The Electron Spin Resonance Spectra of Nitrobiphenyl Radical Anions

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In a study of series of substituted biphenyls, several nitro derivatives have been synthesized and the ESR spectra of their anion radicals investigated. The analysis of the spectra is quite straightforward for the mononitrobiphenyls. Although the hyperfine splitting constant for the nitrogen atom is distinct, those for the hydrogen atoms can not be assigned unequivocally. These splittings can, however, be assigned with reasonable certainty, as shown in Table I, by using the theoretical estimates of the spin density distribution and by comparing the splitting constants of a related series of radicals, including halogenated nitrobenzene and hydrogenated nitrobiphenyl. The results seem to sustain the view that the frame-work of mononitrobiphenyls is similar to that of nitrobenzene as far as the frontier electronic orbital level is concerned. Although they are phenylated, the effect of the conjugation of ortho- and meta-substituents is small because of the sterically-induced decoupling and the small spin density respectively. This observation is contrary to that made of alkyl-[1], methoxyl-,[2] or cyanobiphenyls.[3] For paraphenylnitrobenzene, however, the electron-withdrawing nitro group does not entirely dominate the mesomeric interaction effect of the additional aromatic ring; this results in somewhat smaller splitting constants for the main ring atoms.

TABLE I. HYPERFINE SPLITTING CONSTANTS OF NITROBIPHENYL ANIONS AND RELATED COMPOUNDS

Anion	a^N	a_o^H	a_p^H	a_m^H	
o-Nitrobiphenyl	9.85	3.21	3.99	1.17	
	8.7	3.9	3.9	0.9	
m-Nitrobiphenyl	9.80	3.28	3.78	1.15	
	9.55	3.28	3.36	1.04	
p-Nitrobiphenyl	—	—		—	
	8.79	2.84		0.93	3.34(b) 0.4(c)
o, o'-Dinitro-	9.28	1.42	3.25	1.28	
biphenyl	4.28	1.45	1.84	0.38	
m, m'-Dinitro-	9.49	3.34	3.75	1.09	
biphenyl	4.00	2.92	2.29	1.21	
p, p'-Dinitro-	—	—	—	—	
biphenyl	3.54	1.38	(a)		
p-Cyclohexyl-					
nitrobenzene	8.90	3.20		1.25	

Upper row: reduced by potassium in 1,2-dimethoxyethane
Lower row: reduced electrolytically in *N,N*-dimethylformamide
(a) No discrete structure was evident
(b) Interaction with a proton
(c) Interaction with two protons

Dinitrobiphenyls all give substantially different spectra depending upon the method of reduction used to produce anion radicals. The spectra of electrolytically-generated radicals could be readily interpreted on the basis of symmetry considerations alone. When reduced by alkali metals, the contiguity of the small cation to the nitro group seems to destroy the molecular symmetry, so the unpaired electron tends to localize exclusively only one of the two nitrogens in a molecule, as in the case of dinitrobenzene.[4] A striking feature of the spectra exhibited in Fig. 1(a) and (b) is that the spectrum of metadinitrobiphenyl closely resembles that of metanitrobiphenyl.

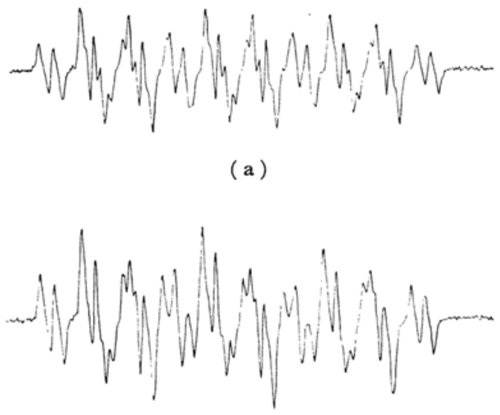

Fig. 1. The electron spin resonance spectra of *m*-nitrobiphenyl (a) and m, m'-dinitrobiphenyl (b) anion radicals.

When the spin density calculations based on the simple Hückel LCAO approximation for these compounds are compared with the experimental data, we find that the internal rotation rather than the cation-induced polarization of the nitro group in dinitrobiphenyl is the more probable model. The o, o'-dinitrobiphenyl anion forms a

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[1] K. Ishizu, This Bulletin, **36**, 938 (1964); **37**, 1093 (1964).

[2], [3] Y. Nakai and H. Shikata, unpublished data.

[4] R. L. Ward, *J. Chem. Phys.*, **36**, 1405 (1962).

stable ion-pair[5] with the alkali metal cation. The metal hyperfine splittings are 0.35 gauss for lithium and 0.18 gauss for sodium. Since one of the benzene rings possesses most of the unpaired spin during the formation of a stable ion pair, the nitrogen in the other ring shows a very small hyperfine splitting, 0.38 gauss.

We have not been able to detect anion radicals with alkali metals in *p, p'*-dinitrobiphenyl.

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[5] H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, ibid., **40**, 241 (1964); *Mol. Phys.*, **9**, 153 (1965).