J. Am. Chem. Soc. **1981**, *103*, 5657-5664

10 kcal/mol at the HF level. At the MP4(SDQ)/6-311G**// MP2/6-31G* level, this reduces to 2.6 kcal/mol. Similarly, the HF/6-31G** value of 29.9 kcal/mol for the ethyl cation is 10 kcal/mol less than the experimental value. Correlation improves the value to 39.0 kcal/mol, in very good agreement with experiment. There is a similar 8 kcal/mol improvement for the propargyl cation **20**; the improvements for **23**, **27**, and **29** are all 5–7 kcal/mol. The overall level of agreement with experiment thus improves considerably from HF theory. This agreement should help in assigning structures to ions for which only the energies are known. For example, the ion with heat of formation 235 kcal/mol, assigned to cyclopropyl cation in ref 1a, cannot be this species because it does not fit in with relative energies listed in Table XV.

Conclusion

Electron correlation methods at the MP4(SDQ) level with reasonably large basis sets have been used to study C_1–C_3 carbocations. Since much experimental data is available in this area, fruitful comparisons between theory and experiment can be made. Such a comparison suggests that this level of theory gives results reliable to within 5 kcal/mol, a considerable improvement over HF theory. The effect of electron correlation on carbocation geometries has been investigated for the smaller systems. Dramatic changes in geometry and energetics of the $C_2H_7^+$ carbocations reveal the importance of electron correlation in such systems. It must be remembered that this level of theory neglects the effect of triple substitutions. A systematic investigation of this and other effects will help in the understanding of these small systems. This understanding could be usefully applied in the case of larger systems on which such large-scale calculations are not feasible.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-79-01061-01), the Fonds der Chemisches Industrie, and was facilitated by a NATO grant. We thank J. Chandrasekhar and M. Saunders for contributions and discussion.

Supplementary Material Available: MP2/6-31G* geometries for C_1–C_2 carbocations (6 pages). Ordering information is given on any current masthead page.

First Determination of the Structure of an Ion-Paired Species in Nonpolar Media: ^1H, ^{13}C, and ^7Li NMR Spectra of Peralkylcyclohexadienyllithium Compounds

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Received January 28, 1981

Abstract: Peralkylcyclohexadienyllithium compounds (**2a**,**b**), formed by addition of alkyllithiums to triene **1**, are shown to exist as ion-paired aggregates containing conjugated anions bent out of the plane at the saturated ring carbon. Both ^{13}C and ^7Li NMR spectra show **2a**,**b** to form two distinctly different ion-paired species—tight peripherally solvated ion-pair aggregates in the presence of mainly tertiary amines and loose separated ion-pair dimers favored with THF, glymes, and HMPT. The latter exhibit two $^7Li^+$ peaks, one due to Li sandwiched between two anions in a *triple ion* and the other situated external to it. In the case of **2b** with THF both ion-pair species are dimers, and the equilibrium $(A^-Li^+)_2{\cdot}(THF)_2 + THF \rightleftarrows (A_2Li)^- + Li\,(THF)_3^+$ is characterized with $\Delta H = -4$ kcal and $\Delta S = -16$ eu. The exchange of ions between ion pairs of **2b** with THF is generally slow on the NMR time scale. However, above 0 °C the lithium exchange rate between the solvated site in the loose ion-pair dimer and the lithium in the tighter ion-pair dimer lies on the NMR time scale. The mean lifetime of lithium in the triple ion is always >10 s. The slow ion-exchange rates are ascribed to the crowded substitution around **2a**,**b**.

Ion pairing in solution has been the object of extensive investigation;[1-8] still several significant questions remain unanswered. They concern the structures of ion pairs, their mode of solvation, and dynamic behavior—how fast and by what mechanisms ions exchange from one ion pair to another.

Most carbanion salts are only soluble in a few ethers and amines. This severely limits what may be learned about solvation and ion pairing from solution spectroscopic investigations. Also, in general, exchange of ions among ion pairs in solution is fast relative to the NMR time scale. Thus NMR spectra of solutions containing different kinds of ion pairs of the same salt show only single averaged spectra.

We have already described how alkyllithium compounds cleanly add, both unsolvated in hydrocarbon solvents and in the presence of ligands, to 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene (**1**) to give stable, soluble, substituted cyclohexadienyllithium compounds (**2**).[9] The latter aromatize on heating to give, in >95% yield, peralkylbenzenes (**3**), with extrusion of methyllithium.

The compounds **2a–c** have unusual properties which render them particularly useful for studies of ion pairing and electronic structure in carbanion salts; **2a–c** are among the few conjugated organolithium compounds which are soluble in many media in-

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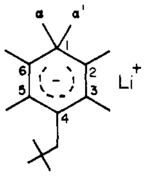
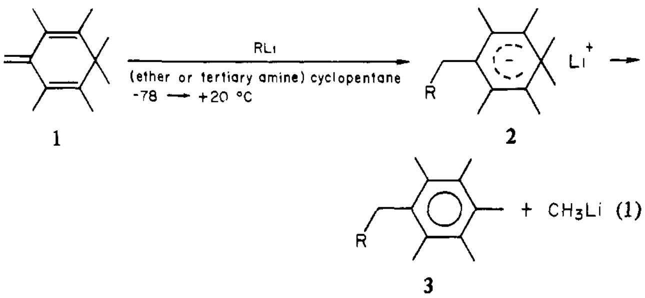
Table I. ^{1}H NMR Shifts[a] of 1 M 2a,b in Cyclopentane with Added Ligands at 0 °C



compd	ligand (quantity, equiv)	1α	1α'	2α	3α'	4α	4γ
2b		0.400	1.130	1.673	1.827	2.363	0.883
2b	NMP (2)	0.360	1.277	1.797	1.883	2.445	0.863
2a	TMEDA (1)	0.330	1.255	1.750	1.855	1.317[b]	
2b	THF-d_8 (2)	0.345[c]	1.242[c]	1.753[c]	1.780[c]	2.417[c]	0.840[c]
		0.228[d]	1.205[d]	1.708[d]	1.710[d]	2.340[d]	0.770[d]
2b	TMEDA (1)	0.367	1.287	1.780	1.855	2.447	0.867

[a] Shifts in ppm with Me$_4$Si as internal standard. [b] Shifts α-δ. [c] High temperature species. [d] Low Temperature species.

cluding *hydrocarbons*.[10] Furthermore, exchange of ions among ion pairs in the systems **2a–c** is slow on the NMR time scale, thereby allowing observation of spectra due to different ion-paired species.



