addition radical at room temperature.[3b] The crystalline field effect on the radical reaction in the crystal may be suggested.

In conclusion, there is a similarity in the decarboxylation process of saturated and unsaturated dicarboxylic acids, where R· is formed from the positive primary *via* the carboxyl radical. There is, however, a significant difference in the following reaction of R produced. Furthermore, the fate of the negative primary is entirely different.

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Studies of the Effects of Ion Pair Formation on the Electron Paramagnetic Resonance Parameters of Radical Anions[1]

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Abstract: A detailed analysis of the effect of ion pair formation on epr parameters such as proton, ^{13}C, and ^{14}N hyperfine splittings and *g* factors was made for several radical anions. The analysis was made by using McLachlan MO's combined with the McClelland approximation. The systems studied were anthracene, fluorenone, anthraquinone, and 2,2′-dipyridyl anions. Using $-e^2/\epsilon r$ as an interaction, it was found that a relatively large ϵ is necessary in order to explain the observed changes in the epr parameters. In general, qualitatively satisfactory agreement was obtained between the observed changes and the ones predicted using the assumed structures. The observed perturbations and the results of calculations are discussed in terms of the possible ion pair structures. The results of the *g*-factor analysis are found to be in excellent agreement with those obtained from carbonyl ^{13}C splittings.

The hyperfine splittings and *g* factors of epr spectra of radical ions are known to be sensitive to environmental perturbations such as ion pair formation or solvation. In principle, such perturbational effects should provide information concerning the structures of ion pairs and the interactions between ions in ion pair systems, if appropriate analysis of such effects can be made. For example, changes in the hyperfine splittings should strongly depend on the position of the cation with respect to the anion. Information on ion pair structures should be obtainable from such data. The magnitude of the perturbation should reflect the strength of the interactions between cation and anion. In spite of the large amount of work carried out on epr spectra of radical ions in ion pair systems, we still have very little knowledge about the actual structures of ion pairs in solution and the strength of the interaction between ions in ion pairs. Although studies of perturbational effects in ion pairs have been made previously by several authors,[2-4] it appears that no comprehensive and detailed analysis in connection with the ion pair structure have been made. Accordingly, we have chosen representative examples of different types of radical ions and investigated perturbational effects on the epr parameters upon ion pair formation. The types of systems and our choice of the representative molecules are: (1) aromatic hydrocarbon, anthracene; (2) ketyls, fluorenone; (3) semiquinones, anthraquinone; and (4) nitrogen heterocyclics, 2,2′-dipyridyl.

Analysis of the data was made by applying McLachlan's MO treatment[5] with the use of the McConnell relationship for proton splittings,[6] the Fraenkel–Karplus[7] formula for ^{13}C splittings, and Stone's theory of *g* factors.[8] Naturally our analysis suffers from any shortcomings inherent in a simple π-electron MO treatment such as McLachlan's. Nevertheless, a great amount of work accumulated in the last decade shows that McLachlan's calculation of spin densities can provide reasonably good agreement with the experimental values if appropriate choices of parameters are made. At present, even more sophisticated unrestricted Hartree–Fock calculations can only give the same order of agreement with the experimental values as the McLachlan method does.[9] Therefore, we have employed McLachlan's method together with the McClelland treatment of the ion pair effect[10] in order to analyze the effect of ion pair formation on the epr parameters. Recently Goldberg and Bolton reported the calculation of potential energies and alkali metal splittings in several alkali metal aromatics.[11] Their calculations also used the McClelland procedure in order to take into account the ion pair effect.

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[1] This work was supported by a grant from the National Science Foundation and a fellowship from the A. P. Sloan Foundation to N. H.

[2] (a) A. H. Reddoch, *J. Chem. Phys.*, **43**, 3411 (1965); (b) M. T. Jones and D. E. Zeller, *ibid.*, **48**, 3341 (1968).

[3] C. Y. Lin and J. Gendell, *ibid.*, **47**, 3475 (1967).

[4] M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, *Bull. Chem. Soc. Jap.*, **41**, 732 (1968).

[5] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[6] H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

[7] M. Karplus and C. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

[8] A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); **7**, 311 (1964).

[9] L. C. Snyder and A. T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

[10] B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458 (1961).

[11] I. Goldberg and J. Bolton, *J. Phys. Chem.*, **74**, 1965 (1970).

Table I. Epr Parameters in Ion Pair Systems

a. Anthracenide Tight Ion Pair (24°)

System	Solvent	A_α, G	A_β, G	A_γ, G
Free	DME	2.743	1.514	5.330
Li	DEE	2.409	1.544	5.598
Na	DBE	2.438	1.553	5.582
	DEE	2.487	1.544	5.526
	MTHF	2.599	1.521	5.440
K	DEE	2.565	1.539	5.465
	MTHF	2.615	1.531	5.413
Cs	MTHF	2.651		5.396

b. Fluorenone Ketyl (24°)

System	Solvent	g value	$A_{^{13}C}$, G	$A_{1,8}$, G	$A_{2,7}$, G	$A_{3,6}$, G	$A_{4,5}$, G
Free	HMPT		1.77	1.76	(−)0.12	3.01	0.63
Free	DMF	2.003750	2.75	1.88	∼0.00	3.07	0.64
Cs	DME		3.90	2.02	0.09	3.11	0.64
K	DME	2.003673	4.20	2.03	0.10	3.12	0.66
Na	DME	2.003625	4.85	2.08	0.16	3.15	0.66
Li	DME	2.003530	6.20	2.32	0.26	3.20	0.67

c. Anthraquinone

Metal	Solvent	Temp, °C	$A_{1,8}$, G	$A_{4,5}$, G	$A_{2,7}$, G	$A_{3,6}$, G
Li	THF	100	1.142	−0.350	0.110	1.884
		60	1.103	−0.331	0.181	1.821
		0	1.058	−0.250	0.230	1.745
		−40	1.038	−0.250	0.250	1.733
		−80	1.009	−0.242	0.242	1.695
Na	THF	70	0.321		0.963	
		30	0.326		0.993	
		−10	0.78	−0.12	0.38	1.51
		−90	0.68	∼0.0	0.43	1.38
K	THF	50	0.301		0.994	
		10	0.298		0.992	
		−50	0.303		0.993	
		−90	0.314		0.982	
Cs	THF	30	0.292		0.968	
		−30	0.294		1.005	

d. 2,2′-Dipyridyl

Metal	Solvent	A_M, G	A_N, G	$A_{3,3'}$, G	$A_{6,6'}$, G	$A_{5,5'}$, G	$A_{4,4'}$, G
K	DMF (free)		2.41	0.57	0.71	1.66	4.91
K	DME		2.58	0.57	1.06	1.20	4.70
K	THF		2.61	0.57	1.06	1.22	4.64
K	MTHF		2.60	0.57	1.07	1.21	4.67
Na	DME	0.57	2.66	0.57	1.14	1.14	4.64
Na	THF	0.57	2.61	0.57	1.21	1.21	4.70
Na	MTHF	0.57	2.63	0.56	1.22	1.22	4.67
Li	DME	0.70	2.77	0.47	1.75	0.69	4.27
Li	THF	0.71	2.76	0.47	1.75	0.69	4.27
Li	MTHF	0.70	2.77	0.47	1.74	0.69	4.28

The purpose of our study here is to see whether or not the observed changes in hfs and g values upon ion pair formation can be explained by a simple MO treatment, and to determine whether information concerning structures of and interactions in ion pairs can be obtained from such a relatively simple treatment.

