Pyracylenes. III.[1] Radical Anions in the Pyracylene System

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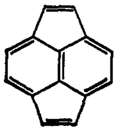
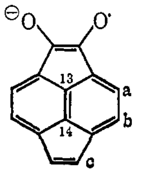
Abstract: The pyracylosemiquinone anion was generated from the quinone under a variety of conditions and compared to the related semiquinones from acenaphthaquinone and 1,2-diketopyracene. The hyperfine splitting constants were found to be dependent upon the method of generation, one set of values obtained by chemical reduction in the presence of base and the other by electrochemical generation. The differences are attributed to the presence of the "free" ion under the base conditions and chelates or tight ion pairs under the electrochemical conditions. The correlation of these spectra with molecular orbital theory is discussed. Stone's theory of *g* factors is modified to allow one to calculate spin density at a heteroatom, oxygen, from two experimental quantities, *g* factors, and half-wave potentials. Thus, pyracyclosemiquinone is found to have approximately one-fifth the spin density at oxygen compared to other semiquinones. This fact plus the large hyperfine splitting constants suggest that this semiquinone anion is more akin to hydrocarbon radical anions than normal semiquinone anions, in excellent agreement with theory. Protonation of the dianion of pyracycloquinone, generated electrochemically, under thermodynamic conditions occurred at carbon to produce diketopyracene. Strain energy and not resonance energy appears to be the determining factor in the equilibrium[1] between diketopyracene and dihydroxypyracyclene.

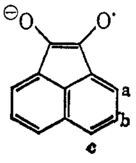
The question of aromaticity is of fundamental theoretical and practical concern and has occupied the attention of many investigators. A particularly interesting compound having $4n + 2$ π electrons and fulfilling Craig's rules of aromaticity is pyracylene (I).[2] Calculations predict a resonance energy of 5.42β,[3,4] whereas the strain of bridging both *peri* positions with sp^2 carbons is estimated to destabilize I by 48 kcal/mole.[5] The unique feature of the electronic structure of this molecule is the prediction that it will have an empty nonbonding molecular orbital, the simplest aromatic hydrocarbon predicted to have this electronic configuration. In order to investigate the properties of the pyracylene system, we synthesized the quinone II related to the parent hydrocarbon.[1b,6] Reduction of this quinone would produce a substituted pyracylene. Since no identifiable products could be isolated by standard reduction procedures,[7] we explored the one electron reduction product (II, pyracylosemiquinone) by the esr technique. This study and some comments regarding correlations between esr spectra and MO calculations form the subject of this paper.



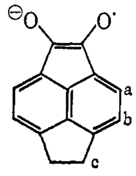
I



II



III



IV

Esr Spectra

To see if unusual electronic distribution attributable to the pyracylyl system in pyracylosemiquinone (II) is realized, the esr spectra of II, III, and IV were compared. Esr data for these semiquinones, prepared by reaction of the quinone with potassium *t*-butoxide in DMSO,[8] appears in Table I.

Table I. Esr Spectral Data (KO-*t*-Bu Reduction in DMSO)

Compd	a_a	a_b	a_c	g
II	1.41 ± 0.02	2.45	2.12	2.0030[a]
III	1.18	0.27	1.28	2.0044[b]
IV	1.15	0.21	1.38	2.0043[b]

[a] Error in *g* is estimated to be ±0.0002. [b] Error in *g* is estimated to be ±0.0001.

The splitting constants of acenaphthasemiquinone (III) are close to those reported[9] for the same species generated electrochemically. Placing a saturated two-carbon bridge across the *peri* positions of III to give IV slightly reduces the ring hydrogen splittings (and hence the ring spin density), which is expected. Because of the slightly electron-releasing character of alkyl compared to hydrogen, electronic density is shifted away from the alkyl group. Unsaturating the *peri* two-carbon bridge (giving II) has a striking effect in that all of the proton splitting constants are raised, which shows that significantly more spin density is on the ring carbons in II than in III or IV. The largest change is at the b position, which has a tenfold increase in spin density, giving it the highest spin density, although the corresponding position of III and IV has the lowest. This is not predictable by simple resonance structure reasoning, for structures with spin at b cannot have the benefit of both benzene resonance and placing the

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(1) (a) For part II, see B. M. Trost and S. F. Nelsen, *J. Am. Chem. Soc.*, 88 2876 (1966). This paper contained a preliminary report of a portion of this work. (b) For part I, see B. M. Trost, *ibid.*, 88, 853 (1966). (c) For part IV, see B. M. Trost and D. R. Brittelli, *Tetrahedron Letters*, No. 2, 114 (1967).

(2) See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 256–304.

(3) R. D. Brown, *J. Chem. Soc.*, 2391 (1951).

(4) (a) B. M. Trost, unpublished calculations; (b) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(5) H. J. Dauben and A. G. Osborne, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., 1956, p 370; we wish to thank one of the referees for pointing out this revised estimate of strain energy.

