

Gibbs surface is placed so that the surface excess of water is zero. Equation A-2 can be substituted into the electrocapillary equation and integrated if x_g is assumed to be constant; this is likely to be true except in very concentrated solutions. The result is

$$\gamma^0 - \gamma = \frac{kT}{\epsilon} \int_{a_{\pm}=0}^{a_{\pm}} \eta_i^d d \ln a_{\pm}^2 + 2kTx_g n_{oi} \left\{ 1 + \int_0^{a_{\pm}} d \ln f_{\pm} \right\} \quad (\text{A-3})$$

where γ^0 is the interfacial tension between mercury and pure water. The first term on the right-hand side of (A-3) is the curve plotted in Fig. A-1. Apart from the activity correction which is not important, the second term on the right-hand side of (A-3) is proportional to the bulk concentration. A plot of the difference of the integrated curve and the interfacial tension from Fig. A-1 against concentration is approximately linear and leads to a value of x_g of about 2.5 Å. Since x_g may be expected to be about equal to the thickness of the outer Helmholtz layer, this value seems reasonable.

It is now necessary to discuss which location for the Gibbs surface is appropriate for the calculation of the amount of

specific adsorption which is the main object of the present paper. When the anion only of a binary electrolyte is specifically adsorbed, equation A-2 becomes

$$\epsilon\Gamma_+(w) = \eta_+^d - n_{oi} \epsilon x_g \quad (\text{A-4})$$

$$\epsilon\Gamma_-(w) = n^i + \eta^d - n_{oi} \epsilon x_g \quad (\text{A-5})$$

if it is assumed that the outer Helmholtz plane is at the same position for each ion. The simple theory of the diffuse layer permits the calculation of η_-^d from η_+^d , but if values of $\Gamma_+(w)$ and $\Gamma_-(w)$ are given, it is then only possible to calculate n^i , the amount of specific adsorption if a value of x_g can be found. On the other hand if the Gibbs surface is fixed at the outer Helmholtz plane, the surface excess of cations and anions is η_+^d and $n^i + \eta_-^d$, respectively, from which n^i is readily obtained. Consequently, it appears preferable for this purpose to fix the Gibbs surface at the outer Helmholtz plane as has been done so far in all calculations based on capacity measurements.

Finally it may be noted that the use of two different locations of the Gibbs surface may account for the discrepancies between the results of Iofa and Frumkin¹³ and those of ref. 5b.

(13) Z. A. Iofa and A. N. Frumkin, *Acta Physicochim. U.R.S.S.*, **10**, 473 (1939).

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An Electron Spin Resonance Study of Nitro Group-Alkali Metal Interactions in Aromatic Hydrocarbons¹

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The reaction of potassium and sodium with nitrobenzene, *o*-dinitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrobenzene, nitromesitylene, dinitromesitylene and trinitromesitylene in 1,2-dimethoxyethane (DME) has been carried out, and the resulting paramagnetic solutions studied using electron spin resonance techniques. The nitrogen hyperfine coupling constants have been determined for each molecule, while proton hyperfine coupling constants have been determined in a few cases. All polynitro compounds studied, except *o*-dinitrobenzene, possess only *one* nitrogen hyperfine interaction. This is in contrast to the results obtained in the electrolytic preparation of these free radicals by Maki and Geske who find two equal nitrogen coupling constants in each of the isomeric dinitrobenzenes. A comparison of the resulting hyperfine structure of the electrolytically and chemically produced free radicals is presented and a strong ion-pair theory proposed for the differences obtained.

In general, dilute solutions of free radicals exhibit a complex hyperfine structure, which is due to an isotropic hyperfine interaction² between the unpaired electron's magnetic moment and the various magnetic moments of nuclei present in the molecule. A detailed analysis of this complex hyperfine structure, usually by means of isotopic substitution, will yield coupling constants for the various magnetic nuclei, and these coupling constants then can be used as a sort of unpaired electron density map of the molecule. Anisotropic hyperfine interactions are, however, averaged to zero by molecular tumbling in solution,^{3a} and therefore the splittings observed must arise from the *s*-character of the odd electron at the nucleus in question.