This article is organized around the influence of potential ligands on the properties of **2a,b** when it is unsolvated and with tertiary amines as well as the THF. Conclusions for the THF complexes are applied to other ligands. Ligand NMR spectra are evidence for complexation and competition for lithium as well as dynamic effects in complexation.

It is shown below that the salts contain conjugated anions in two distinct kinds of ion-paired species and how a structure can be assigned to one of these.

General Behavior of 2b

As previously described, compounds **2a,b** were generated by reacting the appropriate alkyllithium compound with triene **1** in cyclopentane in the presence of ethers and unsolvated.[9] This procedure gave stable solutions of **2a,b** of greater than 95% purity. The salts have now been investigated by using NMR methods, varying temperature, concentration, and ligand.

When glymes and hexamethylphosphoramide (HMPT) were used in reaction 1, they underwent cleavage by alkyllithium under the conditions of the reaction. Instead, these compounds were added to preformed **2a,b** complexed to *N*-methylpyrrolidine (NMP). These preparations were found to be stable. Furthermore, glymes and HMPT displace *N*-methylpyrrolidine from its complex with **2a,b** as the NMR data below will show. Thus we are in a position to investigate ion-pair structure with lithium complexed to HMPT and glymes. The other option, of adding these ligands to unsolvated **2b**, was not practical since the latter is always contaminated by unreacted *tert*-butyllithium.

The NMR results for **2a,b** are naturally separated into data for (a) the unsolvated salts and salts in the presence of simple monoethers and tertiary amines and (b) **2a,b** solvated by THF, glymes, and HMPT; these two sets of data will be discussed separately.

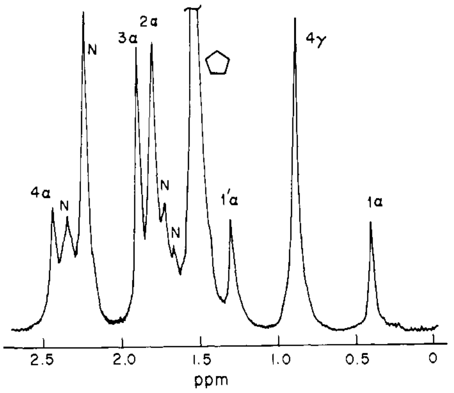
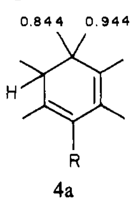
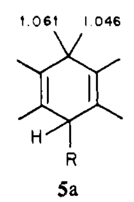


Figure 1. ^{1}H NMR spectrum (60 MHz) of 1.2 M **2b**, in cyclopentane containing 2.4 M; NMP at 20 °C. Numbering C$_1$ saturated, α are CH$_3$ and CH$_2$.

Figure 1 shows the proton NMR spectrum of **2b** in cyclopentane containing 2 equiv of NMP; Table I lists proton shifts of **2b** in the presence of different ligands. The proton resonances are well resolved and vary slightly with temperature in a linear fashion and measurably with ligand. The *gem*-methyls at C$_1$ of **2b** are magnetically nonequivalent, separated by ca. 0.9 ppm, and this shift persists from −80 to at least +40 °C. This is larger than the corresponding value for 1,1-dimethylcyclohexadienes **4a** and **5a** or for CH$_2$ of *cis* and *trans*-10-*tert*-butyl-9-ethyl-9,10-dihydroanthracenes[11] and is reminiscent of the C$_5$ methyl shift in 1,2,3,4,5,6-hexamethylcyclohexenyl cations which have been shown to exist as two bent conformers (**6**).[12] This result implies that

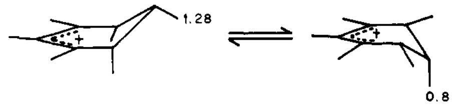


4a



5a

R = *n*-pentyl



(2)

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species **2a,b** are best described as nonplanar about C$_1$, the saturated

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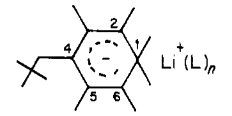
Table II. Carbon-13 Shifts of 1 M **2b** in Cyclopentane with Ligands at 0 °C[a]



ligand(s) (quantiy, mol)	C_1 CH_3	C_1	C_2	C_3	C_4
unsolvated	16.34 30.44	38.67	85.80	132.54	97.50
NMP (2)	17.66 30.57	38.03	84.14	127.78	94.82
TMEDA (1)	16.33 30.57	38.51	83.85	127.96	92.66
diethyl ether (2)		38.13	84.40	127.98	94.40
triethylamine (2)		38.29	84.43	127.96	94.28
NMP (1) + KO-*t*-Bu (1)		36.82	86.47	129.29	91.19
THF (2)		38.24 38.02	83.84[b] 83.63[c]	127.96[b] 127.69[c]	90.39[b] 92.57[c]
HMPA (1) + NMP (2)		38.33	84.01	127.97	90.27
glyme-2 (1) + NMP (2)		38.38 37.90	84.12[b] 83.31[c]	128.02[b] 127.59[c]	90.40[b] 93.02[c]
glyme-5 (1) + NMP (2)		38.39	84.01	128.02	90.39

[a] Shifts in ppm with Me_4Si as internal standard. [b] Low temperatures. [c] High temperatures.

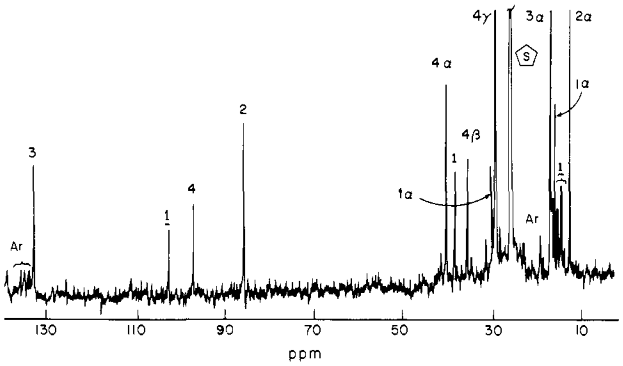


Figure 2. ^{13}C NMR spectrum (22.625 MHz) of 0.77 M **2b** in cyclopentane at 28 °C. Peaks labeled 1 are due to triene **1**; Ar indicates **3b**.

ring carbon, and ring flipping is slow with respect to the frequency shift between the methyls. Since all other cyclohexadienyl ions have been shown to be planar.[13-15] the bent structure of **2b** must be ascribed to destabilization of the hypothetical planar form due to periplanar steric interactions between the substituents.

