

References and Notes

- (1) V. B. Ivanov, V. L. Ivanov, and M. G. Kuzmin, *Mol. Photochem.*, **6**, 125 (1974); S. J. Cristol and G. C. Schloemer, *J. Am. Chem. Soc.*, **94**, 5916 (1972); V. Lilliss, J. McKenna, J. M. McKenna, and I. H. Williams, *J. Chem. Soc., Chem. Commun.*, 473, 474 (1974); A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970).
- (2) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); J. W. Chamberlin, *J. Org. Chem.*, **31**, 1658 (1966); D. A. Jaeger, *J. Am. Chem. Soc.*, **97**, 902 (1975).
- (3) Photosolvolysis of a cyclopropylcarbinol has previously been reported; S. S. Hixson and J. Borovsky, *J. Chem. Soc., Chem. Commun.*, 607 (1975).
- (4) All new compounds had satisfactory elemental analyses and NMR spectra. Except for **3** and **4** new photoproducts were compared with samples synthesized by unambiguous procedures. Photochemical yields were calculated taking into account recovered starting material.
- (5) S. S. Jenkins, J. S. Buck, and L. A. Bigelow, *J. Am. Chem. Soc.*, **52**, 4495 (1930).
- (6) M. Tiffeneau and E. Fourneau, *Bull. Soc. Chim. Fr.*, **14** (43), 971 (1913).
- (7) D. A. Archer, H. Booth, and R. D. Stangroom, *J. Chem. Soc. C*, 2276 (1970).
- (8) Y. Gondo and Y. Kanda, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **5**, 133 (1964).
- (9) The triplet energy for benzyl alcohol was assumed to differ insignificantly from that of toluene ($E_T = 82$ kcal/mol); D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
- (10) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94**, 5077 (1972).
- (11) The absence of quenching by the diazotidene, a radical-chain inhibitor, militates against a possible radical chain reaction.
- (12) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970).
- (13) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975); G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968).
- (14) Photosolvolysis of a benzyl ether bearing a ferrocenyl group may proceed by a similar path; C. Baker and W. M. Horspool, *J. Chem. Soc., Chem. Commun.*, 1236 (1972).

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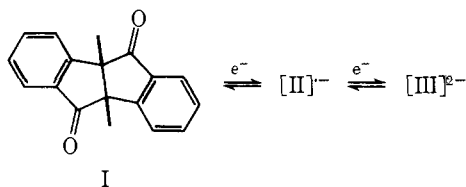
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Symmetry vs. Fluxionality, a Radical Anion with Borderline Properties

Sir:

Electrochemical reduction of the diketone I (*cis*-10,11-dimethyldiphensuccindan-9,12-dione) proceeds via two reversible, one-electron steps at half-wave potentials of -1.75 and -2.23 V vs. $\text{Ag}|\text{AgCl}$.¹ This report concerns the spectroscopic properties of the radical anion II which reveal some unusual and interesting structural properties.



The electron paramagnetic resonance spectrum of II exhibits splittings consistent with four pairs of equivalent protons with hyperfine constants of 2.65, 2.55, 1.3, and 0.2 G. The absence of detectable hyperfines for the methyls effectively rules out structure IIa. The remaining choices, rapidly equilibrating species IIc and IIc' and the fully symmetrical structure IIb, where the dotted lines denote a strong homoconjugative interaction, are equally consistent.

Further insight was provided by the infrared spectrum. An infrared solution cell was modified to include the components of a three-electrode electrochemical cell. The working electrode consisted of a 80-mesh platinum grid fitted between the NaCl windows.² Excellent potential control was achieved with Nernstian equilibrium established within 3 min of commencing electrolysis. The spectrum of II, obtained at -1.85 V, is shown in Figure 1.³ (Upon repolarization of the electrode to -1.0 V the spectrum of I was regenerated.) Table I presents the rele-