(6) Dibenzpyracylene has been reported. See H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

(7) B. M. Trost, to be published.

(8) G. R. Talaty and G. A. Russell, *J. Am. Chem. Soc.*, 87, 4867 (1965).

(9) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, 39, 1793 (1963), give 1.17, 0.27, and 1.27 *g*, respectively.

negative charge on oxygen, the most electronegative atom. The *g* value of II, 2.0030, is quite different from III and IV, and indeed from that of all other hydrocarbon semiquinones,[10] which have *g* factors which fall in the narrow range of 2.0040–2.0048. Both the splitting constants and *g* factor of pyracylosemiquinone (II) are seen to be quite unusual; these facts must be a result of unusual electronic distribution in this system.

Since calculations of electronic distribution are for unperturbed, vapor phase species, it was desirable to generate II under a variety of experimental conditions to see if specific medium effects are important in determining the spin distribution. It was found that II could be formed with the weaker bases NaOH, KOH, and $Ba(OH)_2 \cdot 2H_2O$ if a DMSO solution of the quinone was agitated in the presence of the solid base. II was even formed when a DMSO solution of pyracyloquinone was mixed with tetramethylammonium hydroxide. The need for base being present was eliminated by carrying out the reduction at a mercury cathode using various supporting electrolytes (Figure 1). DMSO solutions 0.1 *M* in tetraalkylammonium perchlorates, sodium perchlorate, lithium chloride, and cesium bromide were all successful. Using DMF which was 0.1 *M* in tetrabutylammonium perchlorate gave no difference in splitting constants for II from those observed in DMSO. The electrolytic reduction fails to give workable radical concentrations in DME or THF with alkali metal supporting electrolytes. Measurable amounts of II are not formed if a DME solution of pyracyloquinone is stirred with sodium hydroxide (in contrast to the results in DMSO), but ultraviolet irradiation (λ 366 mμ) of such a mixture[11] results in formation of II. Although sodium hydroxide is not visibly soluble in DME, the presence of base is necessary, for solutions in pure DME or 0.1 *M* sodium perchlorate in DME fail to give radical upon irradiation. Splitting constants observed under these conditions are summarized in Table II. For the alkali hydroxide/DMSO spectrum (last column of Table II) a difference in splitting constant between the b and c positions could not be resolved. Observed line widths were *ca.* 300 mg in these spectra, compared to 120 to 160 mg for the electrolysis and irradiation spectra, and 240 mg for the potassium *t*-butoxide spectrum. Position assignments for the splitting constants which agree with MO predictions (*vide infra*) were proved by deuteration, the middle-sized splitting being changed as predicted [observed splitting constants 2.93 (2 H), 0.93 (2 H), and 0.44 (2 D)] when pyracyloquinone-*c*,*c*-d_2 was electrolyzed.

There is a large "base effect" on the spectrum of II. Significantly higher spin density at the b and c positions of II is observed in the electrolytic spectra than in the *t*-butoxide spectrum. Since the "electrolytic" spectrum was observed with tetramethylammonium hydroxide, a stronger base than this is necessary to change the splittings. The irradiation spectrum is truly intermediate, the splitting constant observed being exactly (within experimented error) the average of the two extreme spectra. Changing cations does not affect the electrolytic spectrum much; there is a significant difference between tetraalkylammonium and alkali metal, but differences between alkali metals were not measurable.

Table II. Pyracylosemiquinone (II) Esr Splitting Constants, a_H

	Method of generation/solvent				
Position	0.1 *M* KO-*t*-Bu/ DMSO	Irradiation/ NaOH-sat. DME	Electrolysis[b]/ 0.1 *M* M^+– DMSO	0.1 *M* R_4N^+– DMSO[c]	MOH[a]/ DMSO
a	1.41	1.14	0.93	0.90	1.37
b	2.45	2.69	2.83	2.88	~2.37
c	2.12	2.31	2.55	2.57	~2.37

[a] MOH = NaOH, KOH, $Ba(OH)_2 \cdot 2H_2O$. [b] Supporting electrolytes $NaClO_4$, LiCl, CsBr. [c] With Et_4NClO_4, Bu_4NClO_4, and also without electrolysis, just using Me_4NOH in DMSO.

