metal ions bonded to the nitrogens is a dianion so we add two more electrons to the π-system of the sixteen-membered ring. This makes 18 electrons, which is consistent with the $4n + 2$ electrons required by Hückel's rule for a stable aromatic system. The inner ring is similar to the cyclooctatetraene dianion, which has ten electrons. Two protons or a dipositive metal ion added to the center of the dianion ring create a neutral species. The bonding around each nitrogen is similar to the bonding around nitrogen in pyridine. Each nitrogen has a lone pair of electrons, and it may be that two of these lone pairs form N–H bonds as in the pyridinium ion. This would help explain the N–H stretch found in the infrared. Alternatively, the protons may be bound ionically in some fashion. In any case, the molecule can be represented as the sixteen-membered ring with perturbations due to β-pyrrole carbons and the protons or metal atom in the center.

The above argument relies heavily on the observation that the C_β–C_β bond is a double bond. Our argument also predicts that the C_α–C_β bond should be a single bond and that the C_α–N and the C_α–C(methine) bonds should have the same bond order. The observed C_α–C_β bond length is a little short for a pure trigonally hybridized C–C σ-bond. A better description of the molecule may be a combination of the two electronic structures shown in Figures 3 and 4.[10]

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Solvent-Separated Ion Pairs of Carbanions

Sir:

Ionic species are known to associate into ion pairs in low dielectric constant solvents. Two types of ion pairs may be visualized,[1] namely, contact (or intimate) ion pairs which are peripherically solvated, and solvent-separated ion pairs. The existence of such distinct species was invoked by Winstein, *et al.*,[2] to account for the observed salt effects in the solvolysis of certain arene sulfonates. A similar assumption was made by Cram and his co-workers to explain the stereochemical course of electrophilic substitution at saturated carbon.[3] The concept of two chemically distinct ion pairs has also been proved useful in interpreting the absorption spectra of tetraalkylammonium iodide solutions.[4]

We have found direct evidence for the existence of the two kinds of ion pairs from the electronic spectra of fluorenyl carbanion (F⁻). Figure 1 shows the spectrum of its sodium salt in tetrahydrofuran (THF) at three dif-
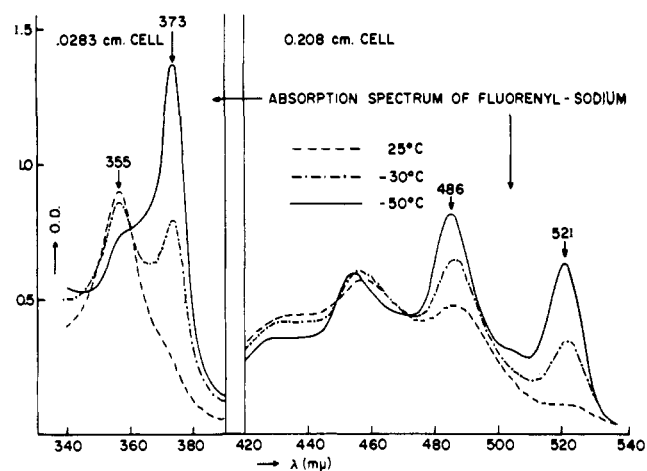
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(2) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).
(3) D. J. Cram, *et al.*, *ibid.*, **81**, 5774 (1959).
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Figure 1.

ferent temperatures. A sharp absorption peak at 355 mμ ($\epsilon_m \sim 10{,}000$) is seen at room temperature in addition to some weaker bands in the visible region. On cooling, a new peak develops at 373 mμ, while the 355 mμ peak decreases, and eventually only the 373 mμ absorption band remains below $-50°$. Simultaneously with this change, an additional peak develops at 521 mμ. The process is reversible, indicating that this new species is in equilibrium with that existing at room temperature. The new entity is not the free fluorenyl ion, although its concentration, like that of the free ion, increases on lowering the temperature. This conclusion is based on the following observations: At any temperature, the relative heights of the two absorption bands (355 and 373 mμ) are not affected by dilution or by the addition of NaB(Ph)$_4$, although the added salt is strongly ionized in THF.[5] Moreover, the dissociation constants for F⁻,Na⁺, calculated from conductivity data, vary from about 7×10^{-7} M at 25° to about 4×10^{-5} M at $-70°$. Hence, under our experimental conditions ([F⁻,Na] between 10^{-2} and 10^{-3} M), only a small fraction of ion pairs dissociates into free ions, not sufficient to be seen in the spectrum.

These observations strongly suggest that the entity formed at low temperatures is a solvent-separated ion pair (F⁻$\parallel$Na⁺). In the sequence F⁻,Na⁺ $\rightleftarrows$ F⁻$\parallel$Na⁺ $\rightleftarrows$ F⁻ + Na⁺, a large gain in solvation energy occurs in the first step, and indeed the temperature dependence of the ratio of the two absorption bands leads to ΔH of about -6 kcal. This value is confirmed by the results derived from the temperature dependence of the conductivity. In the range $+25°$ to $-20°$, ΔH_{total} of the contact ion pair dissociation into free ions has been found to be about -8 kcal., but at very low temperatures ΔH decreases to about -1.5 kcal./mole, since then the ions are formed from solvent-separated ion pairs.