In the presence of THF-d_8, used since it metalates more slowly than protio-THF, fine structure is seen in the proton NMR spectra of **2a,b**. Similar effects take place with **2b** complexed to glyme-2. Suffice it to say that the resonances represent different kinds of ion pairs; this subjected is discussed in detail below.

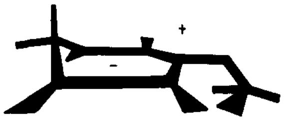
The carbon-13 NMR spectrum of **2b** (see Table II and Figure 2) shows greater resolution and more detail than the proton NMR spectrum due to the higher sensitivity of ^{13}C shifts to molecular environment. As in the proton spectra, the C_1 methyls are magnetically nonequivalent; the methyl at 17 ppm, due to compression from neighboring methyl groups,[16] is assigned as equatorial while that at 30 ppm is axial.

Table III. ^7Li NMR Shifts for **2a,b** in Cyclopentane with Added Ligands at 233 K

			shift, ppm		
2, M	lig 1 (concn, M)	lig 2 (concn, M)	A	B	C
		2b			
0.75				−3.79	
1.22	NMP (2.4)			−3.90	
0.75	TMEDA (0.83)			−3.87	
0.80	TMEDA (0.83)	THF (1.7)		−3.81	
0.96	Et_2O (1.92)			−4.38	
0.82	Et_3N (1.64)			−4.15	
0.75	NMP (1.64)	glyme-2 (1.5)	−1.51	−4.50	−6.97
0.64	THF-d_8 (4.4)		0.02	−4.08	−6.79
0.62	NMP (1.35)	glyme-5 (2.24)	−1.00		−6.93
0.80	NMP (1.73)	HMPA (1.59)	−0.06		−6.89
		2a			
1.03	TMEDA (1.10)	THF (2.10)		−3.50	
1.09	TMEDA (1.27)			−3.58	
0.80	TMEDA (0.94)	glyme-5 (1.98)	−0.98	−3.72	−6.51

[a] With respect to 0.3 M LiCl in methanol.

The ^{13}C shifts of **2b** are well separated. In a gross sense they follow the alternating order one would expect for an odd-alternate pentadienyl anion, i.e., shielding at C_2, C_4, and C_6 due to negative charge[17] and a typical sp^2 shift of 127–132 ppm for C_3 and C_5. However, the shifts do vary with chemical conditions, implying different kinds of ion pairing and solvation. For instance, significant changes in ^{13}C shifts, all in the shielding direction, occur on addition of ethers or tertiary amines to unsolvated **2b** (rows 1–5 in Table II). Thereafter shifts of C_1, $C_{2,6}$, and $C_{3,5}$ change by not more than 0.5 ppm while the C_4 shift changes by 5 ppm. This implicates C_4 as the ring carbon closest to lithium. Inspection of molecular models shows C_4 to be the least obstructed site on the anion. Altogether the results for **2b** presented so far—the magnetic nonequivalence of the *gem*-methyls, the alternating ring ^{13}C shifts, and the sensitivity of the C_4 shift to ligand—are most consistent with partial structure **7**.



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It is also significant that except for unsolvated **2b**, the ^{13}C shifts of **2b** solvated by all ethers or amines vary slightly in a linear fashion with temperature, typically 3×10^{-3} ppm/K; see, for example, Figure 8. This behavior has been ascribed to systems where either only one main species is responsible for the spectra at all temperatures investigated or the distribution of species remains constant with temperature.[18]

Thus so far one can conclude that **2b** contains a conjugated anion, is bent out of the plane about C_1, and exists as various kinds of ion pairs which differ in solvation.

Lithium-7 NMR data for **2a,b** both unsolvated and in the presence of ether and tertiary amines are listed in Table III, rows 1–3, 5, 6, and 12. At 0 °C each sample gives one ^7Li resonance, and the shifts are all around −3.8 ppm with respect to external 0.3 M lithium chloride in methanol. This common chemical shift behavior implies that **2b** in the presence of simple monoethers and tertiary amines forms similar kinds of ion-paired species.

2b Complexed to THF

Compared to the results described above, a striking change takes place in the NMR spectra of **2b** obtained in the presence of THF.

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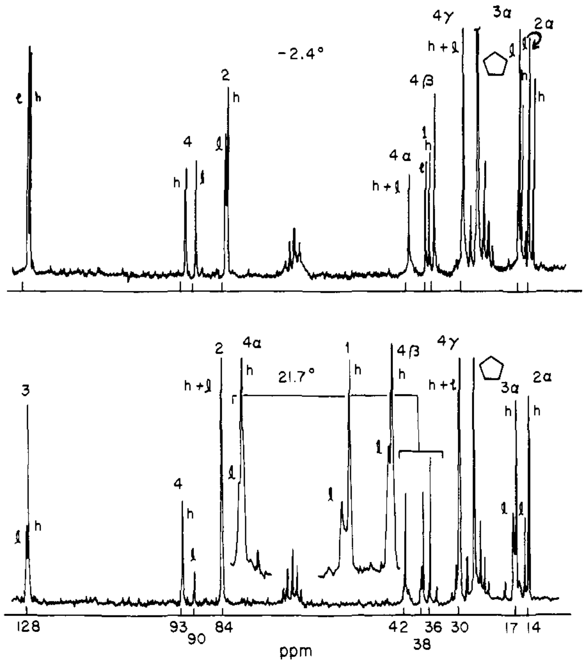


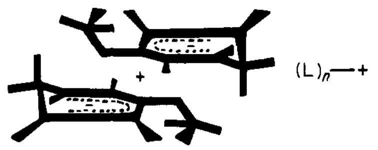
Figure 3. ^{13}C NMR spectrum (22.625 MHz) 1.0 M **2b**, in cyclopentane with 2.0 M THF-d_8 at -2.4 (top) and 21.7 °C (bottom).

Now for the first time we observe fine structure in the NMR spectra. For example, the ^{13}C NMR spectrum of **2** in cyclopentane with 2 equiv of THF-**d**$_8$ at 22 °C has two closely spaced lines for every group of chemically nonequivalent carbons (Figure 3). Within a spectrum the area ratios for each of these doublets are the same, but they vary with THF concentration (Figure 4) and temperature (Figure 3), and the temperature variation is reversible. The resonances which prevail at low and high temperature are labeled l and h, respectively. Note that the shift of C_4 which varies most with ligand in **2b** reaches its most shielded value in the l spectrum of **2b** complexed to THF, compared to the results with tertiary amines, diethyl ether, and **2b** unsolvated (Table II).