Experimental Section

Preparation of samples and the measurements of hyperfine splittings of epr spectra are similar to those described elsewhere and are not repeated here. g-Factor measurements of fluorenone radical anions were made by using potassium napthalenenide as a standard. Two sample cells, one for fluorenone anion and the other a capillary cell containing napththalene negative ion, were placed into the cavity at the same time and the field strengths of the resonance peak positions were determined using a Harvey Wells gaussmeter and a Hewlett-Packard frequency counter. The g values of fluorenone ketyls were calibrated against the known g values of naphthalenide in DME.

Data

Data used for the analysis in this paper are summarized in Table I. The sources of the data are given below.

(1) **Anthracenide.** The experimental values used for the analysis in these studies are mostly taken from the data obtained by Hirota[12] and Reddoch.[2a]

(2) **Fluorenone Ketyl.** Most of the data on ^{13}C splittings and proton splittings of fluorenone are those reported by Hirota.[13] Some new data were obtained in the present studies. g values of fluorenone ketyls were measured in the present studies.

(3) **Anthraquinone Anion.** The data for the anthraquinone ions were taken in the present study. As will be discussed in the later sections, Na anthraquinone at temperatures lower than −40° and Li anthraquinone at all temperatures gave spectra in the slow limit of cation migration between two carbonyl groups. Perturbational effects were investigated in this range.

(4) **2,2′-Dipyridyl.** The data for 2,2′-dipyridyl were taken in the present study. Hyperfine splittings of some ion pair systems were reported previously, and our measured values generally agree well with those obtained by Bolton, *et al.*[14]

Basis of Analysis

MO Calculations of Spin Densities in Ion Pair Systems. (A) Electrostatic Interaction between Ions in Ion Pairs. The effect of ion pair formation on the electronic spectra of radical ions has been investigated previously by Hush and Rowland[15] and McClelland.[10] We combine McClelland's approach with the McLachlan MO treatment. The positive ion is approximated as a point charge Ze located at a distance r from a π electron, and the interaction energy is taken as $-Ze^2/\epsilon r$. In the ion pair considered here, positive and negative ions are relatively close to each other (contact or tight ion pair) and the use of a macroscopic dielectric constant is very questionable. Previous workers often used a $-Ze^2/r$ potential in dealing with ion pair problems. However, it is well known that strong solvation of the cation takes place in the systems of interest here, and the use of $-Ze^2/r$ cannot be justified. In principle, perturbation due to ion pair formation should be given by the sum of all the electrostatic interactions due to cation and solvent dipoles.

$$\begin{aligned} H_{\text{pert}} &= -\frac{Ze^2}{r} - e\sum_i \frac{\boldsymbol{\mu}_i \cdot \mathbf{r}_i}{r_i^3} \\ &= -\frac{Ze^2}{r}\left[1 + \sum_i \frac{r}{r_i}\left(\frac{\boldsymbol{\mu}_i \cdot \mathbf{r}_i}{e r_i^2}\right)\right] \qquad (1) \\ &= -\frac{Ze^2}{\epsilon(r) r} \end{aligned}$$

The second term in the brackets is expected to be negative and can be considered as a screening factor for the coulombic interaction due to the cation. Since we have little knowledge about the solvation structure, it is not possible to calculate this term.

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(12) N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968).

(13) (a) N. Hirota, *ibid.*, **89**, 32 (1967); (b) in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, Chapter 2.

(14) J. dos Santos Veiga, W. L. Reynolds, and J. R. Bolton, *J. Chem. Phys.*, **42**, 1105 (1965).

(15) N. S. Hush and J. R. Rowland, *Mol. Phys.*, **6**, 201 (1963).

Therefore, we simply replace this term by a parameter $1/\epsilon(r)$ instead of trying to estimate the second term. We call ϵ a screening factor. Then the perturbing term still retains the form of a coulombic interaction. In the following analysis we consider $\epsilon(r)$ as an adjustable parameter.

(B) MO Calculation. In the HMO treatment the Hamiltonian for π electrons is given by

$$H_{\mathrm{eff}} = H_0 - Ze^2/\epsilon r \qquad (2)$$

where H_0 is the one-electron Hamiltonian for π electrons in the absence of perturbation. The HMO's are given by solving a secular determinant.

$$\det\left|(H_{\mathrm{eff}})_{ij} - E\delta_{ij}\right| = 0 \qquad (3)$$

If r_i is not very small, $(H_{\mathrm{eff}})_{ij}$ could be approximated in the following way, as pointed out by McClelland.[10]

$$\begin{aligned}(H_{\mathrm{eff}})_{ij} &= \int \Phi_i(H_0)\Phi_j \mathrm{d}\tau - \int \Phi_i(Ze^2/\epsilon r)\Phi_j \mathrm{d}\tau \\ &= \begin{cases} \alpha_i^0 - \dfrac{Ze^2}{\epsilon r_i} = \alpha_i^0 + x\beta_i & \text{for } i = i \\ \beta_{ij} & \text{for } i \neq j \end{cases} \end{aligned} \qquad (4)$$

In going from the first to the second line of eq 4, two approximations were made. First, although ϵ is a function of r, this is assumed to be constant over the space where the integration is made. Second we use the McClelland approximation

$$\int \Phi_i \frac{1}{r} \Phi_j \mathrm{d}\tau \cong \frac{2S_{ij}}{r_i + r_j} = \frac{\delta_{ij}}{r_i} \qquad (5)$$

Here r_i and r_j are the distances between the electrons on atoms i and j, respectively, and the cation.

Therefore, in this simple approach the ion pair effect can be treated by adjusting the coulomb parameters. We adjusted the coulomb parameters according to eq 4 and used McLachlan's method[5] in order to evaluate the spin densities in the ion pair systems.

Calculation of Hyperfine Splittings (hfs). (A) Proton hyperfine splittings were calculated by using the McConnell relation, $a_i^{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho_i$. There have been some discussions on the validity of the simple McConnell relationship. For example, Colpa and Bolton[16] suggested an alternative equation taking into consideration excess charge effect. However, no significant changes in hfs are made in the present analysis by the use of Colpa–Bolton equation. Therefore, we use the McConnell equation throughout this work.

