Table IV. Comparison of Pentavalent Silicon Geometries

Compd	d(Si-N)	d(Si-C)	Av d(Si-O)	Av ∠C-Si-O, deg	Ref
II	2.116 (6)	1.905 (7)	1.656	95.8	1
I	2.193 (5)	1.882 (6)	1.656	97.1	4
IV	2.336 (4)	1.857 (5)[a]	1.666	98.1	This work
III	2.344 (5)	1.853 (6)	1.642	100.0	5
Phenylsilane		1.843 (5)			15

[a] All of the compounds are sp^2 hybridized except IV. The Si-C carbon distance in IV has been corrected by 0.020 A from the observed value of 1.877 Å to take into account the difference between sp^3 and sp^2 covalent radii [L. N. Ferguson "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, p 39].

respectively. The puckering in the rings can be measured in terms of certain dihedral angles formed between planes each defined by three atoms; for example, {Si-N-C(2), C(2)-C(3)-C(4)}, 140.4 ± 0.5°; {Si-N-O(1), O(1)-C(5)-C(6)}, 144.6 ± 0.4°; and {Si-N-O(2), O(2)-C(7)-C(8)}, 146.8 ± 0.4°.

The molecular packing, shown in Figure 3, is dominated by dipole-dipole interactions, and no unusually short intermolecular contacts occur. A characteristic mode of packing[4,5] in these compounds is for one of the bridging groups to tuck in the angle between two bridging groups on an adjacent molecule. In methyl(2,2′,3-nitrilodiethoxypropyl)silane, the bridge O(1)-C(5)-C(6) nests between the bridges C(2)-C(3)-C(4) and O(2)-C(7)-C(8) of the molecule related by a cell translation along *y*.

Acknowledgment. We are grateful to Cecil Frye for kindly providing the sample, and to John J. Flynn for his aid with the data collection and the initial calculations.

Heptafulvalene Cation and Anion Radicals

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Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received October 16, 1968

Abstract: The cation and anion radicals of heptafulvalene (I) have been prepared and their esr spectra have been investigated. This study has been conducted in order to gain information concerning resonance stabilization and spin-density distributions in molecules closely related to the nonbenzenoid hydrocarbon heptafulvalene. The heptafulvalene cation (III) is generated by thermal cleavage of the dication dimer ($30° \lesssim t \lesssim 60°$) and the anion is produced by reaction of potassium with I at *ca.* $-80°$ and by cleavage of the dianion dimer at temperatures greater than 30°. The hyperfine spectrum of the cation radical is consistent with three sets of four protons each with splittings $|a_1^H| = 0.075$ G, $|a_2^H| = 2.90$ G, and $|a_3^H| = 1.72$ G. The anion-radical spectrum is very temperature and solvent dependent due to intramolecular potassium ion migration. Both slow-exchange and rapid-exchange spectra are observed. The slow-exchange spectrum ($-120°$; MTHF) arises from two groups of two protons each with splittings $|a_1^H| = 8.22$ G and $|a_3^H| = 5.02$ G. Comparison of these couplings with those of the rapid-exchange spectra and with calculated splittings reveals a feature of the spin-density distribution which is novel—the unpaired spin in heptafulvalene anion is essentially localized on one of the rings. Two pieces of evidence provide indications that the radical ions of heptafulvalene, in contrast with heptafulvalene itself, may have considerable delocalization energy as predicted by HMO theory: (1) the dimers of the radical ions are appreciably dissociated at room temperature, and (2) good agreement is obtained between the experimental hyperfine splittings and the values computed using approximate π-electron theory in which a uniform nuclear framework is assumed, thus indicating an absence of the alternating single and double bonds which reduce the delocalization energy of I.

The resonance stabilization of nonbenzenoid hydrocarbons is of considerable interest. Heptafulvalene (I) is predicted by HMO theory to possess a large delocalization energy in disagreement with the experimental finding of a small empirical resonance energy.[3] It would be of interest to gain information regarding resonance stabilization for molecules with the same nuclear framework as I which are related to it by π-electron oxidation and reduction.[4] Toward this end we have prepared the heptafulvalene cation and anion radicals and have investigated their esr spectra.