In the planar aromatic hydrocarbon free radicals the isotropic hyperfine interaction at the position of the protons, which lie in the plane of the molecule, is due to a σ - π configuration interaction.^{3b-6} The magnitude of this hyperfine interaction, for

a given proton, is proportional to the unpaired electron density in the π -orbital of the contiguous carbon atom.⁷ In polyatomic free radicals such as nitrobenzene negative ion, which contain a heteroatom, there are two mechanisms whereby an isotropic hyperfine interaction may arise at the nitrogen atom. A σ - π configuration interaction may take place similar to that for protons and/or the spacial overlap of the P_z functions of the carbon and nitrogen atoms may produce appreciable odd electron density at the nitrogen. The former mechanism seems more plausible in a planar configuration with pure sp^2 hybridization, and the latter mechanism plausible in a non-planar configuration. In either case the hyperfine interaction observed is a measure of the *s*-character of the odd electron at the position of the nucleus in question.

Recent studies on the negative ions of nitrobenzene and the isomeric dinitrobenzenes have led to some very interesting results. The observed hyperfine spectrum for the potassium salt of *m*-dinitrobenzene dissolved in 1,2-dimethoxyethane (DME) exhibits a hyperfine interaction with all the protons in the molecule, but with only *one* of the two nitrogens.⁸ This is in great contrast

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(3) (a) S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954); (b) **25**, 890 (1956).

(4) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(5) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

(6) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(7) H. M. McConnell and D. Chestnut, *ibid.*, **28**, 107 (1958).

(8) R. L. Ward, *ibid.*, **32**, 410 (1960).

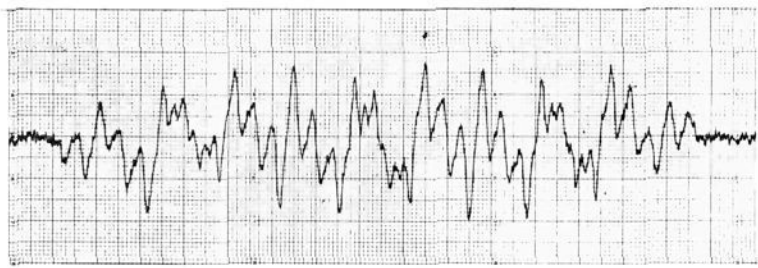


Fig. 1.— dx''/dH vs. H for the potassium salt of nitrobenzene in DME.

to the studies of Maki and Geske⁹ who recently reported two equal nitrogen hyperfine interactions for all the isomeric dinitrobenzene negative ions produced electrolytically in acetonitrile.

This article presents a further study of chemically produced aromatic negative ions containing nitro groups. Nitrobenzene negative ion^{10,11} has been re-examined and the coupling constants refined. Negative ions of *o*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrobenzene, nitromesitylene, dinitromesitylene and trinitromesitylene have been prepared in DME by chemical reduction with an alkali metal, their hyperfine spectra observed, and at least coupling constants for the nitrogens obtained. A comparison with the electrogenerated negative ions will be made and reasons for differences and similarities in the two will be presented.

Experimental

The method of chemically preparing an aromatic negative ion has been thoroughly discussed elsewhere.¹² It is important, however, to stress a few salient points about this procedure. The solvent, usually 1,2-dimethoxyethane (DME) or tetrahydrofuran, is vigorously dried over sodium-potassium alloy until a characteristic blue color is formed in the solvent at Dry Ice-Cellosolve temperatures. The solvent is kept over the sodium-potassium alloy until it is to be used. The reaction vessel, for the preparation of the negative ion, is prepared from new glass each time. The vessel is rinsed with alcohol, evacuated on a vacuum line, flamed out thoroughly with a torch and tested for air leaks before it is used. The alkali metal, used in the reaction, is purified by sublimation until it exhibits mirror-like characteristics. The solvent is distilled into the reaction vessel *in vacuo*, frozen with liquid nitrogen and sealed off. This procedure definitely eliminates the presence of oxygen or water. The reaction between the aromatic compound dissolved in the solvent and the alkali metal is carried out at room temperature or at -70° depending on the substance to be reduced. All samples used in the preparation of the negative ions were recrystallized and dried by pumping.