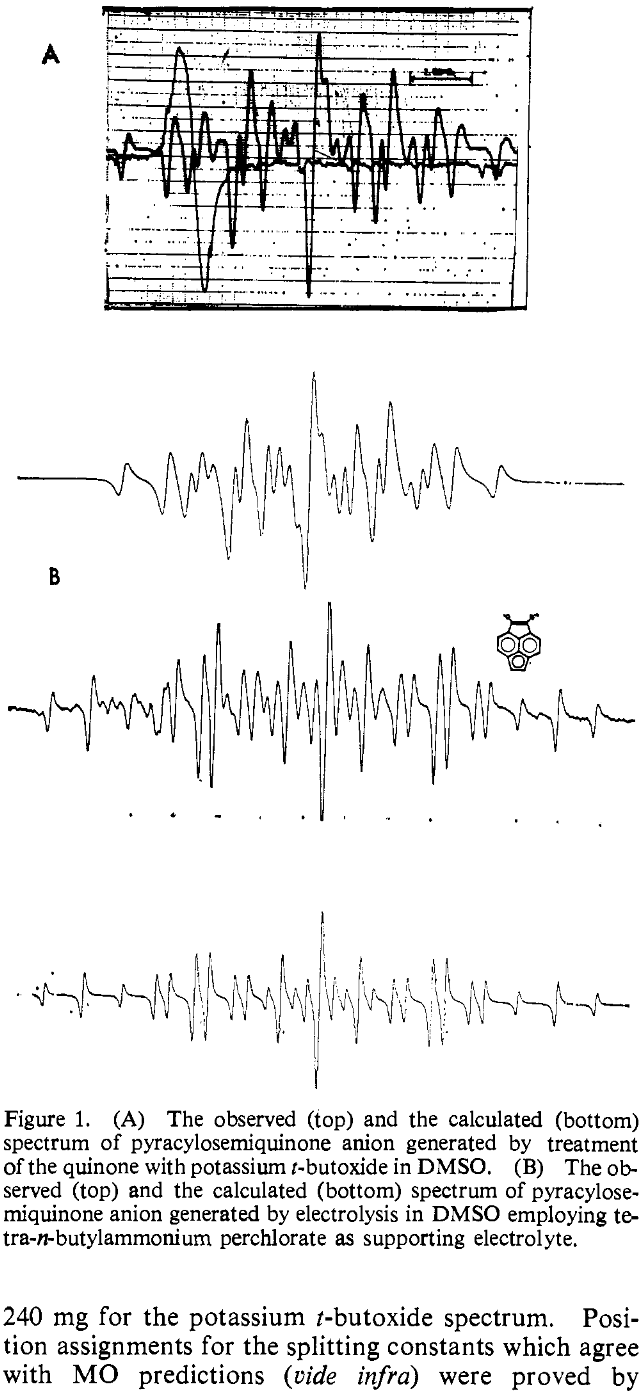

Figure 1. (A) The observed (top) and the calculated (bottom) spectrum of pyracylosemiquinone anion generated by treatment of the quinone with potassium *t*-butoxide in DMSO. (B) The observed (top) and the calculated (bottom) spectrum of pyracylosemiquinone anion generated by electrolysis in DMSO employing tetra-*n*-butylammonium perchlorate as supporting electrolyte.

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[10] (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, Spec. No. 243-ss (1960); *Chem. Abstr.*, **57**, 1770*b* (1961); (c) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 43, 4191 (1965).

[11] Irradiation of basic quinone solutions to give the semiquinones is a known process: E. C. Lucken, *J. Chem. Soc.*, 4234 (1964).

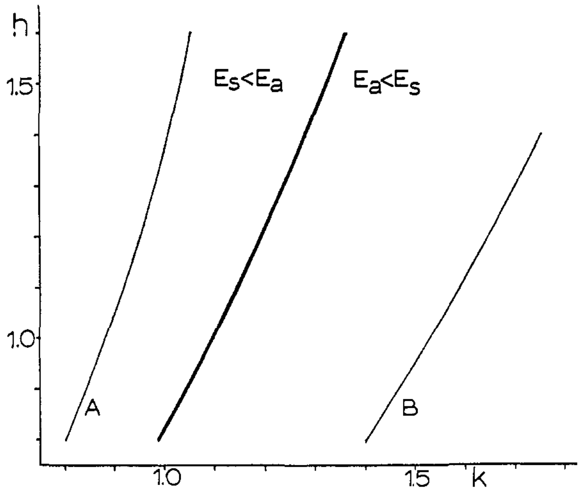
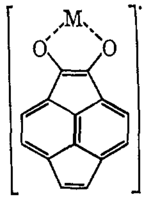


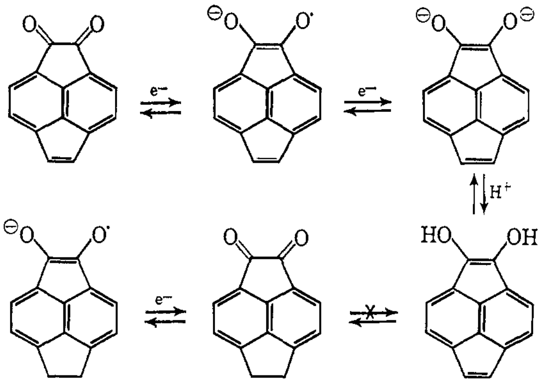
Figure 2. Variation of *h* and *k* in Hückel calculations for pyracyloquinone. The heavy line passes through *h* and *k* values for which $E_A = E_S$. To the right $E_A < E_S$ (experiment shows this is fact), while to the left $E_S < E_A$ ("crossed" region). Lines A and B give *h* and *k* values for best fit to the *t*-butoxide and electrolytic spectra, respectively. For the former, it was assumed the odd electron is in ψ_A in spite of the energy crossing.