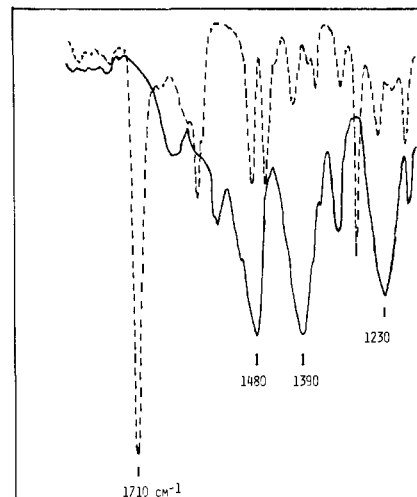
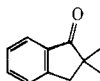
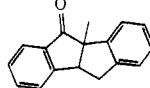
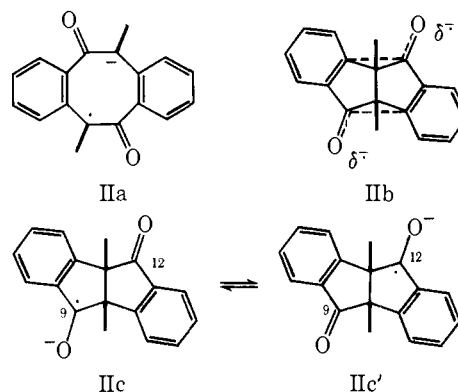


Figure 1. The infrared spectra of I (dotted line) and II (solid line) obtained in dimethyl- d_6 sulfoxide with 0.4 M $(\text{CH}_3)_4\text{NPF}_6$.

Table I. Infrared Absorptions of Carbonyl Radical Anions

Compound	E vs. Ag/AgCl (v)	ν_{CO} (cm^{-1})	$\nu_{\text{CO}}^{\cdot-}$ (cm^{-1})
9-Fluorenone	-1.22	1695	1540
1,4-Naphthoquinone	-0.63	1660	1510
	-2.08	1710	1548
	-2.02	1710	1544



vant absorptions of a series of representative carbonyl compounds and their respective radical anions.

The most striking features of the spectrum of II are: (i) the absence of absorption at 1710 cm^{-1} characteristic of the neutral carbonyl, and (ii) three strong yet broad absorptions at frequencies much lower than those observed for the monoketone anion radicals of Table I. (The latter have only a single strong band in this region.)

Structure IIb might be expected to have a C-O stretching mode as low as 1480 cm^{-1} , but the other two bands and the broadness are difficult to rationalize for this structure. Alternatively, if the fluxional motion of the equilibrating pair $\text{IIc} \rightleftharpoons \text{IIc}'$ is rapid enough to influence the vibrational states of the system, the anomalous features of the spectrum may be accommodated.

Hush's theory for mixed-valence equilibria is relevant to understanding the dynamic properties of IIc.⁴ In this view, the potential surface which includes IIc and IIc' is derived from the weak interaction of two zeroth-order surfaces which

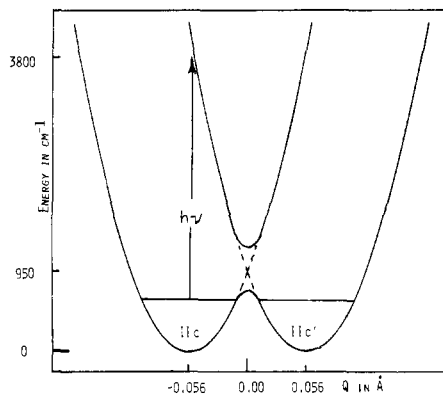


Figure 2. Potential surface and ground-state vibrational level for the interconversion of IIc and IIc'. $Q = \text{reaction coordinate} = \sqrt{2}[R_{\text{CO}}(12) - 1.26 \text{ \AA}] = \sqrt{2}[1.26 \text{ \AA} - R_{\text{CO}}(9)]$.

characterize small amplitude vibrations of the two structures independent of one another. These zeroth-order surfaces may in turn be constructed from knowledge of the force constants for equivalent vibrations in analogous monofunctional molecules. For this case the problem is vastly simplified by the fact that the internal coordinates of greatest importance are just the two C–O bond lengths in each structure, $R_{\text{CO}}(9)$ and $R_{\text{CO}}(12)$. Thus, conversion of IIc to IIc' requires little more than compressing $R_{\text{CO}}(9)$ and stretching $R_{\text{CO}}(12)$. The zeroth-order surface for this motion is readily calculated from the force constants derived from the spectra of the monoketones and their respective anion radicals.⁵ The portion of this surface along the reaction coordinate is shown in Figure 2 (solid lines). In the region where the zeroth-order surfaces cross (dotted lines), the true states will be mixed, splitting the degeneracy. This establishes the height of the barrier and the position of a low lying electronic excited state. If we adopt 0.08 \AA as the difference between $R_{\text{CO}}(9)$ and $R_{\text{CO}}(12)$ ⁶ at the minima, the barrier is calculated to be $\leq 950 \text{ cm}^{-1}$.

