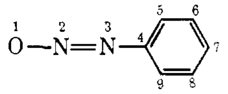
applies McConnell's equation[6] with $Q^{H}{}_{CH} = -23.7$, a

$$a^{H} = Q^{H}{}_{CH}\rho^{C}$$

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 reason to believe that $a^{N}$ should also depend on the spin densities of the neighboring centers[9] 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 $\sigma$–$\pi$ 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.

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



| Atom | $a$,[a] gauss | $\rho_{exptl}$ | $\rho_{calcd}$[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 |

[a] 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 $\lambda = 1.2$, $h_{N} = 0.5$, $h_{O} = 1.0$, $k_{NN} = 1.5$.

We are now in the position to compare the quantities derived from the experiment with theoretically calculated spin densities. The perturbation method of McLachlan[11] 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, $\rho_{calcd}$, in column 4 of Table I were obtained. It can be seen that the spin densities in the aromatic ring are indeed reproduced 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.

**Acknowledgment.** We are indebted to the Computing Center of the Eidgen. Technische Hochschule, Zürich, and the Max-Planck Institut für Plasmaphysik, München, for making computer time available. Thanks are due to Professor H. Zimmermann, München, for allowing us the use of his esr spectrometer, and to Dr. H. Baumgärtl, Dr. K. C. Schilffarth, and Dipl.-Chem. E. Merz for recording the spectrum. Financial support of a NATO Fellowship (G. B.) and by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

---

(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.

(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).

**Gerhard Binsch**
*Organisch-chemisches Laboratorium, Eidgen.*
*Technische Hochschule*
*Zürich, Switzerland*

**Christoph Rüchardt**
*Institut für Organische Chemie, Universität München*
*München, Germany*

*Received September 18, 1965*

---

## 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 radical[1] 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).

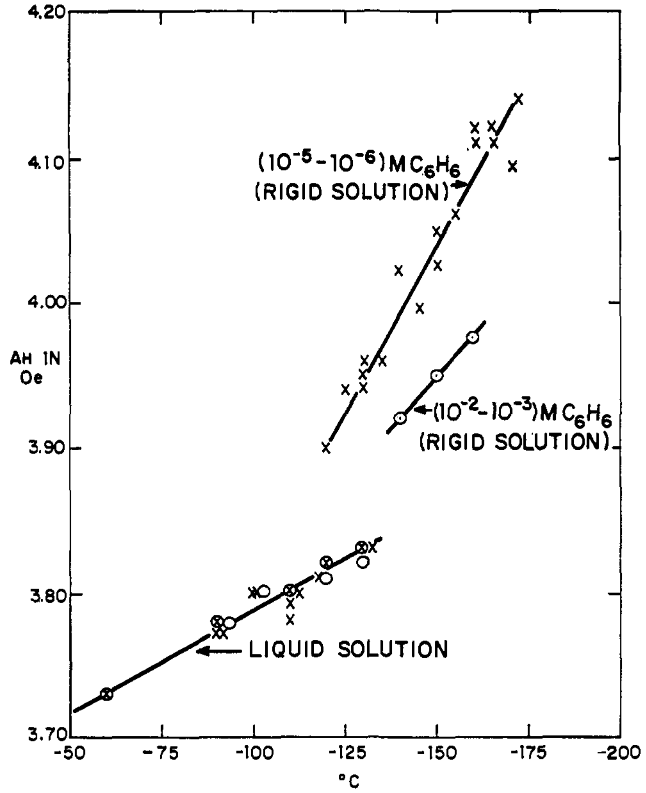


Figure 1. Temperature dependence of benzene anion radical hyperfine splittings. Circled ×'s are the results of Fessenden and Ogawa (ref. 7). The ×'s are from several samples in which the benzene concentration was of the order of $10^{-5}$–$10^{-6}$ *M*. The open circles are from a sample in the concentration range $10^{-2}$–$10^{-3}$ *M*.