The proton NMR spectrum of **2b** complexed to THF also shows doubling of resonances for chemically equivalent hydrogens. This is summarized in Table I and seen in Figure 5.

From the above results, one can see that **2b**·(THF)$_n$ forms two different kinds of ion pairs, l and h. By analogy with previous work the former must be the looser of the two since it prevails at low temperature.[19] It is also evident that the exchange of anions between different ion pairs is slow on the NMR time scale, i.e., τ(anion) > 1.0 s. This is unusual in that exchange processes of this type are generally observed to be very fast, say τ(anion) ~ 10^{-8} s.[20,21]

Lithium-7 data confirm and extend the above conclusions. As noted above, ^{7}Li resonances of **2b** in the presence of tertiary amines or diethyl ether consists of a single line of shift ca. 3.8 ppm from external 0.3 M lithium chloride in methanol. However, in the presence of THF there are three well separated ^{7}Li resonances, over a 7-ppm span, one at -3.8 ppm, B (with respect to lithium chloride in methanol), and the other two flanking it, A and C, at 3 and 4 ppm, respectively, to each side (Figure 6). The latter two resonances always have the same intensity. With increasing THF-d_8 concentration or decreasing temperature, the areas of the outside resonances increase at the expense of the central one (Figure 6). Comparing the ^{1}H, ^{13}C, and ^{7}Li NMR spectra for **2b** with THF-d_8 we learn that the outer ^{7}Li resonances, A and C, and the low temperature peaks in the ^{1}H and ^{13}C spectra represent one ion-pair species while a second kind of ion pair gives rise to the central ^{7}Li peak and the proton and ^{13}C spectra which prevail at high temperature. From the equality of areas for the flanking ^{7}Li resonances, we can conclude that the low-temperature species is at least a dimer. Interestingly, of these two peaks the left hand one (Figure 6) is quite close in shift to lithium chloride in methanol, that is, peak A is due to a symmetrically solvated lithium ion. The other resonance at the opposite end of the spectrum, 7 ppm away, has a shift quite similar to that for cyclopentadienyllithium or fluorenyllithium in diethyl ether.[22] The latter forms contact ion pairs with lithium centered above the five-membered ring. We are now in a position to propose that the low temperature prevailing ion-pair species is best described by



2bl

One lithium is sandwiched between the 4 positions of two anions, forming a triple ion. External to it is a second lithium symmetrically solvated, represented by peak A in the ^{7}Li spectrum (Figure 6).

A series of samples was prepared ca. 0.7 M in **2b** in cyclopentane with 2,4,6 and 13 equiv of THF-d_8 and the ^{7}Li NMR spectra obtained at different temperatures between -75 and -16 °C. Comparison of ^{7}Li peak areas and THF concentrations shows that the equilibrium system most closely in accord with the data obtained so far is one in which a partially solvated tight ion-pair dimer, **2bh** to be discussed below, accepts a molecule of THF-d_8 to form the looser dimer **2bl**.

$$\underset{\mathbf{2bh}}{(A^-Li^+\cdot THF)_2} + THF \underset{-5\,°C}{\overset{K=0.37}{\rightleftharpoons}} \underset{\mathbf{2bl}}{(A^-Li^+A^-)\ Li^+\cdot(THF)_3} \qquad (3)$$

As has been observed for other ion-paired systems, equilibrium 3 is displaced to the loose dimer side at low temperatures.[18] From the variation of the equilibrium constant with temperature, we find $\Delta H = -4 \pm 0.4$ kcal mol^{-1} and $\Delta S = -16 \pm 2$ eu, quite similar to results for fluorenyllithium and indenyllithium using 1,2-dimethoxyethane.[18] Some preliminary data pertaining to dynamic behavior of Li$^+$ in this system also accords with the proposed structure of the loose ion-pair dimer. Above -23 °C the A and B ^{7}Li resonances of **2b**·THF, but *not the C resonance*, undergo progressive broadening and coalescence with increasing temperature (Figure 7). This indicates the operation of a process which exchanges solvated lithium in **2bl** with lithium in the tight ion-pair dimer **2bh** at a rate on the NMR time scale. The suggested sandwiched location of lithium C in the triple ion in the loose ion-pair dimer must be responsible for its much slower exchange rate with lithium.

While the structure of the loose ion-pair dimer **2bl** can be described in some detail, that of the tighter ion-pair species **2bh** is less understood. Species **2bl** is a dimer, and since the system **2b** with THF behaves in accord with equilibrium 3, **2bh** must also be dimeric.

The ^{13}C shifts of **2bh** are different from those of unsolvated **2b**. Also THF in the presence of **2b** has different ^{13}C shifts from free THF. Note, the ^{7}Li shifts of **2b** in the presence of diethyl ether and all tertiary amines and of **2bh** are all nearly the same. Thus **2bh** is best described as a peripherally solvated tight ion-pair dimer.[23-25] The relationship of the above conclusions to previous

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[20] Chang, R.; Johnson, C. S. *J. Am. Chem. Soc.* **1966**, *88*, 2338. Hirota, N. *Ibid.* **1968**, *90*, 3603. Eigen, M. *Proc. Int. Conf. Coord., Chem., 11th* **1968**, 97.

[21] Note, however, slow exchange of ions has been observed among ion pairs of fluorenyllithium complexed to crown ethers: Wong, K. M.; Konizer, G.; Smid, J. *J. Am. Chem. Soc.* **1970**, *92*, 666.

[22] Cox, R.; Terry, H., *J. Magn. Reson.* **1974**, 14, 317. The ^{7}Li NMR shifts were measured with respect to LiCl in water and in ref 10 with respect to *n*-butyllithium in cyclohexane. We measured 1.0M LiCl in water (+1.089 ppm) and *n*-butyllithium (+2.973 ppm) with respect to 0.3 M LiCl in methanol. All shifts including those from ref 10 and 22 are given with respect to LiCl in methanol.

[23] Slates, R. V.; Szwarc, M. *J. Am. Chem. Soc.* **1967**, *89*, 6043.

[24] Chan, L. L.; Smid, J. *J. Am. Chem. Soc.* **1968**, *90*, 4654.

