

mixture thermal conductivity is merely an *ad hoc* assumption; (2) Eq. (7) is only a first approximation and the error involved may be appreciable; (3) the theory of the thermal-diffusion column does not take into account the energy of internal motions; (4) the exponent of T is not the same for λ as for η in the case of polyatomic gases; (5) the theory of the thermal-diffusion

column is probably not quite perfect; (6) the assumed law of molecular interaction with spherical symmetry may not be quite appropriate for polyatomic molecules. More experiments on the experimental determination of α for polyatomic molecules are thus necessary to determine the exact role of internal energies in the process of thermal diffusion.

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ESR Studies of Nitrobenzene, *o*-Dinitrobenzene, and *m*-Dinitrobenzene Alkali-Metal Salts*

CHI-YUAN LING AND JULIEN GENDELL

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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The hyperfine splittings for the lithium, sodium, potassium, and cesium salts of nitrobenzene and the sodium, potassium, and cesium salts of *o*-dinitrobenzene over a range of temperature in DME are reported, as well as the splittings for the nitrobenzene and *o*-dinitrobenzene radicals produced by electrolytic reduction in DME. The sodium salt of nitrobenzene was also studied in a mixture of DME and DMSO. Results for nitrobenzene and *o*-dinitrobenzene are correlated with those previously reported for *m*-dinitrobenzene salts. For all three anions it was found that the perturbation of the anion on ion-pair formation increases along the series Cs⁺ to Li⁺. Line-broadening effects associated with cation motion from one nitro group to the other in the *o*- and *m*-dinitrobenzene salts correlate well with the extent of the perturbation of the anion by the metal cation. On the basis of (1) similar magnitudes and similar variation with temperature of the alkali-metal hyperfine splittings for all three anions, (2) the absence of line-broadening depending on alkali-metal quantum number, and (3) the observations in the mixed solvent system, a model for the ion pairs in DME is proposed in which the cation interacts with a single nitro group at a given instant of time, the cation is tightly bound to the nitro group with a fairly strongly bound cage of DME molecules solvating the nitro group cation complex, and temperature variation of the alkali-metal splitting is attributed to motion of the cation in the vicinity of the nitro group. Simple molecular-orbital calculations were performed in which the electrostatic interaction of the cation with the nitro group was simulated by increasing both the oxygen and nitrogen Coulomb integral parameters and good agreement between calculated and experimental changes of anion hyperfine splittings on going from the nitrobenzene free ion in DME to the sodium salt was obtained.

I. INTRODUCTION

There have been numerous electron spin resonance investigations of radicals containing nitro groups in the past few years. In many situations interesting linewidth effects have been observed and solvent effects have been extensively studied.

Alkali-metal salts of nitrobenzene, *o*-dinitrobenzene, and *m*-dinitrobenzene were initially investigated by Ward¹ who found evidence of strong ion pairing. For example, only one large nitrogen hyperfine splitting in the *m*-dinitrobenzene salts was observed. Most of Ward's results were obtained with equipment of poorer resolution than is now available and only in the case of the *m*-dinitrobenzene salt in DME at 0°C was an alkali-metal splitting reported.²

Recently, Ling and Gendell³ measured the alkali-metal splittings in the sodium, potassium, and cesium

salts of *m*-dinitrobenzene in DME over a range of temperatures, and also found evidence of cation motion from one nitro group to the other. Symons⁴ reported some similar results for *m*-dinitrobenzene salts in THF.

Ling and Gendell³ also observed alkali-metal splittings in *o*-dinitrobenzene salts, and in this case also there was evidence of cation motion between nitro groups. Rather unusual linewidth effects in the ESR spectrum of the sodium salt of *o*-dinitrobenzene at low temperatures were reported by Gendell.⁵

In order to gain a better understanding of the motional effects in *o*- and *m*-dinitrobenzene salts, to increase the knowledge of the nature and structure of the ion pairs formed in these systems, to ascertain the differences in the extent of ion pairing with different alkali-metal cations, and to investigate the origin of the temperature dependence of the alkali-metal splittings, we have measured the hyperfine splittings in nitrobenzene and *o*-dinitrobenzene salts in DME over a range of temperature.

* Supported in part by the American Chemical Society Petroleum Research Fund.

¹ R. L. Ward, J. Am. Chem. Soc. **83**, 1296 (1961).

² R. L. Ward, J. Chem. Phys. **36**, 1405 (1962).

³ C.-Y. Ling and J. Gendell, J. Chem. Phys. **46**, 400 (1967).

⁴ M. C. R. Symons, J. Phys. Chem. **71**, 172 (1967).

⁵ J. Gendell, J. Chem. Phys. **46**, 4152 (1967).

TABLE I. Hyperfine splitting constants of nitrobenzene in gauss.^a

	$T^{\circ}\text{C}$	a_o	a_m	a_p	a_N	a_{cation}
Li salt-DME	0	3.49(2)	1.135(5)	3.94(2)	11.55(5)	0.125(5)
Li salt-DME	-20	3.49(2)	1.135(5)	3.90(2)	11.40(5)	0.145(5)
Na salt-DME	23	3.56(2)	1.12(1)	4.08(2)	11.60(5)	0.40(1)
Na salt-DME	-60	3.54(2)	1.12(1)	4.12(2)	11.25(5)	0.19(1)
K salt-DME	23	3.55(2)	1.12(1)	4.13(3)	11.05(5)	0.23(1)
K salt-DME	-60	3.55(2)	1.12(1)	4.16(3)	10.60(5)	0.18(1)
Cs salt-DME	0	3.54(2)	1.12(1)	4.16(3)	10.80(10)	2.95(2)
Cs salt-DME	-60	3.54(2)	1.12(1)	4.24(3)	10.50(10)	2.62(2)
DME electrolysis	23	3.54(2)	1.12(1)	4.29(2)	10.15(5)	
DMSO electrolysis	23	3.52(2)	1.11(1)	4.18(2)	10.40(5)	

^a The standard deviation assigned to a splitting constant is indicated by a number in parentheses following the splitting constant and referring to the last digit.

We have also compared and correlated the results for nitrobenzene, with one nitro group, with those for *o*- and *m*-dinitrobenzene, where there are two nitro groups and evidence of cation motion between nitro groups. The results of ESR studies of the sodium salt of nitrobenzene in mixtures of DME and DMSO, which have proved extremely valuable in elucidating the nature of the ion pair, are also reported here.

