

## Photoinduced Paramagnetism in Solutions of Nitrobenzene in Tetrahydrofuran

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# Photoinduced Paramagnetism in Solutions of Nitrobenzene in Tetrahydrofuran\*

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RECENTLY Lagercrantz and Yhland<sup>1</sup> reported the observations of photoinduced paramagnetism in solutions of *s*-trinitrobenzene in tetrahydrofuran. They observed that solutions irradiated with a high-pressure mercury lamp, which contained a filter with 10% transmission at 387 m $\mu$  and 50% transmission at 408 m $\mu$ , exhibited an electron spin resonance (ESR) hyperfine spectrum. This spectrum is the result of a single nitrogen hyperfine interaction of 13 Oe and three equivalent proton hyperfine interactions of 3.1 Oe. We wish to report studies of photoinduced paramagnetism in solutions of nitrobenzene in tetrahydrofuran and to offer an explanation for the single "dominant" nitrogen hyperfine interaction of 13 Oe observed in *s*-trinitrobenzene.

The experiments of Lagercrantz and Yhland with *s*-trinitrobenzene have been repeated in this laboratory. In addition to the splittings they report we have observed a further splitting of each line into five lines of approximately 1:2:3:2:1 intensity ratios. This splitting, of  $0.23 \pm 0.02$  Oe, is attributed to the two other nitrogens in the molecule. The observation of a large hyperfine interaction with one nitrogen and a lesser interaction with the remaining nitrogens in polynitro aromatic compounds was first observed in the spectra of chemically reduced nitro compounds.<sup>2,3</sup> In these latter systems the nonequivalence of the nitrogens results

TABLE I. Coupling constants<sup>a</sup> for photoparamagnetic nitrobenzene-tetrahydrofuran system.

$A_N = 15.00 \pm 0.02$	$A_{\beta,\delta} = 1.08 \pm 0.04$
$A_{2,4,6} = 3.1 \pm 0.1$	$A_{\alpha H}(\text{THF}) = 0.38 \pm 0.04$

<sup>a</sup> Measured in Oe.

<sup>b</sup>  $A_2$  is the coupling constant for proton No. 2, etc.

from ion-pair formation between an alkali-metal atom and the polynitro aromatic at the site of one nitro group.

We have observed photoinduced paramagnetism in solutions of nitrobenzene in tetrahydrofuran. The solutions were placed in Pyrex tubes and irradiated continuously with light from a Hanovia 612C-1 low-pressure mercury arc lamp. The ESR spectrum, Fig. 1, exhibits a widely spaced set of identical triplets. The observed spectrum contains more lines than can be attributed to nitrobenzene alone. The spectrum of nitrobenzene has also been observed in tetrahydrofuran-*d*<sub>8</sub>, Fig. 2, and in tetrahydrofuran -3,3,4,4-*d*<sub>4</sub>. The spectrum observed from solutions of the latter solvent is identical to that of Fig. 1. It is therefore obvious from a comparison of the spectra that the "extra" proton hyperfine interaction of  $0.38 \pm 0.04$  Oe is due to a single  $\alpha$  proton of the tetrahydrofuran molecule. Spectra from isotopically substituted nitrobenzenes have also been observed. The coupling constants for the nitrobenzene-tetrahydrofuran system appear in Table I.

Lagercrantz and Yhland<sup>1</sup> attributed the spectrum observed in their experiments to a "promotion of charge transfer in an electron-donor-acceptor complex built up from tetrahydrofuran (donor) and *s*-trinitrobenzene (acceptor) lead to an unpairing of the electrons in-

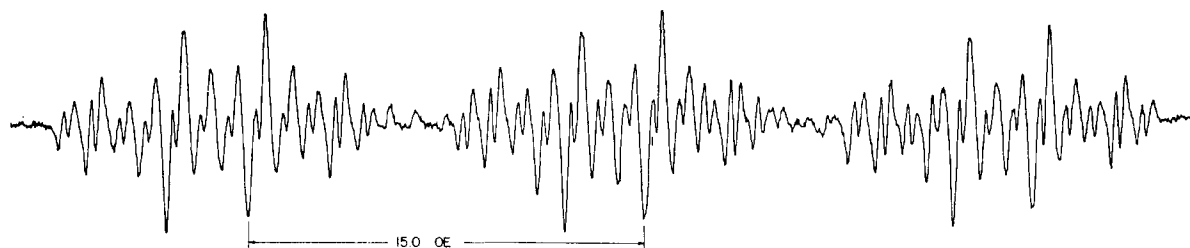


FIG. 1.  $dX''/dH$  vs  $H$  for the photoparamagnetic nitrobenzene-tetrahydrofuran system.

