the following general observations can be made in regard to the mechanisms.

(a) A π-electron (σ–π configuration interaction) mechanism is dominant for *para* H–H coupling in benzene, α-methyl to H coupling in toluene, and methyl to methyl coupling in the xylenes. σ contributions to *ortho* and *meta* coupling in benzene are considerably larger than the π contributions.

(b) An aromatic π-electron system is less effective in transmitting spin information than a linear polyene system; *i.e.*, the magnitudes are smaller.

(c) Contributions to π-electron coupling from different paths are approximately additive.

(d) The VB calculations appear to overestimate the π-electron coupling constants between nuclei which are associated with $2p_\pi$ electrons in the same subset of an alternate system.

Acknowledgments. This work was supported in part by grants from the National Science Foundation. The authors wish to thank the University of Arizona Computer Center for providing computational facilities.

Spectroscopic Studies of Alkali Metal Ions and Ammonium Ions in 2-Pyrrolidones[1]

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Received January 6, 1969

Abstract: The far-infrared spectra of alkali metal salts in 2-pyrrolidones exhibit bands which are not present in either the pure solvent or the pure salt. The band frequencies are dependent on the nature of the cation and solvent but not on the anion. The experimental evidence indicates that the observed bands are due to vibrations of the cations in a solvent cage. Nuclear magnetic resonance and far-infrared mole-ratio studies were used to determine the coordination number of lithium ion in a mixed solvent system, 1-methyl-2-pyrrolidone (1M2PY) and dioxane. Both techniques indicate that the lithium ion is solvated by four molecules of the pyrrolidone. Examination of the carbonyl band frequency in 1M2PY indicates that the cation interacts strongly with the oxygen of the carbonyl group. The absence of Raman lines in 1M2PY solutions of lithium salts suggest that the bond with solvent is essentially ionic.

It was pointed out in our previous publications,[2] as well as those of Edgell and coworkers, that the combination of nmr and far-infrared spectroscopic techniques offers a new approach to the study of ionic solvation. These publications reported spectroscopic studies on solvation of alkali metal salts in dialkyl sulfoxides[2a–c] and other solvents.[2d–f] A model for the alkali metal vibration in solvent cage was proposed.[2d–f] It was of interest to us to extend these studies to other solvents, both polar and nonpolar, so as to determine the influence of solvent properties on the formation, the stoichiometry, and the structure of the solvation cage around metal ions. In this paper, we report the study of the alkali metal ion solvation in 2-pyrrolidone and its derivatives.

In general, 2-pyrrolidones are polar compounds with a dielectric constant of 27[3] for the 2-pyrrolidone and 32[4] for the 1-methyl-2-pyrrolidone (hereafter abbreviated 2PY and 1M2PY, respectively). The pyrrolidones also act as nucleophilic reagents and form complexes with both transition[5] and nontransition metal ions.[6,7] Studies on the solvent properties of 1M2PY indicate that it is an excellent dissociating solvent.[8,9] Preliminary investigation indicated that at least 2PY and 1M2PY have reasonable transparencies in the far-infrared spectral region.

Experimental Section

Apparatus. All far-infrared spectra were obtained with a Perkin-Elmer 301 far-infrared spectrophotometer. Demountable liquid cells with Teflon spacers and polyethylene windows (Barnes Engineering Co.) were used. Cell thicknesses were usually kept at 0.05 or 0.1 mm. Between runs, the cells were flushed with acetone and then with pentane and dried in a current of dry air. The spectrophotometer was used in the double-beam mode. A dry nitrogen purge was always maintained when running below 320 cm^{-1} but the purge was not necessary above this frequency. Concentrations of salt solutions were varied between 0.1 and 2.0 *M*. Most measurements, however, were carried out with 0.5 *M* solutions.

Ultraviolet spectra were obtained on a Cary 14 spectrophotometer. Infrared spectra from 4000 to 600 cm^{-1} were obtained on either a Perkin-Elmer 237B or a Unicam SP 200 spectrophotometer.

The nmr measurements were made on a 60-Mc Varian A-60 spectrometer. All sample tubes were equilibrated at 35° before they were placed in the probe. This practice ensured reaching thermal

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(1) Abstracted in part from the Ph.D. Thesis of J. L. Wuepper, Michigan State University, 1969.