We assign the differences in splitting constants observed to having "free" ions (II plus cation) and chelated ion pairs (V). We attribute the base effect to preferential coordination of the alkoxide with the cation thus liberating the free radical anion II. Thus the electrolytic spectrum represents that of the chelate V. Metal splittings might be expected for V[12] in ether solvents; however, we have been unable to obtain high enough radical concentration for esr spectra by electrolytic reduction in ethers. In agreement with this interpretation is the observed spectrum when the radical was generated by irradiation of a solution of quinone in DME saturated with sodium hydroxide. Rapid equilibrium of chelate and free forms (lifetime less than *ca.* 10^{-7} sec) would lead to the averaged splitting constants observed. Since the hydroxide concentration is extremely low, the semiquinone anion is an effective competitor for chelation (or tight ion-pair formation).



V

When pyracyloquinone is electrolytically reduced at potentials on the second polarographic wave (*vide infra*), II disappears and the dianion VI is presumably formed. If the applied potential is dropped to zero, a negative current is observed and II appears; the reduction is reversed.[13] In unpurified spectro grade DMF, however, III, not II, appears after high-potential reduction is ceased. A reasonable interpretation involves protonation (from solvent impurities?) of the dianion. Although kinetic protonation should occur at oxygen, if the large strain energy[5] overrides the resonance energy[3,4] associated with the pyracylene system, tautomerization would occur to the more stable 1,2-diketopyracene. Further reduction of diketopyracene generates its radical anion, which is observed. This sequence is summarized below.



The formal reverse process, enolization of III to form VI, could have occurred in potassium *t*-butoxide–DMSO, but does not; VI would have oxidized to form II under our conditions and no II was observed. We have been unable to demonstrate that diketopyracene can tautomerize to dihydroxypyracylene.

Molecular Orbital Calculations

HMO calculations of the spin densities of II were performed to examine the agreement of predictions with experiment. Although simple HMO theory does not work particularly well for nonalternate systems (such as IV),[9] II is a special case, in this as in so many other respects. The odd-electron MO, the only one which normally is considered for esr spectra, has zero electron density at carbons 13 and 14. Thus, for the purposes of esr, this molecule can be considered an alternant system.

Values for the Coulomb integral at oxygen and the C–O resonance integral are required. By convention,[14] these are expressed as $\alpha_O = \alpha_C + h_O\beta_{CC}$, $\beta_{CO} = k_{CO}\beta_{CC}$, respectively. Various *h* and *k* parameters have been used; values of $h = 1.2$, $k = 1.6$ gave the best fit in McLachlan calculations on *p*-quinones,[9] while $h = 0.8$, $k = 1.0$ fit several properties of unsaturated ketones best.[15] For II there is another criterion for choosing *h* and *k* besides best fit to coupling constants. As *h* and *k* are varied, the energy levels of the first two empty molecular orbitals cross. With $h = 0.8$, $k = 1.0$, the ninth MO (antisymmetric with respect to the C_{13}–C_{14} axis, ψ_A) is 0.005β lower in energy than the tenth (symmetric, ψ_S), but with $h = 1.9$, $k = 1.0$, ψ_S is 0.030β lower than ψ_A. While ψ_A gives reasonable spin densities for any reasonable *h* and *k*, ψ_S does not (ψ_S has almost zero spin density at position b and much higher spin density at oxygen. At constant *k*, increasing *h* lowers ψ_S much more than ψ_A, causing the crossing). The observed *a* and *g* values show the odd electron is in ψ_A. Figure 2 illustrates the energy level crossing.

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[12] Although the very stable tetracyanoethylene radical anion does not give metal splittings (M.C.R. Symmons, Michigan State University, ESR Symposium, Aug 1–3, 1966) II is considerably stabler than other semiquinones, which do show metal splittings, even in the presence of base.[10]

[13] Breaking the circuit causes appearance of II at a slower rate; presumably quinone diffuses into the region where the dianion is and disproportionation occurs.

[14] Reference 2, Chapter 4.

[15] H. E. Zimmerman, private communication.

Values of h and k were varied to find values for best fit to the observed splitting constants. If the electron were placed in E_A regardless of the energy crossing, a line in the h vs. k plot for best fit (which is very good, <0.003 deviation from experiments for all densities) lies entirely in the crossed region (Figure 2). Table III contains values near the crossing points, the best "uncrossed" values. A similar line may be calculated for the electrolytic spectrum. Here the best fit line lies in the "uncrossed region." McLachlan calculations[16] which allow for electron correlation do not improve the fit to experiment. All of the energy levels, not just ψ_A, are involved in these calculations, so this could have been expected. Best fit lines can be drawn for the McLachlan calculations as well; both lie in the crossed Hückel energy level area of the h,k plot.