This study also comprises a continuation of our investigations of spin density distributions for π-electron hydrocarbon radicals containing seven-membered rings.[5]

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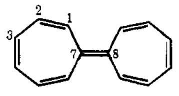
(1) (a) Alfred P. Sloan Research Fellow; (b) to whom all inquiries should be addressed.

(2) Deceased April 3, 1968.

(3) R. B. Turner, "Theoretical Organic Chemistry; Kekulé Symposium," Butterworth & Co. (Publishers), Ltd., London, 1959, p 67.

(4) As far as we are aware only one such molecule has been prepared to date, the heptafulvalene dication [I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, *Tetrahedron Letters*, 5265 (1967)].

(5) (a) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *J. Am. Chem. Soc.*, **87**, 3527 (1965); (b) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968); (c) W. V. Volland and G. Vincow, *ibid.*, **48**, 5589 (1968).

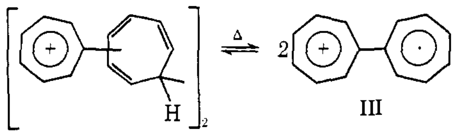


I

Results

A new dicationic substance bi(*x*-tropenyliumyl-2,4,6-cycloheptatrien-1-yl) (II) was synthesized by the reaction of I with silver ion. The one-electron oxidation of I generates the heptafulvalene cation radical (III) which subsequently dimerizes to produce II.

The heptafulvalene cation radical (III) was regenerated by equilibrium thermal cleavage of II. The esr signal can be detected at temperatures as low as 30°.



II

III

Below 60° the intensity of the spectrum varies in the manner expected for a monomer–dimer equilibrium. At higher temperatures the esr signal decays due to a side reaction of the dimer. The measured parameters of the spectrum are listed in Table I.

Table I. Parameters of the Esr Spectra of Heptafulvalene Cation and Anion Radicals

Radical	Solvent	Temp, °C	$\lvert a_1^{\mathrm{H}}\rvert$[a]	$\lvert a_2^{\mathrm{H}}\rvert$	$\lvert a_3^{\mathrm{H}}\rvert$	$\lvert a^{\mathrm{K}}\rvert$[b]	ΔH_{ms}	g
Cation	$C_2H_5NO_2$	50	0.075	2.90	1.72		0.08	2.00263
Anion	MTHF	−120	8.22[c]	*d*	5.02[c]		1.3	
	THF	−90	4.18	*d*	2.53	0.23	0.15	
	THF	+90	4.08	*d*	2.50		0.45	2.00267
	DMF	−70	4.10	*d*	2.49		0.25	2.00266

[a] Splittings and line widths are given in gauss. The splittings are assigned to ring positions with the aid of theory. [b] Potassium hyperfine splitting. [c] All proton splittings cited in this table arise from four protons except for these, which arise from two protons each. [d] This splitting is too small to be resolved.

The heptafulvalene anion radical (red) has been generated by reduction of I with potassium metal and has been detected in several solvents at −80°. If the temperature is raised the esr signal of the radical anion first disappears (*ca.* −50°) and then reappears at higher temperature (*ca.* +30°). This sequence is due to radical dimerization and then equilibrium thermal cleavage of the dimer (purple).

We have measured the equilibrium constant for the cleavage of the dianion dimer in THF relative to that for the dissociation of neat liquid bi-2,4,6-cycloheptatrien-1-yl to form cycloheptatrienyl radical. The equilibrium constant is $\approx 10^{-7}$ at 66° and is *approximately nine orders of magnitude greater* than that for bi-2,4,6-cycloheptatrien-1-yl.[6]

The parameters of the esr spectrum of the anion radical are presented in Table I. It is found that the spectrum is strongly temperature and solvent dependent (Figure 1). The spectrum in DMF at −70° exhibits the binomial intensity ratios expected for two groups of four protons (Figure 1a); hyperfine splitting constants are 4.10 and 2.49 G. The third splitting due to the remaining four protons is not resolved and is therefore less than 0.15 G. In THF (and MTHF) at −90° (Figure 1b) the spectrum shows pronounced line width variations, but essentially the same hyperfine splittings as in DMF. As the temperature is lowered further in MTHF samples the relative intensities of the hyperfine components change. At −120° a hyperfine spectrum is found which can be analyzed as arising from two sets of two equivalent protons with splittings of 8.22 and 5.02 G (Figure 1c).