(B) ^{13}C and ^{14}N Splittings. The ^{13}C splittings were calculated by using the Fraenkel–Karplus formula[7]

$$a_{^{13}\mathrm{C}} = [S^{\mathrm{C}} + 2Q_{\mathrm{CC'}}{}^{\mathrm{C}} + Q_{\mathrm{CO}}{}^{\mathrm{C}}]\rho_{\mathrm{C}}{}^{\pi} + 2Q_{\mathrm{C'C}}{}^{\mathrm{C'}}\rho_{\mathrm{C'}}{}^{\pi} + Q_{\mathrm{OC}}{}^{\mathrm{O}}\rho_{\mathrm{O}}{}^{\pi} \qquad (6)$$

Fraenkel and Karplus suggested $S^{\mathrm{C}} = -12.7$ G, $Q_{\mathrm{CC'}}{}^{\mathrm{C}} = 14.4$ G, and $Q_{\mathrm{CC'}}{}^{\mathrm{C'}} = 13.9$ G. The choices of $Q_{\mathrm{CC}}{}^{\mathrm{C}}$ and $Q_{\mathrm{CO}}{}^{\mathrm{C}}$ are not completely established. However, Bröze and Luz recently analyzed a number of carbonyl molecules and suggested $Q_{\mathrm{CO}}{}^{\mathrm{C}} = 36$ G and $Q_{\mathrm{OC}}{}^{\mathrm{O}} = -24.3$ G from the comparison between the experimental ^{13}C splittings and the calculated ones.[17] Using these parameters

$$a_{^{13}\mathrm{C}} = 52.2\rho_{\mathrm{C}} - 27.8\rho_{\mathrm{C'}} - 24.3\rho_{\mathrm{O}} \qquad (7)$$

The ^{14}N splittings can be calculated by using an equation similar to the McConnell relation[18]

$$a^{\mathrm{N}} = Q^{\mathrm{N}}\rho^{\mathrm{N}} \qquad (8)$$

Calculation of g Values. According to Stone's theory of g values,[8] the g value for a radical ion is given by

$$g = 2.00232 + \Sigma\Delta g_i + \Sigma_{nj}\Delta g_{nj}$$

$$\Delta g_i = (2/3)\sum_m^{a,b} \frac{\rho_{\mathrm{r}}(C_{\mathrm{r}x}{}^m)^2 (C_{\mathrm{r}}{}^{\mathrm{p}}) + \rho_{\mathrm{s}}(C_{\mathrm{s}x}{}^m)^2(C_{\mathrm{s}}{}^{\mathrm{p}})^2 + (\rho_{\mathrm{r}} + \rho_{\mathrm{s}})C_{\mathrm{r}x}{}^m C_{\mathrm{s}x}{}^m C_{\mathrm{r}}{}^{\mathrm{p}} C_{\mathrm{s}}{}^{\mathrm{p}}}{\epsilon^{\mathrm{p}} - \epsilon_i{}^m} + (2/3)\sum_m^{a,b} \frac{\rho_{\mathrm{r}}(C_{\mathrm{r}y}{}^m)^2(C_{\mathrm{r}}{}^{\mathrm{p}})^2 + \rho_{\mathrm{s}}(C_{\mathrm{s}y}{}^m)^2(C_{\mathrm{s}}{}^{\mathrm{p}})^2 + (\rho_{\mathrm{r}} + \rho_{\mathrm{s}})C_{\mathrm{r}y}{}^m C_{\mathrm{s}y} C_{\mathrm{r}}{}^{\mathrm{p}} C_{\mathrm{s}}{}^{\mathrm{p}}}{\epsilon^{\mathrm{p}} - \epsilon_i{}^m} \qquad (9\mathrm{a})$$

$$\Delta g_{nj} = (2/3)\frac{\rho_j[(C_{jx}{}^m)^2 + (C_{jy}{}^m)^2](C_i)^2}{\epsilon^{\mathrm{p}} - \epsilon_j{}^m} \qquad (9\mathrm{b})$$

where Δg_i and Δg_{nj} are the contributions to the g values from the ith σ bond and the jth lone-pair orbital, a and b refer to the bonding and antibonding orbitals of the ith σ bond between atoms r and s, $C_{\mathrm{r}}{}^{\mathrm{p}}$ is the coefficient of the $2\mathrm{p}_z$ atomic orbital of the atom r in the odd-electron orbital, $C_{\mathrm{r}x}{}^m$ and $C_{\mathrm{r}y}{}^m$ are the coefficients of the $2\mathrm{p}_x$ and $2\mathrm{p}_y$ atomic orbitals of the atom r in the mth σ orbital, and the other notations have similar meanings. Our analysis of g factors is somewhat similar to the analysis of the solvent effect on g values in nitroxide radicals made by Kawamura, *et al.*[19] g values of radical ions containing heteroatoms have been studied by several workers,[20–23] but no detailed studies of the ion pair effect have been made in these systems. The only detailed analysis of ion pair effects on g values seems to be limited to the case of the naphthalene negative ion, which was studied by Williams, Pritchett, and Fraenkel.[24]

Structures of Ion Pairs. The ion pair systems we consider in this paper are so-called tight (contact) ion pairs. The assumed structures on which the calculations are based are shown in Figure 1. These structures may be debatable, but the agreements between the experimental spin densities and the calculated ones support the structures. The structure for the anthracene ion pair was also predicted by the potential energy calculation of Goldberg and Bolton.[11]

Results and Discussion

Aromatic Hydrocarbon, Anthracene. Upon ion pair formation, proton splittings at the 1, 4, 5, and 8 positions (α) decrease and the 9, 10 proton (γ) splitting increases. The correlation between the changes among different hfs first noted by Reddoch[2a] seems to be valid in most

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(16) J. P. Colpa and J. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(17) M. Bröze and Z. Luz, *J. Chem. Phys.*, **51**, 9749 (1969).

(18) B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 695 (1964).

(19) T. Kawamura, S. Matsunami, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Jap.*, **38**, 1935 (1965); **40**, 1111 (1967).

(20) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(21) P. J. Zandstra, *J. Chem. Phys.*, **41**, 3655 (1964).

(22) (a) M. Adams, M. S. Blois, and R. H. Sands, *ibid.*, **28**, 774 (1958); (b) M. S. Blois, H. W. Brown, and J. E. Malling, "Free Radicals in Biological Systems," Academic Press, New York, N. Y., 1960, p 117.

(23) C. Heller, *J. Amer. Chem. Soc.*, **89**, 4288 (1967).

(24) W. G. Williams, R. J. Pritchett, and G. K. Fraenkel, *J. Chem. Phys.*, **52**, 5584 (1970).

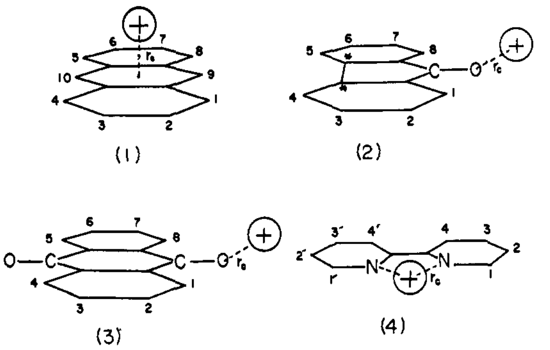

Figure 1. Model of ion pair structures: (1) anthracene, (2) fluorenone, (3) anthraquinone, (4) 2,2′-dipyridyl.

anthracene ion pair systems. The models of ion pairs used in this calculation are shown in Figure 1. Spin densities were calculated using different r_c and ϵ. The results are summarized in Figure 2, together with the representative experimental values. Clearly, the general trends of perturbation agree well with the experimental results. The stronger the perturbation, the smaller the α splittings and the larger the γ splittings. We also note that the relative changes in α and γ splittings are quite consistent. The coulomb interaction $e^2/\epsilon r_c$ has two unknown parameters, ϵ and r_c, and it is not possible to discuss the magnitudes of perturbation or structures of ion pairs unambiguously. However, it seems possible to draw some conclusions concerning the ion pair structures from the results shown in Figure 2.