II. EXPERIMENTAL

Nitrobenzene radical anion alkali-metal cation, ion pairs, in 1,2-dimethoxyethane (DME), were prepared by alkali-metal reduction of nitrobenzene using standard procedures^{6,7}. J. T. Baker nitrobenzene (purified reagent grade) was used with additional degassing on the vacuum line. The *o*-dinitrobenzene used was purified by zone melting. Nitrobenzene anion radicals in DME and dimethyl sulfoxide (DMSO) were prepared by electrolytic reduction in a vacuum electrolytic cell similar in design to the one used by Bolton and Fraenkel⁷ with tetra-*n*-butyl ammonium perchlorate as a supporting electrolyte. Radical concentrations were adjusted either by dilution of more concentrated solutions or by controlling the initial nitrobenzene concentration. On dilution, at room temperature, the widths of the lines in the ESR spectra of the radicals decreased until radical concentrations of 10^{-3} to 10^{-4} *M* were reached. Further decrease in radical concentration did not appear to result in increased resolution. Radical concentrations which were used to obtain the data reported were in the range of 10^{-3} to 10^{-4} *M* and here linewidths (defined as the distance in gauss between maximum and minimum in the derivative of the absorption) were typically about 100 mG. As the temperature was decreased, some improvement in resolution was obtained before lines began to broaden at low temperatures. In some cases, notably with the Li salt at high and low temperatures, we were not able to determine sufficiently accurate hyperfine splitting constants because of prohibitively poor resolution.

⁶ D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.* **78**, 116 (1956).

⁷ J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.* **40**, 3307 (1964).

Where mixtures of DME and DMSO were employed, the sodium salt of nitrobenzene in DME was first prepared and then premeasured amounts of DMSO were added. On addition of the DMSO the amount of DME present was proportionately reduced, so that the total volume and hence the radical concentration was kept constant.

A Varian 4502 spectrometer using a 100-kc/sec field modulation and equipped with a Varian variable temperature control unit, was used to record all spectra. Temperatures are accurate to $\pm 2^{\circ}\text{C}$. A Varian magnet with 12-in.-diam pole caps and a 2-in. air gap was used. Magnetic-field scans were obtained by injecting a constant voltage into a magnet-flux stabilizer in a procedure similar to that described by Gendell *et al.*⁸ As found previously, magnetic-field scans obtained in this manner were extremely linear and stable. Scan rates were periodically calibrated using the accurately known hyperfine splitting of the *p*-benzo-semiquinone radical.⁹

III. ALKALI-METAL SALTS OF NITROBENZENE

A. Results

In Table I, the hyperfine splitting constants for the Li, Na, K, and Cs salts of nitrobenzene at two temperatures (the highest and lowest temperatures for which data were obtained) are presented. In addition, the hyperfine splitting constants for the nitrobenzene radical in DME and DMSO obtained by electrolytic reduction at room temperature are given in Table I. Two typical ESR spectra: that of the nitrobenzene-K salt at -40°C and that of the nitrobenzene-Na salt at 23°C are reproduced in Fig. 1.

On changing temperature, large variations in the alkali-metal and nitrogen hyperfine splitting constants were observed. These quantities as a function of temperature are plotted in Figs. 2 and 3; respectively. As the data in Table I indicate, no significant variation

⁸ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **41**, 949 (1964).

⁹ B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.* **30**, 1006 (1959).

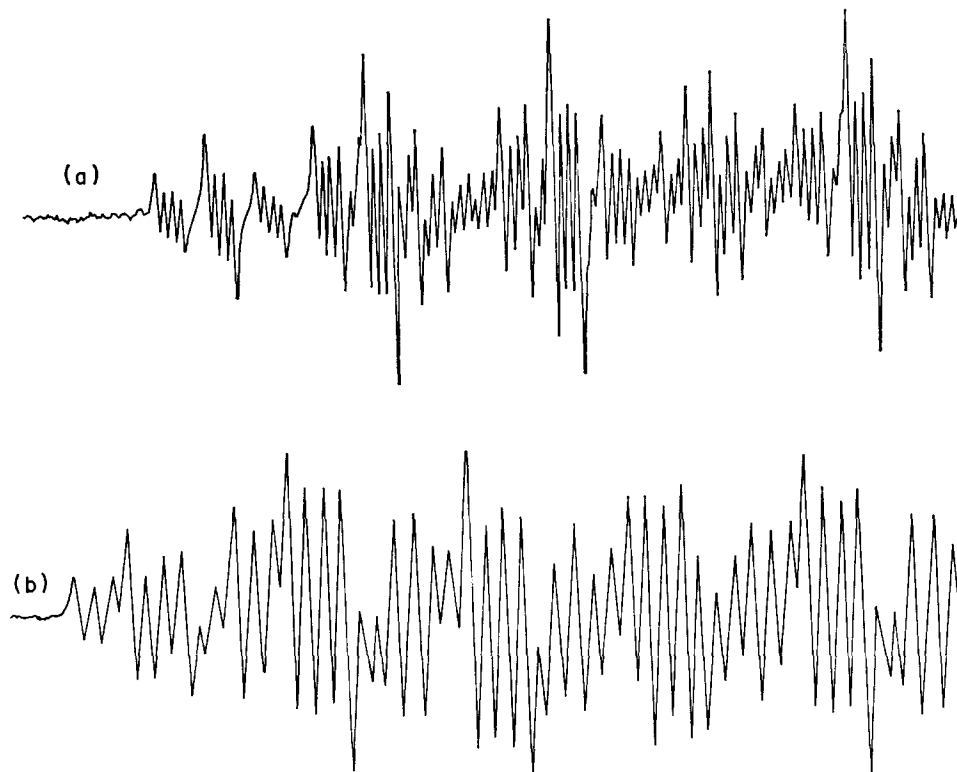


FIG. 1. Electron spin resonance derivative spectra; (a) nitrobenzene—K salt at -40°C in DME, (b) nitrobenzene—Na salt at 23°C in DME. Low-field half of the spectra shown.

with temperature for the *ortho*, *meta*, *para*, proton splitting constants was observed.