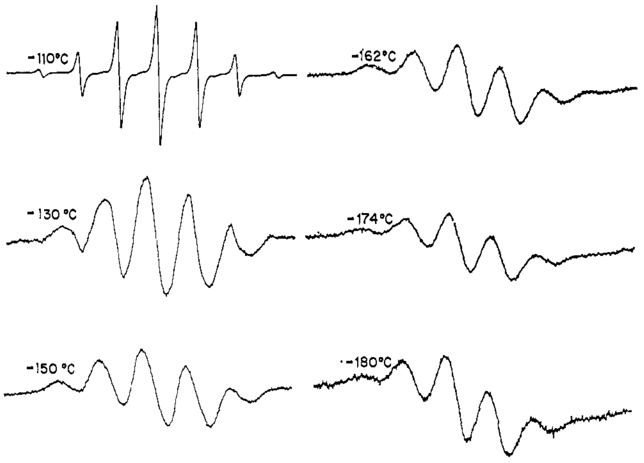


Figure 2. Temperature dependence of the esr spectrum of benzene anion radical. The benzene concentration was of the order of $10^{-2}$–$10^{-3}$ *M*. The solution was frozen at −130°. The spectrometer gain and modulation amplitude were not kept constant. Therefore, these spectra do not show the changes in relative intensity as a function of temperature.

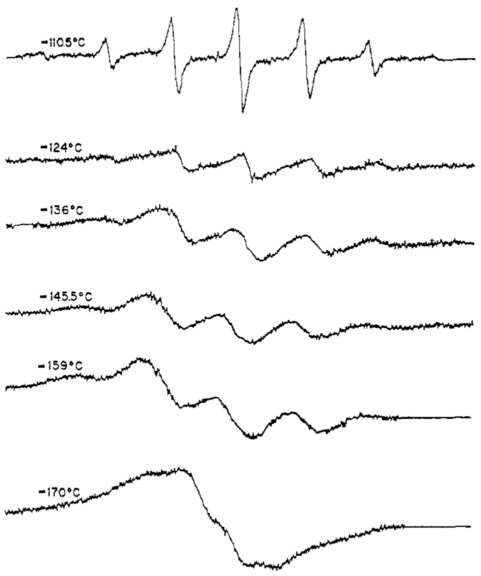


Figure 3. Temperature dependence of the esr spectrum of benzene anion radical. The benzene concentration was of the order of $10^{-5}$–$10^{-6}$ *M*. The solution was frozen at −124°. The spectrometer gain and modulation amplitude were not kept constant. Therefore, these spectra do not show the changes in relative intensity as a function of temperature.

spectrum observed is identical with that of the benzene anion radical.

To establish the equivalence of the two spectra, the effect of temperature upon the apparent hyperfine splitting and the spectrum of the benzene anion radical in rigid solution[3] must be considered.[6] Figure 1 summarizes the effect of temperature upon the hyperfine splittings for two different concentrations of benzene anion radical in both liquid[7] and rigid[8] solutions. Three things are apparent: (1) the temperature dependence of the hyperfine splitting is concentration independent in liquid solutions; (2) the temperature dependence of the apparent hyperfine splitting is greater in rigid solution than in liquid solution;[9] (3) the temperature dependence of the apparent hyperfine splitting is concentration dependent in rigid solutions, the rate of change being less at high benzene concentrations.

Another important feature is shown in Figures 2 and 3. Upon freezing, the spectral line widths increase,

---

(3) The solvent was a 2:1 mixture of tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). It freezes at ∼−110°. However, it is easily supercooled to ∼−125°. Each component of the solvent used in this study was prepared[4] by repeating the sequence of refluxing over sodium–potassium alloy followed by a very carefully controlled distillation until a 2:1 mixture of THF and DME supported a deep blue color in the presence of Na–K at low temperatures and such a solution gave no esr spectrum. All samples were prepared under high vacuum conditions.[5]

(4) Very pure alloy can be obtained from MSA Research Corp., Callery, Pa. This is an important aspect of the solvent and sample preparation since, if the alkali metals are contaminated with aromatics, of one sort or another, they may show up as anion radicals in the samples.

