parison of the optical rotatory properties suggests that the structure of the three polymeric type II complexes are different from each another. The complexes of PLL and PLO exhibit almost identical CD patterns in the visible, characterized by a strong negative band at 510 nm and by a weaker positive band at $\simeq$585 nm. In the charge-transfer transitions region below 400 nm the CD pattern of the PLO complex is similar to that of the PDBA complex, but substantially different from that of the PLL complex. Such variation of the CD properties among type II complexes of the three polymers possibly reflects a different number of amido nitrogens coordinated to Cu(II) at the planar positions and/or different apical interactions of side-chain amino groups in the three cases. Again the CD spectrum of the biuret type complex of PDBA is very similar to the corresponding complex of $[\text{L-His}]_n$ formed at pH 14. As in the latter case it is possible that side-chain amino groups of PDBA occupy apical positions in the coordination sphere of Cu(II).

We have also proved that the α-helical structure of the polypeptide backbone is not compatible with the formation of type II copper complexes of PLL and PLO. If a solution of PLL at pH $\simeq$11.2, (where the polypeptide conformation is 100% α-helix) is titrated with cupric ions, one observes a decrease of helical content which parallels the extent of complex formation (Figure 4). The disruption of the helical structure appears to be noncooperative in character, being linearly proportional to the amount of added metal ions. We can therefore reasonably conclude that cupric ions are coordinated to peptide sequences not in the helical form, and previously proposed models based on coordination to the polypeptide chain in the α-helical form are inconsistent.

More detailed results including potentiometric infrared and CD investigations will be available in due course and will be reported elsewhere.

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Cation Solvation: the Conversion of Contact Ion Pairs to Solvent Separated Ion Pairs

Sir:

Since the proposal by Winstein[1] of two types of ion pairs, many techniques have been developed to differentiate between them,[2] with the distribution depending on solvent donicity, cation size, anion, and temperature. It has also been found that in some systems two or more types of contact ion pairs can be observed,[3] whereas in other systems two or more types of solvent separated ion pairs can exist.[4] Focusing on the contact pairs, it is reasonable to imagine contact pairs with various extents of cation and/or anion solvation (solvated contact pairs). The question then arises as to how many solvent molecules are necessary to convert a contact ion pair to a solvent separated ion pair.

Attempts to answer this question have been complicated because of the nature of the usual electrolyte systems. In a pure solvent, the concentration of the solvating agent cannot be effectively varied, and one typically observes contact, solvent separated, or an equilibrium mixture of the two or more types of ion pairs.[2,5] But it is not possible to determine the extent of solvation of the ions. Mixed solvents could be used to overcome this problem.[2,6] However, they are generally unsatisfactory because of the solubility characteristics of the usual electrolytes, which result in the solvent and the selected donor competing for coordination sites on the ions.

The system sodium tetraethylaluminate ($NaAlEt_4$)-benzene-donor (D) is a particularly unique system for this type of study. $NaAlEt_4$ is soluble in benzene, a nonsolvating solvent. Thus controlled amounts of a solvating agent can be added to a benzene solution of $NaAlEt_4$, thereby permitting one to determine the ion pair type as a function of the D/Na^+ ratio. We wish to report here ratio studies using this system with a number of monodentate and bidentate solvating agents having Gutmann donor numbers ranging from 19.2 to 38.8.[7]

It is possible to distinguish between contact and solvent separated ion pairs in the $NaAlEt_4$-benzene-D system by examining the spin-spin interactions between ^{27}Al and ^1H as reflected in the methylene group proton resonance patterns.[8] In samples containing anions with cubic symmetry, the methylene absorptions appear as well-defined nine-line patterns representing the fortuitous overlapping of resonances resulting from essentially equal spin-spin interactions of methylene protons with both the neighboring methyl protons and the aluminum nucleus. Conversely, in samples containing highly distorted anions, the ^{27}Al-^1H spin interactions are not observed in the ^1H NMR spectra. Rather, the resonance collapses to a 1,3,3,1 quartet resulting from the remaining ^1H-^1H spin interactions. The two extremes, a nine-line pattern representing the anionic T_d symmetry and a quartet corresponding to the highly distorted anion are logically related to solvent separated and contact ion pairs, respectively.[9]

