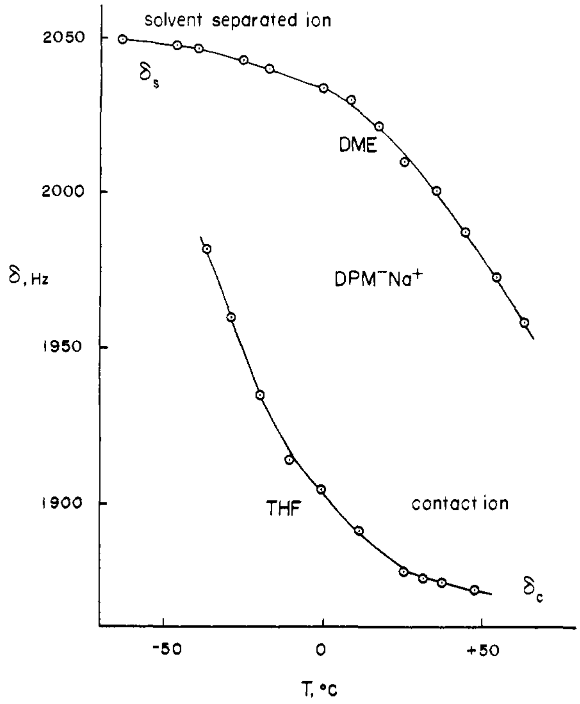

Figure 2. The α-carbon chemical shifts for diphenylmethylsodium.

We have studied the solvation process for all the alkali metal carbanions of diphenylmethane (DPM^-M^+) dissolved in 2-methyltetrahydrofuran (MeTHF), tetrahydrofuran (THF), and dimethoxyethane (DME) using variable temperature carbon-13 magnetic resonance.[11-16] Carbon-13 chemical shift changes give a sensitive overall view of the redistribution of π-electron density at each carbon as the carbanion responds to the solvation process. Very large chemical shift changes are observed for the α and para carbons with the small cations, lithium and sodium. Much smaller changes, if any, occur with potassium, rubidium, and cesium (Table I). Proton decoupled carbon-13 spectra were taken at approximately 8° increments for the carbanions that showed appreciable temperature-dependent chemical shift changes (Figures 1 and 2).[17] Unlike

Table I. Carbon-13 Chemical Shifts of α and Para Carbons at Temperature Extremes and Ambient Equilibrium Constants for Diphenylmethyl Carbanions[a]

	MeTHF				THF				DME			
Solvent cation	C_α	C_p	T, °C	K	C_α	C_p	T, °C	K	C_α	C_p	T, °C	K
Li^+	69.9	110.5	+75	1.53	76.5	107.5	+54	2.99	76.7	107.8	+80	8.00
	80.0	106.1	−46		80.7	106.1	−54		81.3	105.9	−35	
Na^+	73.2	108.8	+46	<0.01	74.8	1108.4	+48	~0.03	78.2	107.2	+64	3.34
			b		79.1	106.4	−36		81.9	106.2	−73	
K^+	78.2	108.8	+40	*d*	79.1	107.8	*c*	*d*	79.8	107.2	*c*	*d*
			b		79.9	107.0	−73		80.8	106.5	−73	
Rb^+	79.5	108.7	*b*	*d*	79.9	107.7	*b*	*d*	80.4	107.3	*b*	*d*
Cs^+	81.3	108.3	*b*	*d*	81.5	108.3	*b*	*d*	81.4	107.9	*b*	*d*

[a] Chemical shifts are in parts per million downfield from tetramethylsilane (internal); spectra obtained with JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer using 1200–1500 average transients; equilibrium constants for ratio of solvent separated to contact ion pairs at 26 °C (ref 28). [b] No chemical shift changes found as temperature lowered. [c] No chemical shift changes found at ambient temperature (26 °C) and above. [d] Equilibrium dominated by contact ion pairs.

Table II. Linear Dependence of the Contact Ion α-Carbon Chemical Shift (δ_c) on Cation Size ($1/M^+$)[a]

Solvent cation	$1/M^+$, Å^{-1}	MeTHF δ_c	THF δ_c	DME δ_c	$\Delta\delta_c$ (DME–MeTHF)
Li^+	1.35	1636[b]	1716[b]	1739[b]	103
Na^+	0.98	1830	1873	1884[b]	54
K^+	0.73	1958	1981	1980	22
Rb^+	0.67	1990	2000	2012	22
Cs^+	0.59	2035	2040	2035	0

[a] Chemical shifts are in hertz downfield from tetramethylsilane (internal). [b] Estimated from linear plot of δ_c's of other cations.

proton magnetic resonance, solvent interference is not a problem. For example, the α-carbon resonance of DPM$^-$Li$^+$ passes through the lowest field MeTHF resonance at 17 °C, preventing chemical shift determination only over a 5° temperature increment (Figure 1).