As DMSO was added at room temperature to the nitrobenzene—Na salt in DME, no change in the ESR spectrum of the radical anion sodium cation, ion pair, was observed until the proportion of DMSO reached 40 volume percent. The ESR spectrum obtained for this mixture was the result of the superposition of the spectra of two species: one of them, the ion pair, characterized by a sodium hyperfine interaction, and the other with no observable sodium splitting and with splitting constants slightly different from those of the ion pair. The latter species we call the free-ion. As the proportion of DMSO was increased, the concentration of the free-ion species (as evidenced by the intensity of its ESR spectrum) increased, and above 60 volume percent DMSO only the free-ion spectrum was observed. Vacuum pumping to dryness of a mixture with a high percentage of DMSO and then addition of pure DME, yielded a solution whose ESR spectrum was that of the ion pair alone. The ESR spectrum obtained for a 50–50 mixture is reproduced in Fig. 4. From the intensities of their respective spectra, the ratio of the ion-pair to free-ion concentration is estimated as 2:3 in this mixture.

The most significant result obtained from the mixed solvent system is that, over the concentration range where the spectrum of the ion pair was observable

(up to 60 volume percent DMSO), all hyperfine splitting constants of the ion pair were the same as those in pure DME within experimental error. There was no observable change in sodium splitting constant. In the case of the free ion, except for nitrogen, all the splitting constants obtained in mixtures of DME and DMSO were the same as in pure DMSO. The nitrogen splitting constant of the free-ion species decreases as the proportion of DME increases, so that in the 50-volume percent mixture a_N is 2.5% less than the value found in pure DMSO.

B. Effect of Alkali-Metal Cation

The data in Table I show that a_N and a_p vary greatly with alkali-metal cation while there are only small changes in a_o and a_m . If one uses the hyperfine splitting constants of nitrobenzene radical produced electrolytically in DME¹⁰ as a base, and considers the changes of these splittings in the alkali-metal salts as a measure of the perturbation of the nitrobenzene anion by the alkali-metal cation, then both the changes of a_N and a_p indicate increasing perturbation along the series Cs^+ to Li^+ . Thus, on this basis, the smaller the size of the cation, the larger the perturbation.

¹⁰ We call the radical produced in DME by electrolytic reduction the free ion in DME.

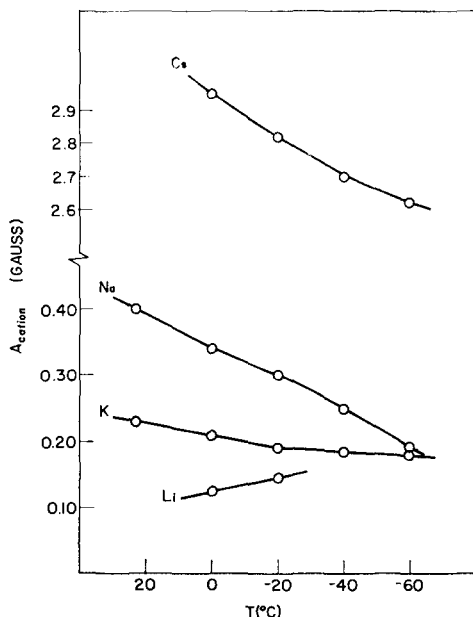


FIG. 2. Alkali-metal cation hyperfine splitting (a_{ion}) as a function of temperature (T) for the Li, Na, K, and Cs salts of nitrobenzene in DME.

Several authors^{11,12} have considered the ratio of the metal hyperfine splitting in the ion pair to that in the free atom as equal to the spin density on the metal in the ion pair, and this in turn as a measure of the extent of ion pairing or the magnitude of the perturbation caused by the alkali-metal cation. Symons⁴ has raised some questions as to the general validity of this approach. If we calculate metal spin densities for nitrobenzene anion alkali-metal cation, ion pairs, by the method just described, then, for Cs⁺, K⁺, Na⁺, and Li⁺, the metal spin densities are, respectively, 0.360%, 0.257%, 0.107%, and 0.087% at 0°C.¹³ The metal spin densities calculated in this manner decrease along the series Cs⁺ to Li⁺.

In the case of these nitrobenzene salts, however, the unknown contributions to the metal hyperfine splitting from indirect spin polarization,¹⁴ nonbonded electrons, and the effects of motion of the cation in the vicinity of the nitro group (see Sec. III.C), make metal spin densities calculated by this crude procedure very questionable indicators of the extent of ion pairing. Hence we regard the magnitude of the changes of a_N and a_p with alkali-metal cation to be a more meaningful measure of the perturbation of the nitrobenzene anion by the metal cation.

¹¹ H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *Mol. Phys.* **9**, 153 (1965).

¹² B. J. Herold, A. F. Nerva-Correia, and J. Dos Santos Veiga, *J. Am. Chem. Soc.* **87**, 2661 (1965).

¹³ Hyperfine coupling constants of the atoms in gauss: $^7\text{Li}=143.3$; $^{23}\text{Na}=316.2$; $^{39}\text{K}=82.4$; $^{133}\text{Cs}=820.1$. P. Kusch and H. Taub, *Phys. Rev.* **75**, 1477 (1949).

¹⁴ E. De Boer, *Rec. Trav. Chim.* **84**, 609 (1965).

C. Nature of the Ion Pair

In order to discuss the nature of the ion pairs formed by nitrobenzene anions and alkali-metal cations, the following experimental observations must be kept in mind:

(1) In the case of Na⁺, K⁺, and Cs⁺, both the alkali-metal splitting and the nitrogen splitting decrease with temperature, and there also appears to be a change of the *para* proton splitting toward the value of the free ion in DME as the temperature is decreased.

(2) Although measurements were made with Li⁺ at only two temperatures, the changes of a_{Li} and a_p with temperature do not follow the trend for Na⁺, K⁺, and Cs⁺.

(3) For the sodium salt in a mixture of DME and DMSO, the value of a_{Na} for the ion pair *did not change* on addition of DMSO.

(4) In all instances for all the nitrobenzene alkali-metal salts in pure DME, for the sodium salt in mixtures of DME and DMSO, and for *o*- and *m*-dinitrobenzene salts where there is evidence of intramolecular motion of the cation (see Sec. IV.A)—no variation of linewidth with alkali-metal quantum number as found in several cases by Hirota^{15,16} was observed.¹⁷

Of prime importance in any discussion of ion pairs is the role that the solvent plays. Do the ions form an intimate or contact ion pair, or is the solvent associated with the ion pair so that a solvent-shared or loosely associated ion pair is formed? Is there more than one distinct form of the ion pair present, and if so what are the rates of conversion from one form to another?