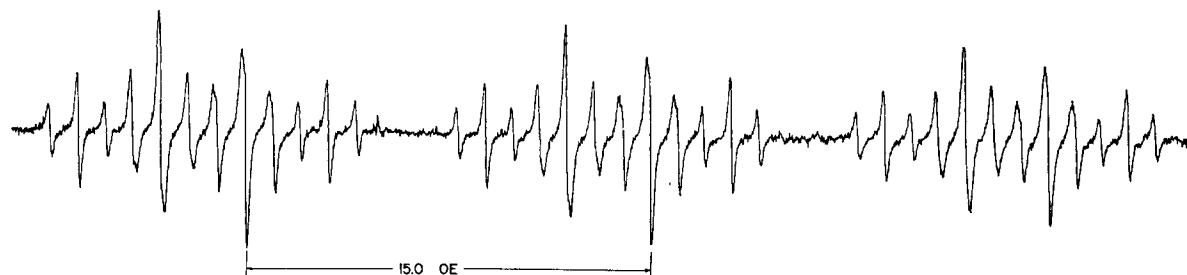


FIG. 2.  $dX''/dH$  vs  $H$  for the photoparamagnetic nitrobenzene-tetrahydrofuran-*d*<sub>8</sub> system.

volved." Our results indicate that a possible mechanism for the production of the paramagnetic species is the following. Light irradiation causes the nitro group to abstract an  $\alpha$  hydrogen atom from the tetrahydrofuran molecule. The resulting tetrahydrofuran free radicals rapidly dimerize or disproportionate, leaving a neutral nitrobenzene free radical in solution. From the small hyperfine interaction of the additional hydrogen we suspect that it resides on an oxygen atom. The total decay time for this radical is approximately 2 sec. We therefore attribute the nonequivalence of the nitrogens in *s*-trinitrobenzene to a mechanism similar to that which exists for the alkali-metal-nitrobenzene-type complexes.<sup>2,3</sup> The possibility of a stable paramagnetic charge transfer complex is in doubt due to a lack of the observation of a superposition of two spectra on the esr signal.

I wish to thank C. Lagercrantz and M. Yhland for preprints of their work and A. Streitwieser for a helpful discussion.

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<sup>1</sup> C. Lagercrantz and M. Yhland, *Acta Chem. Scand.* **16**, 1043 (1962); **16**, 1799 (1962).

<sup>2</sup> R. L. Ward, *J. Chem. Phys.* **32**, 410 (1960); **36**, 1405 (1962).

<sup>3</sup> R. L. Ward, *J. Am. Chem. Soc.* **83**, 1296 (1961).

## Molecular Asymmetry

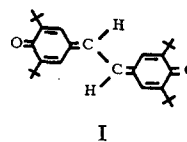
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(Received 26 October 1962)

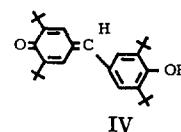
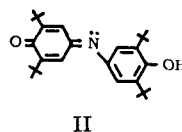
**R**ECENTLY Brownstein and Ingold<sup>1</sup> have described some measurements with NMR that demonstrate *apparent* symmetry in certain molecules is improbable.

They have reported that in the stilbenequinone (I),



methyl hydrogen resonance appears as a doublet and that this multiplicity is due to molecular asymmetry which is not apparent from the simple canonical structure (I). This they have ascribed to hindered rotation about the central carbon-carbon bond.

This interesting behavior has now also been observed in the indophenol system (II), and the quinonemethide system (IV). By virtue of the restricted rotation about



the carbon-nitrogen double bond in II and the central carbon-carbon double bond in IV three methyl hydrogen peaks would be anticipated. These are observed with II in carbon tetrachloride and with IV in benzene with the correct relative intensities of 1:1:2. The less intense pair are from the nonidentical *t*-butyl groups attached to the quinone ring. The methyl hydrogen doublet of equal intensities observed with IV in carbon tetrachloride and deuteriochloroform is something of an anomaly for which there is no ready explanation.

The proton resonance observed upon addition of formic acid implies a totally symmetrical structure. The simplest structure conforming to this implication is (III), with a similar structure corresponding to IV.

TABLE I. Chemical shift.\*

	Solvent	$\delta$ CH <sub>3</sub>	$\delta$ benzenoid	$\delta$ quinonoid	$\delta$ vinyl	$\delta$ OH
II	CCl <sub>4</sub>	1.25, 1.35, 1.56		6.73, 6.98 <sup>b</sup>		5.7
	CCl <sub>4</sub> (HCO <sub>2</sub> H)	1.35		7.0 <sup>b</sup>		
	C <sub>6</sub> H <sub>6</sub> N	1.48				
	CH <sub>3</sub> CN	1.35		6.85 <sup>b</sup>		
	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	1.32		6.88 <sup>b</sup>		
IV	CCl <sub>4</sub>	1.28, 1.42	7.20	7.92, 7.95 6.82, 6.86	6.98	5.45
	C <sub>6</sub> H <sub>6</sub>	1.35, 1.45, 1.51				5.21
	C <sub>6</sub> H <sub>6</sub> (HCO <sub>2</sub> H)	1.46				
	C <sub>6</sub> H <sub>6</sub> N	1.53				
	CH <sub>3</sub> CN	1.38		7.42		
	(CD <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	1.35 <sup>c</sup>		7.65		
	CDCl <sub>3</sub>	1.37, 1.47	7.30	6.92, 6.98 7.51, 7.58	7.10	5.48
	CDCl <sub>3</sub> (HCO <sub>2</sub> H)	1.38				

\* Relative to tetramethylsilane at ambient temperature.

<sup>b</sup> Assignment uncertain.

<sup>c</sup> Broad band 0.15 ppm at half-height.