(2) (a) B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **90**, 4470 (1968); (c) *ibid.*, **91**, 20 (1969); (d) W. F. Edgell, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. R-149; (e) W. F. Edgell, J. Lyford, and J. Fisher, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, No. S-136; (f) W. F. Edgell, personal communication.

(3) R. L. Blumenshine and P. G. Sears, *J. Chem. Eng. Data*, **11**, 141 (1966).

(4) P. G. Sears, W. H. Fortune, and R. L. Blumenshine, *ibid.*, **11**, 406 (1966).

(5) J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *Inorg. Chem.*, **4**, 18 (1965).

(6) P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem.*, **27**, 2301 (1967).

(7) S. K. Madan, *Inorg. Chem.*, **6**, 421 (1967).

(8) M. D. Dyke, P. G. Sears, and A. I. Popov, *J. Phys. Chem.*, **71**, 4140 (1967).

(9) M. Breant, personal communication.

equilibrium quickly. Tetramethylsilane was used as an internal standard for all samples. The resonance being studied was scanned repeatedly until at least three identical values to the nearest tenth of a cycle were obtained. All mole ratio experiments were repeated at least twice.

Reagents. Eastman practical grade 1-methyl-2-pyrrolidone was stored over Linde 4A molecular sieves for several days and then distilled under reduced pressure through a 100-cm packed column. The water content as determined by Karl Fisher titration was between 0.001 and 0.01 *M*.

2-Pyrrolidone was obtained from the Aldrich Chemical Co. The yellowish crystals were subjected to fractional freezing until a product freezing at 25.6 ± 0.2° was obtained. The product was less than 0.02 *M* in water.

1-Vinyl-2-pyrrolidone was obtained from Aldrich Chemical Co. and was used without further purification.

Fisher technical grade dioxane was refluxed over metallic sodium and distilled through a 100-cm helicies packed column. The 60% middle fractions of distilled solvent were retained.

Anhydrous lithium perchlorate was purchased from G. F. Smith Chemical Co. and dried at 215° for 24 hr. Fused anhydrous lithium iodide was obtained from K & K Chemical Co. and used without further purification.

Potassium and rubidium tetraphenylborates were prepared by mixing water solutions of sodium tetraphenylborate and the respective chloride. The resulting precipitate was washed with water until a negative test for chloride ion was obtained.

All other salts were obtained commercially in the purest form available and used without purification except for drying.

Preparation of Solid Solvates. Solid solvates $Li(1M2PY)ClO_4$ and Li(1M2PY)SCN were prepared by slowly adding 1M2PY to a concentrated solution of the respective salt dissolved in nitromethane. The resulting precipitates were briefly washed with nitromethane and dried *in vacuo* at 30°. The complex halides Li(1M2PY)I, Li(1M2PY)Br, and Li(1M2PY)Cl were precipitated by the addition of dry benzene to saturated solutions of the salt in 1M2PY. The resulting fluffy white precipitates were filtered and dried *in vacuo* at 30°. Sodium and ammonium complexes were made by cooling warm saturated solutions of the salts in 1M2PY. The precipitates were filtered and dried *in vacuo*. The halogen or thiocyanate ions in several of the complexes were determined by argentometric titrations. Carbon-hydrogen analysis was obtained for complexes which did not contain a titratable anion.

Results and Discussion

Infrared Spectra. The positions of the far-infrared bands in 2-pyrrolidone, 1-methyl-2-pyrrolidone, and 1-vinyl-2-pyrrolidone which are unique to the solution are given in Table I. In the case of 1-vinyl-2-pyrrolidone, the opacity of the solvent prevented measurements beyond 300 cm^{-1}, and thus only the data for the lithium salts could be obtained. It is seen from the data in Table I that the frequencies of the bands are dependent only on the nature of the cation and decrease progressively with the increase in the atomic number of the metal ion. In the case of the ammonium ion, however, the frequency of the cation band in 1M2PY is about equivalent to the frequency of the sodium band, while in 2PY the frequency is higher than expected from the mass effect.

