Detailed electronic structural calculations and single-crystal esr experiments on $V(S_2C_2Ph_2)_3$ are in progress and will be reported in full in a forthcoming paper.

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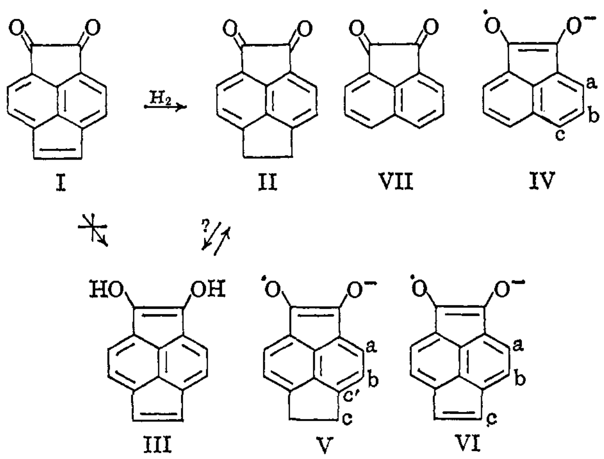
## Pyracylenes. Radical Anions Related to Pyracyloquinone

*Sir:*

Recently,[1] one of us reported the preparation of a pyracylene derivative, pyracyloquinone (I). Theoretically, reduction of this compound could lead to the much sought after pyracylene system; however, catalytic reduction produced[1] only 1,2-diketopyracene (II). Other reducing agents such as trimethyl phosphite, zinc, and sodium have led only to undefined products. Since it appeared the derivatives of III were highly unstable, more suitable techniques for studying such systems were necessary.



I II VII IV

III V VI

The initial products of reduction of quinones and oxidation of hydroquinones in alkaline media involve semiquinone anions as intermediates.[2] These species can be detected and their structures deduced from esr measurements. The conversion of the quinone (I) and the keto form of the hydroquinone (II), both of which were in hand,[1] to pyracylosemiquinone would demonstrate the existence and relative stability of the pyracylene aromatic system.

The anion radicals IV, V, and VI were generated from the corresponding quinones VII, II, and I by the method of Russell[2a] (solution in 0.1 *M* potassium *t*-butoxide in freshly distilled DMSO). The esr spectral data[3] are summarized in Table I. Whereas IV and V were stable for many hours at room temperature, VI slowly decomposed to produce a very complicated spectrum over a period of a few hours. The coupling constants observed for acenaphthasemiquinone (IV) agree well with the reported values[4] for the same radical species generated electrolytically. The values of $a_a$ and $a_b$ found for V are quite close to the corresponding ones for IV, as might be anticipated. Unfortunately, no satisfactory model for comparison with the splitting by the methylene hydrogens, $a_c$, of V exists. As expected, calculations[5] employing the experimental[6] charge density ($\rho_c$ of IV) indicate a value of 2.03 gauss[7] for $a_c$ of V, somewhat higher than that observed. The inductive effect of the methylene bridge should reduce the odd-electron density at the aromatic carbon C′ of V corresponding to position C of IV, thus reducing the splitting by the methylene hydrogens.

**Table I.** Esr Spectral Data[a]

| Semiquinone | $a_a$ | $a_b$ | $a_c$ | $g$ |
|---|---|---|---|---|
| IV[b] | 1.18 | 0.27 | 1.28 | 2.0044 |
| V[b] | 1.15 | 0.21 | 1.38 | 2.0043 |
| VI[c] | 1.41 | 2.45 | 2.12 | 2.0030 |

[a] Coupling constants are reported in gauss. [b] $a$ value $\pm0.02$ gauss, $g$ value $\pm0.0001$. [c] $a$ value $\pm$ 0.02 gauss, $g$ value $\pm0.0002$.

The higher coupling constants for pyracylosemiquinone (VI) indicate the presence of substantially greater spin density in the carbon framework of VI than for IV or V. These coupling constants, converted to spin densities by the McConnell relationship, are compared to values calculated by Hückel molecular orbital theory in Table II. The excellent agreement of the experimental and calculated spin densities provides the assignment of the coupling constants as presented in Tables I and II. Of particular interest is the prediction that the largest spin density resides at position b. This result is not predicted by naïve valence bond methods, for resonance structures which put an odd electron at b do not have the benefit of benzene resonance stability as do those structures with an odd electron at a or c.