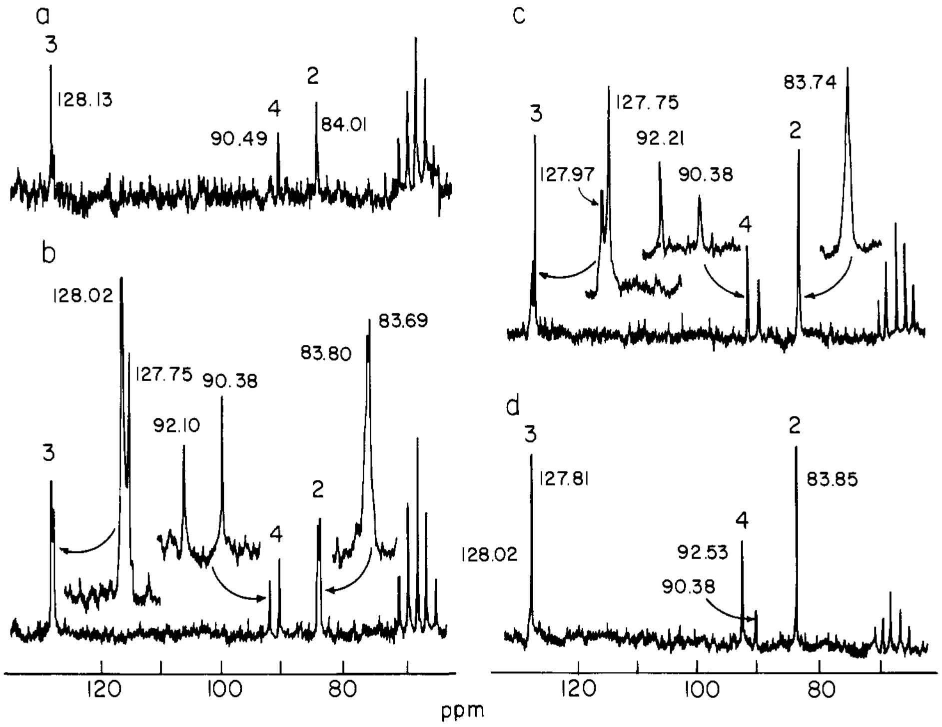

Figure 4. ^{13}C NMR spectrum of **2b** (C_2–C_4, ring carbons) at −11.8 °C with varying concentrations of **2b** and THF-d_8: (a) 0.71, 9.3; (b) 0.64, 4.4; (c) 0.64, 2.7; (d) 064, 1.4; (e) 0.67, 0.71 M of **2b** and THF-d_8, respectively.

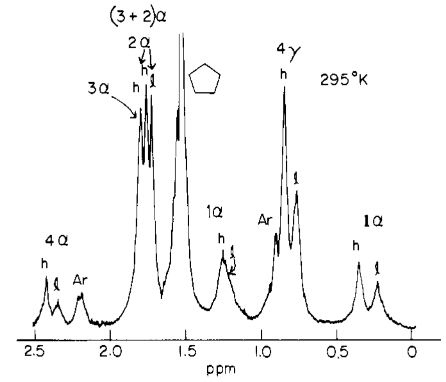

Figure 5. ^{1}H NMR spectrum (60 MHz) of 1 M **2b** in cyclopentane with 2 M THF-d_8 at 21.7 °C.

results from the literature will be discussed below.

2b with Amines, Ethers, and Polyethers—General Behavior

Altogether the NMR data for **2b** in the presence of all potential ligands tried out so far fall into a common pattern which is typified by the results for **2b**·THF. Thus under all circumstances so far we observe no more than three lithium resonances, and their shifts are close to those seen for **2b** complexed to THF (Table III). Compound **2b** with diethyl ether or tertiary amines gives rise to only the central resonance in the ^{7}Li NMR spectrum, −3.8 ppm. Use of diglyme as ligand gives results very similar to THF; HMPT or pentaglyme with **2b** give only the flanking resonances A and C, and they are of equal area. It is significant that these ^{7}Li C resonances obtained by using the glymes, HMPT, and THF have almost identical shifts. This is consistent with the assignment of this resonance to lithium sandwiched between two anions; its shift should not depend on the ligand since the ligand is bonded only to the second external lithium. In contrast the A resonances in these spectra do vary slightly with the ligand, as would be expected for ligand solvated lithium.

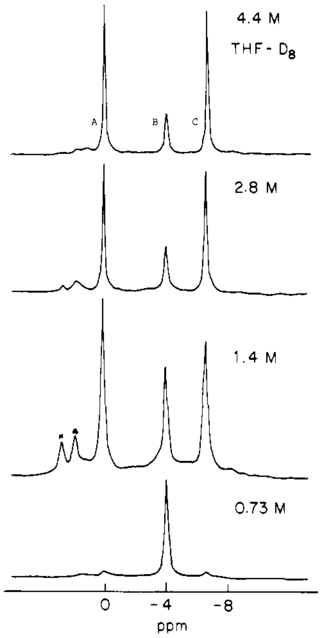

Figure 6. ^{7}Li NMR (23.319 MHz) of 0.64 M **2b** in cyclopentane with THF-d_8 at −40 °C at different concentrations (noted on plot). Stars indicate impurities due to CH_3Li (1.86 ppm) and lithium acetaldehyde enolate (2.76 ppm).

The **2b**–ligand complexes which give rise to the flanking A and C resonances in the ^{7}Li NMR spectra have ^{13}C ring shifts *identical* with those obtained at low temperature in the complexes **2b**·THF and **2b**·glyme-2. These resonances are assigned to the triple ion and should not depend on ligand. In contrast the ^{13}C shifts of **2b** with tertiary amines and diethyl ether and the high temperature prevailing spectra obtained from **2b** complexed to THF or glyme-2 do vary with ligand and have been assigned, above, to tight ion-paired species. This is seen most clearly in Figure 8 in which the C_4 ^{13}C shift vs. temperature of **2b** in the presence of different ligands is plotted.

Thus the common features of the NMR spectra of **2b** in the presence of different ethers and amines lead us to propose that the two kinds of ion-paired species found for **2b** with THF also obtain in the presence of other ligands.

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(25) Chan, L. L.; Wong, K. H.; Smid, J. *J. Am. Chem. Soc.* **1970**, *92*, 1955.

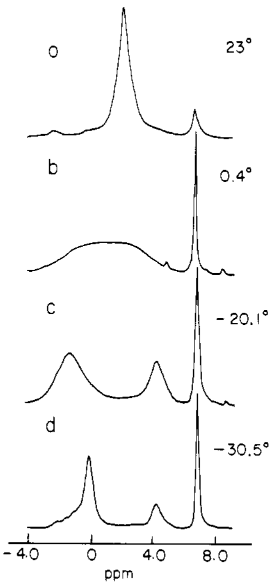


Figure 7. ^{7}Li NMR spectra (23.319 MHz) of 1 M **2b** in cyclopentane with (a)-(c) 2 M THF-d_8 and (d) 4 M THF-d_8 at different temperatures.