For given cations, the band intensities were proportional to the concentrations of the respective salts. The absorptivities of the different cations progressively decreased with increasing atomic number of the cations. Here again the ammonium band does not fall into the general pattern, being approximately equal to the intensity of the lithium band (Figure 1).

The positions of the far-infrared bands do not change upon the addition of small amounts of water (~1%). The only noticeable effect is the upward shift of the base line due to water absorption. Since most of the measurements were done with 0.5 *M* solution of salts and the water content of the solvent was <0.01 *M*, it is seen that even if water had greater solvating power than the pyrrolidones (which in itself is doubtful), the effect of water would be minimal.

Table I. Absorption Spectra of Alkali Metal Ions in 2-Pyrrolidones

	ν_{max}, cm^{-1}		
Salt	2PY	1M2PY	1V2PY
LiI	400 ± 4	398 ± 4	419 ± 4
LiBr	400	398	419
LiCl	400	377 (398)	419
$LiClO_4$	400	398	419
$LiNO_3$	397	398	419
LiSCN	402	398	419
NH_4I	216 ± 4	206 ± 4	
NH_4Br	217	207	
NH_4ClO_4	218	207	
NH_4NO_3	218	213	...
NH_4BF_4	218	207	
NH_4HSO_4	...	207	
$NH_4B(Ph)_4$	218	...	
NH_4SCN	219	207	
NaI	207 ± 4	204 ± 4	
NaBr	206	204	
$NaClO_4$	207	204	
$NaNO_3$	207	206	...
NaSCN	206	207	
$NaB(Ph)_4$	...	205	
$NaBF_4$	206	207	
KI	147 ± 5	140 ± 5	
$KClO_4$	145	140	
KSCN	144	138	...
$KB(Ph)_4$	147	138	
RbI	...	106 ± 6	
$RbClO_4$	...	106	...
$RbB(Ph)_4$	...	106	

Anomalous results were obtained with lithium chloride in 1M2PY solutions. Usually, two bands were observed with the frequency of the most intense band being at 377 cm^{-1}. Since lithium chloride is an extremely hygroscopic substance, it was suspected that traces of water may be responsible for the deviation. Addition of small amounts of water to a dry solution of lithium perchlorate in 1M2PY, however, did not shift the position of the maximum.

Since it was conceivable that the 377-cm^{-1} band may be due to a Li^+Cl^- ion pair, an excess of tetrabutylammonium chloride was added to lithium perchlorate solutions in this solvent, but once again a shift in the solvent-cation band was not observed.

Following the procedure used in the DMSO studies,[2c] the isotopic shift resulting from the replacement of NH_4^+ ion by ND_4^+ ion was calculated on the basis of a simple "diatomic" model NH_4^+–1M2PY. The calculated value was 17 cm^{-1}, while the observed value is 16 cm^{-1}. While this close agreement does not necessarily indicate that there is truly a 1:1 interaction between the cation and the solvent, it does confirm that the observed band is due to the vibration of the solvated cation.

Study of the $\nu_{C=O}$ Frequency. In order to obtain some idea on the stoichiometry of the solvation sphere, an inert solvent had to be found in which mixtures of varying concentrations of the 1M2PY and alkali metal salts could be studied. This problem cannot be solved easily, since the solvent must not only be inert, but also it must be transparent in the far-infrared spectral region and have good dissolving properties. Of the numerous solvents investigated, only dioxane

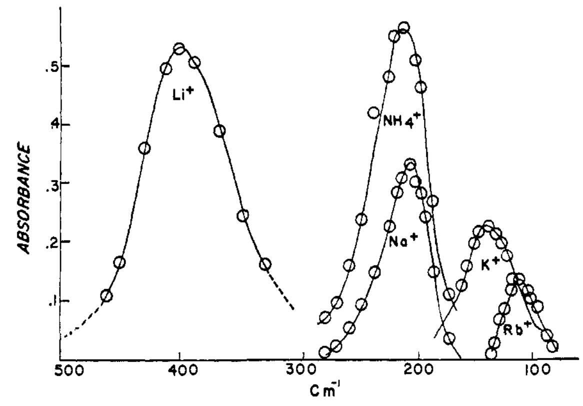

Figure 1. Far-infrared absorption bands of alkali metal ions in 1-methyl-2-pyrrolidone.