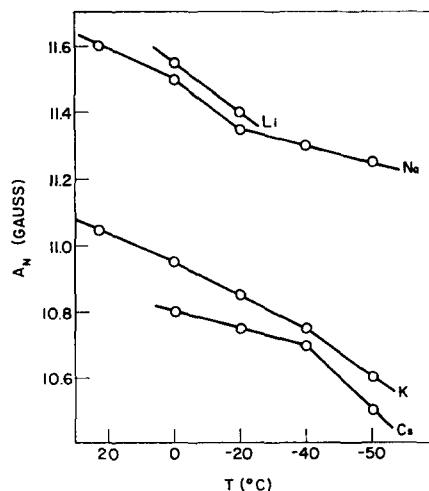


FIG. 3. Nitrogen hyperfine splitting (a_N) as a function of temperature (T) for the Li, Na, K, and Cs salts of nitrobenzene in DME.

¹⁵ N. Hirota and R. Kreilick, *J. Am. Chem. Soc.* **88**, 614 (1966).

¹⁶ N. Hirota, *J. Phys. Chem.* **71**, 127 (1967).

¹⁷ For all the radicals, there was a linear variation of linewidth across the ESR spectrum (the high-field lines being broader than those at low field), and this effect became more pronounced as the temperature was decreased.

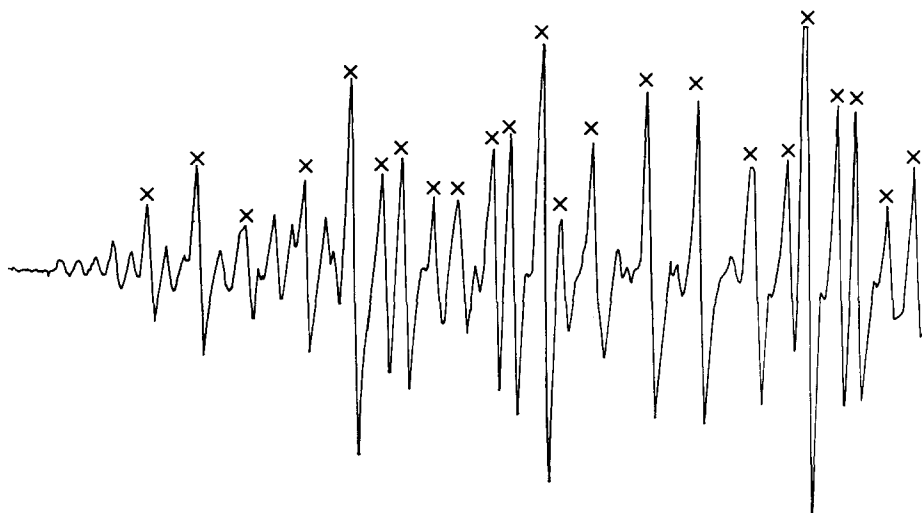


FIG. 4. Electron spin resonance derivative spectrum of the sodium salt of nitrobenzene in a 50 volume percent mixture of DME and DMSO at 23°C. Two radical species—the ion pair and the free ion—are observed, and the lines in spectrum attributed to the free ion are labeled with a cross (×). Low-field half of the spectrum is shown.

The magnitude of the metal splittings and their variation with temperature have been used in an attempt to answer these questions about ion pairs. As far as the temperature variation of the alkali-metal splitting is concerned, it appears that two different explanations have been proposed. One explanation offered by Atherton and Weissman,¹⁸ and used by several authors,¹⁹ is based on a model in which the anion and the cation form a contact ion pair and an increase or decrease of the metal splitting with decrease of temperature is attributed to a decrease of motion of the cation with respect to the anion, the cation settling down in either a region of high or low spin density.

Hirota¹⁶ has proposed a model involving a rapid equilibrium between an intimate ion pair and a more loosely associated ion pair, the loosely associated ion pair favored at low temperatures so that the metal splitting decreases with decreasing temperature.

In the case of nitrobenzene anion alkali-metal cation, ion pairs, Observation (1) above for Na⁺, K⁺, and Cs⁺ is consistent with the rapid equilibrium model of Hirota. The results with Li⁺, Observation (2), would be anomalous on the basis of this model. However, the absence of any observable linewidth effects associated with motion of the alkali-metal cation, Observation (4), under a variety of conditions, is difficult to reconcile with an equilibrium-type model. One might expect to see evidence of slow equilibrium and hence line broadening under some set of conditions if a model involving distinct species was appropriate. Moreover, Observation (3), obtained in the mixed solvent system is extremely difficult to reconcile with the Hirota model of a rapid

equilibrium between a loosely bound and a tightly bound ion pair or a "pulling off" mechanism proposed by Symons⁴ in which at low temperatures, increased solvation of the cation is assumed to cause a reduction in the strength of the interaction between anion and cation. On the basis of either of these models, we would expect that addition of DMSO to the ion pair in DME, which favors dissociation and shifts the equilibrium between ion pair and free ion toward the free ion, would cause a decrease of the sodium splitting of the ion pair.²⁰

The fact that the sodium splitting remains constant on addition of DMSO implies to us that the cation must be bound quite tightly to the nitro group and that a fairly strong bound cage of DME molecules solvates the nitro group-cation complex.

We then propose to explain the temperature variation of the alkali-metal, nitrogen, and *para* proton splittings on the basis of a decrease in vibration motion of the cation in the vicinity of the nitro group. If there is a fairly strongly bound cage solvent molecules around the nitro-group-cation complex, one cannot speak of motion of the cation with respect to the nitro group without involving this solvent cage as well. Thus a decrease in motion of the cation can cause an effective contraction of the solvent cage and a reduction of the perturbation of nitro group while the cation is still closely and strongly bound to the nitro group. The different behavior of Li⁺ from Na⁺, K⁺, or Cs⁺, Observation (2), can be rationalized on the basis of the small size of Li⁺ which allows it to be in more direct contact with all three atoms of the nitro group.

In conclusion, we feel that the potential well caused

¹⁸ N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.* **83**, 1330 (1961).

¹⁹ E. De Boer and E. Mackor, *J. Am. Chem. Soc.* **86**, 1513 (1964); H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *J. Chem. Phys.* **40**, 241 (1964); J. Dos Santos Veiga, and A. F. Nerva-Correia, *Mol. Phys.* **9**, 395 (1965).

²⁰ Gough and Symons found in mixtures of *t*-pentanol and *i*-propanol, a decrease in the sodium splitting of the durosemi-quinone-sodium ion pair as the polarity of the solvent system was increased by increasing the proportion of *i*-propanol. T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.* **62**, 269 (1966).

TABLE II. Calculated and experimental spin densities.