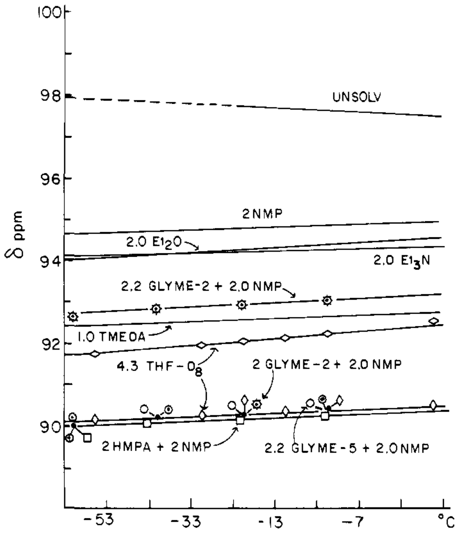


Figure 8. ^{13}C NMR shift of C_4 of 1 M **2b** in cyclopentane vs. temperature, with different ligands (labeled on plot).

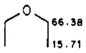
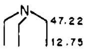
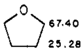
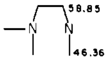
One can apply the above conclusions also to ^{7}Li NMR data reported in the literature for other lithium salts. Both (1,3-diphenylallyl)lithium and (triphenylmethyl)lithium were reported to form separated ion pairs in THF, glyme-2, and HMPA. These solutions gave ^{7}Li NMR shifts from -1.3 to +0.55 ppm (vs. LiCl in external methanol),[22] the shift region we assign to solvated lithium ion.

A comment is in order here on the origin of ^{13}C NMR shifts in ion pairs. The linearity of charge with ^{13}C chemical shift in π-electron systems is based on data from separated ion pairs where the counterion exerts minimal influence in ^{13}C shifts.[17] In the past it has been implied that ^{13}C shift changes among contact ion pairs and between contact and separated ion-pairs are due to changes in charges, i.e., development of carbon-metal covalency. There is no evidence of such effects. It is more likely that electric fields due to neighboring ions in the ion pairs or ion-pair aggregates are responsible.

Ligand NMR Spectra of Solvated 2b

Carbon-13 shifts of tertiary amines and ethers in the presence of **2a,b** are all significantly different, by as much as 2.3 ppm, from those of the free ligand in hydrocarbon solvents. Table IV lists effects of **2b** on ^{13}C NMR shifts of simple ethers and amines. These results clearly show that all the ligands in Table IV are, at least in part, complexed to lithium in **2b**. With few exceptions, see below, these preparations give single NMR spectra for all contained ligand; thus exchange of free ligand into the complexes of **2b** must be fast on the NMR time scale. Table V lists ^{13}C shifts of NMP under different conditions. Addition of **2b** to NMP changes the NMP shifts, implying interactions between lithium and NMP. Addition of diethyl ether to this solution does not change the NMP shifts; therefore NMP is still complexed to lithium. In this general way using mixtures of potential ligands with **2b**, one can establish an order of strengths of complexation of **2b** to different amines and ethers. For instance adding THF to preformed **2b** with NMP causes the ^{13}C and ^{7}Li NMR spectra to change to those characteristic of **2b** with THF alone (Tables II-V). So we learn that THF displaces NMP from its complex with **2b**. In this fashion we find that THF, glyme-2, glyme-5, and HMPT all displace NMP from its complex with **2b**. All these results are confirmed by the ^{13}C NMR spectra of the anion, (Table II), the ligand (Table VI), and ^{7}Li NMR (Table III).

Table IV. Influence of 2b on ^{13}C Shifts in Ether and Tertiary Amines at 0 °C

2b concn, M	ligand concn, M	lig 1[a]	shift increment,[b] ppm
0.96	1.92		0.39 -0.24
0.80	1.60		-0.40 -0.57
0.75	2.07		0.73 -0.02
0.75	0.83		-1.67 -0.13

[a] Shifts are in ppm with Me_4Si as internal standard. [b] Shift from pure ligand due to complexation with 2b.

Table V. ^{13}C Shifts of *N*-Methylpyrrolidine in Cyclopentane in the Presence of 2b and Secondary Ligands at 250 K

2b concn, M	NMP concn, M	lig 2 (concn, M)	shift,[a] ppm CH$_3$	CH$_2$ (1)	CH$_2$ (2)
	2.00		56.92	42.4	24.71
1.22	2.44		57.05	42.51	24.42
0.75	1.62	Et_2O (1.50)	57.00	42.45	24.43
1.00	2.00	THF-d_8 (2.13)	56.93	42.50	24.70
0.75	1.64	glyme-2 (1.50)	56.92	42.5	24.70
0.62	1.35	glyme-5 (1.46)	56.92	42.5	24.70
0.80	1.72	HMPA (1.59)	56.92	42.5	24.70

[a] With respect to Me_4Si.

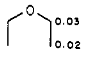
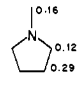
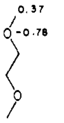
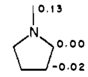
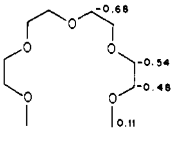
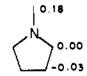
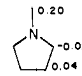
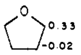
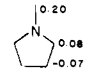
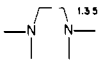
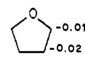
Table VI shows that in a solution containing **2b**, TMEDA, and THF in the molar ratio ca. 1:1:2, TMEDA is mainly complexed to **2b** while THF is not. In contrast Table VII shows that for **2a** in the presence of TMEDA and glyme-5, the anion spectrum resembles that of **2b** with THF, i.e., glyme-5 partly displaces TMEDA from the **2a**-TMEDA complex.

On the basis of the foregoing experiments, the order of increasing strengths of complexation of **2b** with different ligands is diethyl ether < *N*-methylpyrrolidene < THF < TMEDA ~ glyme-2 < glyme-5 < HMPT.