As a consequence of this very low barrier, molecular vibrations involving change in $R_{\text{CO}}(9)$ and $R_{\text{CO}}(12)$ must be strongly anharmonic. Both the vibrational splittings and the selection rules for dipolar transitions between them should deviate greatly from the monofunctional cases. Also, local solvation inhomogeneities should result in fluctuations in the barrier height (and therefore the vibrational states) resulting in the observed line broadening. Calculation of the vibrational states for the full two-dimensional surface are currently in progress.

As shown in Figure 2, there should exist an electronic transition at about 3800 cm^{-1} ⁷ (the exact value depending upon the vibrational levels). In fact, the electronic spectrum of II includes a strong absorption at very long wavelength ($\lambda_{\text{max}} 1590 \text{ nm}$ in Me_2SO , $\lambda_{\text{max}} 1700 \text{ nm}$ in CH_3CN , $\epsilon 4030$).⁸ Applying the correction for the solvent effect proposed by Hush,⁴ we obtain 4018 cm^{-1} as the "gas phase" optical intervalence transition, in surprisingly good agreement.⁹

It is interesting to note the possibility that the ground vibrational state for the fluxional system may exceed the barrier for interconversion. If such were the case, the nuclear configuration would effectively be symmetrical and it is ironic that this may be the case even in the absence of strong transannular interaction.¹⁰

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References and Notes

- (1) Data from cyclic voltammetry in $(\text{CH}_3)_2\text{SO}$, $0.10 \text{ M } (\text{CH}_3)_4\text{NPF}_6$.
- (2) The cell represents a modified version of that described by W. R. Heineman, J. N. Burnett, and R. W. Murray, *Anal. Chem.*, **40**, 1974 (1968).

- (3) That the spectrum does represent the anion radical is supported by (i) the reversible oxidation to I, (ii) the observation of isosbestic points when the electrode was held at intermediate potentials, and (iii) Beer's law behavior for the corresponding electronic absorption spectrum, *vide infra*.
- (4) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).
- (5) These are 13.0 and 10.6 mdyne/\AA for the ketones and radical anions, respectively.
- (6) Bond lengths of 1.22 and 1.30 \AA were used for the ketone and radical anions, respectively. The latter is based on an INDO calculation for indanone radical anion.
- (7) This transition is analogous to the intervalence transition characteristic of binuclear mixed valence complexes.¹¹
- (8) None of the radical anions in Table I absorbed beyond the visible.
- (9) It should be pointed out that an error in the extrapolation of solvent effects could be as great as $\pm 1000 \text{ cm}^{-1}$.
- (10) This interaction is apparently not negligible since the reduction potential of I is 0.27 V more positive than the equivalent monoketone.
- (11) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973); G. M. Tom and H. Taube, *ibid.*, **97**, 5310 (1975); R. W. Callahan, G. M. Brown, and T. J. Meyer, *ibid.*, **96**, 7830 (1974).

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The Conversion of Berberine into (\pm)- α - and (\pm)- β -Hydrastine¹

Sir:

A useful landmark in the topography of ideas concerning biogenetic interrelationships among monomeric isoquinoline alkaloids can be traced back to 1910 when William H. Perkin, Jr., and Sir Robert Robinson observed that: "These (berberine and phthalideisoquinoline) alkaloids are, indeed, so closely related as to suggest that hydrastine is either formed in the plant from berberine, or that they are both derived from some common parent."² We now wish to report the first known in vitro conversion of berberine (**1**) into (\pm)- α -hydrastine (**5**) and (\pm)- β -hydrastine (**6**) by a simple and efficient route which may emulate in part the biogenetic process.

The key to the transformation of berberine (**1**) to the hy-