	ρ_o or $\Delta\rho_o$	ρ_m or $\Delta\rho_m$	ρ_p or $\Delta\rho_p$	a_N or Δa_N (G)
Free ion experimental ^a	0.149	-0.047	0.181	10.15
Free ion calculated ^b	0.146	-0.048	0.182	9.92
Δ experimental ^c	0.001	0.000	-0.009	1.45
Δ calculated ^c	0.001	-0.001	-0.009	1.81

^a Experimental spin densities for the free ion in DME using $a = -Q\rho$ and $Q = 23.7$.

^b Calculated spin densities and nitrogen splitting for the free ion. See text.

^c Δ refers to the value of the quantity in the sodium salt minus the value for the free ion.

by the nitro group and the solvent cage traps the alkali-metal cation in close contact with the nitro group and that this well is deep enough to consider the system tightly bound but broad enough to allow considerable cation motion. This view of the ion pair is not essentially different from that of Atherton and Weissman¹⁸ if one includes the effect of the solvent around the ion pairs and, for nitrobenzene salts, we feel it is preferable to the rapid equilibrium model of Hirota.

If one observes line-broadening effects associated with the alkali-metal cation, or observable evidence of two species, then the Hirota model¹⁶ of an equilibrium between two distinct species is reasonable, but if all evidence points to a tightly bound ion pair and for a given ion pair a rapid equilibrium between the species must always be assumed then we feel that to postulate the existence of distinct species becomes somewhat artificial.

D. Calculation of Cation Perturbation

The formation of a nitrobenzene radical anion alkali-metal cation ion pair changes the spin density distribution in the radical as evidenced by the different hyperfine splitting constants in the metal salts and the free ion in DME. The nature of the ion pair (see Sec. III.C) makes it likely that the major perturbing influence of the alkali-metal cation is an electrostatic interaction of the cation with the nitro group. The perturbation of the spin density on the nitro group is then transmitted to the ring. Using this model we have attempted to calculate the changes in spin density distribution on ion-pair formation by an extension of a method proposed by Gendell *et al.*²¹ and used by Rieger and Fraenkel²² to explain solvent effects in radicals containing nitro groups.

Spin densities were calculated using Huckel LCAO theory including McLachlan's²³ procedure for approximately treating configuration interaction. Hyperfine splittings were related to spin densities by using a

²¹ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962).

²² P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.* **39**, 609 (1963).

²³ A. D. McLachlan, *Mol. Phys.* **3**, 233 (1960).

Q of 23.7 in the McConnell relationship $a = -Q\rho$ for the protons and the expression $a_N = 99\rho_N^\pi - 71.6\rho_O^\pi$ which Rieger and Fraenkel²² proposed on the basis of a semiempirical correlation of many nitro-group nitrogen splitting constants. Coulomb and resonance integral parameters for the nitro group were adjusted to give a good fit to the splitting constants for the free ion in DME. The values used were $\delta_O = 1.40$, $\delta_N = 2.05$, and $\gamma_{CN} = 1.20$ ²⁴.

The presumed electrostatic interaction of the nitro group with the alkali-metal cation was then simulated in the calculation by increasing the Coulomb integral parameter of *both* the oxygen and the nitrogen atoms. In previous treatments of this kind, which attempted to explain solvent effects in radicals containing nitro groups, the effect of changing to a more polar and more hydrogen-bonding solvent was simulated by increasing only δ_O and in general this adequately reproduced the trends in the changes of splitting^{22,25}.

In the case of the ion pair, however, we believe that the electrostatic perturbation of the nitro group by the alkali-metal cation is of a more general nature and that it is not unreasonable to suppose that both δ_O and δ_N should be increased on ion-pair formation. We therefore attempted to fit the changes in splitting on going from the free ion in DME to the sodium salt, at room temperature, on this basis. The results in Table II show very good agreement between experimental and theoretical changes when δ_O is increased by 0.10 and δ_N increased by 0.05.

Gulick and Geske²⁶ have made measurements of the O^{17} hyperfine splitting in nitrobenzene radicals in DMF, DMF-H₂O mixtures and in 0.1 *M* NaNO₃ in DMF. The effect of adding the sodium salt was to increase a_O by 0.10 G and to increase a_N by 1.13 G. Gulick and Geske argued that if one uses the model proposed by Rieger and Fraenkel²² in which the effect of more polar solvents is simulated by an increase in the oxygen Coulomb integral then, since $|a_O|$ increases while ρ_O^π is calculated to decrease, one must describe a_O by an expression of the form $a_O = Q_1\rho_O^\pi + Q_2\rho_N^\pi$. However, if the perturbation of the nitro group is simulated by an increase in both oxygen and nitrogen Coulomb parameters then ρ_O^π is calculated to increase. For example, with the parameter changes used above, the calculated increase in ρ_O^π on going from the free ion to the sodium salt is 0.0025. If one does not include the term involving Q_2 in the expression for a_O then, from Gulick and Geske's determination of a_O in DMF (8.84 G) and the value of ρ_O^π in DMF (0.1988) calculated by Rieger and Fraenkel, we obtain a Q_1 of 44.5. Using this value for Q_1 , if $\Delta\rho_O^\pi$ is 0.0025, then an increase of 0.11 G in the ^{17}O splitting is predicted on going

²⁴ The parameters used for the nitro group of the free ion in DME are very close to those used by Rieger and Fraenkel for a series of radicals containing nitro groups in DME. See Ref. 22.

²⁵ D. H. Levy and R. J. Myers, *J. Chem. Phys.* **42**, 3731 (1965).

²⁶ W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.* **87**, 4049 (1965).

TABLE III. Hyperfine splitting constants of *o*-dinitrobenzene in gauss.^a

	$T^{\circ}\text{C}$	$a_{\text{H}(3)}, a_{\text{H}(6)}$	$a_{\text{H}(4)}, a_{\text{H}(5)}$	$a_{\text{N}(1)}, a_{\text{N}(2)}$	a_{cation}
Na salt-DME	23	0.81(1)	1.62(2)	4.05(5)	0.38(1)
Na salt-DMF ^b	-40	0.81(1)	1.62(2)	3.90(5)	0.20(1)
K salt-DME	23	0.62(2)	1.65(2)	3.60(5)	0.22(1)
K salt-DME	-60	0.62(2)	1.65(2)	3.40(5)	0.14(1)
Cs salt-DME	23	0.43(1)	1.64(2)	3.30(5)	3.30(5)
Cs salt-DME	-60	0.43(1)	1.64(2)	3.16(5)	2.73(5)
DME electrolysis ^c	23	0.21(1)	1.71(2)	2.79(4)	

^a The standard deviation assigned to a splitting constant is indicated by a number in parentheses following the splitting constant and referring to the last digit.

