

Electron spin resonance study of the geometry of 9-phenylacridine

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(5.0, 5.1 Å), mandelate (4.5, 3.9 Å), hydroxyisobutyrate (4.1, 3.4 Å), lactate (4.0, 3.2 Å), and glycolate (3.8, 2.6 Å). A similar calculation for vanadyl bis(acetylacetonate) with $\rho = 1.49$ g/cc from the reported crystal structure²⁹ yields $R = 3.7$ Å compared to $r = 3.3$ Å for toluene solutions. Except for the benzilate, in general, the closest packing crystal radii are larger than hydrodynamic radii. We discover an exception to this "general rule" with vanadyl sulfate, $\text{VO}\text{SO}_4 \cdot 5\text{H}_2\text{O}$, with $R = 2.9$ Å compared to $r = 3.4$ Å (R was calculated with $\rho = 2.00$ g/cc from the crystal structure¹⁹ and W corresponding to $\text{VO}(\text{H}_2\text{O})_5^{2+}$). Such a large value of r relative to R is a further indication that the vanadyl species in aqueous solution is larger than $\text{VO}(\text{H}_2\text{O})_5^{2+}$ as discussed earlier. For vanadyl bis(acetylacetonate) in seven different solvents Wilson and Kivelson have found variations in r from 3.01 to 3.56 Å which can be explained in terms of differences in solvent coordinating ability.²²

Conclusion

Due to the similarities in g and hyperfine anisotropies for all the hydroxycarboxylate chelates, we expected variations in their line widths to primarily reflect differences in the viscosity of the medium and molecular size. Indeed, τ_R , which is a measure of molecular tumbling rates in solution, correlates quite well with the molecular weights. In general, the theory satisfactorily explains the principal features of the spectra although the same τ_R is still not obtained from different parameters. The rotational correlation time and residual line width for vanadyl sulfate in aqueous solution appear to be anomalous with respect to the hydroxycarboxylates, perhaps because of strong metal ion-solvent interactions in the former.

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An Electron Spin Resonance Study of the Geometry of 9-Phenylacridine

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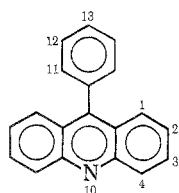
The electron spin resonance spectrum of the radical anion of 9-phenylacridine (9PAC) was obtained and the coupling constants were assigned. Correlation of the coupling constants with Hückel molecular orbital calculations indicated that the phenyl ring was twisted approximately 65° out of the plane of the acridine nucleus. The effect of the value of the Coulomb integral on the twist angle determination is discussed.

In a previous paper¹ we discussed the relative importance of resonance energy and steric interactions in determining the molecular geometry of a group of highly hindered molecules (the aryl-substituted polynuclear aromatic hydrocarbons) and concluded that the overriding influence was steric. The steric strain was assumed to be relieved by twisting of the aryl substituent out of the plane of the other ring system, the degree of twisting being related to the type and number of steric interactions present in the molecule. Molecules with steric repulsions like those in 9-phenylanthracene have been found to exhibit a twist angle lying between 60 and 72° ,²⁻⁸ to test further the direct relation of twist angle to steric strain, we have investigated the geometry of 9PAC, the *N*-heterocyclic analog of 9-phenylanthracene. The instability of the cation radi-

cal precluded its study; however, we have prepared the anion radical and have determined its twist angle to be approximately 65° .

Experimental Section

The 9PAC was prepared according to Albert.⁹ Hexamethylphosphoramide (HMPA) was triply distilled under vacuum from a solution of 9PAC and sodium; *N,N*-dimethylformamide (DMF) was dried over Linde 4A molecular sieves and vacuum distilled under nitrogen from a suspension of anhydrous copper sulfate; 1,2-dimethoxyethane (DME) was dried and distilled over lithium alumi-



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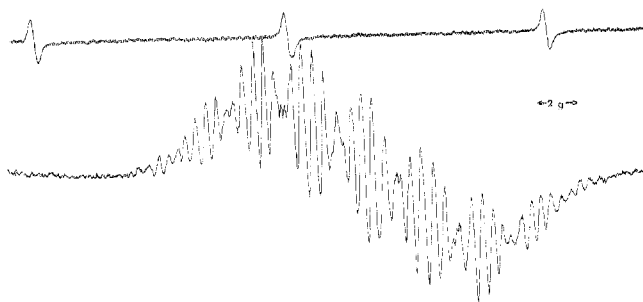


Figure 1. Poorly resolved esr spectrum of the 9PAC anion radical.