Dynamic Effects in Complexation

While exchange of free with complexed ligand in solutions containing **2a** or **2b** is generally fast on the NMR time scale, there are two cases where exchange is slow enough to give separate spectra for the two ligand environments. A cyclopentane solution of **2b** (0.75 M) with TMEDA (0.83 M) gives a CH_2N ^{13}C resonance at 56.7 ppm. However, TMEDA (1.6 M) with **2b** (0.8 M) gives rise below -50 °C to two ^{13}C CH_2N resonances of equal amplitude at 56.7 and 58.3 ppm. The latter shift is identical with that of free TMEDA. This shows that **2b** forms a 1:1 complex with TMEDA and exchange of ligand between its free and complexed environments is slow on the NMR time scale below -50

Table VI. Competition Experiments. Complexation of 2b with Tertiary Amines and Ethers

2b concn, M	ligand(s)[a] (molarity, M)	
0.75	 (1.5)	 (1.6)
0.75	 (1.5)	 (1.64)
0.62	 (1.64)	 (1.6)
0.84	$O{=}P(N{<})_3{}^{0.13}$ (1.6)	 (1.7)
0.97	 (1.94)	 (2.09)
0.90	 (0.99)	 (1.92)

[a] ^{13}C NMR shift increments in ppm.

Table VII. Ring ^{13}C NMR Shifts of 2a in the Presence of Ligands at 233 K

			concn, M		
δ_2	δ_3	δ_4	glyme-5	TMEDA	2a
82.84	127.17	95.23		1.24	1.09
82.69	127.05	94.97[a]	1.98	1.17	0.94
82.26	126.63	92.83[b]			

[a] Species predominant at high temperatures. [b] Species predominant at low temperatures.

°C. Above this temperature the CH_2N resonances broaden and coalesce, indicating faster ligand exchange. Similar results are seen with triethylamine. A cyclopentane solution 0.8 M in **2b** and 1.6 M in triethylamine shows two methyl resonances of equal area at 11.15 and 12.50 ppm, respectively. The latter shift is that seen for free triethylamine.

Discussion

Although little work has been reported on ion pairing in hexadienylic metal compounds, the results of this work are consistent with data for other ion-paired systems reported in the literature as shown by the selected examples described below.

In general, separated ion pairs (SIP) are recognized when spectral data for carbanion salts become independent of ligand and counterion. These effects are more likely to be observed with smaller cations and at low temperatures, the latter because the formation of a SIP from a contact ion pair (CIP) is accompanied by a negative entropy due to freezing out of ligand (S) motions.

$$R^-M^+ + S \rightleftarrows R^-MS^+ \qquad (4)$$

The state of aggregation of an ion-paired species can vary. However, it is interesting that where molecular weights of carbanion salts have been measured or indirectly inferred, dimers are often detected, as seen for **2bl** and **2bh**. Ebulliometry showed [9-(2-hexyl)fluorenyl]lithium to be dimeric in cyclohexane and equal parts monomers and dimers in THF.[10] Of related structure, [9-propylfluorenyl]lithium was found to consist mainly of dimers in toluene and cyclohexane.[10] Polystyryllithium in benzene consisted of dimers.[26,27]

From kinetics of anionic polymerization, polystyryllithium[28] in benzene–glyme was proposed to form, in part, triple ions and polystyrylcesium to exist as intramolecular triple ions.[29] These species are also dimeric in "R^-Li^+".

Distinct solvates of ion-paired species, as of **2b** with THF, have been reported before. Thus (1,1-diphenylhexyl)lithium in hexane with THF forms two complexes with Li–THF in ratios 1:2 and 1:4.

$$A^-Li^+ + 2THF \xrightleftharpoons{K_5} A^-Li^+{\cdot}(THF)_2 \qquad (5)$$

$$A^-Li^+{\cdot}(THF)_2 + 2THF \xrightleftharpoons{K_6} A^-Li^+{\cdot}(THF)_4 \qquad (6)$$

with $\Delta H_5 = -4.6$ kcal and $\Delta S_5 = -15.6$ eu.[30] Also (1,1-diphenylbutyl)lithium was shown to form a tight complex with average Li^+–THF ratio of 1:2.4, thus mainly a 1:2 complex.[31]

The lithium-7 shifts of a variety of lithium carbanion salts in HMPT are essentially the same, ascribed to separated ion pairs, while the shifts for these salts in diethyl ether vary considerably, due to contact ion pairing.[22] Also it is interesting that the ^{7}Li shift of −11.8 ppm for [9-(2-hexyl)fluorenyl]lithium in cyclohexane changes to −6 ppm on addition of 2 equiv of THF to the solution.[10] If this latter salt, with THF, exists as an ion-pair dimer with triple ion, $A_2Li^-Li^+$, as seen for **2bl**, the observed −6-ppm shift could be the result of averaging a −12-ppm shift of ^{7}Li in the triple ion with a solvated ^{7}Li shift of ca. 0 ppm. Note that with excess THF or HMPT the ^{7}Li shifts change to −1.2 and −2.0 ppm, respectively, representing a species more solvated than with just 2 equiv of THF.

A combination of UV and ^{1}H, 13C, and ^{7}Li NMR spectra showed that for fluorenyllithium, DME, THF, glyme-3, glyme-4, Me_2SO, and HMPT favored the formation of SIP, especially at low temperatures and also displaced *p*-dioxane from its complex with fluorenyllithium, the latter being a contact ion pair.[7,18,24,25,32,33] In similar fashion O'Brien, Russell, and Hart, using ^{13}C NMR showed THF and DME to favor the formation of separated ion pairs from fluorenyllithium, (diphenylmethyl)lithium, trityllithium and [(trimethylsilyl)benzyl]lithium, especially at low temperatures.[8] The sodium compounds formed mixtures of separated and contact ion pairs while the potassium, rubidium, and cesium salts formed only contact ion pairs.[8]

The published findings, quoted above, qualitatively parallel our results for compound **2b**. However, the advantages of **2b** are its stability, high solubility in all media tried, and the slow exchange of ions among ion pairs. This has allowed us to investigate **2b** under numerous conditions and led to some highly detailed information on the structure of an ion pair–dimer which contains a triple ion.

The stability of **2b** was ascribed to destabilization of the transition state for aromatization due to steric interactions among the substituents.[9] The crowded substitution in **2b** is most likely also responsible for its bent structure, about the saturated carbon, and the detection of only conjugated anions in all solutions investigated, included the unsolvated species. In this system bridged carbon–lithium bonds may be energetically prohibited by the large substituents around the ring.

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(26) Johnson, A.; Worsfold, D. J. *J. Polym. Sci. Part A* **1965**, *2*, 449.

(27) Worsfold, D. J.; Bywater, S. *Can. J. Chem.* **1960**, *38*, 1891.

(28) Ise, N.; Hirohara, H.; Makino, T.; Takaya, K.; Kakayama, M. *J. Phys. Chem.* **1970**, *74*, 606.

(29) Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1964**, *86*, 5024.

(30) Waack, R.; Doran, M. A.; Stevenson, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 2109.