The electron spin resonance spectrometer used in these experiments is one of conventional design operating at 9300 Mc./sec. All the spectra presented, with the exception of trinitromesitylene negative ion, were observed with a 250 Kc./sec. field modulation and a synchronous detector. The negative ions, which were stable only at low temperatures, were cooled, while observing the resonance, by using a conventional gas-flow technique.

All spectra presented were recorded as the derivative of the absorption as a function of the magnetic field. Each spectrum was calibrated with an auxiliary proton resonance probe as the spectrum was being recorded. The splittings observed were obtained by measuring distances between the maximum of different peaks.

Results

Nitrobenzene.—This negative ion has been investigated^{10,11} previously using nitrogen-15 and

(9) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

(10) R. L. Ward and M. P. Klein, *ibid.*, **28**, 518 (1958).

(11) R. L. Ward, *ibid.*, **30**, 852 (1959).

(12) D. E. Paul, D. Lipkin and S. I. Weissman, *THIS JOURNAL*, **78**, 116 (1956).

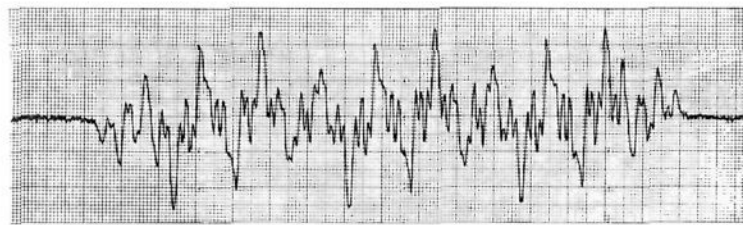


Fig. 2.— dx''/dH vs. H for the sodium salt of nitrobenzene in DME.

deuterium substitution. Lack of resolution, however, failed to yield a *meta* proton coupling constant or to show a difference in the *ortho* or *para* proton coupling constants. A better resolved spectrum of this negative ion, prepared with potassium in DME, appears in Fig. 1. A knowledge of the relative sizes of the coupling constants, from the isotopic species, allows an exact evaluation of these coupling constants. These values are

$$\begin{aligned} |A_N| &= 10.33 \text{ gauss} \\ |A_o| &= 3.46 \text{ gauss} \\ |A_m| &= 1.13 \text{ gauss} \\ |A_p| &= 3.86 \text{ gauss} \end{aligned}$$

where $|A_N|$ is the absolute value of the nitrogen coupling constant, and $|A_o|$ is the absolute value of the *ortho* proton coupling constant, etc. These values agree quite well with those of Geske and Maki,¹³ who prepared nitrobenzene negative ion electrolytically in acetonitrile.

The sodium salt of nitrobenzene negative ion, Fig. 2, however extends over 36.9 gauss compared to 33.7 gauss for the potassium salt. The sodium salt also exhibits at least 80 hyperfine components compared to the expected value of 54 for the unperturbed nitrobenzene negative ion. This additional structure in the sodium salt is attributed to an alkali metal hyperfine interaction similar to that observed in benzophenone negative ion in DME¹⁴ and naphthalene negative ion dissolved in tetrahydrofuran.¹⁵

***m*-Dinitrobenzene.**—The reaction between *m*-dinitrobenzene and potassium metal has been studied thoroughly and reported earlier.⁸ The observation of a single nitrogen hyperfine interaction in this alkali metal salt was indeed unexpected and led to further studies of the reaction between an alkali metal and aromatic hydrocarbons containing nitro groups. This single nitrogen hyperfine interaction of *m*-dinitrobenzene has been observed in the salts of Li, Na, K, Rb and Cs at room temperature. The potassium salt has been prepared and studied at temperatures between -70 and 40° with no change in the single nitrogen hyperfine interaction.