As the temperature is raised, the α-carbon chemical shifts of the lithium and sodium salts move upfield and approach a constant, shielded value (δ_c). At high temperature, the equilibria contain mainly contact ion pairs.[1-10] In the contact ion, the cation is close to the α-carbon and strongly polarizes the π-electron density toward this site,[18-23] thus accounting for the shielded value of δ_c. The polarizing effect of the cation on the π-electron density at the α-carbon is proportional to the size of the cation. The contact ion α-carbon chemical shift, δ_c, is linearly related to the reciprocal of the cation's ionic radius (Table II). This linear relationship is observed for the sodium, potassium, rubidium, and cesium salts in MeTHF and THF and for the potassium, rubidium, and cesium salts in DME, where δ_c is experimentally accessible at high temperature. From this linear relationship, a reasonable estimate can be obtained for the inaccessible δ_c's of the lithium salts in all solvents and for the sodium salt in DME (Table II).[17] These chemical shifts are approached but not reached near the boiling points of solvents. Similar linear relationships have been observed in UV and proton magnetic resonance measurements of carbanions. Bathochromic shifts in absorption maxima have been found for carbanionic species as the radius of the cation increases.[1b,2,6,24] Proton shifts of the contact ions are related to the size of the cation for fluorenyl,[9] triphenylmethyl,[8] and for 1- and 2-methylnaphthyl[25] carbanions.

The contact ion α-carbon chemical shifts are solvent dependent. For the same cation, δ_c is shielded in the order MeTHF > THF > DME. This small effect shows the influence of the *external* solvent shell on the π-electron density at the α-carbon. DME, with two donor sites, disperses the cation's charge slightly better than THF. THF is much more effective than MeTHF due to its less hindered donor site. Thus, the cation polarizes the π-electron density toward the α-carbon most effectively in MeTHF where the cation-solvent interaction is the weakest. This solvent dependence diminishes as the cation becomes larger (Table II, last column). With cesium, no solvent effect is seen.

As the temperature is lowered and the ion pair becomes solvated, the α-carbon chemical shifts approach a constant, deshielded value (δ_s). In the solvent separated state, the cation is wrapped with solvent and the carbanion responds by spreading the π-electron density more evenly over the π-system. Therefore, solvation results in a decrease in π-electron density and gives deshielded values for δ_s. δ_s's for the lithium salts (δ_s = 2003 Hz, MeTHF; 2019 Hz, THF; and 2036 Hz, DME) are much less solvent dependent than δ_c's because the solvent wrapped cation is effectively larger and its charge more disperse. From these δ_s values, one may estimate that the "size" of a solvated lithium is about the same as that of an unsolvated rubidium cation (Table II).

The α-carbon chemical shift change is largest for the smallest cation, lithium. For DPM$^-$Li$^+$ in MeTHF, a downfield 10.1 ppm change is observed in going from +75 to −46 °C (Table I). This represents a *decrease* in π-electron density at the α-carbon of approximately 0.07 electrons.[16,26] The para carbons undergo smaller variations with temperature in the opposite direction. The upfield shift change for the para carbons of DPM$^-$Li$^+$ in MeTHF ($2 \times 4.4 = 8.8$ ppm), an *increase* in π-electron density, accounts for most of the decrease at the α-carbon in going from contact to solvent separated ions. The other carbons show only small chemical shift changes with temperature (<1 ppm).[27] These temperature dependent chemical shift changes are completely reversible and concentration independent. The potassium, rubidium, and cesium salts remain as primarily contact ion pairs throughout the temperature range investigated in MeTHF, THF, and DME. Only the potassium salt in DME and THF shows small downfield α-carbon chemical shift changes as the temperature is lowered (0.8 ppm in THF and 1.0 ppm in DME).

These sigmoidal curves graphically display how the equilibria between contact and solvent separated ions change with temperature and solvent. DPM$^-$Li$^+$ shows only the solvated end of the equilibrium in the powerful solvating medium, DME. In THF the middle portion is observed while in MeTHF more than 70% of the conversion from solvent separated to contact ions may be followed (Figure 1). In contrast, the sodium salt is appreciably solvated only in THF and DME because solvation is thermodynamically less favorable for larger cations (Figure 2). For those salts where more than 50% conversion is experimentally accessible (Li$^+$, MeTHF, 72%; Na$^+$, THF, 61%; and Na$^+$, DME, 55%), van't Hoff plots of the equilibrium constants give excellent straight lines and yield the following enthalpy and entropy of solvation values: Li$^+$, MeTHF, $\Delta H = -6.3 \pm 0.2$ kcal/mol, $\Delta S = -20 \pm 1$ eu; Na^+, THF, -7.4 ± 0.4, -30 ± 2; and Na^+, DME, -7.4 ± 0.3, -22 ± 2.[28] These values compare favorably with values for delocalized carbanions determined by proton magnetic resonance[8] and UV.[1b,2]

This great sensitivity of carbon-13 shifts of carbanions to solvent, temperature and cation accounts for the differences in chemical shifts that have been reported for the *same* carbanion.[29] It is especially important to emphasize the danger of comparing chemical shifts of lithium salts to those of the other alkali metals because, even when the shifts are very close, the state of solvation may be significantly different.