^b From Ref. 5.

^c From Ref. 3.

from the free ion in DME to the sodium salt. As the change in the nitrogen splitting on adding NaNO_3 to pure DMF (1.31 G) is close to the change on going from the free ion in DME to the sodium salt (1.45 G) we might expect that the changes in a_{O} in the two situations are comparable. Thus, since the calculated estimate of 0.11 G for the change in a_{O} is very close to the experimental value of 0.10 it may mean that the relationship $a_{\text{O}} = Q_1 \rho_{\text{O}}^*$ is sufficient to describe ^{17}O splitting constants and the term $Q_2 \rho_{\text{N}}^*$ may not be significant.

The formation of an ion pair between the nitro group and the alkali-metal cation can destroy the molecular plane of symmetry unless the cation is situated in the plane of the molecule. This effect could possibly be simulated in these calculations by a decrease in the resonance integral parameter γ_{CN} between the aromatic ring and the nitro group. Attempts to vary γ_{CN} did not yield results in agreement with experiment.²⁷ This does not exclude the possibility, however, that the interaction of the cation with the nitro group could give rise to a small tetrahedral distortion of the nitro group which would result in an increase of the nitrogen splitting.²⁸

IV. ALKALI-METAL SALTS OF *o*- AND *m*-DINITROBENZENE

A. Results

In Table III the hyperfine splitting constants for the Na, K, and Cs salts of *o*-dinitrobenzene at two temperatures (the highest and lowest temperatures for which data were obtained) and the splitting constants for the radical produced in DME by electrolytic reduction are given. The spectrum of the potassium salt at 0°C is reproduced in Fig. 5.

We previously reported the fact that in the cesium salt equivalent nitrogen splittings are observed, and

²⁷ Ludwig *et al.* studied the solvent effects on coupling constants in nitrobenzene anion and concluded that formation of a solvent complex does not produce a significant twisting of the nitro group. P. Ludwig, T. Layloff, and R. N. Adams, *J. Am. Chem. Soc.* **86**, 4568 (1964).

²⁸ D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.* **83**, 3532 (1961).

no linewidth effects associated with a slow motion of the cation from one nitro group to the other are detectable, while in the sodium salt at low temperatures line broadening due to a dynamical inequivalence of the nitro group occurs.³ The linewidth effects in the sodium salt have been discussed by Gendell.⁵ In the case of the potassium salt, at higher temperatures, the ESR spectra (see Fig. 5) show no significant line-broadening effects, but at -60°C line-broadening effects similar to those of the sodium salt are observed.

The spectrum at -60°C shows a peculiar pattern of well resolved (wr.) and poorly resolved (pr.) quartets. For each nitrogen quantum number M_{N} the nine quartets form a wr., pr., wr.; pr., wr., pr.; wr., pr., wr. sequence. The five outermost quartets labeled by quantum numbers ($M_{\text{H}_I}, M_{\text{H}_{II}}$) are shown in Fig. 6. Protons 3, 6 form set H_I and Protons 4, 5 form set H_{II} . If we assume that, as in the sodium salt, cation motion from one nitro group to the other causes $a_{\text{H}(3)}$ and $a_{\text{H}(6)}$ as well as $a_{\text{H}(4)}$ and $a_{\text{H}(5)}$ to be instantaneously inequivalent, and if we use the linewidth contributions for this model which have been calculated by Gendell,⁵ then the observed sequence of linewidth variations is predicted if $|a_{\text{H}(3)} - a_{\text{H}(6)}| \approx |a_{\text{H}(4)} - a_{\text{H}(5)}|$.

For in this case lines ($M_{\text{H}_I} = \pm 1, M_{\text{H}_{II}} = \pm 1$) are not broadened, lines with either M_{H_I} or $M_{\text{H}_{II}}$ zero are broadened, and line $M_{\text{H}_I} = M_{\text{H}_{II}} = 0$ is composed of two broad components which are not observed and two observable narrow components.

In all cases, even where other linewidth effects are observed, we detect no evidence for any linewidth variation dependent on alkali-metal quantum number for any of the *o*-dinitrobenzene salts.

In order to correlate the previous results which have been reported for *m*-dinitrobenzene salts with those of *o*-dinitrobenzene and nitrobenzene salts we briefly review some of the pertinent observations that have been made on the *m*-dinitrobenzene system.¹⁻⁴

In the sodium salt in DME, two different nitrogen splitting constants of 9.85 and 0.29 G³ are observed at room temperature and no linewidth effects associated with cation motion from one nitro group to the other are observed. The behavior of the potassium salt is similar to that of the sodium at low temperatures

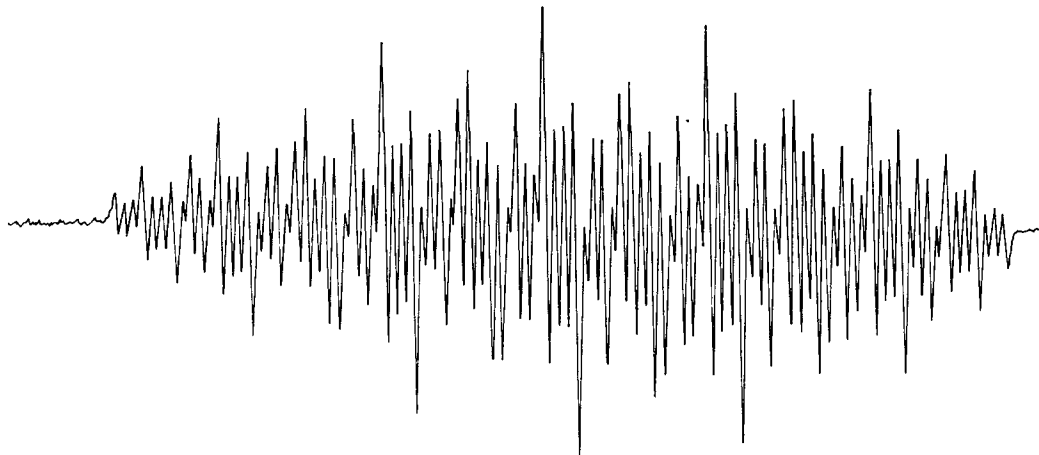


FIG. 5. Electron spin resonance derivative spectrum of the potassium salt of *o*-dinitrobenzene at 0°C in DME.

but at room temperature line broadening is observed which is taken as evidence for slow motion of the cation between nitro groups. The cesium salt at room temperature exhibits a pronounced alternating line-width effect associated with the nitrogen quantum number, which on the basis of the model in which the cation is associated with a single nitro group at a given instant of time implies considerable cation motion between nitro groups. At low temperatures, the rate of this motion is sufficiently reduced so that two different nitrogen splitting constants are observed.