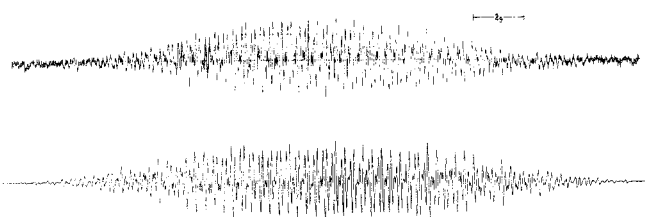


Figure 2. Esr spectrum (top) of the 9PAC anion radical and its computer simulation using the coupling constants of Table I, a 0.06-G line width, and a completely Lorentzian line shape.

TABLE I: Coupling Constants for the 9PAC Anion Radical

Position	Type	No. of nuclei	a , G
1	H	2	2.936
2	H	2	1.094
3	H	2	1.964
4	H	2	1.822
11	H	2	0.385
13	H	1	0.526
10	N	1	3.665

num hydride and stored under vacuum over pieces of sodium. Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from Southwestern Analytical Chemical Co. (Austin, Tex.) and dried in a vacuum oven before use. The esr spectrometer used was a Varian V-4502 with standard accessories; both the spectrometer and the spectral simulation program have been previously described.^{3,4}

Results and Discussion

The radical anion of 9PAC was prepared by alkali metal reduction of the parent in DME and by electrochemical reduction in DMF; in both cases the poorly resolved spectrum shown in Figure 1 was obtained. Alkali metal reduction in HMPA, however, yielded a highly resolved spectrum; this spectrum and its computer simulation, using the coupling constants in Table I, a 0.060-G line width, and a completely Lorentzian line shape, are shown in Figure 2. Though the noise level obscures the outer lines, the sensitivity of the central portion of the spectrum to small changes in the coupling constants allows a high degree of confidence in positing that the coupling constants of Table I are those giving rise to the experimental spectrum.

The assignment of the coupling constants to positions in the molecule was based on Hückel calculations. Assignment on this basis was straightforward with the exception of positions 3 and 4; for these positions the relative magnitude of the calculated spin densities was a function of the value chosen for the Coulomb integral of the nitrogen

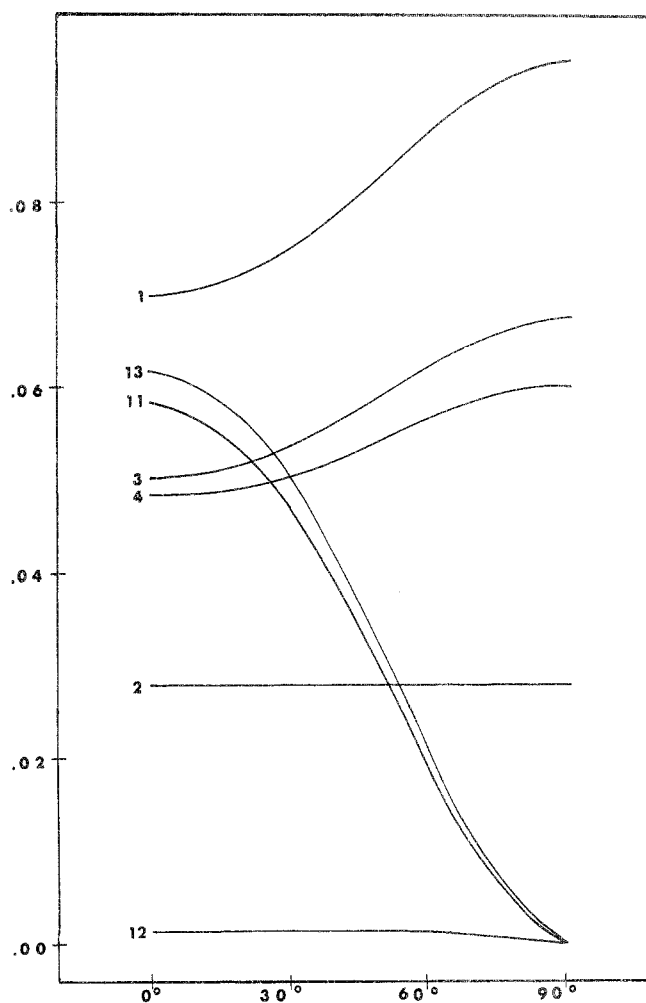


Figure 3. Ued's of the 9PAC anion radical as a function of the twist angle θ . The ued's were calculated using $h_N = 0.7$, $k_{CN} = 1.0$; similar curves were obtained using other values of h_N .

atom. Szwarc, *et al.*,¹⁰ used nmr line broadening results to assign these positions in the acridine anion radical; we have assumed that the ordering would be unchanged by the presence of the phenyl substituent and have followed their assignment.