Acknowledgment. Support of this work by the Robert A. Welch Foundation (Grant A331) is gratefully acknowledged. The authors wish to thank the National Science Foundation (GP-32912) for providing funds for the JEOL PFT-100 used in this work.

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(18) Crystal structure studies for $Ph_3C^-Li^+$ (ref 19), fluorenyl Li^+ and K^+ (ref 20, 21), indenyl Li^+ (ref 22), and $PhCH_2^-Li^+$ (ref 23) show that the cation is close to the α and Cl carbons and is coordinated to the donor site(s) of solvent molecule(s) in the solid state.

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(26) Compared to proton shift changes, a change of 10 ppm in the same solvent is quite large. For example, the *largest* proton shift change observed for trityl carbanions (para hydrogen) was for tritryllithium in THF compared to its shift in diethyl ether, 0.37 ppm (ref 8).

(27) For example, for DPM^-Li^+ in MeTHF, where chemical shift changes are largest, the following chemical shifts are observed at high and low temperatures, respectively: Cl, 146.9, 146.1; C_m, 128.7, 127.8; C_o, 117.6, 112.5, and 121.4 (average shift = 117.0, ortho carbons are nonequivalent at low temperatures due to slow rotation about the Cα–Cl bond).

(28) Equilibrium constants for the ratio of solvent separated to contact ion pairs were determined using the relationship: $K = \delta_o - \delta_c/\delta_s - \delta_o$, where δ_o, δ_c, and δ_s are the observed, contact, and solvent separated α-carbon chemical shifts, respectively. For DPM^-Li^+ in MeTHF and for DPM^-Na^+ in DME, δ_c's were estimated from the linear δ_c vs. $1/M^+$ plot. For DPM^-Na^+ in THF, δ_s in DME was used as the solvent separated shift. These estimated values of the experimentally inaccessible δ_c's and δ_s's probably cause the greatest share of the error in the thermodynamic values.

(29) For example, compare the carbon-13 shifts for the lithium and potassium salts of diphenylmethane and triphenylmethane (ref 14–16).

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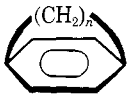
Received August 4, 1976

Electron Paramagnetic Resonance of Metastable [7]Paracyclophane: Out-of-Plane Distortions of a Triplet Benzene

Sir:

The recent syntheses of the [7]- and [6]paracyclophanes (I) have made available compounds in which a single benzene ring experiences substantial out-of-plane distortions.[1-3] Unlike the previously prepared [*m*,*m*]paracyclophanes (II), the nonplanar π-electron systems are not complicated by inter-ring interactions.[4]



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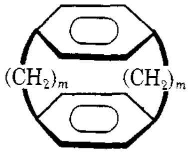

II

III

We have observed the EPR spectrum of the metastable triplet of [7]I (T_{7I}). The average distance between the two unpaired electrons is found to be substantially greater than that observed in triplet benzene or *p*-dialkylbenzenes. The observations are readily explained by the changes in energy of the π-molecular orbitals as ring carbons 1 and 4 are raised out of the aromatic plane. The degeneracies of the pairs of bonding and antibonding orbitals are split and the two unpaired electrons are largely localized on the out-of-plane carbons. These results also bear on the interpretation of the EPR[5] and optical[6] measurements of [*m*,*m*]II.

The EPR spectra of T_{7I} were determined in methylcyclohexane glasses. The zero-field parameters were[7] $D = 0.1108$ cm^{-1} and $E = 0.0122$ cm^{-1}. In the range of 5-20 K no significant changes with temperature were detected. For [2,2]II, $D = 0.1037$ cm^{-1} and $E = 0.0155$ cm^{-1}. With [3,3]II two isomers were observed; $D = 0.0916$ cm^{-1}, $E = 0.019$ cm^{-1} and $D = 0.077$ cm^{-1}, $E = 0.009$ cm^{-1}. For the relatively strainless [4,4]- and [6,6]II and for *p*-xylene we were only able to determine $D^* = (D^2 + 3E^2)^{1/2}$. For each of the three $D^* \simeq 0.169$ cm^{-1}. The measurements of de Groot et al. of metastable benzene in a single crystal gave $D = 0.1590$ cm^{-1}, $E = 0.0064$ cm^{-1}; $D^* = 0.1594$ cm^{-1}.[8]

The zero-field parameters D and E are dependent on the distribution of the unpaired spins: $D \propto \langle 3z^2 - r^2/r^5 \rangle$ and $E \propto \langle y^2 - x^2/r^5 \rangle$ where r is the distance between unpaired electrons and x, y, and z are the projections along a set of axes fixed in the molecule. In our systems z will be perpendicular to the plane of the four central carbons, 2, 3, 5, and 6, and y along the C_1–C_4 direction. D crudely provides an inverse distance between the spins and E a measure of the deviation from threefold or higher symmetry. The nonzero E found for benzene indicates that the average structure is not a regular hexagon.[8]