(5) M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(6) The spectrum reported for the adamantane anion radical in ref 1 is not due to benzene anion radical in liquid solution: (1) at −150° the solvent must have been frozen; (2) an extrapolation of the benzene anion radical hyperfine splitting in liquid to 3.90 oersteds predicts a sample temperature of −180°; (3) no matter how dilute the benzene anion radical solution, even if only five lines are observed, the relative intensities are those expected for seven lines.

(7) R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).

(8) One might ask how or why the benzene anion radical hyperfine splitting is still observed after the solution is frozen. There are several plausible explanations: (1) there may be small pockets of liquid left; (2) the benzene anion radical may be rotating about its hexad axis, as benzene is known to do (see D. R. F. Gelson and C. A. McDowell *J. Chem. Phys.*, **40**, 2413 (1964), and references cited therein); (3) the anisotropy of the benzene anion radical may be small.

(9) Some, perhaps all, of this larger apparent hyperfine splitting probably results from decreased motional averaging which leads to an increased anisotropic hyperfine contribution.

and the outer two lines become difficult to observe. As the temperature is decreased, the line widths continue to increase, and it ultimately becomes impossible to observe the outer two lines; hence the spectrum appears to consist of five lines. As the line width increases in magnitude relative to the line separation, one also finds that the observed relative intensities of the spectral lines change from 1:6:15:20:15:6:1 to 1:4:6:4:1. This is a general phenomenon and has been very well demonstrated by Lebeder, *et al.*,[10] by means of detailed calculation of the spectral patterns to be expected as one allows the line width to increase relative to the line separation.

Finally, samples containing $10^{-1}$–$10^{-3}$ *M* adamantane have been studied. At the higher concentrations, spectra identical with that of benzene anion radical were observed, *i.e.*, seven lines, $a_H = 3.80\ (\pm 0.01)$ oersteds and $g = 2.00277\ (\pm 0.00005)$ between $-110$ and $-120°$. Upon lowering the temperature below the freezing point of the solvent, spectra such as those shown in Figures 2 and 3 were obtained. In the more dilute samples, a seven-line pattern (sometimes a five-line spectrum with an intensity distribution expected for seven lines) was observed with $a_H \sim 3.90$–$4.00$ oersteds and $g = 2.0027\ (\pm 0.0001)$ at $\sim -125°$. Some of the latter solutions may have been frozen. Lowering the temperature beyond $-125°$ gave results similar to those shown in Figures 2 and 3. Qualitatively, the dilute samples gave less intense spectra by at least an order of magnitude than that used to record Figure 3.

There is no doubt that the above spectra could be derived from benzene present as a contaminant in the adamantane. Benzene concentrations as low as one part in $10^7$ on a mole-to-mole basis can probably be detected in a $10^{-1}$ *M* solution of adamantane.[11] It is estimated from esr and ultraviolet measurements that the benzene concentration in the adamantane samples studied was approximately two orders of magnitude greater than this minimum value. The adamantane was purified by two sublimations, the first at atmospheric pressure and the second under high vacuum conditions.

The possibility also exists that benzene is derived from adamantane itself by reaction with sodium–potassium alloy. A distinction between these two possibilities could be made by an independent determination of the amount of benzene present in samples of adamantane. Such a determination might be possible through the use of isotopic dilution techniques.[12]

After consideration of the above evidence one concludes the parameters reported by Bowers, *et al.*,[1] for adamantane anion radical, *i.e.*, five broad lines ($\sim$2 oersteds in width), of relative amplitudes approximately given by the binomial distribution expected for five lines (1:4:6:4:1), hyperfine splitting $a_H = 3.90$ oersteds and $g = 2.0029$ at $-150°$ in a 2:1 mixture of THF and DME, could equally well have been those of the benzene anion radical under rigid solution conditions.