The room-temperature values for the alkali-metal splittings of nitrobenzene, *o*-dinitrobenzene, and *m*-dinitrobenzene are given in Table IV. In the *m*-dinitrobenzene salts the temperature variation of the alkali-metal splittings as previously reported³ is very similar to that in the nitrobenzene and *o*-dinitrobenzene salts.

B. Correlation with Nitrobenzene Results

The changes with alkali-metal cation of a_N in *m*-dinitrobenzene and of a_N and $a_{H(3)}$, $a_{H(6)}$ in *o*-dinitrobenzene suggests that the perturbation of these radicals by the alkali-metal cation increases along the series Cs^+ to Na^+ , just as in the case of nitrobenzene.

The absence of any line-broadening effects associated with alkali-metal cation in cases where there is evidence of intramolecular motion of the cation implies that the cation is jumping between well-defined and equivalent sites. The data also reveal that there are similar changes with temperature for the alkali-metal and nitrogen splitting in nitrobenzene, *o*-dinitrobenzene

and *m*-dinitrobenzene. In addition, the magnitudes of the alkali-metal splittings (see Table IV) are approximately the same in all three cases. These observations suggest that the same type of tightly bound ion pair is present in *o*- and *m*-dinitrobenzene as in nitrobenzene that in the two dinitrobenzene compounds as well as in nitrobenzene the alkali-metal cation is intimately associated with a single nitro group and that the variations of splitting constants with temperature all have as a common cause the motion of the cation in the vicinity of the nitro group.²⁹

C. Cation Perturbation

If the alkali-metal cation in the *o*- and *m*-dinitrobenzene cases can be considered bound to a single nitro group at any instant of time, one might attempt to extend the previous calculation for the sodium salt of nitrobenzene to the dinitrobenzene salts by using the nitro group parameters found for the sodium salt for one nitro group and for the other nitro group the parameters appropriate for the free ion. This calculation for the sodium salt of *m*-dinitrobenzene gives two nitrogen splitting constants of 8.13 and 2.11 G. The experimental values are 9.85 and 0.29 G.³ Considering the crudeness of this approach the calculation

TABLE IV. Alkali-metal splitting constants of nitrobenzene and *o*- and *m*-dinitrobenzene in gauss at 23°C.

	Nitrobenzene	<i>o</i> -dinitrobenzene	<i>m</i> -dinitrobenzene
Na salt	0.40	0.38	0.29 ^a
K salt	0.23	0.22	0.21 ^a
Cs salt	2.95 ^b	3.30	2.46 ^a

^a From Ref. 3.

^b Value at 0°C.

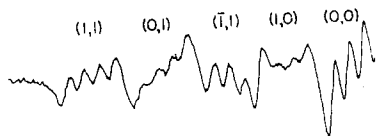


FIG. 6. Electron spin resonance derivative spectrum of the potassium salt of *o*-dinitrobenzene at -60°C in DME. Five outermost quartets, at low magnetic field, labeled by (M_{HI} , M_{HII}).

²⁹ Ward (see Refs. 1 and 2), on the basis of his observation of a single large nitrogen splitting in *m*-dinitrobenzene salts, considered the cation associated with one nitro group, but he observed equivalent nitrogens and no alkali-metal splittings in the case of *o*-dinitrobenzene salts.

seems to account for the major portion of the splitting changes on the basis of an electrostatic perturbation of a single nitro group. It is also to be noted that on the basis of this calculation the sodium cation is associated with the nitro group with the higher nitrogen splitting constant. Thus, association of the sodium cation with a nitro group effectively traps the unpaired electron on that nitro group.³⁰ This is consistent with the experimental observation of similar alkali-metal splittings for nitrobenzene and *m*- and *o*-dinitrobenzene. The conclusion that the unpaired electron density is higher on the nitro group with the associated cation is not an obvious consequence of the fact that two nitrogen splittings are observed in, for example, *m*-dinitrobenzene.

If association of the cation with the nitro group was such as to cause sufficient twisting of that nitro group out of the plane of the ring, the unpaired electron would localize more on the in-plane nitro group and hence the nitro group which *was not* associated with the alkali-metal would have the larger nitrogen splitting.³¹ The observation of similar alkali-metal splittings and changes with temperature for nitrobenzene, *o*- and *m*-dinitrobenzene seems to us to rule out this possibility.

Gendell⁵ previously postulated that the rather unusual linewidth variations in the sodium salt of *o*-dinitrobenzene was due to motion of the sodium cation from one nitro group to the other, causing modulation of all three isotropic hyperfine splittings. Two states, A and B due to the position of the cation, were assumed for 1,2-dinitrobenzene. In State A, nuclei 1,2,3,4,5,6 have splittings $a_1, a_2, a_3, a_4, a_5, a_6$, while in State B these nuclei have splittings $a_2, a_1, a_6, a_5, a_4, a_3$. In order to explain the cancellation of broadening effects for particular lines in the ESR spectrum it was necessary to assume that $|a_3 - a_6| \approx |a_4 - a_5|$ and that $|a_1 - a_2| \approx 2|a_3 - a_6|$.

We can estimate these differences in *o*-dinitrobenzene by a calculation similar to the one that was made for *m*-dinitrobenzene if we consider that the cation is associated with a single nitro group at a given instant of time. The result of this calculation is: $|a_3 - a_6| = 0.61$ G; $|a_4 - a_5| = 0.64$ G; and $|a_1 - a_2| = 2.40$ G. The calculation predicts $|a_4 - a_5| \approx |a_3 - a_6|$ but gives $|a_1 - a_2| \approx 4|a_3 - a_6|$. Considering the various approximations that have been made we conclude that this calculation shows that the relationships between the differences $|a_3 - a_6|$, $|a_4 - a_5|$, and $|a_1 - a_2|$ introduced as *ad hoc* assumptions by Gendell are not unreasonable for the model of a single nitro group perturbed by the

sodium cation at a given time and cation motion between nitro groups.