Table III. Calculated Spin Densities for Pyracylosemiquinone (II)

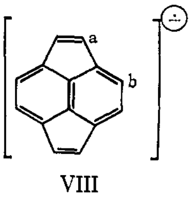
		Base spectrum				
		Hückel		McLachlan		
Pos	Exptl (Q = 24)	h = 0.8, k = 1.0	h = 1.2, k = 1.2	h = 0.8, k = 0.74[a]	h = 1.2, k = 0.78[a]	SCF
4	0.059	0.048	0.049	0.048	0.059	0.053
5	0.102	0.106	0.108	0.113	0.103	0.110
7	0.088	0.086	0.088	0.088	0.091	0.089

		Electrolytic spectrum			
		Hückel		McLachlen	
Pos	Exptl (Q = 24)	h = 0.8, k = 1.4	h = 1.2, k = 1.7	h = 0.8, k = 0.85[a]	h = 1.2, k = 1.0
4	0.038	0.038	0.038	0.035	0.040
5	0.120	0.120	0.120	0.121	0.126
7	0.107	0.091	0.093	0.090	0.090

[a] Hückel energies crossed. Calculation at crossing of Hückel energy levels gives ρ_4 far too low, ρ_5 far too high; ρ_2 is quite insensitive to h and k.

Finally, a closed shell SCF calculation[17] (which gives remarkable agreement with the ultraviolet spectrum[7]) gives spin densities slightly closer to experiment than the best "uncrossed" Hückel calculations for the base spectrum, which we assign to the "free" anion.

The above discussion assumes constant Q's at all positions to get the "experimental" spin densities. Fraenkel[18a] and Higuchi[18b] have calculated that Q_H increases if the C–CH–C angle is decreased. Recent work[19] has shown that for pyracylene anion (VIII) itself, Q_b = 22.6, Q_a = 30.0[20] are required to fit the spectrum using Hückel spin densities. Since bond angles at position a of VIII and c of II should be similar, Q = 30 for position c of II might be expected. This would make ρ_c = 0.071 for the base spectrum and 0.086 for the electrolytic spectrum, which improves agreement with the latter, but makes it worse for the former. Since ρ_7 is very insensitive to h and k variations, changing h and k does not account for using a larger Q at position c than positions a and b. The value of Q is claimed to be dependent upon charge density as well as bond angle. The Colpa and Bolton[21] modification of the McConnell equation, $a_i = (Q' + k\epsilon_i)\rho_i$, where ϵ_i is the excess charge at position i, does not improve the fit, nor justify use of a larger Q' at position c than positions a or b. The Giacometti modification,[22] $a_H = Q_1\rho_2 - Q_2 \left|\sum_j c_i c_j\right|$ where j are atoms bonded to i, does not produce significant changes from the regular McConnell equation; to obtain as good a fit, Q_1 must be about 24 instead of the 31.5 which fits best.



VIII

Thus the excellent agreement of simple Hückel theory with experiment using constant Q's seems to be fortuitous, since Q_c ought to be larger than Q_a and Q_b.

The esr spectrum of III was calculated using the method of Levy[23] to predict the methylene splitting constants. Table IV gives results for the extreme h_O and k_{CO} values used for II; agreement is considerably less favorable for the ring protons of III than II, as is expected.[9] The methylene splitting constants agree about as well as other examples.

Table IV. Calculated Spectrum for Diketopyracene Anion (III)

	Exptl	HMO, Q = 24 h = 0.8, k = 1.0	HMO, Q = 24 h = 1.2, k = 1.6	McLachlan
a_a	1.15	0.49	0.60	0.60
a_b	0.21	0.00	0.00	0.38
a_c (methylene)	1.38	0.92[a]	1.22[a]	1.29[a]

[a] Calculated by the method of Levy.[23]

Neither III nor IV shows the "base effect" on the splitting constants which is so prominent in the spectrum of II, although geometry at the carbonyls must be very similar. We suggest that the greater resonance energy and lower oxygen charge density of II could allow free II to be formed in base, but not in III and IV, which would have stronger chelates (or tighter ion pairs) and thus are not as easily broken up.

In addition to the correlation of splitting constants with molecular orbital theory, Stone[24] developed a correlation of hyperfine splitting factors (g factors) with molecular orbital theory. For semiquinone anions, he found this relationship could be expressed by eq 1.[25]

$$\Delta g = b + \lambda c + \rho_O\gamma_O \qquad (1)$$

Since the half-wave potential of the quinone also is related to the energy coefficient (λ) of the lowest unoccupied molecular orbital, this equation can be modified so that the g factor shift is expressed as a function of the

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(16) A. D. McLachlan, *Mol. Phys.* 3, 233 (1960). We thank Professor Holme for the use of his computer program for McLachlan calculations.

