

and diphenylmethyl radicals. The latter was identified by its fluorescence spectrum with λ_{\max} at 535 m μ . A diphenylmethane⁹ was also detected at longer exposure times. *We postulate that the products at long exposure times result from reactions of photoexcited diphenylmethylene or by photolysis of products formed by reaction of photoexcited diphenylmethylene with the matrix.*

Light of wavelength 3500 Å⁸ was also used to photolyze solutions of diphenyldiazomethane in methylcyclohexane at 77°K. The products at small exposure times were the same as those using 2537-Å irradiation. At longer exposure times, diphenylmethylene disappearance was much slower than with 2537-Å irradiation and was not accompanied by formation of detectable amounts of diphenylmethyl radicals. Phosphorescence of a substituted diphenylmethane was also observed.⁹

Diphenyldiazomethane photolysis was also studied as a function of exposure time and wavelength of incident light in a 2-methylpentene-2 glass at 77°K. The luminescence results coupled with the esr measurements show that *ground-state diphenylmethylene can be formed and is stable in a simple olefin glass* without serious complications from insertion, addition, or abstraction reactions. It is also stable in 2-methyltetrahydrofuran, methanol, ethanol, triethylamine, benzene, and fluorocarbon matrices at 77°K.

The photolysis of 9-diazo fluorene, substituted phenyl- and diphenyldiazomethanes, and some aromatic azides (nitrene precursors) in organic glasses at 77°K have also been studied and will be reported later.¹⁰

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(10) NOTE ADDED IN PROOF. G. L. Closs, C. A. Hutchison, Jr., and B. E. Kohler, *J. Chem. Phys.*, in press, have observed the optical absorption spectrum of diphenylmethylene oriented in single crystals. Our absorption work in glasses indicates bands with λ_{\max} 465, 290–300, and 240 m μ , the lower wavelength bands being much more intense than the 465 m μ band.

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Electron Spin Resonance Study of the Phenyl diazotate Free Radical, the Key Intermediate in Phenylations with Aromatic Diazo Compounds

Sir:

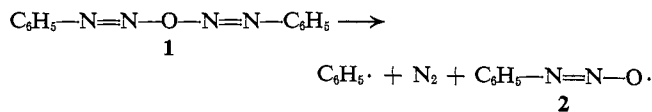
Recent evidence^{1,2} strongly demanded a revised mechanism for the Gomberg reaction³ and phenylations with N-nitrosoacetanilides,³ according to which the diazoanhydride **1**⁴ is formed as a common intermediate. This species was postulated to decompose into a phenyl radical, nitrogen, and the supposedly long-lived diazotate radical **2**. The occurrence of a paramagnetic intermediate in the course of these reactions has been confirmed by electron spin resonance

(1) C. Rüchardt and E. Merz, *Tetrahedron Letters*, **36**, 2431 (1964); E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, **30**, 2451 (1965).

(2) C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, **48**, 3623 (1964).

(3) Cf. ref 1 and 2 for a literature survey.

(4) T. Kauffmann, H. O. Friestad, and H. Henkeler, *Ann.*, **634**, 64 (1960).



spectroscopy and it will now be shown that the spectrum of this radical is consistent with the proposed structure **2**.

When a freshly prepared solution of 400 mg of N-nitrosoacetanilide in 3 ml of benzene was placed into the microwave cavity of an AEG esr spectrometer, the spectrum shown in Figure 1a could be observed. A g value of 2.0055 was determined using DPPH for calibration. The deceptively simple spectrum, apparently caused by a high degree of accidental degeneracy, yielded only the largest and smallest hfs constants directly, together with the information that the other coupling constants involved must be approximately integral multiples of the smallest one. On rejection of all possibilities which are not consistent with the total width of the spectrum and the number of lines, or which give grossly wrong intensity ratios, one is left with two sets of approximate parameters differing by interchange of two splitting constants to two equivalent protons and a nitrogen nucleus, respectively. This ambiguity could be resolved by computer simulation.⁵ Figure 1b shows the spectrum calculated

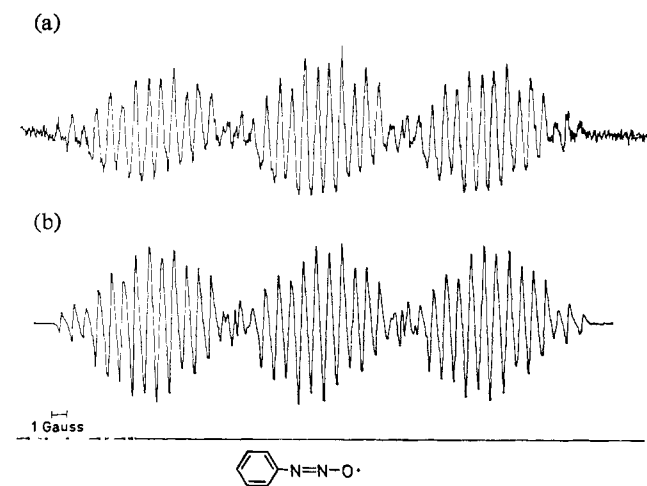


Figure 1. Electron spin resonance spectrum of the phenyldiazotate free radical. (a) Observed spectrum; magnetic field increases to the right. The decrease of intensity from right to left (downfield spectrum) is due to the decreasing radical concentration during the time of recording (20 min at 30°). (b) Calculated spectrum with hfs constants of Table I, using Lorentzian line shape and a line width of 0.18 gauss.

with the parameters of Table I, column 2. From the sensitivity of the computed spectrum to changes in the parameters the standard deviations of the hfs constants can be estimated to ± 0.03 gauss.