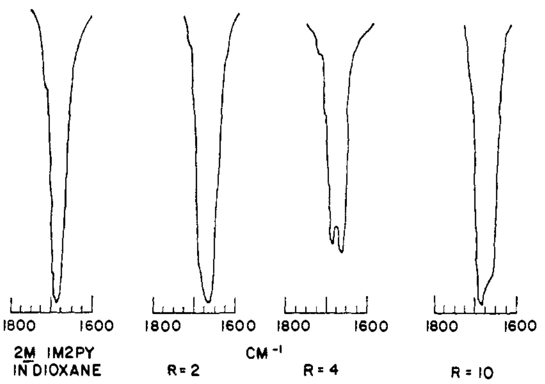

Figure 2. The $\nu_{C=O}$ band of 1-methyl-2-pyrrolidone at various mole ratios of 1M2PY/Li$^+$.

seems to possess some of the required properties although the possibility of a weak interaction between dioxane and the alkali metal ions could not be excluded. Even in this system, however, only lithium salts were sufficiently soluble for the measurements.

The carbonyl band of 1M2PY in dioxane solution appears at 1692 cm^{-1} characteristic of uncomplexed pyrrolidone. As lithium iodide is progressively added to the solution and the 1M2PY/Li ratio is varied, another band appears at 1671 cm^{-1}. The intensity of this band increases with increasing concentration of the lithium ion (Figure 2). It is reasonable to assume that the band shift is due to the interaction of the carbonyl oxygen with the metal ion. Replacement of lithium iodide with lithium perchlorate leads to identical effects. Results are also identical, regardless of whether the ratio is varied by changing the ligand or the salt concentration.

It is obvious from the above results that the bonding between the lithium ion and the pyrrolidone occurs through the carbonyl oxygen. At the mole ratio 1M2PY/Li$^+$ = 10, most of the organic ligand is present in uncomplexed form. Since similar shift of the carbonyl band can be observed upon addition of water, a rigorously anhydrous system was used in the above study. Examination of the 1M2PY spectrum in the 4000–600-cm^{-1} spectral region showed that with the exception of the carbonyl band, the spectrum is not affected by the addition of lithium salts.

Infrared Spectra of Solid Solvates. The far-infrared spectra of most of the solid complexes usually were not well defined. Reproducible sharp bands at 375 and 395 cm^{-1} were observed for Li(1M2PY)Cl and Li(1M2PY)SCN complexes, respectively. In all other cases, only very broad bands were obtained in the general region of the corresponding cation–solvent bands obtained in solutions.

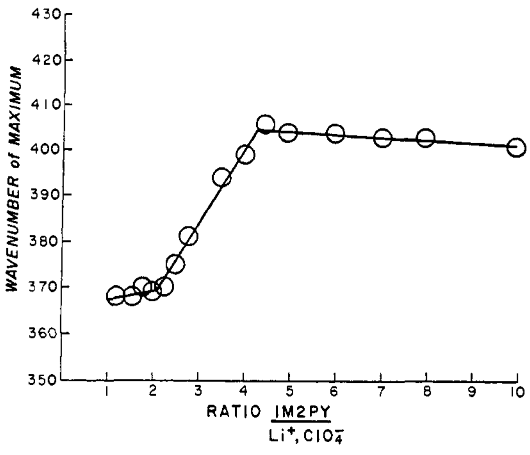

Figure 3. The position of the solvent–cation absorption band as a function of 1M2PY/LiClO$_4$ mole ratio in dioxane solutions.

The positions of the $\nu_{C=O}$ band of the solid complexes of alkali salts with 1M2PY are shown in Table II. It is seen that for the lithium salts, the band shifts to lower frequencies by ≈42 cm^{-1} and the shift is completely independent of the nature of the anion. It should be noted that the band shift is considerably greater than the one observed in solutions showing that in the solid complex there is a stronger interaction between the carbonyl group of 1M2PY and the lithium ion. On the other hand, in the case of sodium and ammonium salts, the magnitude of the band shift seems to be dependent on the nature of the anion.