We attribute this large variation of proton splitting constants to the occurrence of intramolecular "jumping" of the potassium cation from one ring to the other. At −120° (MTHF) this motion is slow compared with the reciprocal of the hyperfine frequency and the ion-pair spectrum corresponds to 2 groups of two equivalent protons. On the basis of the excellent agreement between calculated and experimental splittings to be presented below we assert that (1) both splittings arise from protons in the *same ring*[7] and (2) there is essentially no unpaired π spin density on the other ring. If these proposals are correct we would expect that as the rate of K^+ "hopping" increases to the fast-exchange case,[8] a characteristic pattern of line width alternation[8] would be exhibited and the averaged spectrum would be consistent with two groups of four protons with just *half* the coupling constants measured for the slow-exchange spectra. This behavior is indeed noted in THF and MTHF at −90°.

From details of the line shape in THF at −90° (Figure 1b) we estimate that the rate of hopping of K^+ is $\approx 7 \times 10^8$ sec^{-1}. The resolution of a potassium hyperfine splitting in this spectrum is good evidence for the intramolecular nature of the ion migration.[8] The spectrum in DMF at −70° exhibits binomial intensity ratios and the averaged couplings and thus corresponds to a much faster exchange rate than that found in THF.

Discussion

Spin Density Distributions. The most striking feature of our results is the contrast between the spin density distributions of the cation and anion. In the case of the cation the unpaired spin is delocalized throughout the molecule whereas for the anion it is essentially *localized on a single ring*. Such a spin-density distribution is novel for a π-electron radical.

We can explain these results qualitatively in terms of an HMO theory model in which it is proposed that heptafulvalene consists of two almost independent cycloheptatrienyl (C_7H_7) halves. The Hückel molecular-orbital energy levels for C_7H_7 are shown in Figure 2a and those for a noninteracting dimer are portrayed in Figure 2b. The bond between carbon atoms 7 and 8 constitutes a weak perturbation of the dimer which lifts some but not all of the molecular-orbital degeneracy. The symmetry of this perturbation is such that the

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(6) (a) W. V. Volland, Ph.D. Thesis, University of Washington, 1967; (b) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969); (c) the equilibrium constant for the thermal cleavage of neat liquid bi-2,4,6-cycloheptatrien-1-yl is 10^{-12} at 133°[6a] and has been extrapolated to 66° using the enthalpy of cleavage, 35 kcal/mol.[6b]

(7) The splitting of the remaining pair of protons in this ring is too small to be resolved.

(8) (a) E. de Boer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964); (b) E. de Boer, *Rec. Trav. Chim.*, **84**, 609 (1965); (c) M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, *Bull. Chem. Soc. Japan*, **40**, 2754 (1967).

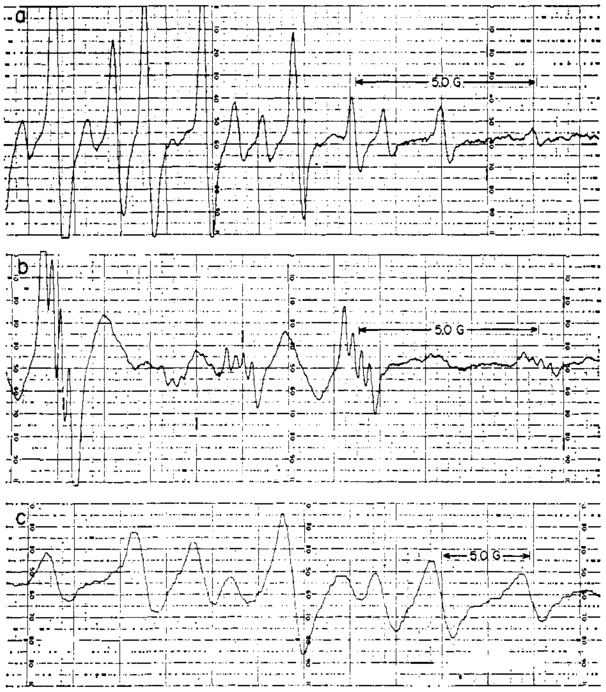

Figure 1. Hyperfine spectrum of the heptafulvalene anion radical: (a) DMF at −70° (half the spectrum shown), (b) THF at −90° (half the spectrum shown), (c) MTHF at −115° (entire spectrum shown).

