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Publication Date

1965

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AEC Contract No. W-7405-eng-48

Electron Spin Resonance Spectra of the Radical Anions of
Nitrosobenzene and Nitrobenzene in Liquid Ammonia

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ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS OF
NITROSOBENZENE AND NITROBENZENE IN LIQUID AMMONIA

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The ESR spectra of the nitrosobenzene (C_6H_5NO) and nitrobenzene ($C_6H_5NO_2$) radical anions prepared by electrolytic reduction¹ have been observed in liquid ammonia. The nitrosobenzene radical anion shows two ortho and two meta proton coupling constants which can be explained by simple theoretical models. The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.²

The observed spectrum of the reddish-brown nitrosobenzene radical anion is shown in Fig. 1a. This radical appears to be quite stable at $-78^\circ C$ in liquid ammonia solution, particularly compared to 1,3-butadiene.¹ The spectrum consists of 30 principal lines which are further split by small amounts. On the basis of the 30 principal lines one can readily determine the N^{14} , the single para proton, and average values for both the ortho and meta coupling constants. The larger value can be assigned to the ortho protons in analogy to nitrobenzene. The additional splittings can only be accounted for if it is assumed that nitrosobenzene has two ortho protons differing by 0.30 g. A similar difference for the meta protons of 0.18 g. can be determined from the intensity ratios within its triplets. The calculated spectrum in Fig. 1b shows the excellent agreement with experiment for the constants in Table I.

The two ortho and two meta coupling constants must arise from the effects of a non-linear C-N-O group. This group must be held fairly

rigidly in a planar conformation. This is similar to the case of nitrobenzene, but the symmetry of nitrobenzene does not allow us to determine directly the effects of the N-O bond on the coupling of the ring protons.

A theoretical interpretation of this effect can be included in a Hückel LCAO molecular orbital calculation of the spin densities in either of two ways. One can either utilize a small resonance integral between the oxygen and the nearby ortho carbon, (between positions 1 and 8) or describe the polarization effects of the nitroso group by changing the Coulomb integral of one ortho carbon atom. Rieger and Fraenkel³ used the latter method and Stone and Maki⁴ used both methods to account for similar asymmetries in substituted benzaldehydes. Stone and Maki referred to these as the β and α effects respectively. If one uses the approximate configuration treatment of McLachlan⁵ with the parameters recommended by Rieger and Fraenkel² but with $\delta_{\dot{N}} = 1/3 \delta_{\ddot{N}}$ ⁶ and with $\gamma_{18} = 0.05$ or $\delta_8 = -0.07$, then one obtains the theoretical proton coupling constants given for nitrosobenzene in Table I.

It can be seen from Table I that either a small value for the resonance integral between the oxygen and its nearby ortho carbon or a small change in the nearby ortho carbon Coulomb integral yields a satisfactory explanation of the two ortho and meta coupling constants. As previously observed,⁴ these two effects are seen to work in opposite directions and we are unable to distinguish between them. An arbitrary adjustment of parameters can improve the agreement with the values in Table I particularly for the para position, but the purpose of our calculation was to use only one completely adjustable parameter (γ_{18} or δ_8) to explain the two ortho and meta coupling constants.

In Table I we also give our observed values for the radical anion

of nitrobenzene in liquid ammonia. The radical anion was prepared by the electrolytic reduction of a $5 \times 10^{-3} M$ solution 0.1M in sodium iodide. The spectrum was independent of temperature from -40 to $-78^\circ C$. The values in parenthesis are for nitrobenzene dissolved in methylformamide,² acetonitrile,⁷ and 50% water in acetonitrile,⁸ respectively. It can be seen from Table I that the solvent shift for nitrobenzene in liquid ammonia is intermediate between acetonitrile and 50% water in acetonitrile. Ludwig et al.⁶ have recently related the large solvent shifts for nitrobenzene radical anion to the formation of hydrogen bonds with the solvent. Since acetonitrile and liquid ammonia have essentially the same dielectric constants the shift cannot be explained entirely by the simple polarity of the solvent. Since liquid ammonia is a more protic solvent than is acetonitrile its position in the solvent shifts in Table I is consistent with some type of hydrogen bonding. However, it can also be seen from Table I that the calculation of Rieger and Fraenkel² which is based upon a variable oxygen Coulomb integral is a very satisfactory qualitative interpretation of the shift in the nitrogen and proton coupling constants in a wide variety of solvents.

This work was performed under the auspices of the United States Atomic Energy Commission.