Generally speaking, the size of the perturbation required to reproduce the observed spin density changes upon ion pair formation is not very large. This implies that in using an $e^2/\epsilon r_c$ potential for the interaction, one has to use a relatively large ϵ if a relatively small r_c is to be used. Previous workers often used the e^2/r potential to represent the ion pair interaction, but this potential produces much changes in spin densities which are much too large for reasonable tight ion pair structures. In all ion pair systems, solvents are expected to solvate the cation in the open space. First, this reduces the electrostatic interaction, as discussed before, and a relatively large screening factor may be necessary even in the tightest ion pair systems. Second, even in the contact ion pairs the interaction between solvated solvent molecules and anions may tend to make the distance between ions larger than those expected from the ionic radii and van der Waals radii. These expectations seem to be borne out in our results.

The largest changes in spin densities so far observed are those found in poor solvating solvents such as diethyl ether (DEE), where the macroscopic dielectric constant is 4.18 at 25°. If we assume the possible distance r_c for Li pairs to be 2.5–3.5 Å, for Na 3–4 Å, and for K 3.5–4.5 Å, the corresponding ϵ to produce the observed changes in DEE is 5–2.5. If we take ϵ to be about 4 (which is close to macroscopic dielectric constant), the corresponding r_c's are 3 Å for Li, 3.3 Å for Na, and 4 Å for K. These values are already larger than the sums of ionic and van der Waals radii. If we assume smaller ϵ values, the corresponding r_c values would be even larger. This situation is even more pronounced for the ion pairs in MTHF and THF.

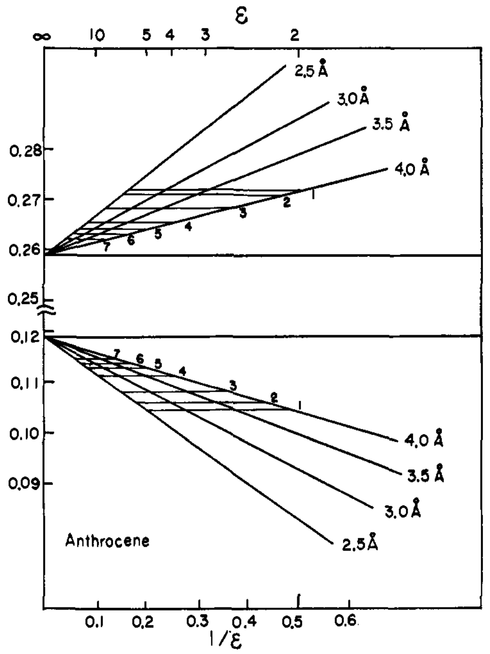

Figure 2. Spin densities at the α and γ positions of anthracene anion at various strengths of the ion pair interactions. Each line was drawn with a fixed value of r_c (r_c = 2.5, 3.0, 3.5, and 4.0 Å) and as a function of screening factor ϵ. Horizontal lines indicate the experimental spin densities for various anthracene ion pairs. Q values were chosen so that the calculated spin densities for free anions agree with the experimental values: (1) Li,diethyl ether (DEE); (2) Na,*n*-butyl ether (DBE); (3) Na,DEE; (4) K,DEE; (5) Na,MTHF; (6) K,MTHF; (7) Cs,MTHF.

From the observed relatively large alkali metal splittings, these ion pairs are thought to be tight ion pairs. However, perturbation of proton splittings is relatively small. Since the calculation is very approximate, one cannot take the numerical results very seriously, but perhaps one can safely conclude the following. (1) Relatively large screening factors have to be used in expressing the electrostatic interactions in ion pairs. The screening factors are closer to macroscopic dielectric constants rather than to 1. (2) Even in the so-called contact ion pairs, the distances between ions may be significantly larger than those expected from ionic and van der Waals radii. The use of the macroscopic dielectric constant as a screening factor is obviously very questionable and cannot be justified. However, $\epsilon \simeq 7$ and $\epsilon = 4$ for MTHF and DEE require r_c to be 3 Å for Li, 3.5 Å for Na, 4 Å for K, and 4.5 Å for Cs. The use of macroscopic dielectric constants together with a reasonable ion pair separation seems to give changes in spin densities close to those observed.

Fluorenone Ketyl. The ^{13}C and proton splittings of various ketyls have been reported previously.[12,13] We supplemented them with more new data in this work. g factors of fluorenone ketyl were investigated in this work. In determining experimental spin densities $Q = -29$ G was used for proton splittings. For carbonyl molecules such as fluorenone, there is not a unique choice of MO parameters or of Q. One may obtain reasonably good fits to experimental values with different sets of parameters if one uses different Q values. In the present study, we varied the parameters in the following ranges in order to determine the parameters which best fit the free-ion spin den-

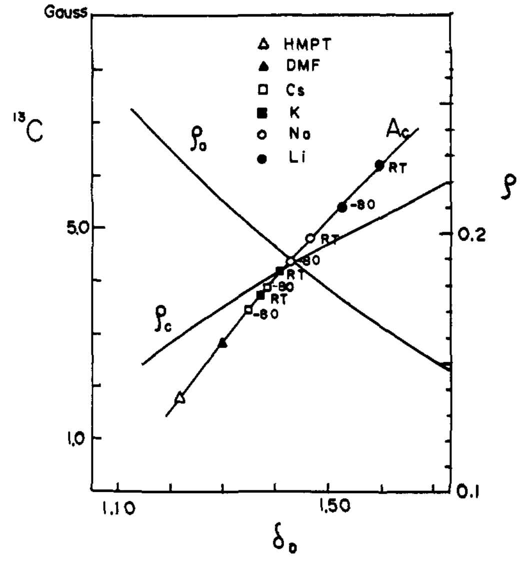

Figure 3. Changes of ^{13}C splittings and spin densities on carbon and oxygen atoms as functions of oxygen coulomb parameters. The lines give the calculated ^{13}C splittings A_C, the spin density on the carbon atom ρ_C, and the spin density on the oxygen atom ρ_O as functions of oxygen coulomb parameters. Points on the curve are experimental values taken in THF. RT and −80 indicate values at room temperature and −80°, respectively.