The preparation of $NaAlEt_4$, solvent, and sample preparation are described elsewhere.[10] The solvating agents were distilled over CaH_2 and handled as described earlier.[10] NMR spectra were obtained on Varian A-60A and HA100 spectrometers. Solutions of these systems tend to form two phases in benzene at certain ratios of donor/Na^+ with the salt and the solvating agent being predominantly in the lower phase. Some of the spectra shown are of the lower phase. Consequently, the concentrations of the salt and the solvating agent will show considerable variation, but since both remain in the lower phase, the D/Na^+ ratio is as listed. Except for a possible effect due to viscosity, the spectra are, in general, independent of this behavior. In those instances where a single phase is formed, the salt concentration is 0.26 M.

In Figure 1, a comparison of the methylene resonances is shown for $NaAlEt_4$ in benzene using diethyl ether (Et_2O), teterahydrofuran (THF), and hexamethylphosphoramide (HMPA) as solvating agents. For the 1:1 ratios of D/Na^+, the expected quartet characteristic of contact ion pairs is observed. However, using HMPA as the donor, a 4:1 ratio of HMPA/Na^+ gives a ^1H NMR spectrum characteristic of solvent separated ion pairs. In contrast, a 4:1 ratio of THF/Na^+ gives a ^1H NMR spectrum indicative of a preponderance of contact ion pairs. Finally, if we consider the limit where the donor is used as the solvent, it is seen that the methylene resonance in HMPA is essentially the same as it is for the 4:1 ratio of D/Na^+. When THF is used as the solvent, the nine-line pattern characteristic of solvent separated ion pairs is also observed. However, the resolution is poorer than that observed with

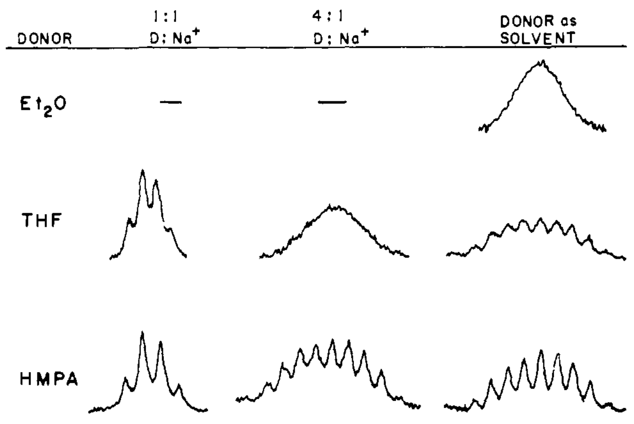

Figure 1. Methylene group resonance patterns in $AlEt_4^-$ for different ratios of donor/Na^+.

Table I. Donor/Na^+ Ratio to Give Solvent Separated Ion Pairs

Donor	D/Na^+ to give $[M^+//X^-]^0$	DN
Ethylenediamine (en)	2:1	
Dimethoxyethane (DME)	3:1-4:1	
Hexamethylphosphoramide (HMPA)	4:1	38.8
Dimethylformamide (DMF)	4:1-5:1 (probably 4:1)	30.9
Dimethyl sulfoxide (Me_2SO)	4:1-5:1	29.8
Pyridine (py)	>18:1	33.1
Tetrahydrofuran (THF)	>18:1	20.0
Diethyl ether (Et_2O)		19.2

HMPA. This has been attributed to an equilibrium between contact and solvent separated ion pairs,[9] but the distinctiveness of the nine-line pattern indicates a predominance of solvent separated ion pairs. On the other hand, when Et_2O is used as the solvent, the methylene resonance is indicative of a preponderance of contact ion pairs, thereby emphasizing the poor donor ability of Et_2O. Thus we see three cases; HMPA is a strong donor giving solvent separated ion pairs at a 4:1 ratio of D/Na^+; THF is an intermediate donor giving solvent separated ion pairs at high D/Na^+ ratios; and Et_2O is a sufficiently poor donor that it does not form solvent separated ion pairs with $NaAlEt_4$.