***p*-Dinitrobenzene.**—It has been observed that the reaction between potassium and *p*-dinitrobenzene dissolved in DME at -70° produces a green paramagnetic solution, while the reaction at room temperature produces a yellow non-paramagnetic solution. This same sequence is observed in the electrolytic generation of *p*-dinitrobenzene negative ion at room temperature when the electrolysis current is discontinued. The spectrum of the potassium salt appears in Fig. 3. Nitrogen-15

(13) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

(14) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

(15) S. I. Weissman, private communication.

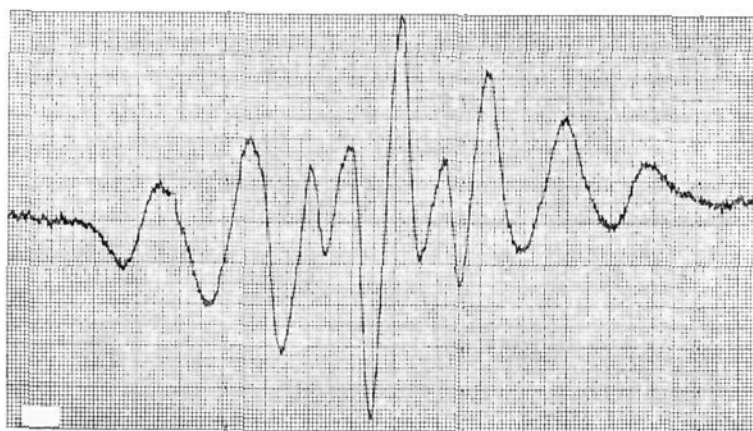


Fig. 3.— $-dx''/dH$ vs. H for the potassium salt of *p*-dinitrobenzene in DME.

has been substituted for one of the nitrogens in this molecule and its hyperfine spectrum also observed. The intensity distribution, number of lines observed and nitrogen-15 substitution indicate that the potassium salt of *p*-dinitrobenzene possesses one nitrogen hyperfine interaction and two equivalent proton hyperfine interactions. It is believed that the two protons *ortho* to the interacting nitrogen yield the coupling constants observed. These coupling constants are

$$\begin{aligned} |A_N| &= 4.5 \text{ gauss} \\ |A_P| &= 2.3 \text{ gauss} \end{aligned}$$

The total spread of the pattern is 13.3 gauss. It was necessary to use a fairly large value of field modulation amplitude to observe the spectrum in Fig. 3, and therefore it is possible that a small *meta* proton hyperfine interaction has not been observed.

***o*-Dinitrobenzene.**—This negative ion has been prepared with potassium in DME at room temperature and its hyperfine pattern appears in Fig. 4. This spectrum is comparable to the one reported by Maki and Geske,⁹ which exhibits *two* equal nitrogen hyperfine interactions of 3.2 gauss. This hyperfine pattern extends over 17 gauss.

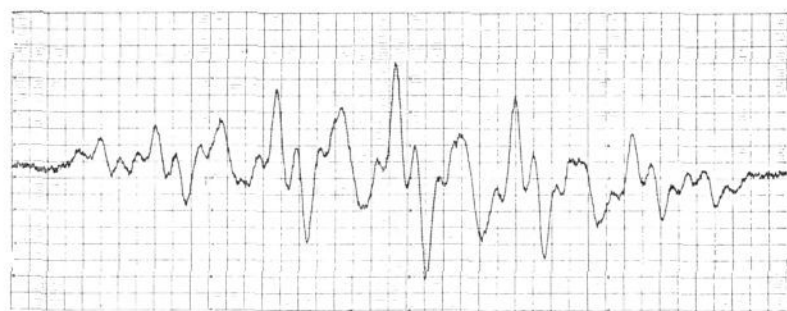


Fig. 4.— $-dx''/dH$ vs. H for the potassium salt of *o*-dinitrobenzene in DME.

