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ELECTRON SPIN RESONANCE STUDY OF ARYLDIAZENYL RADICALS IN SOLUTION

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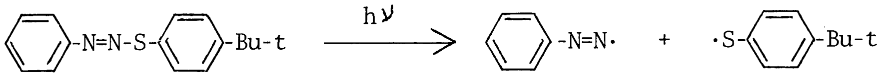
Esr spectra of phenyl- and p-substituted phenyl-diazenyl radicals in solution give $a_{N^1} \simeq 23$ G, a_{N^2} - 9.4 G, and $a_H \simeq 1.1$ G (two meta hydrogens), suggesting a free rotation of the $N^1{=}N^2$ group around the $C^1{-}N^1$ bond. o-Monosubstituted phenyldiazenyl radicals prefer to take a planar conformation, and show a hyperfine coupling constant of only one meta hydrogen-5.

Aryldiazenyl radicals have been subjects of much interests in chemistry as intermediates of thermolyses of arylazo-t-alkanes,[1)] and can proceed in some combination reactions[2a,b)] and probably also in hydrogen abstraction reactions.[2c)] But they could not be observed directly by spectroscopic methods and were therefore studied by theoretical calculations, indicating that they should be sigma radicals.[3)] In this report we present an esr study of a number of aryldiazenyl radicals in solution.

Photolysis of a solution of phenylazoarylsulfide (aryl = p-t-butylphenyl) in cyclopropane at -100 ∿ -125 °C (Eq. 1) gave an esr spectrum (g value = 2.0005 ± 0.0001) consisting of nine 1:2:1 triplets (1.2_0 G separation) in an arrangement of 1:1:1 triplet (22.5 G separation) of 1:1:1 triplets (9.4_5 G separation) (Experiment No. 1 of the Table). The substitution of the para hydrogen of the phenyl group in the azo compounds by methoxyl and chloro groups did not alter the esr spectrum (Experiments Nos. 3 and 5). In Fig. 1 the spectrum obtained from the reaction with p-chlorophenylazophenylsulfide is illustrated.



(1)

Phenyl-d_5-azoarylsulfide gave however an esr spectrum of nine singlets, in a pattern of 1:1:1 triplet (22.6 G separation) of 1:1:1 triplets (9.2_8 G separation) (Experiment No. 2, Fig. 2). This indicates that two equivalent hydrogens in the phenyl ring have the hyperfine coupling constant of 1.2 G.

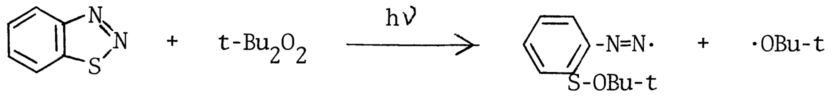
The deuterations of the two hydrogens ortho to the azo linkage in the p-methoxyphenyl- and p-chlorophenyl-azo compounds did not converge the 1:2:1 triplets of the esr spectra from the parent compounds to singlets (Experiments Nos. 4 and 6). These results imply that the two meta hydrogens to the azo group have the hyperfine coupling constant of 1.2 G.

Photolysis of 1-(4-chlorophenyl)diazenylphenylsulfide-2-^{15}N gave an esr spectrum consisting of six 1:2:1 triplets (1.1 G separation) in a pattern of 1:1:1 triplet (23 G separation) of doublets (13.3 G separation) (Experiment No. 7). This leads to the conclusion that a_{N^1} = 23 G, $a_{^{15}N^2}$ = 13.3 G, and $a_{^{14}N^2}$ = 9.2_4 G. The hyperfine coupling constants observed are summarized in the Table.

The characteristic properties of the free radicals observed are as follow: a) the low g value, 2.0006, accords very well with 2.0007 of nitrosobenzene cation radical,[4c)] b) N^1 has a larger coupling constant ~23 G than that of N^2 (~9.4 G) as suggested for phenyldiazenyl radicals,[3)] and c) the two hydrogens in the meta positions have the hyperfine coupling constants, ~1.1 G, as those of benzoyl radicals.[4a)] They all support that the radicals are nitrogen-centered sigma radicals, possibly aryldiazenyl radicals. A possiblility for another nitrogen radicals which are alike to 1-phenyl-2-arylthiyl-2-X-1-hydrazyl, can be excluded because the sigma radicals of phenyldiazenyl would be much more unstable than the pi radicals,[5a)] and because the substitution by arylthiyl group at N^2 of the phenylhydrazyl would cause an increase in the g value up to 2.0028[5b)] to 2.007[5c)] and also spin couplings with ortho and para hydrogens of the arylthiyl group.

Based on the results of the theoretical studies on phenyldiazenyl radicals,[3)] on benzoyl radicals,[4a)] and on nitrosobenzene cation radicals,[4b)] the coupling constants for the two meta hydrogens can well be explained by supposing that in the phenyldiazenyl and p-substituted phenyldiazenyl radicals in solution, the N^1=N^2 group is rotating freely around the C^1-N^1 axis, as in the case of the C=O group in benzoyl radicals.[4a)] In the case of rotation with high energy barriers, taking a planar conformation, only one ortho hydrogen and one meta hydrogen should show measurable hyperfine coupling constants, respectively.[3b,4a)] Nitrosobenzene cation radical is the case.[4c)]

When phenyldiazenyl radicals carry ortho substituents, the rotation of the N^1=N^2 group around the C^1-N^1 bond should have high energy barriers. Photolysis of 1,2,3-benzothiadiazole in cyclopropane in the presence of di-t-butyl peroxide (Eq. 2) gave an esr spectrum (g value = 2.0005)