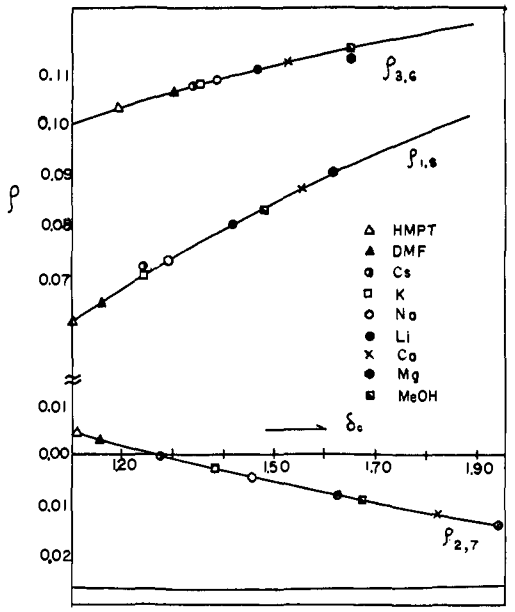

Figure 4. Calculated spin densities on the ring as functions of oxygen coulomb parameter. Points on the curve indicate the experimental values.

sities. The ranges are $1.00 \leq \delta_O \leq 2.00$, $0.80 \leq \gamma_{CC'} \leq 1.50$, $0.70 \leqq \gamma_{C^*C^*} \leqq 1.00$, and $1.00 \leq \gamma_{CO} \leq 2.00$. The notations for δ and γ are the same as those made for previous studies.[25] Reasonably good agreement with experimental spin densities was obtained using the following parameters and $Q = -29$ G: $\delta_O = 1.15$, $\delta_{C'} = 0.10$, $\gamma_{CO} = 1.60$, $\gamma_{CC'} = 1.30$, and $\gamma_{C^*C^*} = 0.8$. An MO calculation of fluorenone anion was previously done by Dehl and Fraenkel.[25] Our parameters are similar to theirs.

The calculated spin densities for the free ion are $\rho_{1,8} = 0.064$, $\rho_{2,7} = 0.003$, $\rho_{3,6} = 0.102$, and $\rho_{4,5} = -0.027$. The experimental values are $\rho_{1,8} = 0.061$, $\rho_{2,7} = 0.004$, $\rho_{3,6} = 0.106$, and $\rho_{4,5} = \pm\ 0.022$.

As discussed previously, the ion pair effect can be treated by changing the coulomb integral to $\alpha_i = \alpha_i^0 - Ze^2/\epsilon r_i$. To be accurate, the coulomb integral of all carbon and oxygen atoms should be changed. However, the cation is in the vicinity of oxygen and the effect of the cation on the other carbon atoms is expected to be relatively small. Also, it was shown that the coulomb integral of the carbon atom adjacent to the negative oxygen atom (C_1 and C_8) should be smaller than those of other carbons in the case of benzophenone.[26] This effect would tend to cancel the effect of the cation. Since $\epsilon(r)$ depends on the distance, it is also difficult to correctly take into account the cation effect for all the atoms in the molecule. Therefore, as a first approximation, we adjusted the oxygen coulomb parameters in order to see the cation effect. This approximation may not be very satisfactory for proton splittings, but carbonyl ^{13}C and g factors depend primarily on the relative spin densities on the carbonyl carbon and oxygen atoms and probably do not suffer much from this simplification. The other ambiguity involved in this calculation is the uncertainty in the structure of ion pairs. It has been suggested that the cation moves more to an off-nodal plane of the $2p\pi$ orbital at higher temperatures.[27] The relative position of the cation also depends on the type of cation. These uncertainties should be kept in mind in analyzing the data.

(A) ^{13}C Splittings. Using the spin densities obtained from the MO calculation, the carbonyl ^{13}C splittings are calculated as a function of the oxygen coulomb parameter. They are plotted together with the experimental values in Figure 3. The change of 0.44 in δ_0 gives the observed change in the ^{13}C splitting in going from the free ion in HMPT to the Li ion pair.

(B) Proton Splittings and Spin Densities at Ring Carbon Atoms. The spin densities are calculated as functions of oxygen coulomb parameters, and the proton splittings are estimated using McConnell's relationship. The results are shown in Figure 4 together with the experimental values. It is seen that the general trends of the spin density changes are predicted correctly by this calculation. However, the quantitative consistencies among the changes in spin densities at various positions are not very satisfactory. The required change in δ_O in going from the free ion to to the Li ion pair is approximately 0.3–0.5.

(C) g Values. The contribution to the g values for the fluorenone radical anion can be divided into three parts: the contribution from the aromatic carbon frame (Δg_{hc}), from the nonbonding orbital in oxygen (Δg_n), and from the σ-bonding in the carbonyl (Δg_{CO}). According to Segal, Kaplan, and Fraenkel Δg_{hc} is given by[28]

$$\Delta g_{hc} = \sum_i \rho_i(31.9 - 16.6\lambda) \times 10^{-5} \qquad (10)$$

where λ is the parameter in the expression of orbital energy obtained by the HMO theory. Δg_n can be

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(25) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(26) T. Takeshita and N. Hirota, *ibid.*, **51**, 2146 (1969).

(27) K. Nakamura and N. Hirota, *Chem. Phys. Lett.*, **3**, 137 (1969).

(28) B. Segal, M. Kaplan, and G. K. Fraenkel *J. Chem. Phys.*, **43**, 4191 (1965).

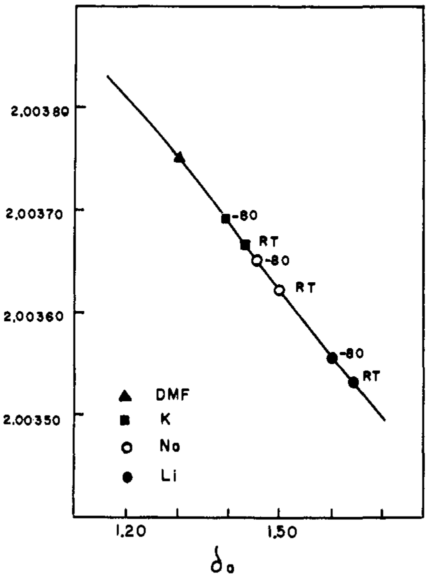

Figure 5. Calculated g value as a function of oxygen coulomb parameter. Points on the curve indicate the experimental values taken in THF. RT and −80 indicate room temperature and −80°, respectively.

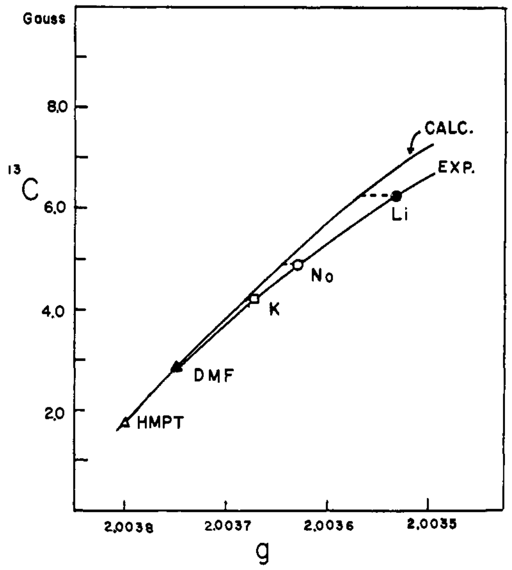

Figure 6. Correlation between ^{13}C splittings and g values. The calculated curve shows the correlation between the calculated ^{13}C splittings and g values with the same oxygen coulomb parameters. Constant $\Delta E(n-\pi^*)$ was assumed for the g-value calculation. The experimental curve indicates the correlation among the observed ^{13}C splittings and the g values.

given by

$$\Delta g_n = (2/3)[\zeta_O\rho_O/\Delta E(n-\pi^*)] \qquad (11)$$

where ρ_O is the odd-electron spin density on the oxygen atom, ζ_O is the spin-orbit coupling of the oxygen atom, and $\Delta E(n-\pi^*)$ is the transition energy of the n–π* transition.