(17) We are deeply indebted to Dr. Howard E. Simmons for this calculation. This calculation shows that ψ_A is of lower energy than ψ_S.

(18) (a) I. Berual, D. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 1489 (1962); (b) J. Higuchi, *ibid.*, 39, 3455 (1963).

(19) B. M. Trost, S. F. Nelsen, and D. Brittelli, to be published.

(20) This angle is estimated to be approximately 106°. Fraenkel's calculation gives a Q of about 38 for this angle.

(21) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 6, 273 (1963).

(22) G. Giacometti, P. L. Nurdio, and M. V. Pavan, *Theoret. Chim. Acta*, 1, 404 (1963).

(23) D. H. Levy, *Mol. Phys.*, 10, 233 (1966).

(24) A. J Stone, *ibid.*, 6, 509 (1962)

(25) In this equation, Δg is the difference between the observed g factor and that for a free electron, 2.00232; λ refers to the energy of the odd electron orbital of the semiquinone; γ_O is a function of λ; ρ_O is the spin density at oxygen; b, c, and γ_O are experimental constants.

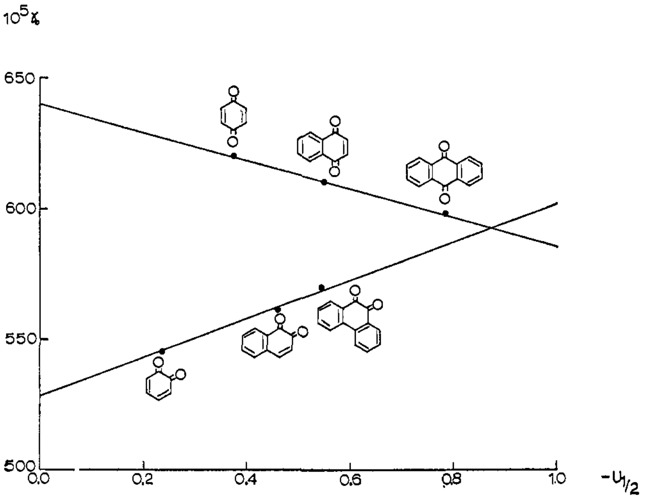

Figure 3. A plot of γ_0, which is a function of the energy of the first unoccupied molecular orbital (λ), *vs.* the half-wave potentials of the same quinones employed by Stone.[24]

half-wave potential and the oxygen spin density. Such a modification allows one to calculate the spin density at a heteroatom, oxygen, from two experimental quantities, g factors and half-wave potentials.

To examine this possibility, we undertook a study of the half-wave potentials of the same quinones chosen by Stone for his correlations.[26] For our polarographic studies, we employed DMSO as solvent since we had employed this solvent for our esr studies and since it gave the best polarographic results. The half-wave potentials ($U_{1/2}$) are summarized in Table V. For the molecular orbital calculations, we chose the oxygen parameters suggested by Fraenkel as those giving best fit for esr spectra, $h = 1.2$ and $k = 1.6$. Plotting λ *vs.* $U_{1/2}$ for the first wave gives two straight lines, one for *o*-quinones (eq 2) and one for *p*-quinones (eq 3).[27]

$$\lambda = 0.626U_{1/2} + 0.115 \quad (2)$$

$$\lambda = 0.580U_{1/2} + 0.187 \quad (3)$$

Table V. Half-Wave Potentials of Selected Quinones[a]

Quinone	Wave 1, v	Wave 2, v
1,4-Benzoquinone	−0.376	−1.174
1,4-Naphthoquinone	−0.550	−1.289
9,10-Anthraquinone	−0.784	−1.454
1,2-Benzoquinone[b]	−0.220	. . .
1,2-Naphthoquinone	−0.463	−0.772
9,10-Phenanthroquinone	−0.545	−1.277

[a] Values reported are *vs.* a standard calomel electrode. [b] Assuming $\Delta U_{1/2}$ on changing from DMF to DMSO is similar to that for the other quinones.