Bathochromic shifts were observed in absorption maxima of ion pairs on increasing the interionic distance.[6] Hence, it is not surprising that F⁻$\parallel$Na⁺ absorbs at higher wave length than F⁻,Na⁺. Variation of counterion has a similar effect, as shown by the

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Table I. Absorption Maxima of Contact and Solvent-Separated Fluorenyl Ion Pairs in Various Solvents

Counterion	Solvent	ϵ	λ_{max} F⁻,M⁺	λ_{max} F⁻‖M⁺	Fraction of F⁻‖M⁺ at 25°
Li	Toluene	2.38	348	...	0.0
Li	Dioxane	2.20	346	...	0.0
Na			353	...	0.0
Li	Me–THF	4.6	347	373	0.25
Na			355	373	0.0
Li	THF	7.40	350	373	.80
Na			356	373	0.05
Cs			364	...	0.0
NBu₄			368	...	0.0
Na	THF at −80°	12.2	...	373	1.00
Li	DME[a]	7.10	...	373	1.00
Na			359	373	.95
Cs			364	...	0.0
Li	Pyridine	12.3	...	373	1.00
Na			...	373	1.00

[a] 1,2-Dimethoxyethane.

results listed in Table I. It is apparent from the last column in the table that at any temperature the Li salt always yields the highest fraction of solvent-separated ion pairs, whereas the poorly solvated Cs⁺ or NBu₄⁺ salt shows no evidence of solvent-separated pairs in THF even at −80°. Note also that the positions of the absorption bands are very little, if at all, affected by the polarity of the medium. Studies of spectra of F⁻,Li⁺ in mixtures of dioxane and THF indicate that the formation of F⁻‖Li⁺ probably involves two molecules of THF.

Investigation of dianions of tetraphenylethylene, the dimeric dianions of 1,1-diphenylethylene, etc., again indicates existence of solvent-separated ion pairs in equilibrium with the contact ion pairs. Apparently, recent data[7] relating to shifts in absorption spectra of carbanions with changing solvent polarity should be interpreted in terms of formation of two distinct ion pairs rather than in terms of a shift induced by the polarity of the medium.

Shifts in absorption bands to higher wave length at low temperature have also been observed for aromatic radical ions.[8] The change was attributed to formation of free ions. However, reinvestigation of some of these spectra (*e.g.*, sodium and lithium naphthalenide) in the presence of sodium tetraphenylboron again indicates that an equilibrium between contact and solvent-separated ion pairs is the most probable cause of the observed phenomena.

It may be anticipated that the reactivity of solvent-separated ion pairs approaches that of the free carbanions and this may account, at least partly, for the higher reaction rates observed in the more polar solvents. This problem is currently under investigation. The study of solvent-separated carbanion pairs will undoubtedly shed more light on the role of solvent in such reactions as electrophilic substitutions on saturated carbon, etc.

A more detailed description of these investigations will be published later.

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Enediol Cyclic Phosphates[1]

Sir:

Five-membered cyclic phosphates derived from 1,2-glycols and from *o*-dihydroxyarenes have received much attention[2]; however, enediol cyclic phosphates are virtually unknown.[3] We report here a novel approach to this highly reactive type of phosphate.

$\delta_{P^{31}} = +48.9$ p.p.m. $\delta_{P^{31}} = -11.5$ p.p.m.
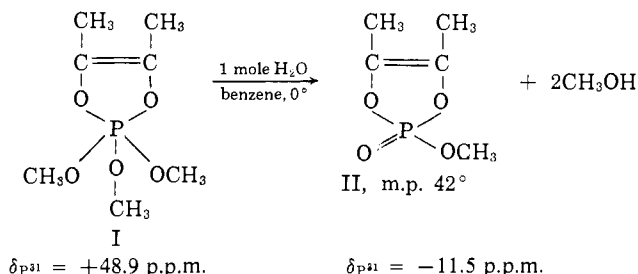
A stirred solution of the biacetyl–trimethyl phosphite *1:1* adduct,[4] I (19.97 g.) in benzene (20 ml.) was cooled in an ice–salt bath and treated with 1 mole equiv. of water (1.71 g.). The solution temperature went up from −4° to +18° within 2 min.; the solvent was *immediately* removed, under vacuum at 25°. The H¹ and P³¹ n.m.r. of the liquid residue showed the presence of the cyclic phosphate II and of dimethylphospho-acetoin[2e,5] (V) in a 1:2.4 proportion; only traces of trimethyl phosphate (VII) were present. Distillation in a 24-in. spinning-band column gave acetoin-enediol cyclophosphate[6] (II), b.p. 48–49° (0.06 mm.), n^{25}D 1.4310, in 30% yield. On standing at 20°, the liquid II crystallized to colorless needles, m.p. 42–43°, not changed by recrystallization from benzene–hexane; the properties of the crystals and of the liquid were identical. *Anal.* Calcd. for $C_5H_9O_4P$: C, 36.6; H, 5.5; P, 18.9. Found: C, 36.1; H, 5.6; P, 18.4.

(1) Investigation supported by Public Health Service Research Grant No. CA-04769-06 from the National Cancer Institute, and the National Science Foundation (G-19509).
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(3) *Index Chemicus*, No. **5**, 15, 46132 (1964), lists the title of a preliminary communication by V. A. Kukhtin and I. P. Gozman, *Dokl. Akad. Nauk USSR*, **158**, 157 (1964), claiming the preparation of an enediol cyclic phosphate by a procedure different from ours.
(4) The literature was reviewed by F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).
(5) $\delta_{P^{31}}$ in p.p.m.: dimethylphosphoacetoin, keto-V, +0.25; enol-IV, +2.5; trimethyl phosphate, VII, −2.5.
(6) 4,5-Dimethyl-2-methoxy-2-oxo-1,3,2-dioxaphospholene.