A certain ambiguity also exists in the assignment of the splittings on the phenyl ring. The simulation in Figure 2 is based on a 0.526-G splitting from the single para proton and a 0.385-G splitting from the two equivalent ortho protons. A simulation based on a 0.526-G splitting from three equivalent protons (ortho and para) and a 0.385-G splitting from two equivalent protons (meta) is indistinguishable at the intensity of the experimental spectrum from that shown in Figure 2. On the basis of the Hückel calculations we decided that the meta proton splittings would be too small to be detected and thus made the assignment given in Table I.

The method and assumptions involved in determining the twist angle, θ , have been previously discussed.¹ The unpaired electron density (ued) at each atom was calculated using Hückel molecular orbital theory and is shown as a function of twist angle, θ , in Figure 3. To ensure that the value of θ_{9PAC} determined does in fact reflect the molecular geometry and not simply a particular HMO con-

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TABLE II: Twist Angles Determined from the Ratios of the Ued's^a

	1/11	2/11	3/11	4/11	Av
Case 1	67	70	65	68	67
Case 2	66	68	65	66	66
Case 3	66	66	65 ^b	64 ^b	65

^aAll values are in degrees. ^b These values were obtained by inverting the assignment of the two positions.

struct, we used three sets of values for the parameters and determined θ_{9PAC} for each set. From among the values cited in calculations on heteromolecules,¹¹ we chose three sets which would span the commonly used range of values: case 1,¹² $h_N = 0.84$, $k_{CN} = 1.0$; case 2,^{13,14} $h_N = 0.7$, $k_{CN} = 1.0$; case 3,^{10,15} $h_N = 0.5$, $k_{CN} = 1.0$.

The effect of the value of h_N on the twist angle is small; the average θ_{9PAC} value varies by only 2° (Table II). With $h_N = 0.5$ the order of the ued's at positions 3 and 4 is inverted; however, if we also invert the assignment of the

coupling constants at these positions, the value of θ_{9PAC} is in good agreement with that derived from the other sets of parameters. A similar inversion was noted by Pedersen and Muus¹⁴ for the quinoxaline anion radical upon changing the value of h_N from 0.7 to 0.4.

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Electronic and Electron Spin Resonance Spectra of the Anion Radicals of Phenyl- and Diphenylethylenes

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A number of previously unknown esr and uv spectra have been observed for aryl- and diarylethylene anion radicals generated by IG (internal generation) and EG (external generation) electrolytical reductions in dimethyl sulfoxide and acetonitrile, respectively. Semiempirical self-consistent field calculations combined with limited configuration interaction (LCI-SCF), according to Longuet-Higgins and Pople and Roothaan methods, allow a satisfactory interpretation of the electronic spectra of the anion radicals. Also uv spectra of parent neutral molecules have been taken into consideration and discussed. Spin densities, obtained by the aforementioned and McLachlan's methods, have been translated into coupling constants through McConnell's relationship and compared with experimental data. These three methods allow an unequivocal assignment of proton hyperfine splitting (hfs) constants for all considered anion radicals.

Introduction

While the esr spectra of ion radicals have been the subject of extensive experimental and theoretical investigations¹ only scanty information about the ultraviolet spectra of the same compounds has been collected. Recent literature references in the field can be found in papers by Zahradnik and Čársky² and by Shida and Iwata.³ In the present work we present the uv and esr spectra of a series of anion radicals as well as the uv spectra of the parent neutral molecules. An attempt is made to interpret all the experimental data by means of a single MO calculation. The latter has been performed according to different

methods in order to confront the merits of the different semiempirical MO theories in predicting both energy and electron distribution in radical anions. The skeleton of *p*-nitrophenylethylene was present in all compounds under examination. The formulas together with twist angles are shown in Figure 1, where the twist angles are taken counterclockwise looking from the ethylenic carbon.

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