**Table II.** Comparison of Experimental and Calculated[a] Quantities for Pyracylosemiquinone (VI)

| | Spin density at position | | | | |
|---|---|---|---|---|---|
| | a | b | c | λ[b] | $g$ |
| Calculated | 0.048 | 0.106 | 0.086 | 0.1192 | 2.0028 |
| Experimental | 0.059[c] | 0.102[c] | 0.088[c] | | 2.0030 |

[a] This calculation employed $h_O = 0.8$ and $k_{CO} = 1.0$. The results are relatively insensitive to variation in these parameters. See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 117. [b] Refers to $E = \alpha + \lambda\beta$ for the highest occupied molecular orbit of VI. [c] Obtained from $a_r = Q\rho_r$ with $Q = 24$.

The significance of the $g$ value for organic molecules has virtually been ignored until very recently.[8] Pub-

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(1) B. M. Trost, *J. Am. Chem. Soc.*, **88**, 853 (1966).

(2) For leading references see (a) E. R. Talaty and G. A. Russell, *ibid.*, **87**, 4867 (1965); (b) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(3) A dual cavity-equipped Varian V-4502 spectrometer with 9-in. magnet was employed. As a reference standard, peroxylamine disulfonate ($a$ = 13.0 gauss, $g$ = 2.0055) was used.

(4) Dehl and Fraenkel report $a_a$ = 1.17 gauss, $a_b$ = 0.27 gauss, and $a_c$ = 1.27 gauss. See R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(5) Using $Q$ (aliphatic) $= A + B\cos^2\theta$ where $A = -1.1$ (J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1963)), $B = 50$ (R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963)), and $\theta$ is the angle between the axis of the p orbital at the aromatic carbon C′ and the C′–C–H plane (in this case $\theta \cong 30°$).

(6) Using the McConnell relationship $a_c = Q\rho_c$ where $\rho_c$ is the spin density at position c of IV and $Q$ (aromatic) = 24.

(7) If the best HMO value calculated by Dehl and Fraenkel[4] is employed, the predicted $a_c$ value is 1.46 gauss for V—a fortuitous agreement with the experimental value.

(8) For an excellent discussion of the importance of the $g$ value in interpretation, see ref 2b.

lished $g$ values for semiquinone anions with no halogen substitution fall in the narrow range of 2.0044 ± 0.0004.[2b,9] The values for IV and V (see Table I) occur within this range; however, the value for VI is significantly lower, closely approaching the range 2.0026 ± 0.0001 reported[2b,8] for hydrocarbon radical anions. The nature and unusually low energy of the molecular orbital containing the odd electron anticipates this result. Furthermore, the quantitative theory of $g$ values developed by Stone[10,11] predicts a value of 2.0028, in excellent agreement with the observed one (see Tables I and II). The abnormal $a$ and $g$ values of VI strongly suggest it is not a normal semiquinone anion but more akin to a hydrocarbon anion radical. Since the energy level in which pyracyloquinone can accommodate an extra electron is very low lying and because of the nature of this orbital, the species formed might better be described as a perturbed hydrocarbon radical anion than the semiquinone anion. Theory and experiment and the excellent correlation between them attest to this conclusion.

The distribution of the odd-electron density in this molecule indicates the presence of the pyracylene aromatic system. We have already noted its instability. Furthermore, III is not formed from II under these conditions nor does V, the semiquinone anion of II, decompose to VI. Since diketopyracene (II) may be considered[12] a tautomer of dihydroxypyracylene (III), we might have anticipated interconversion of II and III or of V and VI. This observation and the relative instability of VI suggest the pyracylene aromatic system does not possess the substantial stability predicted by molecular orbital theory.

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[9] (a) M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958); (b) M. S. Blois, H. W. Brown, J. S. Hyde, and J. E. Maling, *Arch. Sci.* (Geneva), **13**, spectrum no. 243–255 (1960); *Chem. Abstr.*, **57**, 1770*b* (1961).

[10] A. J. Stone, *Mol. Phys.*, **6**, 509 (1962).

[11] $g = g_{el} + b + \lambda c + \rho_O \gamma_O$ where $g$ is the observed value; $g_{el} =$ 2.00232, the value for a free electron; $b = 0.000247$; $\lambda$ refers to the energy of the odd-electron orbital in the hydrocarbon to which the semiquinone is related (for pyracylene $\lambda = 0.000$); $c = -0.000193$; $\gamma_O = 0.00550$; $\rho_O$ is the spin density on oxygen with $b$, $c$, and $\gamma_O$ experimental constants as determined by Stone.