***sym*-Trinitrobenzene.**—This negative ion has been prepared with both potassium and sodium metal in DME. The sodium salt, whose spectrum appears in Fig. 5, is more stable and was chosen for this study. Nitrogen-15 and deuterium substitution have been performed in this molecule and the corresponding negative ions prepared. There is only *one* nitrogen hyperfine interaction of 7.0 gauss and three equivalent proton interactions of 4.1 gauss. The pattern extends over approximately 26.4 gauss. A fairly large value of field modulation also was required for this spectrum and therefore small differences in the proton

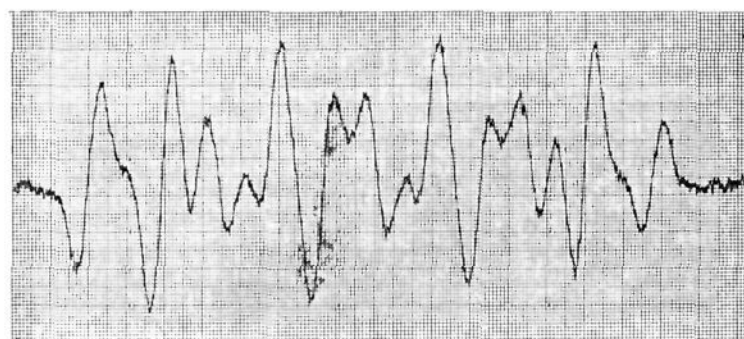


Fig. 5.— $-dx''/dH$ vs. H for the sodium salt of *sym*-trinitrobenzene in DME.

coupling constants or a possible alkali metal splitting may not have been observed.

Nitromesitylenes.—As noted in reference 8, nitro-, dinitro- and trinitromesitylene react with potassium in DME to yield a rich hyperfine pattern. Trinitromesitylene, Fig. 6, yields a basic triplet with each triplet split into ten lines. This

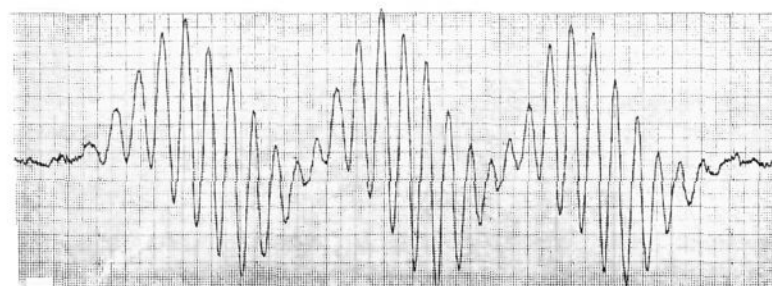


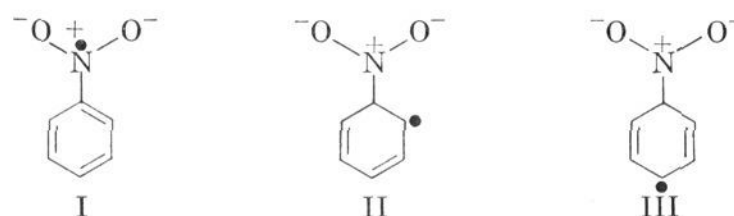
Fig. 6.— $-dx''/dH$ vs. H for the potassium salt of trinitromesitylene in DME.

spectrum is attributed to one nitrogen hyperfine interaction and nine equivalent proton interactions. The other two nitro-mesitylenes each exhibit one nitrogen interaction. The spectra, in each case, exhibit a sufficient number of lines that all the protons must be included to interpret the results. The single nitrogen coupling constants for trinitro-, dinitro- and nitromesitylene negative ions are, respectively

$$\begin{aligned} |A_N| &= 12.6 \text{ gauss} \\ |A_N| &= 14.6 \text{ gauss} \\ |A_N| &= 16.5 \text{ gauss} \end{aligned}$$