Table II. Solid Complexes of 1M2PY with Alkali Metal Salts

Salt	Calcd, %			Found, %			$\nu_{C=O}$,
	C	H	MX	C	H	MX	cm^{-1}
1M2PY	...	...	...	...	...	...	1687
Li(1M2PY)ClO$_4$	29.22	4.41	...	29.31	4.30	...	1645
Li(1M2PY)SCN	...	...	39.61	...	...	39.08	1645
Li(1M2PY)Cl[a]	...	...	29.95	...	...	29.48	1645
Li(1M2PY)Br	32.29	4.89	...	33.15	5.79	...	1645
Li(1M2PY)I	...	...	57.45	...	...	57.52	1645
Na(1M2PY)$_3$I	...	...	33.51	...	...	33.25	1655
Na(1M2PY)$_2$ClO$_4$	37.45	5.65	...	38.38	6.05	...	1670
NH$_4$(1M2PY)NO$_3$	33.52	7.31	...	34.62	7.70	...	1658
NH$_4$(1M2PY)$_2$SCN	...	...	27.74	...	...	26.66	1644

[a] P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem.*, **27**, 2301 (1965).

Stoichiometry Studies. In order to establish the stoichiometry of the solvated species, both infrared and nmr studies were performed on the Li$^+$–1M2PY system in dioxane solutions. Figure 3 shows the shift of the solvated cation band frequency brought about by a change in the 1M2PY:Li$^+$ ratio (designated by R). The position of the band remains essentially constant at 396 cm^{-1} with $R > 4$. At smaller values of R, the band progressively shifts to 369 cm^{-1}. The limiting value is reached at $R = 2$.

It appears, therefore, that the lithium ion has four molecules of 1M2PY in its primary solvation sphere.

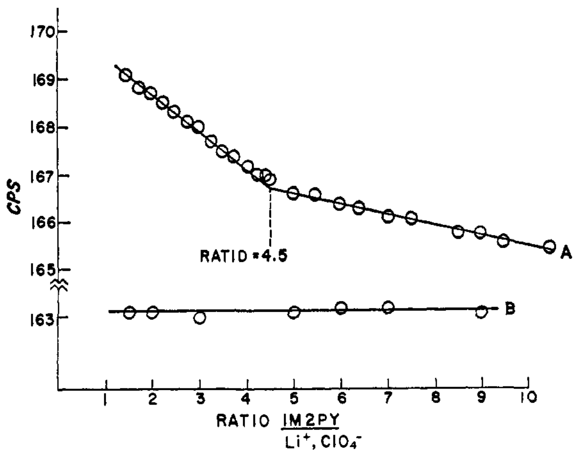

Figure 4. Chemical shift of the methyl protons of 1M2PY *vs.* 1M2PY/LiClO$_4$ mole ratio; concentration of 1M2PY varied: (A) 1M2PY + LiClO$_4$ solutions in dioxane; (B) 1M2PY in dioxane.

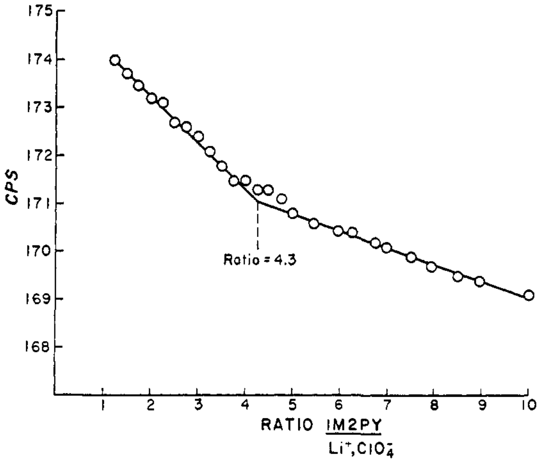

Figure 5. Chemical shift of the methyl protons of 1M2PY *vs.* 1M2PY/LiClO$_4$ mole ratio; concentration of LiClO$_4$ varied.

As the ratio of 1M2PY to lithium falls below this figure, either a new complex, such as Li(1M2PY)$_2^+$, is formed, or the 1M2PY molecules are gradually replaced with dioxane to give Li(1M2PY)$_2$(diox)$_2^+$ solvate which is responsible for the band at 369 cm^{-1}.