Although we have concluded that in the dinitrobenzene salts the cation is associated with a single nitro group at a given instant of time and this pulls the unpaired electron density onto that nitro group, the nitrogen splittings differ in nitrobenzene and *o*- and *m*-dinitrobenzene, implying somewhat different spin densities on the nitro group in the three cases. The observation that the alkali-metal splittings in nitrobenzene and *o*-dinitrobenzene salts are so close in magnitude is perhaps due to the fact that the size of the alkali-metal splitting is not an extremely sensitive function of the magnitude of the spin density on the nitro group because of a significant contribution to the alkali-metal splitting from an interaction with the nonbonded electrons of the oxygen atoms.³²

D. Cation Motion

The motion of the cation from one nitro group to the other in *o*- or *m*-dinitrobenzene causes modulation of the nitrogen splitting and line broadening. If we assume two states A, B, where in state A one nitro group has splitting a_N^A and the other a_N^B while in State B the splittings are reversed, then line broadening will be observed when $\Delta a_N \tau \approx 1$, where $\Delta a_N = |a_N^A - a_N^B|$ and τ is the lifetime of State A or B.

We have concluded on the basis of similar observations for nitrobenzene, and *o*- and *m*-dinitrobenzene salts that the perturbation of the nitro group decreases along the series Na^+ to Cs^+ and Δa_N should follow the same trend. In addition, the lifetime τ of the cation in the vicinity of a given nitro group will depend upon the barrier to hopping from one nitro group to the other and this in turn will be a function of the extent to which the cation perturbs the nitro group and polarizes the surrounding solvent cage. Thus we expect τ to decrease along the series Na^+ to Cs^+ as well. Hence the product $\Delta a_N \tau$ should exhibit the same behavior and we would expect increasing evidence of the breakdown of static inequivalence of the nitro groups as we go from Na^+ to Cs^+ . The observed line-broadening effects in the ESR spectra of both *o*- and *m*-dinitrobenzene alkali-metal salts are in complete accord with these expectations.

E. Correlation with Solvent Effects

The results for *o*-dinitrobenzene salts show that the proton triplet splitting $a_{H(3)}, a_{H(6)}$, changes radically with the nature of the cation and it also varies greatly with solvent.²² For all the ion pairs, however, there is no change of this splitting with temperature. Freed and Fraenkel³³ found, however, a substantial change in

³⁰ Ward (see Ref. 1) came to the same conclusion for *m*-dinitrobenzene ion pairs by considering valence-bond structures.

³¹ Geske *et al.* found in the anion radical of 2, 6-dimethyl-1, 4-dinitrobenzene that the nitrogen coupling constant for the flat nitro group was 5.66 G while that for the nitro group twisted out of the molecular plane was only 0.14 G. D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.* **86**, 987 (1964).

³² N. M. Atherton and A. E. Goggins, *Trans. Faraday Soc.* **62**, 1702 (1966).

³³ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **40**, 1815 (1964).

this splitting with temperature when the radical was prepared electrolytically in DMF. They suggested that a possible explanation for the temperature dependence was a change in the fluctuating solvent interactions. If this explanation is correct, then a absence of temperature variation in the case of the alkali-metal cation, ion pairs, supports the model of a tight ion pair with a surrounding solvent cage which insulates the radical from the fluctuating solvent interaction experienced by the free ion.

Ling and Gendell⁹ noted previously that the splittings for the cesium salt of *m*-dinitrobenzene in DME at room temperature are almost identical to those of *m*-dinitrobenzene produced electrolytically in acetonitrile. In the cesium salt we conclude there is rapid motion of the cation from one nitro group to the other and thus the observed splittings are an average of those for the two positions of the cation. The fact that the splittings in acetonitrile are identical to those of the cesium salt suggests that in acetonitrile, as well, the observed splittings result from an average over states in which the nitro groups are instantaneously inequivalent. This agrees with the argument of Rieger and Fraenkel²² who maintained that the spin density distribution in *m*-dinitrobenzene radicals cannot be treated by any static model but one must take into account fluctuating solvent interactions which make the two nitro groups instantaneously inequivalent.

V. CONCLUSIONS

On the basis of changes in hyperfine splittings of the anion which ensue on ion-pair formation, we conclude that in all of the alkali-metal salts of nitrobenzene, *o*-dinitrobenzene, and *m*-dinitrobenzene, which were observed, there is increased perturbation of the anion along the series Cs⁺ to Li⁺.

For a given alkali metal, similar magnitudes and similar variations with temperature of the metal hyperfine splittings were observed with all three anions, even though there is evidence of motion of the alkali-metal cation from one nitro group to the other in the dinitro salts. Throughout the temperature range which was used, line broadening depending on alkali-metal quantum number was not observed for any of the salts. In the case of the sodium salt of nitroben-

zene in mixtures of DME and DMSO, although addition of DMSO shifted the equilibrium between the ion-pair and free-ion species in favor of the free ion, the sodium splitting of the ion pair *did not* change.

On the basis of these observations we have postulated a model for the ion pair in DME, in which for all three anions, the cation interacts with a single nitro group at a given instant of time. The cation is considered to be tightly bound to the nitro groups, and in addition, a fairly strongly bound cage of DME molecules solvates the nitro-group-cation complex. The observed temperature variation of the alkali-metal splitting is attributed to motion of the cation with respect to the nitro group. This motion also involves the molecules of the DME solvent cage.

Line-broadening effects associated with cation motion from one nitro group to the other in the *o*- and *m*-dinitrobenzene salts depends upon the magnitude of $\Delta a_N \tau$, where Δa_N is the instantaneous difference between nitrogen splittings when the cation is associated with a given nitro group, and τ is the lifetime of this state. The change in line-broadening effects along the series Na⁺ to Cs⁺ have been correlated with the extent of the perturbation of the nitro group by the alkali-metal cation which changes the magnitudes of Δa_N and τ .

The similarities of alkali-metal splitting in the dinitro salts with those in nitrobenzene salts is taken as evidence that complexing of the cation with a nitro group traps the unpaired electron on that nitro group, and that the dominant effect of ion pairing is an electrostatic interaction of the cation with the nitro group. Twisting or bending of one nitro group out of the molecular plane, by interaction with the cation, would favor the localization of the unpaired electron on the other nitro group without the associated cation and this effect is therefore not considered to be significant.

Simple molecular-orbital calculations were performed in which the electrostatic interaction of the cation with the nitro group was simulated by increasing both the oxygen and nitrogen Coulomb integral parameters of the nitro group. Calculated and experimental changes of anion hyperfine splittings on going from the nitrobenzene free ion in DME to the sodium salt were in good agreement.