**Acknowledgment.** Helpful correspondence and conversations with Professors K. W. Bowers and F. D. Greene and the long and continued interest of Dr. T. L. Cairns are acknowledged.

**M. T. Jones**
*Contribution No. 1154, Central Research Department*
*E. I. du Pont de Nemours and Company*
*Experimental Station, Wilmington, Delaware 19898*
*Received October 26, 1965*

---

(10) Ya. S. Lebeder, D. M. Chernikova, N. N. Tekhomirova, and V. V. Voevodskii, "Atlas of Electron Spin Resonance Spectra," Consultants Bureau, New York, N. Y., 1963.

(11) The extreme sensitivity of esr should be noted. It is obvious from Figure 3, where the benzene concentration is between $10^{-5}$ and $10^{-6}$ *M*, that a 10- to 100- dilution would still yield an observable esr spectrum (with appropriate changes in spectrometer parameters). This corresponds to $10^{-11}$ or $10^{-12}$ mole of benzene anion radical for a sample of 0.1 ml. This is within the nominally quoted esr spectrometer sensitivity.

(12) This experiment was suggested by Professor C. Gardner Swain.

---

## Stereoregular Modes of Double Bond Opening Determined in the Initial Short Period of the Anionic Polymerization of Isopropyl Acrylate

*Sir:*

We report in this communication that in the anionic polymerization of isopropyl acrylate initiated with phenylmagnesium bromide or diphenylmagnesium: (a) different modes of monomer double bond opening, *i.e.*, the *cis* mode,[1] the *trans* mode, and a 1:1 mixture of them, occur in different temperature ranges separated by narrow boundary regions, (b) the opening mode is determined in the initial very short period, and (c) the initially determined mode persists against temperature change beyond the boundary of its characteristic range.

It was reported previously[2] that when isopropyl acrylate-$\alpha,\beta$-$d_2$ with the ratio, $\gamma$, of the $\alpha$,*trans*-$\beta$-$d_2$ to the $\alpha$,*cis*-$\beta$-$d_2$ isomer equal to 5 is polymerized in toluene at $-78°$ using phenylmagnesium bromide as catalyst, two diisotactic processes with *cis* and *trans* opening of the double bond take place in the polymerization to give a polymer with $\kappa \approx 1$. Here $\kappa$ is the intensity ratio of the lower to the higher field nmr signal of the *meso*-methylene protons, and $\kappa = \gamma$ and $\kappa = 1/\gamma$ mean *trans* and *cis* opening of the double bond, respectively, according to the assignment of the two *meso*-methylene signals.[3] It was found, however, that polymerization in toluene[4] at $-57.5°$ or higher temperatures (confirmed up to 0°) gives a polymer with $\kappa \approx \gamma$, while polymerization at $-62.5°$ or lower temperatures (confirmed down to $-83°$) gives a polymer with $\kappa \approx 1$. When ethyl ether was used as solvent, polymers with $\kappa \approx \gamma$ and $\kappa \approx 1$ were obtained in the polymerizations at temperatures above $-63°$ and below $-73°$, respectively.

When polymerization was performed in toluene or ether at 0° for an initial 30 sec and then at $-83°$ for a succeeding 6 hr, a polymer with $\kappa \approx \gamma$ (Figure 1) was obtained, the same as in the polymerization at 0° throughout. The polymer may be regarded as mostly formed at $-83°$, because the temperature reached $-60°$ and $-83 \pm 0.5°$ within 20 and 80 sec, respectively, and because only a small amount of polymer was obtained by polymerization for 1 min at 0°. *trans* opening of the double bond in the polymerization at $-83°$ after the rapid fall of temperature from 0°

---

(1) Was not confirmed for the Grignard-initiated polymerization.

(2) T. Yoshino and K. Kuno, *J. Am. Chem. Soc.*, **87**, 4404 (1965).

(3) T. Yoshino, M. Shinomiya, and J. Komiyama, *ibid.*, **87**, 387 (1965).

(4) Contains ether (5% in volume) from the Grignard solution.