Table I

Coupling Constants for Nitrosobenzene and Nitrobenzene Radical Anions^a

Position	Nitrosobenzene		Nitrobenzene	
	Obs. ^b	Cal. ^c	Obs. ^f	
		β effect ^d	α effect ^e	
Nitrogen-2	7.97	-	-	11.46(9.70, 10.32, 13.59)
Para H-6	2.97	4.43	4.54	3.89(4.03, 3.97, 3.54)
Ortho H-4	3.84	3.68	4.02	3.42(3.36, 3.39, 3.44)
-8	4.14	4.03	3.67	
Meta H-5	0.96	1.08	1.22	1.11(1.07, 1.09, 1.12)
-7	1.14	1.22	1.06	

^a Absolute magnitudes in gauss.

^b Bracketed values may be interchanged.

^c Calculated with $\delta_O = 1.4$, $\delta_N = 0.733$, $\gamma_{NO} = 1.67$, $\gamma_{CN} = 1.2$, and $Q_{CH} = 23.7$. The meta positions have negative spin density.

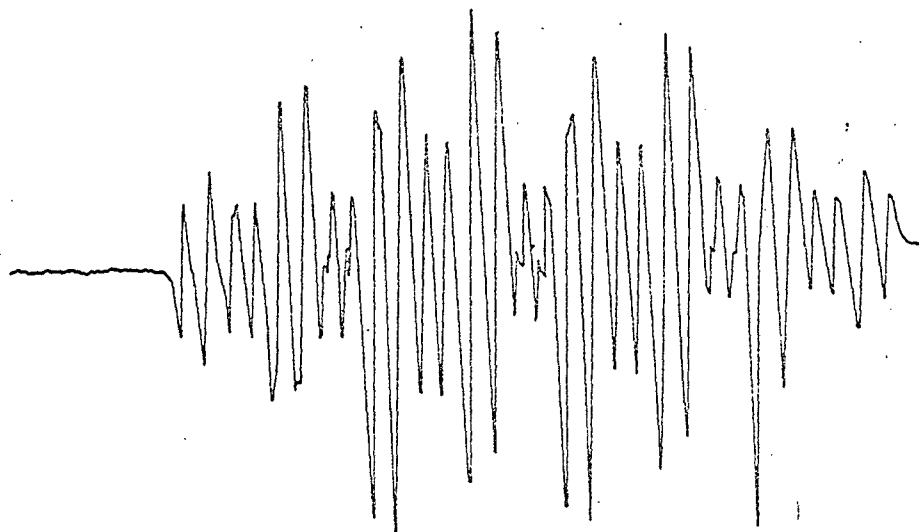
^d Using $\gamma_{CO} = 0.05$ between positions 1 and 8. $\rho_1 = 0.2629$, $\rho_2 = 0.3138$, $\rho_3 = 0.0086$.

^e Using $\delta_8 = -0.07$. $\rho_1 = 0.2652$, $\rho_2 = 0.3121$, $\rho_3 = 0.0026$

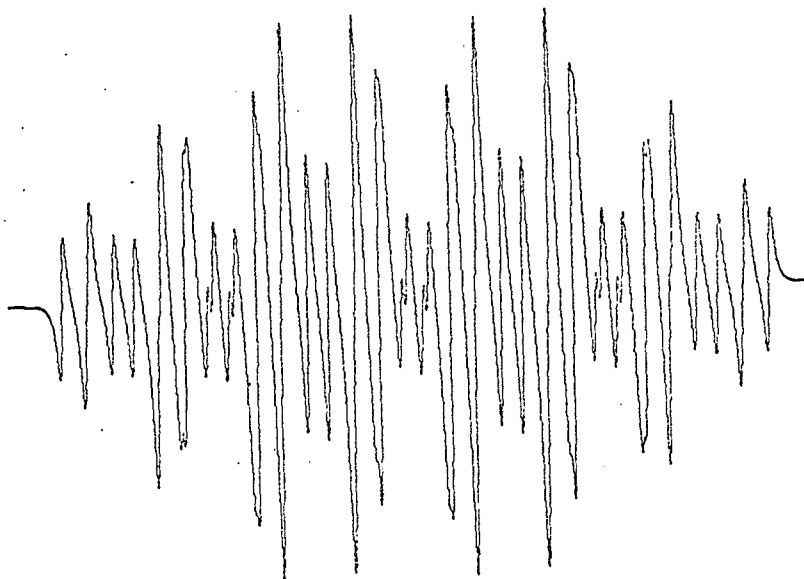
^f Our value in liquid ammonia followed by dimethylformamide (ref. 2), acetonitrile (ref. 7) and 50% water in acetonitrile (ref. 8), respectively.

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(a)



(b)

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