To compute "experimental" spin densities, ρ_{expt} , from the observed coupling constants is a straightforward problem for the aromatic carbon atoms. If one

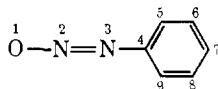
(5) A Fortran II coded program was developed for an IBM 7090 computer equipped with a Mosley plotter and the necessary plotter routines on the system tape. Output is thereby directly obtained as a plot of the first derivative of the absorption spectrum in a predetermined scale. Part of the computational scheme is based on a program originally designed by E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963). We are indebted to Professor Maki, University of California, Riverside, Calif., who kindly provided us with a copy of his program.

applies McConnell's equation⁶ with $Q_{\text{CH}}^{\text{H}} = -23.7$, a

$$a^{\text{H}} = Q_{\text{CH}\rho}^{\text{H}} C$$

value which seems to be well documented by now,⁷ one obtains the numbers in column 3 of Table I. Although the same type of relationship has been claimed to hold as well for coupling constants to nitrogen nuclei in certain classes of compounds,⁸ there is good theoretical

Table I. Hyperfine Splitting Constants and Spin Densities of the Phenyldiazotate Free Radical



| Atom | $a,^{\circ}$ gauss | ρ_{exptl} | $\rho_{\text{calcd}}^{\text{b}}$ |
|------|-----------------------|-----------------------|----------------------------------|
| 1 | | | 0.5442 |
| 2 | ± 1.67 | | -0.0244 |
| 3 | ± 11.61 | | 0.2179 |
| 4 | | | 0.0264 |
| 5,9 | -2.60 | 0.1095 | 0.0944 |
| 6,8 | 0.89 | -0.0375 | -0.0407 |
| 7 | -2.73 | 0.1152 | 0.1286 |

^o The signs of the nitrogen hfs constants are not known; for the signs of the proton coupling constants compare T. H. Brown, D. H. Anderson, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 720 (1960).

^b McLachlan calculations with $\lambda = 1.2$, $h_{\text{N}} = 0.5$, $h_{\text{O}} = 1.0$, $k_{\text{NN}} = 1.5$.

reason to believe that a^{N} should also depend on the spin densities of the neighboring centers⁹ and the charge distribution in the molecule.¹⁰ Since these factors must play a more important role in the species under consideration than in anion radicals derived from nitrogen heterocycles,⁸ it is rather unlikely that good results will be obtained with a single constant. Unfortunately, the σ - π interaction parameters required for a more elaborate treatment still have to be determined empirically and are not known for the present case. More data are obviously needed before one can attempt to establish a quantitative correlation.

We are now in the position to compare the quantities derived from the experiment with theoretically calculated spin densities. The perturbation method of McLachlan¹¹ has been adopted for these calculations, since it appears to be one of the best theories presently available,¹² clearly superior to calculations of odd electron densities by the unmodified Hückel method. Taking account of the hetero atoms by a reasonable set of parameters,¹³ the spin densities, ρ_{calcd} , in column 4 of Table I were obtained. It can be seen that the spin densities in the aromatic ring are indeed reproduced

(6) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(7) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2795 (1962); *ibid.*, **39**, 609 (1963).

(8) A. Carrington and J. dos Santos Veiga, *Mol. Phys.*, **5**, 21 (1962); E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963); C. A. McDowell and K. F. G. Paulus, *Mol. Phys.*, **7**, 541 (1964).

(9) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(10) J. C. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(11) A. D. McLachlan, *ibid.*, **3**, 233 (1960).

(12) Recent unrestricted Hartree-Fock calculations of L. C. Snyder and T. Amos [*J. Chem. Phys.*, **42**, 3670 (1965)] on a much higher level of sophistication produced an about equally good agreement with experiment.

(13) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

remarkably well. Although for the reasons stated above a direct quantitative comparison between theory and experiment is not feasible for the nitrogen nuclei at this stage, the approximately equal ratios of the calculated spin densities and the observed coupling constants hardly leave any doubt that the assignment as given in the table is correct.

There is one interesting alternative, however, that should be considered. It is conceivable that the 2.60-gauss hfs constant has to be assigned to one *ortho* and one *para* proton and the 2.73-gauss coupling constant to the other *ortho* proton. A difference of this kind could be expected on the basis of the angular structure of the nitrogen-nitrogen double bond segment provided the rotation around the carbon-nitrogen bond is sufficiently hindered. Analogous effects have been reported for radicals derived from azobenzene,¹⁴ aromatic aldehydes,¹⁵ and nitroso compounds.¹⁶

This question is now being investigated in a series of *para*-substituted aryldiazotate radicals. The assignment of the coupling constants to the two nitrogen nuclei will be tested by introduction of a nitrogen-15 label, and an attempt will be made to generate aryldiazotate radicals by oxidation of *syn*- and *anti*-aryldiazotate anions.

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(14) E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, **1**, 13 (1965).

(15) D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 1852 (1961); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

(16) G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, **87**, 122 (1965); D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **42**, 3731 (1965).

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The Reported Adamantane Anion Radical. Its Relationship to Benzene Anion Radical

Sir:

The report by Bowers, *et al.*,¹ of the preparation of the adamantane anion radical has generated considerable interest.² The purpose of this communication is to demonstrate that under conditions reported for the preparation of adamantane anion radical¹ the esr

(1) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963).

(2) See, for example, R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964), and P. T. Lansburg and J. D. Sidler, *Chem. Commun.*, 373 (1965).