Δg_{CO} for free ions in DMF is taken as the difference between Δg_{obsd} and $\Delta g_e + \Delta g_{hc} + \Delta g_n$. The n–π* transition energy $\Delta E(n-\pi^*)$ for fluorenone is not established experimentally. However, $\Delta E(n-\pi^*) = 2.7 \times 10^4$ cm^{-1} seems to be a reasonable estimate from analogy with many other carbonyl compounds.[29] For the free ion in DMF, each contribution was estimated to be as follows: $\Delta g_{hc} = 36 \times 10^{-5}$, $\Delta g_{CO} = 27 \times 10^{-5}$, and $\Delta g_n = 80 \times 10^{-5}$ g values of ion pairs were calculated by using eq 7 as a function of the oxygen coulomb parameter. $\Delta E(n-\pi^*)$ is expected to depend on the cation. However, this change is not known. In Figures 5 and 6, calculated g values using constant $\Delta E(n-\pi^*)$ are plotted. Since a small blue shift for $\Delta E(n-\pi^*)$ is expected upon ion pair formation, g factors calculated with constant $\Delta E(n-\pi^*)$ are expected to be slightly larger than they should be. Δg_{CO} for ion pairs was calculated in the following way. If one assumes that the carbonyl σ bond consists of the oxygen $2p_y$ orbital and the carbon sp^2 orbital then Δg_{CO} is given by

$$\Delta g_{CO} = (2/3)(\zeta_O\rho_O + (2/3)\zeta_C\rho_C)[1/\Delta E(\sigma - \pi^*)] \qquad (12)$$

Using $\Delta g_{CO} = 27 \times 10^{-5}$ for the free ion, $\Delta E(\sigma-\pi^*)$ is estimated to be 8.74×10^4 cm^{-1}. For ion pairs this value of $\Delta E(\sigma-\pi^*)$ is used and Δg_{CO} is estimated using eq 12 and the calculated spin densities. In Table II, the experimental g values and the required δ_O to fit the experimental g values for different ion pairs are given together with those for ^{13}C splittings. The agreement between ^{13}C splittings and g values is very good. The calculation of g values is done by assuming constant $\Delta E(n-\pi^*)$. It is seen that the calculated g values are systematically slightly larger than those obtained experimentally, if we use the δ_O which fits the ^{13}C splittings. It is tempting to attribute these differences to neglect of the blue shift due to ion pair formation. If one takes this difference as the correction to the Δg_n due to the blue shift, one can obtain estimates of $\delta\Delta E(n-\pi^*)$ due to ion pair formation. They are calculated to be 600 cm^{-1} for Na and K and 1000 cm^{-1} for Li ketyls. In other words, g values and ^{13}C splittings can be fit with the exactly same δ_O, if the above values are assumed for the blue shift of n–π* transition. These values of $\delta\Delta E(n-\pi^*)$ seem to be quite reasonable for this type of blue shift. In conclusion, the consistency between the changes in g values and ^{13}C splitting seems to be excellent. The spin densities at the carbonyl carbon and oxygen which give the best fit to ^{13}C splittings and g values in various ketyls are given in Figure 3.

Table II. The Oxygen Coulomb Integral Parameters to Fit the Carbonyl Carbon Hfs and g Values

Metal	Solvent	δ_O Carbonyl ^{13}C hfs	 g factors
	Free	1.15	1.15
K	HMPT	1.22	
K	DMF	1.30	1.30
Cs	DME	1.39	
K	DME	1.41	1.44
Na	DME	1.47	1.50
Li	DME	1.59	1.64

(D) Interaction between Ions. As in case of anthracene ion pairs, we estimate ϵr_c which fits the data from the required change of δ_O in ion pairs to fit g factors and ^{13}C splittings. These values are 13 for Li, 17 for

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[29] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963, Chapter 8.

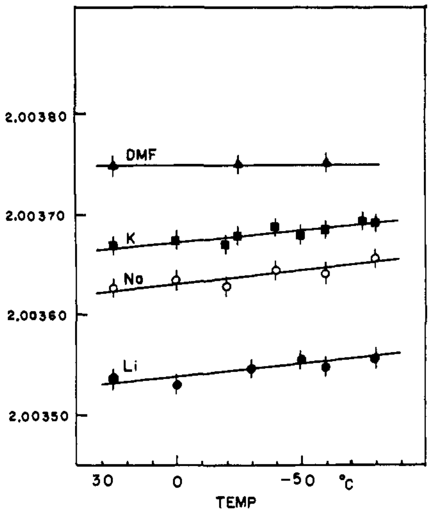

Figure 7. Temperature dependence of *g* values of fluorenone ketyls.

Na, 22 for K, and 24 for Cs in THF (Table III). If we assume r_c to be 2.5 Å for Li, 3.0 Å for Na, 4 Å for K, and 4.5 Å for Cs, the screening factor is about 5.5. The correct values of r_c for ketyls may even be smaller than those used above. In that case, ϵ is larger. These values of r_c and ϵ are very similar to those required to produce the observed perturbations in anthracenide case. However, as stated earlier, the effect of the cation on other carbon atoms are not accurately taken into consideration in this treatment. If we use $X\beta_i = e^2[(1/\epsilon r_c) - (1/\epsilon' r_i)]$ in order to take into account of this effect, the appropriate values of ϵr_c and accordingly ϵ become smaller. Nevertheless, strong solvation of the cation seems to reduce the electrostatic interaction, and relatively large ϵr_c has to be used in order to account for the observed changes in epr parameters.

Table III. Changes in the Oxygen Coulomb Integral Parameter, $\Delta\delta_O$, Screening Factor, ϵ, Distance, r_c, and Blue Shift, ΔE(n–π^*)

Metal	Solvent	$\Delta\delta_O$	ϵr_c	r_c (ϵ 7), A	ΔE(n–π^*)
	Free	0.00			
K	HMPT	0.07			
K	DMF	0.15			
Cs	DME	0.24	23.7	3.4	
K	DME	0.26	21.9	3.1	0.03β
Na	DME	0.32	17.3	2.5	0.03β
Li	DME	0.44	13.0	1.8	0.05β

(E) **Temperature Dependence.** Quite a large temperature dependence was observed for the ^{13}C splittings and *g* values. The temperature dependence of *g* values is shown in Figure 7. These changes indicate a decrease in the electrostatic interactions between ions as the temperature decreases. There are two possible causes for this: first, change in r_c because of the structural changes in ion pairs; secondly, weaker electrostatic interaction due to increased solvation at lower temperatures. The required changes in ϵr_c in going from 22° to −80° are 2.8 for Li, 3.4 for Na, and 3.4 for K. If we assume the same r_c as we used in the previous section, the change in $\epsilon(\delta\epsilon)$ is about 1. Since the change in the macroscopic dielectric constant over the same temperature range is about 5, the obtained $\delta\epsilon$ is much smaller than the change in dielectric constant. Since the ion pair structure changes with temperature, as indicated by the large temperature dependence of the alkali metal splittings, it is difficult to know the exact cause of this change. However a small increase in screening factor can easily be accounted for by the increased solvation at lower temperatures.