appropriate zeroth-order linear combinations of the fourfold-degenerate molecular orbitals are either symmetric (designated S_1 and S_2) or antisymmetric (designated A_1 and A_2) with respect to reflection in a plane perpendicular to the aromatic plane and passing through the C_7–C_8 bond. At the 7 (or 8) position the symmetric C_7H_7 orbitals have nonzero coefficients whereas the antisymmetric orbitals have nodes. In the HMO approximation a perturbation applied at that position will lift the degeneracy of the S orbitals and will mix them (S_1 and S_2 yield S_{12} and S_{12}') but will neither perturb nor mix the antisymmetrical orbitals nor will it lift their degeneracy. The resulting molecular orbital pattern for the perturbed dimer is shown in Figure 2c and is qualitatively identical with that predicted by HMO theory for heptafulvalene. The interesting features of this model are that (1) the unpaired electron in the cation occupies a delocalized orbital formed by mixing two perturbed symmetrical C_7H_7 orbitals and (2) the unpaired electron of heptafulvalene anion is in either of two degenerate molecular orbitals which have coefficients identical with those of the A orbital of C_7H_7 on one ring and zero coefficients on the other. The accidental molecular-orbital degeneracy predicted for the heptafulvalene anion (Figure 2c) is likely lifted primarily by the potassium counterion which is not expected to modify the localization of the unpaired electron.[9] The location of the counterion dictates which ring will possess the unpaired spin. As the potassium ion "jumps" from ring to ring the unpaired spin also "jumps" to accommodate the change in position of the perturbation. The various features of the model presented above are indeed reflected in our experimental esr results.

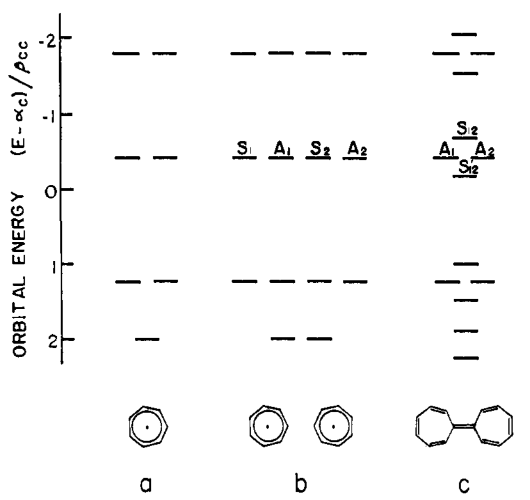

Figure 2. Hückel molecular orbital energy levels, $(E - \alpha_c)/\beta_{cc}$: (a) C_7H_7, (b) noninteracting dimer of C_7H_7, (c) heptafulvalene.

The magnitudes of the proton hyperfine splittings have been computed using the Hückel MO and McLachlan SCFMO methods. Calculated splittings for the cation are listed in Table II. The resonance integral β_{78} has been allowed to vary in order to reflect some twisting of the C_7H_7 rings due to steric repulsions at the 1,6 and 9,14 positions. Very good agreement with experiment is obtained using the McLachlan method with $\beta_{78} = 0.9\beta_{cc}$, *i.e.*, percentage deviations for the two larger splittings are 10% or less.

Table II. Heptafulvalene Cation, Calculated and Experimental Splittings

		Calcd			
		HMO[a]	McLachlan SCF-MO[b,c]		
	Exptl	$k_{78} = 1$	$k_{78} = 1$	$k_{78} = 0.9$	$k_{78} = 0.8$
$\lvert a_1^H \rvert$	0.075	1.03 G	0.45	0.29	0.10
$\lvert a_2^H \rvert$	2.90	2.33	2.73	2.83	2.94
$\lvert a_3^H \rvert$	1.72	1.67	1.55	1.50	1.46

[a] All splittings are calculated using McConnell's relationship with $|Q| = 26$ G. [b] $k_{78} = \beta_{78}/\beta_{cc}$. [c] $\lambda = 1.1$.