(2)

consisting of nine doublets (1.3 G separation) in a pattern of 1:1:1 triplet (20.9 G separation) of 1:1:1 triplets (9.3 G separation) (Experiment No. 8, Fig. 3). 4,6-Dideuterio-1,2,3-benzothiadiazole gave the same esr spectrum as that of the parent compound (Experiment No. 9). Only one of the two

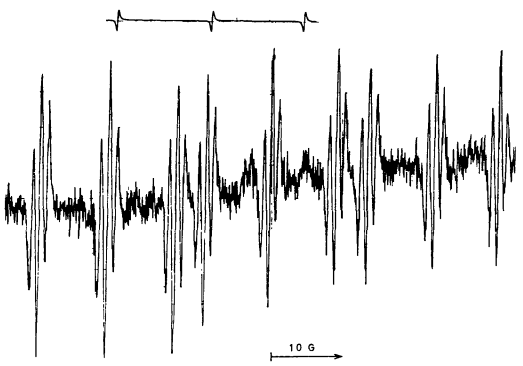


Fig. 1. Esr spectrum of p-Cl-C_6H_4-N=N·

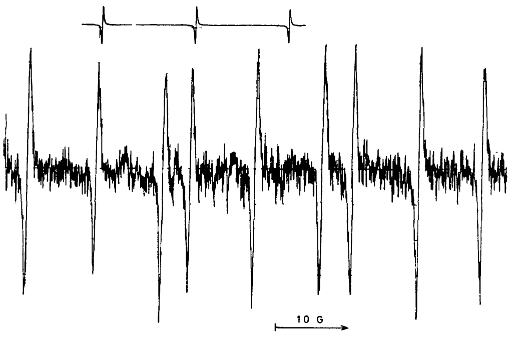
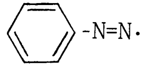
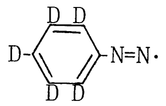
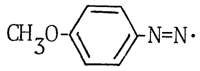
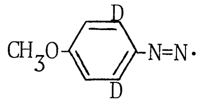
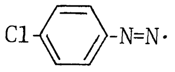
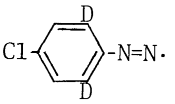
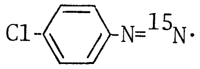
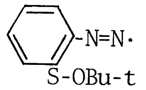
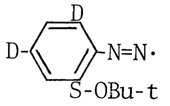


Fig. 2. Esr spectrum of C_6D_5-N=N·

TABLE. HYPERFINE COUPLING CONSTANTS OF ARYLDIAZENYL RADICALS

Run	Ar-N^1=N^2·	g Value ($\pm$0.0001)	Coupling Constant (G) a_{N^1}	a_{N^2}	$a_{m\text{-}H}$ (nH)[a)]
1		2.0005	22.5	9.4_5	1.2_0 (2H)
2		2.0006	22.6	9.2_8	none
3		2.0007	22.5	9.6_0	1.0_0 (2H)
4		2.0007	22.5	9.4_8	1.1_0 (2H)
5		2.0006	22.8	9.1_3	1.2_0 (2H)
6		2.0007	23.1	9.3_5	1.1_0 (2H)
7		2.0005	23.0	13.3	1.1_0 (2H)
8		2.0005	20.9	9.3_2	1.3_2 (1H)
9		2.0005	20.8	9.3_5	1.3_0 (1H)

a) n is the number of the equivalent hydrogens.

hydrogens meta to the azo group in the radicals has the hyperfine coupling constant of 1.3 G:. this suggests that the aryldiazenyl radicals carrying a substituted thiyl group at the ortho position probably has a planar conformation as shown in Fig. 4. The hydrogen-5 should have the hyperfine coupling constant of 1.3 G, taken into the consideration the results of the calculation for a planar phenyldiazenyl radical.[3b)]

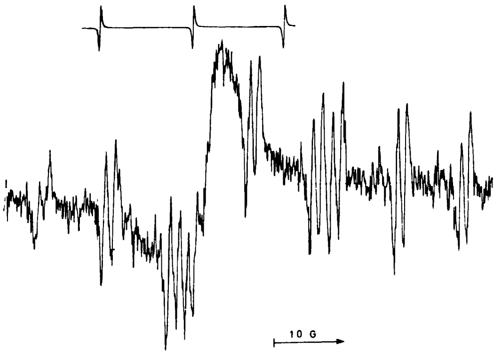


Fig. 3. Esr spectrum of o-t-BuO-S-C_6H_4-N=N·

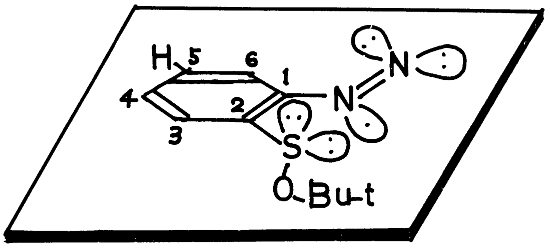


Fig. 4. Planar conformation of o-t-BuO-S-C_6H_4N=N·

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b) N. A. Porter, G. R. Dubay, and J. G. Green, J. Am. Chem. Soc., 100. 920 (1978),

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b) L. F. Kasukhin, M. P. Ponomarchuk, and A. L. Buchachenko, Chem. Phys., 3, 136 (1974),

4) a) P. J Krusic and T. A. Rettig, J. Am. Chem. Soc., 92, 722 (1970),

b) M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, J. Phys. Chem., 76, 553 (1972),

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b) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, Chem. Commun., 1965, 319,

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