

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

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

### Permalink

<https://escholarship.org/uc/item/12p7h22r>

### Authors

Levy, Donald H.

Myers, Rollie J.

### Publication Date

1964-12-01

**University of California**  
**Ernest O. Lawrence**  
**Radiation Laboratory**

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

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

**Berkeley, California**

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted for publi. in J. of Chem.  
Physics.

UCRL-16060

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

Contract No. W-7405-eng-48

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

Donald H. Levy and Rollie J. Myers

December, 1964

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

Donald H. Levy and Rollie J. Myers

Inorganic Materials Research Division,  
Lawrence Radiation Laboratory and  
Department of Chemistry, College of Chemistry,  
University of California, Berkeley, California

The e.s.r. spectra of the nitrosobenzene ( $C_6H_5NO$ ) and nitrobenzene ( $C_6H_5NO_2$ ) radical anions have been observed in liquid ammonia by means of electrolytic reduction.<sup>1</sup> The nitrosobenzene radical anion shows a doubling of the ortho and meta proton coupling constants which can be explained by a simple theoretical model. The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.<sup>2</sup>

The observed spectrum of the reddish-brown nitrosobenzene radical anion is shown in Figure 1a. This radical appears to be quite stable at  $-78^\circ C$  in liquid ammonia solution, particularly compared to 1,3-butadiene.<sup>1</sup> 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 Figure 1b shows the excellent agreement with experiment for the constants in Table I.

The doubling of the ortho and 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 confirmation. 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 by utilizing a small resonance integral between the oxygen and the nearby ortho carbon (between positions 1 and 8). If one uses the approximate configuration treatment of McLachlin<sup>3</sup> with the parameters recommended by Reiger and Fraenkel<sup>2</sup> but with  $\delta\dot{N} = 1/3 \delta\ddot{N}$ <sup>4</sup> and with  $\gamma_{18} = 0.05$ , then one obtains the theoretical proton coupling constants given for nitrosobenzene in Table I.

It can be seen from Table I that a small value for the resonance integral between the oxygen and its nearby ortho carbon yields a satisfactory explanation of the doubling of both the ortho and meta coupling constants. It seems clear that this is a convenient formal method of calculation that neglects the large interaction in the

$\sigma$ -system between the oxygen and the close ortho proton. It also appears to be unnecessary to include any  $Q$  value between the oxygen and this proton. 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 ( $r_{18}$ ) to explain the doubling of the 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 dimethylformamide<sup>2</sup>, acetonitrile<sup>5</sup> and 50% water in acetonitrile<sup>6</sup>, 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.<sup>6</sup> 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 value for their dielectric constants the shift can not 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 Reiger and Fraenkel<sup>2</sup> 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.

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

Table I

Coupling Constants for Nitrosobenzene and Nitrobenzene Radical Anions<sup>a</sup>

| Position   | Nitrosobenzene |                   | Nitrobenzene              |
|------------|----------------|-------------------|---------------------------|
|            | Obs.           | Cal. <sup>b</sup> | Obs. <sup>c</sup>         |
| Nitrogen-2 | 7.97           | —                 | 11.46(9.70, 10.32, 13.59) |
| Para H-6   | 2.97           | 4.43              | 3.89(4.03, 3.97, 3.54)    |
| Ortho H-4  | 3.84           | 3.68              | 3.42(3.36, 3.39, 3.44)    |
| -8         | 4.14           | 4.03              |                           |
| Meta H-5   | 0.96           | 1.08              | 1.11(1.07, 1.09, 1.12)    |
| -7         | 1.14           | 1.22              |                           |

<sup>a</sup> Absolute magnitudes in gauss.

<sup>b</sup> Calculated with  $\delta_O = 1.4$ ,  $\delta_N = 0.733$ ,  $\gamma_{NO} = 1.67$ ,  $\gamma_{CN} = 1.2$ ,  $Q_{CH} = 23.7$  and  $\gamma_{CO} = 0.05$  between positions 8 and 1. The meta position has negative spin density and  $\rho_1 = 0.2629$ ,  $\rho_2 = 0.3138$  and  $\rho_3 = 0.0086$ .

<sup>c</sup> Our value in liquid ammonia followed by dimethylformamide (ref. 2), acetonitrile (ref. 5) and 50% water in acetonitrile (ref. 6), respectively.