Analagous studies were made with a number of other donors, and the D/Na^+ ratios necessary to convert contact ion pairs to solvent separated ion pairs are given in Table I.

The observations for pyridine are particularly interesting. The Gutmann donor number for pyridine is 33.1, a very high value, and the correlation by Popov et al. of the ^{23}Na NMR chemical shifts with donor numbers substantiates this value.[11] More recently data has been obtained that brings the donicity of pyridine toward the Na^+ ion into question.[12] Although the results were logically rationalized in terms of solvent-solvent interactions, the observations reported here indicate that pyridine is, in fact, a rather poor donor toward the Na^+ ion. Based on the results of this study, a donicity toward the Na^+ ion similar in magnitude to that of THF would seem to be more reasonable. It is also interesting to note that DME is not as strong a donor as might be expected.

It is apparent from the above that for strong donors, a D/Na^+ ratio of 2:1 for bidentates and 4:1 for monodentates is sufficient to convert a contact ion pair to a solvent separated ion pair. But this is not to be construed to mean that the solvation number of the Na^+ ion is four. In previous studies, a solvation number of four has been proposed for the Na^+ ion,[13] but using Me_2SO as the donor, Wuepper and Popov reported a value of six.[14] Recent studies in this laboratory give support to the Wuepper and Popov value.[15]

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Symptoms of 1,3 Carbon–Carbon Interactions in Cyclobutane and the Cyclobutyl Cation

Sir:

The 1,3 carbon/carbon covalent interaction across a four-membered ring has recently been shown to exert tremendous effects on spin density distributions in cyclobutenoid ion radicals[1] and in cyclobutyl radicals.[2] More than 20 years ago, Dunitz and Shomaker[3] proposed that such interactions are repulsive in cyclobutane and account for a large fraction of its strain energy. This attractive theory seems not to have gained widespread acceptance, though without the postulated effect that near equality of cyclobutane's strain (26.4 kcal) to that of cyclopropane (27.6) appears awkward to rationalize. It should be emphasized that 1,3 strain is absent in cyclopropane, by defintion, and is therefore at a maximum in cyclobutane. The purpose of the present communication is to more convincingly document the role of 1,3 carbon/carbon interactions in cyclobutane strain and, indeed, in a variety of properties of cyclobutane and the cyclobutyl cation.

Semiempirical SCF MO calculations (CNDO/I, CNDO/II, and MINDO/3) were used to estimate the contribution of 1,3 carbon/carbon interactions to the strain energy of cyclobutane. The 1,3 perturbation energy ($\Delta E_{1,3}$) was calculated (Table I) as the difference between the energy obtained in a normal calculation and that obtained in a corresponding calculation in which the Fock matrix elements representing the 1,3 interactions were zeroed. The geometry was held static in the CNDO cases, but is individually optimized in the MINDO/3 calculations. The perturbation energy is seen to range from 20 to 33 kcal (destabilizing), compatible with the suggestion of a major contribution of the effect to the cyclobutane strain.

Explanations of the puckered conformational minimum of cyclobutane emphasize torsional effects, but the results in Table I implicate differential 1,3 interaction energies as a major contributor to this property as well ($\Delta\Delta E_{1,3} = \Delta E_{1,3}(\text{planar}) - \Delta E_{1,3}(\text{puckered}) = 4$ kcal). This conclusion can be tested still more systematically. Contrary to the pub-