Lithium perchlorate is only very slightly soluble in pure dioxane. When $R = 1.25$, a 0.5 M lithium perchlorate concentration is attainable. The limited solubility of the salt in pure dioxane along with the large increase in solubility when small amounts of 1M2PY are added suggest that a pure Li–dioxane solvate does not exist in the presence of 1M2PY.

Scale molecular models show that four molecules of 1M2PY can easily fit around a lithium ion. Although the solid Li(1M2PY)ClO$_4$ complex prepared in this laboratory contains only one molecule of 1M2PY, it is interesting to note that Li(1M2PY)$_4$ClO$_4$·H$_2$O, which contains four molecules of 1M2PY, has been prepared by other investigators.[7]

Three mole-ratio studies on the pyrrolidone–Li$^+$ system have also been carried out using proton nmr spectra. In the first study, the position of the methyl protons resonance of 1M2PY was followed as a function of the 1M2PY/LiClO$_4$ ratio. The concentration of 1M2PY was varied so as to produce ratios from 1.0 to 9.5. The concentration of lithium perchlorate was held constant at 0.5 M. Figure 4 shows the results. There is a definite break at a ligand to salt ratio of 4.5. The base line illustrates that the position of the methyl protons resonance of 1M2PY is not a function of the 1M2PY concentration.

In the second nmr experiment, the 1M2PY concentraction was held constant and that of LiClO$_4$ was varied. The methyl protons resonance was again plotted as a function of the ligand to salt ratio. Figure 5 shows that the extrapolated value of 4.3 for the coordination agrees quite well with the value of 4.5 obtained by varying the ligand.

A third mole ratio experiment was performed using lithium iodide instead of lithium perchlorate. The difference in the nature of the anions should produce a change in the coordination number value if the anion is significantly involved in the coordination sphere of the lithium ion in solution. The salt concentration was varied and the mole ratio plot shown in Figure 6 produced a value of 4.5 for the coordination number of lithium ions. This value agrees well with the values obtained previously.

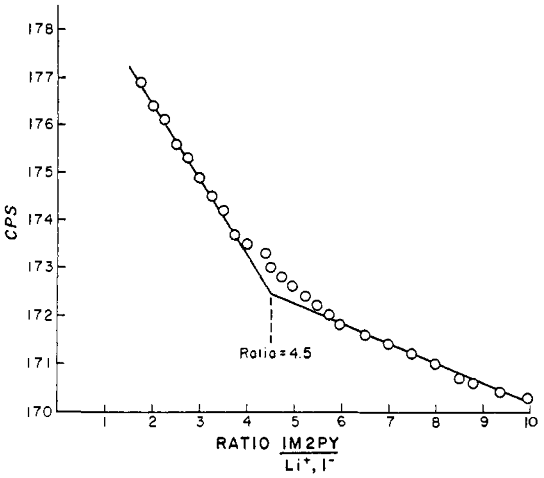

Figure 6. Chemical shift of the methyl protons of 1M2PY *vs.* 1M2PY/LiI mole ratio; concentration of LiI varied.

Table III summarizes the results of these studies. It is seen that all data indicate a solvation number of four for the lithium ion in 1M2PY solution. A survey of literature shows that this coordination number is commonly encountered for lithium ion,[10] but that it is not unique. It is interesting to note that recently Schaschel and Day reported a similar solvation study by the nmr technique.[11] Their results indicate that the

Table III. Coordination Number of Li$^+$ Ion in 1M2PY

Method	Salt	Variable	Coord no.
Nmr	LiClO$_4$	LiClO$_4$	4.3
Nmr	LiClO$_4$	1M2PY	4.5
Nmr	LiI	LiI	4.5
Far-ir	LiClO$_4$	1M2PY	4.2

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(10) G. Donnay and J. M. Gryder, *J. Chem. Educ.*, **42**, 223 (1965).

(11) E. Schaschel and M. C. Day, *J. Am. Chem. Soc.*, **90**, 503 (1968).