Discussion

The spectra observed from the chemically and electrolytically produced nitrobenzene negative ion agree quite well and yield essentially the same coupling constants. The values observed are in good agreement with a valence-bond picture of the molecule using the canonical structures as was



pointed out by Geske and Maki.¹³ The hyperfine interaction with the nitrogen atom arises from the contribution of structure I, while the hyperfine interactions with the *ortho* and *para* protons arise from the contribution of structures II and III. Cross terms of the bond eigenfunctions for structures II and III yield a nonvanishing electron density at the *meta* carbons and therefore

a *meta* proton hyperfine interaction.^{16,17} The agreement of the spectra of the chemically and electrolytically produced nitrobenzene negative ions is indeed gratifying. The difference obtained, however, for the isomeric dinitrobenzenes is interesting and requires further comparison and discussion.

The electrolytic method of preparation of free radicals is a skillful combination of the techniques of polarography and electron spin resonance spectroscopy. This method definitely has some advantages over chemically produced free radicals. A controlled potential for the reduction or oxidation may be used at all times, and a continuous generation of free radicals is possible while the spectrum is being recorded. The possible interference of a small positive ion can also be removed by using a solution of high dielectric constant with a rather large "bulky" supporting electrolyte, e.g., tetra-*n*-propylammonium perchlorate.

Alkali metal reactions with aromatic hydrocarbons, however, have been a fruitful field of study,¹⁸⁻²² and the differences in the resulting spectra from the two techniques are usually insignificant. A few definite examples of a positive ion influence do exist,^{14,15} however, and their study leads to valuable information concerning the identity of the species in solution.

We therefore will attempt to explain the differences in the spectra of the electrogenerated and chemically produced dinitrobenzene negative ions by a comparison of the species existing in solution. It is believed by the author that the results of Maki and Geske are due to an essentially "unperturbed" dinitrobenzene negative ion. The method of preparation and observed spectra, which are consistent with the symmetry of the parent dinitrobenzene, certainly substantiate these views. The aforementioned results on the chemically produced dinitrobenzene negative ions are, however, believed to be due to a chemical complex formation and not to a chemical change of the parent dinitrobenzene. The following arguments, it is hoped, will support this view.

The observation that a definite alkali metal splitting exists in a solution of naphthalene negative ion dissolved in tetrahydrofuran¹⁵ indicates that a very tight ion-pair complex must exist in these solutions of fairly small dielectric constant. A more polar substance than naphthalene would therefore be expected to exhibit an alkali metal splitting more readily as, indeed, is the case with benzophenone and nitrobenzene negative ions.

We assume, therefore, that the existence of a complex between the alkali metal and the nitro-containing hydrocarbon has been substantiated. A set of canonical resonance structures for the

(16) P. Brovotto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

(17) H. M. McConnell, *J. Chem. Phys.*, **29**, 244 (1958); **30**, 328 (1959).

(18) D. Lipkin, D. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

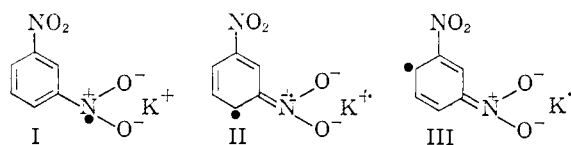
(19) R. L. Ward and S. I. Weissman, *THIS JOURNAL*, **79**, 2086 (1957).

(20) T. R. Tuttle, Jr., R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

(21) T. R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **25**, 189 (1956).