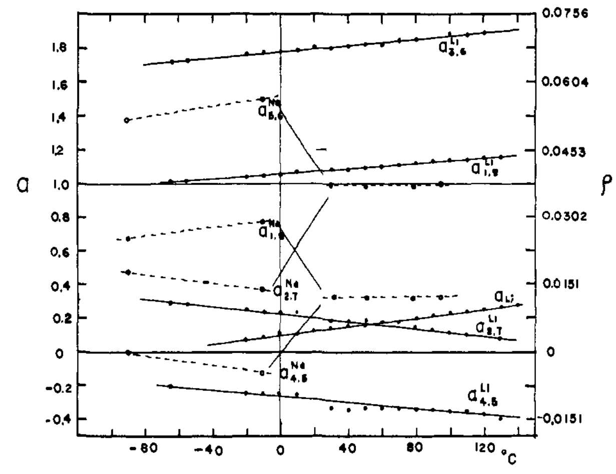

Figure 8. Proton splittings and estimated spin densities of the anthraquinone ion pairs: ‒‒‒, Na anthraquinone; ——, Li anthraquinone.

(F) **Effect of Solvent.** Although we have made no quantitative studies of solvent effects in this work, changes of proton splittings have been detected when DMF replaces ethereal solvents. From the direction of the changes, it is clearly seen that the replacement of THF by DMF increase ϵr_c. The more polar solvent DMF increases the screening factor as expected.

Anthraquinone. Since there are two equivalent carbonyl groups in anthraquinone, it is interesting to see how ion pair formation on one carbonyl site changes the spin distribution, and how this unsymmetric spin distribution can be predicted by this simple approach. The large distortions of the spin densities of radical anions by ion pair formation have been observed in many molecules such as dinitro compounds[30] and benzosemiquinones.[31–34] The unsymmetric spin densities in monoprotonated durosemiquinones have been discussed in terms of the valence-bond approach by Symons and his coworkers.[34]

The epr spectra of Li anthraquinone and Na and K anthraquinone anion at very low temperatures show the spectra in the slow limit of cation migration.[35] The proton splittings are extremely sensitive to changes in perturbation. The experimental splittings are shown in Figure 8. The MO calculation was made

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(30) R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 1996 (1961); *J. Chem. Phys.*, **36**, 1405 (1962).

(31) D. H. Chen, E. Warhurst, and A. M. Wilde, *Trans. Faraday Soc.*, **63**, 2561 (1967).

(32) T. A. Claxton, J. Oakes, and M. C. R. Symons, *ibid.*, **64**, 596 (1968).

(33) M. P. Khakhar, B. S. Prabhananda, and M. R. Das, *J. Amer. Chem. Soc.*, **89**, 3100 (1967).

(34) T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 279 (1966).

(35) Epr spectra of Na anthraquinone were previously reported by E. Warhurst and A. W. Rutter, *ibid.*, **64**, 2338 (1968). Our interpretation of the spectra is somewhat different from theirs. Very recently, T. E. Gough and P. R. Hindle, *ibid.*, **66**, 2450 (1970), reported an analysis of the Na anthraquinone spectrum. Our analysis agrees with theirs.

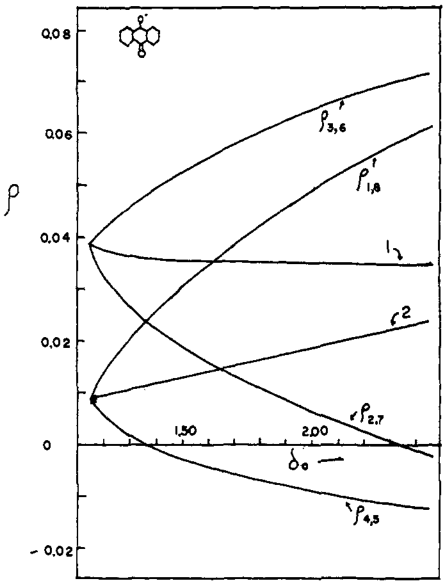

Figure 9. Calculated spin densities of anthraquinone anion ion pairs as functions of oxygen coulomb parameters.

along the same lines as in fluorenone ketyls. First the parameters which best fit to the free-ion spin densities are determined. The choices of parameters are $\delta_O = 1.15$, $\delta_{C'} = 0.11$, $\gamma_{CO} = 1.55$, and $\gamma_{CC'} = 1.00$. Using $Q = -26.5$ G, these parameters give spin densities $\rho_1 = 0.0393$ and $\rho_2 = 0.0090$. Since the experimental spin densities are dependent on the solvent, it is difficult to make a precise comparison between the experimental values and the calculation. The experimental spin densities taken as the reference for the free-ion values were those measured in HMPT (hexamethylphosphoramide). In order to take into account the ion pair effect, we changed the oxygen coulomb parammeters. However, as we have commented before, this neglects the effect of cation on the ring. In order to see this effect, we have changed the coulomb parameters of the carbon atoms near the metal ion (C_1 and C_8) by small amounts. These are shown in Figure 9. Cs anthraquinone shows the epr spectra in the limit of rapid ion migration, and K and Na anthraquinone at higher temperatures show the spectra in the intermediate region. In all these cases one can only determine the average splittings. The average values of ρ_1 and ρ_4 are relatively cation dependent. The comparisons between the experimental values and the calculated ones are also given for these spin densities. As shown in Figure 8, it is clear that the qualitative agreements between the experimental spin densities and the calculated ones are quite good. All the features of the unequivalent spin densities, including the signs, are correctly predicted. However, the quantitative agreements are not very satisfactory, particularly for Li ion pairs. Generally, the calculation seems to predict smaller ρ_3 and larger ρ_4 than the experimental ones. It is seen that the spin distributions are quite sensitive to the adjustments of the coulomb parameters of the carbons at positions 1 and 8. Since it is difficult to accurately take this effect into consideration, good quantitative agreement may be difficult to obtain. In our calculation $\delta_C'' = 0.10$ was used. This value may be too small for the ion pairs of small cations, such as Li pairs. Also, the calculation of spin densities using McConnell's equation may not be exactly correct.

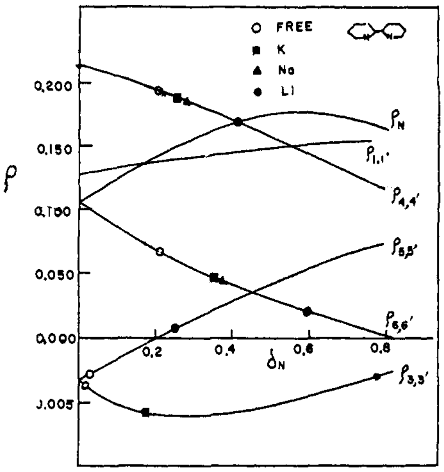

Figure 10. Calculated spin densities of 2,2′-dipyridyl as functions of nitrogen coulomb parameters. Points on the curves are experimental values.