Since Stone's constant γ_0 is a function of λ, we replotted γ_0 in terms of half-wave potentials to obtain the two lines in Figure 3. Substituting these values into Stone's equations leads to eq 4 for *o*-quinones and eq 5

$$\Delta g = 22.5 \times 10^{-5} - 12.1 \times 10^{-5}U_{1/2} + \rho_0\gamma_0 \quad (4)$$

$$\Delta g = 21.1 \times 10^{-5} - 11.2 \times 10^{-5}U_{1/2} + \rho_0\gamma_0 \quad (5)$$

for *p*-quinones. The success of the method can be illustrated by the striking agreement between the spin densities obtained from eq 5 and Hückel spin densities for a series of *p*-quinones in Table VI. *For the latter, best fit was not attempted;* the oxygen parameters are those used in developing the equations (Fraenkel's best fit values) and the methyl group parameters are those suggested by Coulson and Crawford.[28]

Table VI. Spin Densities at Oxygen

Quinone	Eq 5[a]	Hückel
2-Methylbenzoquinone	0.33 ± 0.03	0.346
2-Methyl-1,4-naphthoquinone	0.28 ± 0.03	0.228
Duroquinone	0.38 ± 0.03	0.332

[a] Obtained employing the literature values for g factors and half-wave potentials,[26] the latter adjusted for change in solvent. The error is principally due to the uncertainty in the g factor.

Table VII summarizes the polarographic data and spin density calculations for the quinones of interest in this study. These data confirm the previous conclusion that the oxygens of pyracylosemiquinone anion bear extremely low spin density, approximately one-fifth that for normal semiquinone anions. Since presently we are unable to measure g factors more accurately, a large error exists in the spin densities calculated from eq 4.[29] Nevertheless, the quantitative agreement within our experimental error is excellent. These results in conjunction with the abnormally large hyperfine splitting constants of II indicate the unique nature of the pyracylene system and suggest its semiquinone anion is more akin to a hydrocarbon radical anion rather than a quinone radical anion. Theory and experiment and the excellent correlation between them attest to this conclusion.

Experimental Section

Materials. The quinones, pyracyloquinone and 1,2-diketopyracene, were prepared as previously described.[5,7] Acenaphthaquinone, *p*-benzoquinone, 9,10-phenanthraquinone, and 9,10-anthraquinone were obtained from Aldrich Chemical Co. 1,2-Naphthaquinone and 1,4-naphthaquinone were obtained from Eastman Kodak Co. Pyracyloquinone-5,6-d_2 was prepared as described for the undeuterated compound[6,7] except acenaphthene-d_4 was employed in the initial step. Mass spectral analysis[30] indicated the deuterated compound was 97% d_2 and 3% d_1. Dimethyl sulfoxide and dimethoxyethane were dried by distillation from calcium hydride. Tetra-*n*-butylammonium perchlorate was dried *in vacuo* at 68°. Tetra-*n*-butylammonium iodide was dried *in vacuo* at room temperature.

Esr Determinations. Esr spectra were recorded using a Varian V4502 instrument with a 9-in. magnet. Fremy's salt in saturated sodium carbonate was used as a calibration standard (g = 2.0055, a_N = 13.0 gauss) with dual cavity. The Varian electrolytic cell was used for *in situ* reductions. Solutions were deoxygenated by bubbling nitrogen through them and sample tubes were either 1-mm Pyrex capillaries or the Varian electrolytic cell. Ultraviolet irradiation was carried out using a Bausch and Lomb "high intensity" monochromater with Osram HBO-200W superpressure source.

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(26) For a similar correlation under a different set of conditions and employing different parameters of h and k for oxygen for molecular orbital calculations, see M. E. Peover, *J. Chem. Soc.*, 4540 (1962).

(27) Equations are for the best least-squares lines.

(28) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(29) It is important to point out that methods for more accurate g factor determinations are becoming available. The main source of error to the spin densities calculated by eq 4 and 5 is the uncertainty in this value.

(30) Mass spectral determinations were performed by Morgan-Schaeffer Corp., Montreal, Quebec, and by Professors Larry A. Singer and Joseph Ciabattoni. We are deeply indebted to them for these determinations.

Table VII. Half-Wave Potentials[a] and Oxygen Spin Densities of Semiquinones

Quinone	First wave	Second wave	Oxygen Spin Densities: Eq 4[b]	Oxygen Spin Densities: Hückel	Oxygen Spin Densities: McLachlen
Pyracyloquinone	−0.738	−1.305	0.06 ± 0.02	0.0478	0.0554
Diketopyracene	−0.908	−1.726	0.29 ± 0.03	0.388	0.414
Acenaphthaquinone	−0.807	−1.656	0.30 ± 0.03	0.356	0.352

[a] *Vs.* a standard calomel electrode. [b] The error derives mainly from the uncertainty in our measurement of the *g* factor.

Half-Wave Potentials. A Sargent Model XV polarograph was converted to a three-electrode, controlled potential instrument by utilizing the output of its motor-driven slide-wire potentiometer as the control potential input of a battery-operated, solid-state potentiostat based on operational amplifier circuitry.[31] The polarographic current was passed through the load resistor network of the Sargent XV and was recorded on its 2.5-mv strip-chart recorder.

The polarographic cell was a water-jacketed, all glass assembly with a 10-cc sample compartment. The anode was a platinum spiral. The reference electrode capillary tip was within 1 cm of the mercury drop. The reference electrode bridge was filled with supporting electrolyte and was separated from the aqueous sce compartment by a fine porosity sintered-glass disk, a renewable electrolyte bridge containing 0.1 *M* tetrabutylammonium iodide in DMSO, and a second sintered-glass disk.