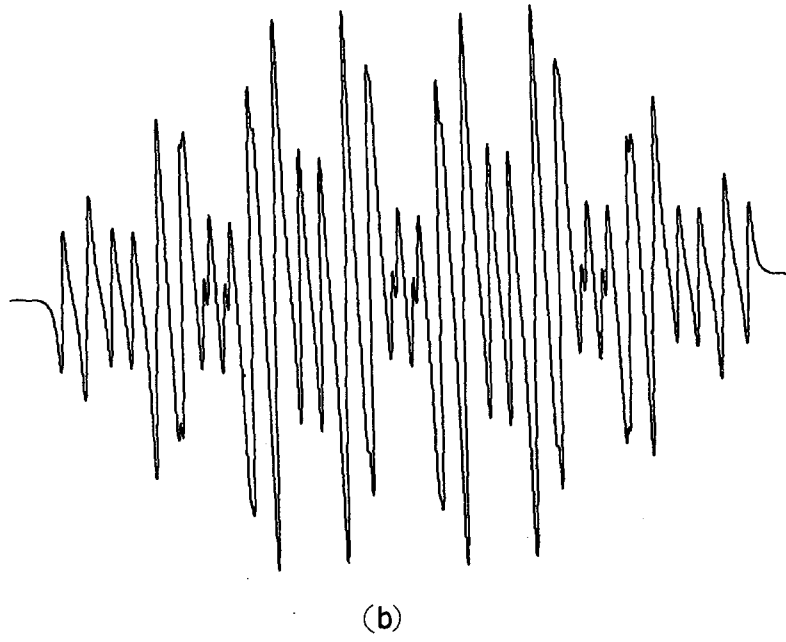
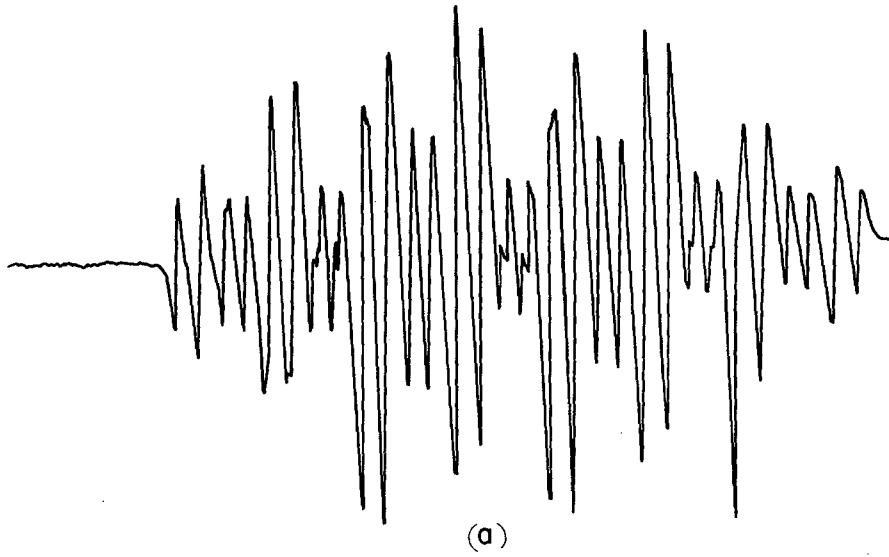
References.

1. D. H. Levy and R. J. Myers, J. Chem. Phys., 41, 1062 (1964).
2. P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. 39, 609 (1963).
3. A. D. McLachlin, Mol. Phys. 3, 233 (1960), we used a  $\lambda = 1.00$  for our calculations.
4. A. Streitwieser, Molecular Orbital Theory (John Wiley and Sons, New York, page 135, 1961).
5. D. H. Geski and A. H. Maki, J. Am. Chem. Soc. 82, 2671 (1960).
6. P. Ludwig, T. Layloff and R. N. Adams, J. Am. Chem. Soc. 86, 4568 (1964).

Figure Caption

Figure 1. The E.S.R. spectrum of nitrosobenzene

- (a) The observed spectrum in liquid ammonia at  $-78^{\circ}\text{C}$  prepared by the electrolytic reduction of a  $5 \times 10^{-3}\text{M}$  solution saturated with tetra-n-propylammonium perchlorate.
- (b) The calculated spectrum using a line width of 0.23 g. and the constants in Table I, for details of the calculation see ref. 1.



MUB-4524

Fig. 1

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Faint, illegible text covering the majority of the page, possibly bleed-through from the reverse side.