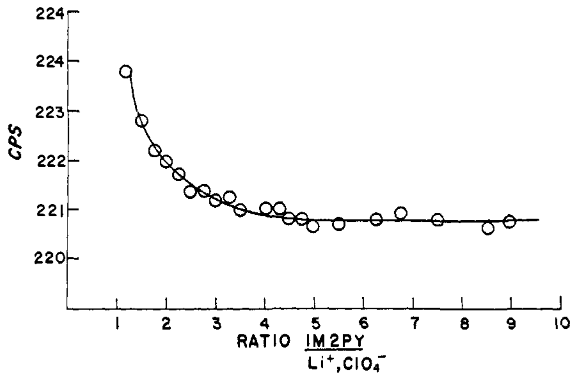

Figure 7. Chemical shift of the dioxane protons *vs.* 1M2PY/LiClO$_4$ mole ratio.

Na$^+$ ion is solvated by four molecules of tetrahydrofuran.

The resonance of the dioxane protons was also studied as a function of lithium perchlorate concentration. The results are shown in Figure 7. At low ratios of 1M2PY:LiClO$_4$, the dioxane protons undergo an appreciable shift. It is possible, therefore, that at low concentration of 1M2PY dioxane participates in the solvation of the lithium ion. These results also support the hypothesis that the low-energy far-infrared band, which appears at low ratios, is a result of the participation of the dioxane in the solvation of the lithium ion.

Attempts were made to study the solvation of alkali metal ions in 1M2PY by ultraviolet and Raman spectroscopy. The ultraviolet spectrum of 1M2PY is featureless from 380 mμ to the solvent cutoff at 265 mμ. Spectra of solutions of 1.0 *M* lithium perchlorate, 0.6 *M* sodium tetraphenylborate, and 0.8 *M* sodium perchlorate were obtained from 380 to 265 mμ with negative results. The sodium tetraphenylborate solution exhibited absorption due to the anion.

Raman spectra in the 1700–200-cm^{-1} spectral regions were obtained of 1.0 *M* solutions of lithium chloride, lithium bromide, and lithium perchlorate in 1M2PY. Three anions were chosen in order to observe possible anion effects. Lithium perchlorate solution showed a band near 400 cm^{-1}, but this band was not present in the chloride or bromide solutions and was due to the perchlorate anion. No bands which could be attributed to salt–solvent interaction were discovered. The absence of Raman bands seems to indicate that the ion–solvent interaction is largely ionic as postulated by Edgell, *et al.*[2e]

Acknowledgment. The authors gratefully acknowledge the support of this work by the National Science Foundation. One of us (J. L. W.) wishes to thank Socony-Mobil Corp. for a fellowship.

Dynamic Polarization of Phosphorus-31 Nuclei. Some Effects of Chemical Environment

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Abstract: Quantitative phosphorus nmr enhancements, determined from dynamic nuclear polarization measurements at 74 G, are reported for a variety of phosphorus-containing compounds in solution with the free radical bisdiphenylenephenylallyl. The wide range of observed enhancements, from −650 for (MeO)$_3$PO to +1610 for PCl$_3$, indicates that ^{31}P contact relaxation components are particularly responsive to changes in the chemical environment of phosphorus. For substituted phosphates, phosphites, and phosphines, the magnitude of the scalar interaction depends critically on the substituents at P. In order of increasing scalar interaction H < Cl < Br < C$_6$H$_5$ < RO. This, coupled with the irregular behavior of thio-substituted compounds, suggests the presence of both direct and indirect coupling mechanisms, the former related to electron–nucleus distance of closest approach, the latter to changes in complexation tendencies.

Previous dynamic nuclear polarization studies of ^{31}P nuclei at both low[2] and high[3] external magnetic fields have shown that the coupling between P nuclei and the electrons of dissolved free radicals is strongly dependent upon the chemical composition of the system. With tri-*t*-butylphenoxyl (TTBP) as the free radical, many systems were unstable and only the sign of the enhancement could be obtained. However, this was sufficient to demonstrate several broad features, the most striking of which was the observation that trivalent phosphorus compounds gave more positive enhancements than their pentavalent counterparts. Recently, we discovered that the free radical bisdiphenylenephenylallyl (BDPA) forms solutions with almost any phosphorus-containing compound which are stable indefinitely; this allowed quantitative measurements to

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