The sample solution was deaerated with high-purity nitrogen (Linde). Measurements were made at 25.0 ± 0.1°. Half-wave potentials were reproducible to at least ±5 mv. Reported half-wave potentials are averages of cathodic and anodic scans. The potential of the dropping mercury electrode *vs.* the sce was measured at the cell terminals with a Rubicon portable potentiometer at the beginning and end of each scan. The reported half-wave potentials include the liquid junction potential between the aqueous and DMSO solutions.

Acknowledgment. We wish to thank the Petroleum Research Foundation, Grants No. 539-Gl (to B. M. T.) and No. 541-Gl (to S. F. N.), and the Wisconsin Alumini Research Foundation for partial support of this work.

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(31) W. M. Schwarz and I. Shain, *Anal. Chem.*, **35**, 1770 (1963).

Sequence Peptide Polymers. III. Poly Asp(OH)-Ser(H)-Gly and Other Serine-Containing Polymers[1,2]

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Received September 6, 1966

Abstract: Poly Asp(OCH_3)-Ser(H)-Gly and poly Asp(OH)-Ser(Ac)-Gly have been prepared from the corresponding tripeptide *p*-nitrophenyl ester hydrobromides with molecular weights from 3000 to 11,000. The sequence Asp-Ser-Gly occurs at the active site of several hydrolytic enzymes and the acetylated polymer is a model of the acylated enzymes which are intermediates in the hydrolysis process. The rate of hydrolysis of the acetyl group is, however, comparable to that of certain simple serine derivatives, and much slower than that of the acylated enzymes. Poly Asp(OH)-Ser(H)-Gly and poly Gly-Ser(H)-Gly have been studied briefly.

Sequence peptides which repeat a portion of the active site of an enzyme are of particular interest for the light they may shed on the catalytic process. The present work is concerned with poly Asp(OCH_3)-Ser(H)-Gly and with related polymers.[4,5]

Several quite different lines were explored for the synthesis.[6] The preferred route involves the preparation and polymerization of the nitrophenyl ester (**7**) as shown in eq 1–5.[7] Yields of purified product were 60–80% for each step.

$$\underset{\mathbf{2}}{\text{Z-Ser(H)-OH}} + \text{HBr-H-Gly-ONP} + \text{DCC} + \text{TEA} \longrightarrow \underset{\mathbf{5}}{\text{Z-Ser(H)-Gly-ONP}} \quad (1)$$

$$\mathbf{5} + \text{HBr} \xrightarrow{CH_3NO_2} \underset{\mathbf{4}}{\text{HBr-H-Ser(H)-Gly-ONP}} \quad (2)$$

$$\text{Z-Asp(OCH}_3\text{)-OH} + \mathbf{4} + \text{DCC} + \text{TEA} \longrightarrow \underset{\mathbf{8}}{\text{Z-Asp(OCH}_3\text{)-Ser(H)-Gly-ONP}} \quad (3)$$

$$\mathbf{8} + \text{HBr} \xrightarrow{CH_3NO_2} \underset{(cf.\ 7)}{\text{HBr-H-Asp(OCH}_3\text{)-Ser(H)-Gly-ONP}} \quad (4)$$

$$\underset{\mathbf{7}}{\text{(tosylate)}} + \text{base} \longrightarrow \text{poly Asp(OCH}_3\text{)-Ser(H)-Gly} \quad (5)$$

$$\underset{\mathbf{12}}{\text{Z-Asp(OBl)-Ser(H)-Gly-ONP}} + \text{AcOH} + \text{Ac}_2\text{O} + \text{HBr} \longrightarrow \underset{\mathbf{11}}{\text{HBr-H-Asp(OH)-Ser(Ac)-Gly-ONP}} \quad (6)$$

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(1) This work was supported by the unsolicited Petroleum Research Fund Grant 33C and by the Public Health Service under Grant RG-7828. It was also supported in part by Contract No. AT-(40-1)-2690 under the Division of Biology and Medicine, U. S. Atomic Energy Commission.

(2) Much of this work is taken from the Ph.D. Thesis of Fulton F. Rogers, Jr., Florida State University, 1963.

(3) Public Health Fellow 1962–1964.

(4) Part I: D. F. DeTar M. Gouge, W. Honsberg, and V. Honsberg, *J. Am. Chem. Soc.*, **89**, 988 (1967).

(5) D. F. DeTar and N. F. Estrin, *Tetrahedron Letters*, **5985** (1966).

(6) Some of these are discussed in ref 4.

(7) The abbreviations are mostly standard, and are described in detail in footnote 4 of ref 4. Numbers identifying peptides are keyed to the Experimental Section for convenience of cross reference.