The oxygen coulomb parameters required to fit the observed spin density changes are 1.45 ± 0.05 for Na, 1.8 ± 0.1 for Li using ρ_1 and ρ_2. If one uses the average splitting of ρ_1 and ρ_4, the required oxygen coulomb parameters are 1.35 for Cs, 1.38 for K, 1.42 for Na, 1.62 for Li, and 1.15 for free ions. These oxygen parameters are very similar to those required for fluorenone ketyls, and the discussion about the screening factors given in that section should also be applied to this case. Similar temperature and solvent effects were observed in the anthraquinone case, and the same discussion given in the fluorenone case should be applied here. In summary, qualitative features of the unsymmetric spin distribution in anthraquinone anion can be well explained by a simple MO treatment.

2,2′-Dipyridyl. Alkali metal ions are chelated between two nitrogen atoms of 2,2′-dipyridyl. Therefore, the positions of the alkali metal ions are well fixed in this system. This expectation is supported by the fact that the alkali metal splittings do not depend on temperature or solvent.

The epr spectra of 2,2′-dipyridyl have been investigated by several workers,[14,36–38] but there seem to be no systematic studies of the ion pair effect. The values of splittings in different ion pairs are given in Table Id. First, in order to fit the free-ion spin densities, the nitrogen coulomb parameter, δ_N, and the resonance integral parameter of the 1–1′ bond, $\gamma_{CC'}$, were varied over the ranges $0.00 \leq \delta_N \leq 1.00$ and $0.70 \leq \gamma_{CC'} \leq 1.00$. The spin densities obtained with $\gamma_{CC'} = 1.00$ as a function of δ_N are given in Figure 10. The agreements between the experimental values and the calculated ones are not good even for free ions. It is seen that the trend of the changes of spin densities upon ion pair formation is qualitatively predicted by changing δ_N from 0.2 for free ion to 0.5 for lithium pair. However, the agreement is generally not very good. The ion pair effect on the spin densities in 2,2′ dipyridyl is rather

(36) A. Zahlen, F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, 44, 2214 (1962).
(37) E. Konig and H. Fischer, *Z. Naturforsch.*, 170, 1063 (1962).
(38) J. C. M. Henning, *J. Chem. Phys.*, 44, 2139 (1966).

small and again the electrostatic interaction seems to be rather small. However, the present approach seems to be least successful in this system.

Concluding Remarks

It is shown that a simple calculation using McLachlan MO's combined with the McClelland treatment based on assumed structure can explain ion pair effects fairly well, although there is much to be improved in order to obtain good quantitative agreement between experimental spin densities and calculated ones. The trends in changes in epr parameters predicted by the calculation agree very well with the observed trends. This implies the basic correctness of the assumed structures. The MO calculations suggest that the relatively small coulombic interaction, $Ze^2/\epsilon r$, is operating in ion pair systems. We think that the reason for this is the effect of strong solvation by solvent molecules (dipole) of cations, which cancels the potential due to the cations. The screening factors which fit the experimental values are closer to the macroscopic dielectric constant rather than to 1.

Even though our calculations are crude, we believe that the results of the present analysis indicate that erroneous results might be obtained in calculation on ion pair systems unless proper consideration is taken of the effects of solvation.

g values of organic radicals have not been used widely for spin density studies. However, the extremely good agreement between ^{13}C splittings and g values seems to indicate that the careful use of g values can provide additional information concerning spin densities on atoms such as oxygen, where the determination of spin density from hfs is not easy.

Acknowledgment. We thank Dr. K. Nakamura for some data on sodium and lithium anthraquinone and helpful discussions concerning assignments of splittings for anthraquinone anions.

Absorption and Emission Spectra of Aromatic Ketones and Their Medium Dependence. Excited States of Xanthone[1]

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Abstract: A detailed examination of the absorption spectra, the polarized phosphorescence spectra, and the polarized excitation spectra of xanthone (C_{2v} symmetry) in polar and nonpolar media has been carried out at 77°K. Five electronic transitions in the absorption region between 27,000 and 44,000 cm^{-1} have been assigned. They are, in order of increasing energy: $^1A_2$ (n,π^*) ← $^1A_1$, $^1A_1$ (π,π^*) ← $^1A_1$, $^1B_2$ (π,π^*) ← $^1A_1$, $^1A_1$ (CT) ← $^1A_1$ (tentative), and $^1A_1$ (π,π^*) ← $^1A_1$ (tentative). Lifetime and polarization measurements, as well as vibrational features, indicate that the configuration of the lowest triplet state is nπ^* in the 3-methylpentane (3-MP) solvent but $\pi\pi^*$ in polar solvents. In both EPA and 3-MP the phosphorescence kinetics of xanthone are nonexponential. Time-delayed phosphorescence and excitation spectra show that the mixed kinetics in 3-MP are due to a small amount of the same phosphorescent species ($^3\pi,\pi^*$) which is dominant in EPA. Moreover, polarization spectra indicate that a small amount of the phosphorescent species (^{3}n,π^*) which is dominant in 3-MP produces the deviation from the exponential decay in EPA. This phenomenon is suggested to arise mainly from two types of solute–solvent cage configurations.

Owing to their role in photochemical and photobiological reactions, the triplet states of aromatic ketones and aldehydes continue to receive considerable attention from both experimental and theoretical points of view.[2–10] It has been shown that the configuration of the lowest triplet state of these compounds can be correlated with properties such as photochemical reactivity and relaxation behavior. A series of diagnostic criteria has therefore been developed which can guide the assignment of the configuration of the lowest triplet state.[2,3] In some cases, however, these criteria do not allow a clear-cut decision to be made. For instance, it appears that carbonyl compounds with very small energy gaps between ^{3}(n,π^*) and ^{3}(π,π^*) configurations have lowest triplet states of a substantially mixed character. This mixing is generally considered to arise by vibrational coupling between the two closely spaced electronic states; experimentally, it is manifested in the polarization characteristics of the phosphorescence.[10–13] A further consequence of the energetic proximity of the triplet states is that a relatively small perturbation of

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(1) This research was supported by HEW, Public Health Service, Grant No. ES 00376.

(2) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(3) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley-Interscience, New York, N. Y., 1969.

(4) R. Shimada and L. Goodman, *J. Chem. Phys.*, 43, 2027 (1965).

(5) A. A. Lamola, *ibid.*, 47, 4810 (1967).

(6) M. Vala and J. Tanaka, *ibid.*, 49, 5222 (1968).

(7) S. Dym, R. M. Hochstrasser, and M. Schafer, *ibid.*, 49, 971 (1968).

(8) S. Dym and R. M. Hochstrasser, *ibid.*, 51, 2458 (1969).

(9) W. A. Case and D. R. Kearns, *ibid.*, 52, 2175 (1970).

(10) Y. H. Li and E. C. Lim, *Chem. Phys. Lett.*, 7, 15 (1970).

(11) R. M. Hochstrasser and C. A. Marzzacco, "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 631.

(12) E. C. Lim, R. Li, and V. H. Li, *J. Chem. Phys.*, 50, 4925 (1969).

(13) E. C. Lim, ref 11, p 469.