[12] The tautomerism required here cannot be considered the normal enol–keto type since enolization requires disruption of one of the benzene rings. This question will be more fully considered in a future communication.

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## Substitution Reactions of Sulfitopentaamminecobalt(III) and Its Derivatives. Evidence for a Limiting SN1 Mechanism

*Sir:*

One of the central themes of recent studies on the mechanisms of substitution reactions of octahedral cobalt(III) ammine complexes has been the question of whether substitution proceeds *via* an SN1 or SN2 mechanism. Arguments in favor of a limiting SN1 mechanism involving a pentacoordinated cobalt(III) intermediate have been advanced for such reactions, but the evidence appears to be inconclusive and the issue has remained a lively and controversial one.[1] We now wish to present definitive kinetic evidence that certain substitution reactions of $Co(NH_3)_5SO_3^+$ and its derivatives do proceed by limiting SN1 mechanisms involving the intermediate $Co(NH_3)_4SO_3^+$.[2] Our evidence is essentially similar to that advanced by Haim and Wilmarth[3] for a limiting SN1 mechanism, involving the pentacoordinated intermediate $Co(CN)_5^{2-}$, in the substitution of water in $Co(CN)_5OH_2^{2-}$ by various nucleophiles.

Our investigations relate to the series of substitution reactions (where $A = NH_3$)

$$Co^{III}A_4SO_3(X) + Y \longrightarrow Co^{III}A_4SO_3(Y) + X \qquad (1)$$

$X = NH_3$; $Y = {}^{15}NH_3$, $OH^-$, $CN^-$, $NO_2^-$, or $SCN^-$
$X = OH^-$; $Y = NH_3$ or $CN^-$
$X = NO_2^-$; $Y = NH_3$ or $OH^-$
$X = SCN^-$; $Y = NH_3$

The occurrence of these reactions apparently reflects the marked *trans*-labilizing influence on the S-bonded sulfito ligand.[4–6] Confirmation of this is provided by our observation that under the conditions of these experiments only one (1.1 ± 0.1) of the five ammonia ligands in $CoA_5SO_3^+$ exchanges with excess $^{15}NH_3$ (reaction 2). The configurations of the other disubstituted complexes are not known with certainty but are presumably also *trans*.

$$Co(NH_3)_5SO_3^+ + {}^{15}NH_3 \longrightarrow Co(NH_3)_4({}^{15}NH_3)SO_3^+ + NH_3 \qquad (2)$$

The kinetics of the above reactions (apart from reaction 2 whose kinetics were not studied) were examined at 25° in solutions of ionic strength 0.46 (maintained with $NaClO_4$). The reactions were followed spectrophotometrically, using a stopped-flow apparatus in the cases where the rates were too fast for conventional measurement.

All of the reactions examined exhibited kinetic behavior consistent with the general rate law

$$\frac{-d[CoA_4SO_3(X)]}{dt} = \frac{k_1^X k_2^Y[CoA_4SO_3(X)][Y]}{k_2^X[X] + k_2^Y[Y]} \qquad (3)$$

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[1] See, for example, A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964); C. H. Langford, *ibid.*, **4**, 265 (1965).

[2] The designation SN1 as used here conforms to the widely accepted definition, namely that of a substitution mechanism in which a unimolecular dissociation step generates an intermediate which is sufficiently long-lived to exhibit a selective reactivity pattern toward different nucleophiles, which is independent of the leaving group. While we believe that the $CoA_4SO_3^+$ intermediate in the present case is pentacoordinated, the evidence does not preclude the possibility of rearrangement to a configuration in which $SO_3^{2-}$ acts as a bidentate ligand.

[3] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962); A. Haim, R. J. Grassi, and W. K. Wilmarth in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31; R. Barca, J. Ellis, M. Tsao, and W. K. Wilmarth, presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, Paper O-83.

[4] J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

[5] A. V. Babaeva and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, **7**, 404 (1962).

[6] W. K. Wilmarth (private communication) and his co-workers have observed what is apparently an analogous labilizing influence of the sulfito ligand in the complex $Co(CN)_4(SO_3)_2^{5-}$, which undergoes ready aquation to $Co(CN)_4(H_2O)SO_3^{3-}$.