Anion splittings are presented in Table III. These are computed (using McConnell's relationship, $a_k^H = Q\rho_{kk}^\pi$) from an unpaired electron molecular orbital with zero coefficients on one ring and coefficients identical with those of the cycloheptatrienyl radical on the other (Figure 2). A general expression for the π-spin density distribution of the A orbital of $C_7H_7\cdot$ is given by[5b]

Table III. Heptafulvalene Anion, Calculated and Experimental Splittings

		Calcd[a]		
	Exptl	HMO	McLachlan	$P = 1.3$[b]
$\lvert a_1^H \rvert$	8.22	7.06	9.37	8.06
$\lvert a_2^H \rvert$	(<0.3)[c]	1.40	0.33	0.70
$\lvert a_3^H \rvert$	5.02	4.54	4.93	4.79

[a] Splittings calculated using $|Q| = 26$ G. [b] Computed using eq 1. [c] Estimated from the rapid-exchange spectra.

$$\rho_{kk}^\pi = {}^1\!/_7[1 - P\cos(8\pi k/7)] \qquad (1)$$

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[9] This assertion is based on the results of HMO calculations in which the effect of the K^+ perturbation has been simulated by small changes in the Coulomb integrals at the 1, 2, or 3 positions.

where $P = 1$ and 1.742, corresponding to HMO and McLachlan SCFMO theories, respectively.[10] We have also computed splittings for $P = 1.3$, a value which gave optimum agreement for tri-*t*-butylcycloheptatrienyl radical,[5b] a molecule whose spin distribution is expected to be very similar to that of the A orbital of $C_7H_7\cdot$. Best agreement with experiment in the case of heptafulvalene is indeed obtained for $P = 1.3$ (deviations for the larger splittings are <5%).

Resonance Energy. It is interesting to compare the resonance stabilization of the ion radicals investigated in this work with that of their parent hydrocarbon, heptafulvalene. The empirical resonance energy of I is only 28 kcal/mol,[3] which is considerably less than the delocalization energy predicted by HMO theory, $4\beta_{cc}$ or *ca.* 64 kcal/mol. This apparent discrepancy is explained by the fact that a uniform molecular geometry is assumed in HMO theory whereas more refined calculations[11] have demonstrated that I consists of alternate single and double bonds. Such bond alternation is characterized by a reduction in the stabilization energy.

The Hückel MO theory also predicts large delocalization energies for the cation and anion radicals, namely $4.18\beta_{cc}$ and $3.56\beta_{cc}$, respectively. In this work we have found two pieces of evidence which *indicate* that the ion radicals may have considerable delocalization energy as predicted and may thus differ from heptafulvalene itself.

(1) The fact that the application of approximate π-electron theory, in which a *uniform* nuclear framework is assumed, leads to the calculation of proton hyperfine splittings which are in good agreement with experiment argues against the occurrence of alternate single and double bonds in the ion radicals (with concomitant reduction of delocalization energy).

(2) A qualitative indication that these radicals are extensively stabilized by resonance is given by the fact that their dimers are both appreciably dissociated into radicals at room temperature. The equilibrium constant for the thermal cleavage of the dianion dimer is approximately nine orders of magnitude greater than the corresponding quantity for bicycloheptatrienyl. We have shown elsewhere[6b] that $C_7H_7\cdot$ is an extensively stabilized free radical with a total empirical resonance energy of 31 kcal/mol.

Experimental Section

Materials. Heptafulvalene was synthesized according to the method of Mayer.[12] Silver tetrafluoroborate was obtained from Ozark-Mahoning, Tulsa, Okla. Nitroethane (practical grade) was fractionally distilled, redistilled from P_2O_5, and passed over an alumina column. THF (tetrahydrofuran) and MTHF (2-methyltetrahydrofuran) were stored over CaH_2, dried over sodium, distilled onto $LiAlH_4$ plus triphenylmethane, and then redistilled. DMF (N,N-dimethylformamide) was stored over CaH_2 and distilled from sodium. Toluene was stored over sodium wire. All other solvents used were reagent grade.