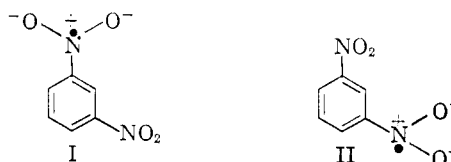
(22) E. de Boer and S. I. Weissman, *THIS JOURNAL*, **30**, 4549 (1958).

potassium salt of *m*-dinitrobenzene would therefore be



These structures will yield the observed coupling constants. Structure I will lead to a single nitrogen hyperfine interaction, while structures II and III will yield proton hyperfine interactions at the *ortho* and *para* positions. Again the cross terms between the bond eigenfunctions of II and III yield an odd electron density at the *meta* carbon and through σ - π configuration interaction a proton splitting. This splitting is actually observed. The equivalence of the two nitrogens in the unperturbed dinitrobenzene negative ion is completely removed by the formation of this complex. The reasons, however, for a complete lack of a second nitrogen hyperfine interaction are unknown at this time. The set of structures where the odd electron resides on the nitro group, which is not complexed by the alkali metal, is of higher energy and apparently does not contribute.

In the case of the electrolytically produced *m*-dinitrobenzene negative ion there is no difference between the two structures, *i.e.*, covering operations



of the parent molecule will convert one form into the other, and therefore the two nitrogens are identical. This symmetry property is possessed by all the isomeric dinitrobenzene negative ions produced electrolytically.

The aforementioned complex formation and appropriate canonical structures can explain the spectra observed for *m*-dinitrobenzene, *sym*-trinitrobenzene and the nitromesitylene negative ions. The reasoning in the *p*-dinitrobenzene case is identical for the lack of equivalence of the two nitrogens. Reasons for the complete lack of a second nitrogen splitting are again lacking. The lack of *m*-proton splitting may be due to the large value of sweep modulation use as mentioned in the section on results.

The agreement of the *o*-dinitrobenzene negative ion spectra, helps to substantiate this "tight-complex" theory. The two nitro groups are close enough together that the alkali metal tends to be complexed by both nitro groups.

A question that might arise in this interpretation is—if a tight complex exists and an alkali metal splitting is observed in certain cases, then why are the coupling constants the same for those negative ions whose spectra do agree? In the case of the sodium salt of naphthalene in tetrahydrofuran, it has been observed that the alkali metal splitting is continuously variable and decreasing with decreasing temperature, whereas the proton splittings

are essentially independent of this temperature change and the change in the alkali metal splitting.¹⁵ This would therefore explain the agreement of the spectra even though a tight complex has been formed.

The question also arose as to whether a chemical reaction had taken place, such as a reduction of a nitro group. This seems implausible, first, because of the equivalence of the nitrobenzene negative ion hyperfine spectra, regardless of the method

of preparation and secondly because the complete lack of any hyperfine interaction at the position of the non-interacting nitro group does not indicate that any change of the nitro group has taken place.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

Nuclear Magnetic Resonance Spectra of Acrylonitrile and Mono-methyl Substituted Acrylonitriles¹

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Complete analyses of the n.m.r. spectra of acrylonitrile and all the three monomethyl substituted products, *i.e.*, α -methacrylonitrile and *cis*- and *trans*-crotonitriles, were carried out and the shifts and coupling constants obtained at infinite dilution in tetramethylsilane which also served as an internal reference. The spectrum of acrylonitrile was very complicated and has been solved by preparing and analyzing the spectrum of α -D-acrylonitrile as an ABX system and converting the H-D couplings into H-H coupling by the factor of 6.5. The isotope effect both in coupling constants and resonance frequencies is within the limits observed by Gutowsky.^{2a} The fact that the α -proton in acrylonitrile comes at higher field than the β -protons has been explained by estimating the diamagnetic anisotropic shielding due to the C \equiv N group on all the protons and making the corresponding corrections in their shifts. A linear relationship between the shifts of *cis*- and *trans*-

protons in the series $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{X} \end{array}$ and the group dipole moment of X, with X = H, CH₃, C₆H₅, CN, Cl and OCH₃, was obtained only after making anisotropic corrections in H₂C=CHCN and H₂C=CHC₆H₅ due to C \equiv N and C₆H₅ groups, respectively.