(31) Okamoto, Y.; Yuki, H.; *J. Organomet. Chem.* **1971**, *32*, 1.

(32) Smid, J.; Chan, L. *J. Am. Chem. Soc.* **1967**, *89*, 4547.

(33) Hogen-Esch, T.; Smid, J. *J. Am. Chem. Soc.* **1965**, *87*, 669; **1966**, *88*, 318; **1967**, *89*, 2764.

Triple ion formation in these complexes of **2a,b**, which is favored by the glymes and HMPT, is not in general dependent on the strength of complexation of lithium with ligand. It is interesting that, except for diethyl ether, oxygen ligands favor triple ions while tertiary amines with **2b** give rise to tight ion paired species. This difference in complexation behavior could be connected with the fact that a tertiary amine has three organic groups bonded to nitrogen while an ether has two.[34,35]

Experimental Section

The origin, preparation, and manipulation of all compounds used in this work is as described by us previously.[9] NMR equipment was also described before.[9]

Preparation of Solutions of 2b with THF. The reaction vessel consisted of a 10-mL 14/20 round bottom flask with side arm protected by a 2-mm straight bore stopcock. The entire system was dried in a current of argon with flaming. A mixture of triene **1** (1.84 g, 10.4 mmol) with THF-d_8 (2.5 g, 31.3 mmol) was syringed in via the stopcock. The apparatus was cooled to 0 °C and a solution of *tert*-butyllithium in cyclopentane (4.25 mL, 11.48 mmol, 2.7 M) added to **1** over a period of 6 min. The reaction mixture was allowed to warm to room temperature and then stirred for another 10 min. Total volume of the reaction mixture was 8.75 mL, measured by syringe. A 0.4-mL aliquot of the reaction mixture was hydrolyzed with O_2-free water in a test tube protected with a serum cap. Gas chromatography (150 °C) using an Aerograph model 700-A instrument with a column (5ft × 0.25 in.) packed with SE-30 on glass beads showed >99.8% conversion of **1** to **4** + **5**. The stock solution just described was concentrated to 1.19 M by evaporating excess solvent in a current of argon. Final concentration of **2b** was 1.19 M. A 2.0-mL aliquot of this solution was introduced into each of three 10-mm o.d. NMR tubes under argon. These tubes were protected with 2-mm straight bore stopcocks. For 3 equiv of THF per equiv of **2b**, the solution was made up to 3.5 mL with cyclopentane. For samples to contain 4,5 and 6 equiv THF for 1 equiv of **2b**, 0.18, 0.36, and 0.54 mL of THF-d_8, respectively, were added, individually, to the 2.0-mL aliquots of stock solution in three NMR tubes and each sample made up to 3.5 mL with cyclopentane. This produced four samples 0.68 M in **2b** containing 3,4,5, and 6 equiv of THF. NMR samples were degassed using the freeze-thaw cycle and sealed off under vacuum.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE-8807439AOI. G.F. thanks Professor John Waugh and the Department of Chemistry of the Massachusetts Institute of Technology for their generous hospitality during 1980–1981.

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(34) Similar results have been observed for fluorenyllithium: Sinyk, R. M.Sc. Thesis, College of Forestry, Syracuse, NY, 1968.

(35) A referee has suggested that the high concentrations of **2b**·THF used in this work favor the loose ion-pair dimer; dilution would tend to dissociate the latter.

Structure of Moderately Strong Acids in Aqueous Solution

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Contribution from the Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02125. *Received January 22, 1981*

Abstract: A general hypothesis is made that the undissociated forms of moderately strong acids exist in aqueous solution as ion-pair complexes in equilibrium with covalently bonded structures. This suggestion has been made earlier by others for the specific cases of trifluoroacetic, trichloroacetic, and hydrofluoric acids and the present paper offers photometric evidence that squaric, butynedioic, di- and monochloroacetic, and difluoroacetic acids also exist partly as ion pairs. The general hypothesis is supported by ^{13}C NMR and thermodynamic data in the form of a correlation between the carboxylate carbon-13 resonance displacement and the standard entropy change $\Delta S°_a$ accompanying acid dissociation. This correlation is interpreted in terms of a model featuring enhanced solvent structuring around highly polar undissociated ion pairs. The observed correlation parameters predict that those acids with $\Delta S°_a$ near -13 and -5 cal mol^{-1} K^{-1} have approximately 50% and 90%, respectively, of their undissociated forms as ion pairs.

Nearly a decade ago we reported[1] the rather surprising result that the undissociated form of squaric acid (1,2-dihydroxycyclobutenedione) formed complexes with two unprotonated acid–base colorimetric indicators, cresol red and 4-phenylazodiphenylamine (PDPA), which are anionic and neutral species, respectively. Each of the complexes had a visible spectrum virtually indistinguishable from that of the protonated indicator species and the affinities of the unprotonated indicators for hydronium and undissociated squaric acid were similar. This discovery had important ramifications for acid–base colorimetry which relies on the assumption that spectral differences between protonated and unprotonated indicator depend solely on the solution pH so that the spectral difference serves as a measure of pH. For squaric acid solutions sufficiently concentrated to contain a significant amount of undissociated squaric acid, the indicator spectrum depends on the concentration of molecular acid as well as on the pH. Since then we have found similar complexes in several other systems and these discoveries have important implications not only for the practice of acid–base colorimetry but also for an understanding of the nature and structure of solute species in aqueous solutions of moderately strong acids.

Each system studied consists of two acid–base conjugate pairs. One pair is to be called the controlling acid or pair because its relatively high analytical concentration controls the solution pH, and the other pair, which is present at much lower concentration, is termed photometric because its UV-visible absorbance is measured and used to monitor the presence of complex species. The complex is between the acidic form of the controlling pair and the basic form of the photometric pair and will be referenced in this paper by the term "acid–base complex". If B and Φ denote general controlling and photometric species, respectively, with electric charge on Φ not designated, then the aqueous equilibria are

$$HB + H_2O = B^- + H_3O^+$$

$$H\Phi + H_2O = \Phi + H_3O^+$$

and an acid–base complex has the nominal formula $BH\Phi$. In ref 1, squaric and oxalic acids were the controlling species while the two colorimetric indicators were the photometric species. Both controlling and photometric acids are moderately strong in the sense suggested by others[2] of having aqueous acid dissociation

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(1) Gelb, R. I.; Schwartz, L. M. *Anal. Chem.* **1972**, *44*, 554-559.

0002-7863/81/1503-5664$01.25/0 © 1981 American Chemical Society