Dication Dimer (II). A solution of heptafulvalene (180 mg, 1.0×10^{-3} mol) in 50 ml of dry toluene was added to a solution of $AgBF_4$ (*ca.* 300 mg, 1.5×10^{-3} mol) in 50 ml of dry toluene under a nitrogen atmosphere at room temperature. The greenish black precipitate which immediately results was filtered, and washed with acetonitrile to separate the oxidized organic material from the silver metal. It was found (in one run) that 0.9 mol of silver metal was produced per mole of I consumed. The orange solution containing a mixture of isomers of the dimer was evaporated to yield a semicrystalline material which could not be recrystallized.

Mass spectral technique was used in order to obtain analytical evidence for the dimeric nature of II. Compound II was reduced by hydride transfer from 1-benzyl-1,4-dihydronicotinamide.[13] The neutral tetramer exhibited a parent peak in the mass spectrum of *m/e* 362.206 (calcd 362.203).

The ultraviolet spectrum of this tetramer (uv $\lambda_{max}^{n\text{-pentane}}$ 263 and 300 mμ) is quite similar both in position and relative intensity to that reported for a thermally isomerized bitropenyl, 1,1′-bis-(1,3,5-cycloheptatrienyl) (uv $\lambda_{max}^{(C_2H_5)_2O}$ 261 and 308 mu),[14] which is further evidence for the proposed structure of the neutral tetramer.

The nmr and uv spectra of II are also consistent with the proposed structure. The nmr in nitroethane or acetonitrile consists of a broad peak at *ca.* τ 1.2 and broad multiplets between τ 2.3 and 4.0.[15] These bands are located in the regions of the protons of a tropenylium ion substituted with an electron-donating group and vinyl protons, respectively. The multiplet due to the methine protons is obscured by the solvent spectrum.

The ultraviolet spectrum of II (uv $\lambda_{max}^{CH_3CN}$ 270 and 353 mμ) is quite similar to that expected for a tropenylium ion substituted with a group which can exert an intramolecular charge-transfer effect.[16]

Heptafulvalene Anion Radical. The heptafulvalene anion radical was generated by the reaction of a DMF, THF, or MTHF solution of I with a potassium mirror *in vacuo* at low temperature (*ca.* −80°).

Esr. A Varian Associates V-4500 esr spectrometer was employed. Details of the experimental techniques have been reported elsewhere.[5b]

The equilibrium constant for the thermal dissociation of the dianion dimer was determined as follows. A solution of I in THF was allowed to react with excess potassium at room temperature for 15 min. Assuming complete reaction the concentration of dianion dimer produced is 0.0095 *M*. The esr spectrum of the anion radical at +66° was compared in intensity[17] with that of the cycloheptatrienyl radical ($C_7H_7\cdot$) produced by thermal cleavage of neat liquid bi-2,4,6-cycloheptatrien-1-yl at 130°. From the known equilibrium constant and enthalpy of cleavage[6] of bi-2,4,6-cycloheptatrien-1-yl an approximate concentration of 2.6×10^{-5} *M* was computed for the heptafulvalene anion;[18] hence $K \approx 10^{-7}$ (66°).

Acknowledgment. This work was partially supported by the U. S. Army Research Office, Durham, and by the Petroleum Research Fund, administered by the American Chemical Society.

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[10] Vibronic coupling effects are omitted from this equation since the heptafulvalene anion, from its molecular symmetry, cannot be orbitally degenerate.

[11] A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962); T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

[12] J. R. Mayer, Ph.D. Thesis, Yale University, New Haven, Conn., 1955.

[13] We are thankful to Mr. Richard Roesler of these laboratories for a sample of 1-benzyl-1,4-dihydronicotinamide.

[14] F. R. Hunter, Ph.D. Thesis, University of Washington, Seattle, Wash., 1966.

[15] The broadening of lines in the nmr spectrum is probably due to the presence of an appreciable concentration of the free radical cation III.

[16] K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Am. Chem. Soc.*, 91, 323 (1969), and references cited therein.

[17] The standard formula area $\propto KW^2H$ was employed ("EPR Operational Techniques," Publication No. 87-114-402, Varian Associates, Palo Alto, Calif.) with the line shape factor *K* taken to be the same for both radicals.

[18] Estimated maximum limits of error for this concentration are a factor of 2.