Experimental

All the spectra were obtained at 21° on a Varian Model 4300B High Resolution Spectrometer equipped with a Flux Stabiliser operating at 40 mc./sec. Spinning 5 mm o.d. Pyrex glass sample tubes were used and the solvent in all the cases was tetramethylsilane purified by distilling over concentrated sulfuric acid to remove the traces of diethyl ether. Calibrations were done by the side band technique, using a Krohn-Hite Model 440B Push-Button Oscillator and Hewlett-Packard Model 522B frequency counter, with tetramethylsilane solvent as internal reference. A commercial sample of α -methacrylonitrile was fractionated and the portion boiling between 89 and 90°, which did not show any impurities in its n.m.r. spectrum, was used. *cis*- and *trans*-crotonitriles were obtained by separating a 70:30 *cis* to *trans* commercial mixture by gas chromatography using a Carbowax 20 M column at 100°. The acrylonitrile used was a commercial sample purified by distillation, the fraction boiling at 78 \pm 0.5° being used. α -D-acrylonitrile was prepared by treating acrylonitrile with D₂O in presence of pure CaCl₂.²

All the frequencies are expressed in cycles per second with respect to the TMS solvent as internal reference. The coupling constants are given directly in c.p.s. The reproducibility in the calibrations of the frequencies is within \pm 0.2 c.p.s. An uncertainty of \pm 0.1 c.p.s. in the coupling constants is allowed. However, a margin of \pm 0.5 c.p.s. should be left in the frequencies at infinite dilution obtained by extrapolation.

Analysis.—The analyses of the spectra of the three monomethyl substituted acrylonitriles, α -methacrylonitrile and *cis*- and *trans*-crotonitriles, were straightforward. These molecules constitute five-spin ABX₃ systems and their complete 32 \times 32 matrices can be factored into submatrices, the largest of which is a 10 \times 10 block, utilizing the eigen-

values of the total spin angular momentum. Assuming free rotation and using the symmetry properties of the methyl group around the C-C bond, further reduction in the size of the matrices was made possible leaving sixteen unconnected elements and eight 2 \times 2 blocks, of which four are degenerate and in each case the off diagonal element is $\frac{1}{2}J_{AB}$. It was thus necessary to solve only quadratic equations to obtain the eigenvalues and eigenfunctions. In all these compounds there was no overlap of the spectra of different protons (there is some overlap in the vinyl proton spectra of α -methacrylonitrile; however, the protons can easily be identified) and the appearance of the spectra was essentially first order. Thus, there was no difficulty encountered in identifying the protons and obtaining initial values of the coupling constants and resonance frequencies. The methyl group spectra were at much higher fields than those of the vinyl protons and provided good initial values for all the H-CH₃ coupling constants, as the second order corrections are quite small in these cases.

The spectra of α -methacrylonitrile and *cis*- and *trans*-crotonitriles are shown in Figs. 1-3. Allowed transitions and the corresponding frequencies and intensities for the ABX₃ system were worked out by Whipple, *et al.*³ The agreement between the observed and calculated spectra, as shown in Tables I-III, is within the experimental uncertainty, estimated at \pm 0.2 c.p.s.

Acrylonitrile is a three-spin ABC system, the analysis of which has been reported previously.⁴ The complete 8 \times 8 matrix of this system consists of two 1 \times 1 and two 3 \times 3 blocks, with no further factorization possible because of lack of symmetry in the molecule. The coupling constants are large compared to the differences in the frequencies and hence reduction of the size of the matrix using perturbation methods is not possible. There are six unknowns: three frequencies and three coupling constants, hereafter referred to as ω 's and J 's. The observed spectrum is so compli-

(1) This research was supported in part by grants from the National Institutes of Health [Research Grant A-2397 (C2)] and Schering Corporation, Bloomfield, N. J.

(2) (a) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959). (b) L. C. Leitch, *Canad. J. Chem.*, **35**, 345 (1957).

(3) E. B. Whipple, J. H. Goldstein and Leon Mandell, *THIS JOURNAL*, **82**, 3010 (1960).

(4) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).