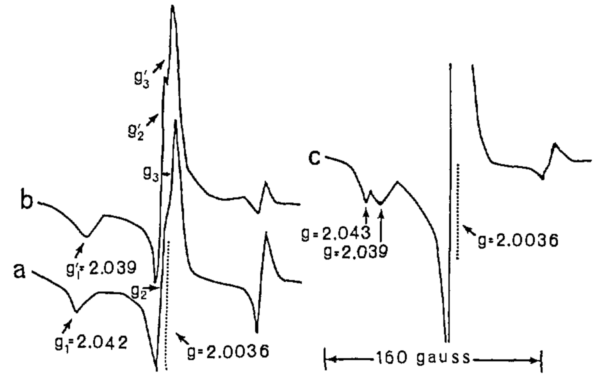

Figure 1. Esr spectra of zinc oxide (a) vacuum heated 2 hr at 500° and *n*-butane added; (b) vacuum heated 2 hr at 500°, oxygen added and evacuated; (c) 20% zinc dust added, vacuum heated 2 hr at 500°, oxygen added and evacuated. The field increases from left to right; spectra recorded at −196°.

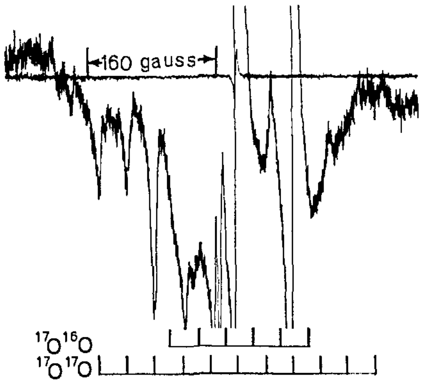

Figure 2. Esr spectrum of zinc oxide vacuum heated 17 hr at 500°, oxygen-17 added and evacuated. The hyperfine splitting constant in the direction of the $2p\pi_g$ orbital is 34.6 G. DPPH (upper spectrum) is used as a standard for the *g* value. Spectrum recorded at −196°.

O^- and O_2^- ions formed on TiO_2 has been shown recently by Micheikin, *et al.*[5]

While the mechanism of O^- formation is presently not very clear, it seems to us that in the presence of chemisorbed hydrogen (from a hydrocarbon), an electron transfer from the valence band (essentially O^{2-} electrons) to a Zn^+ species would be possible.

Using enriched oxygen (63.6% ^{17}O) a well-resolved spectrum of O_2^- (Figure 2), which shows the hyperfine lines due to the configurational interaction with the oxygen nuclei, has also been obtained for the first time on ZnO, which proves beyond doubt that molecular ions ($^{16}O^{17}O^-$, $^{17}O^{17}O^-$) are formed on its surface, following oxygen treatment of a sample which was previously heated *in vacuo* for 17 hr at 500°. However, it is obvious that such a study cannot give information on O^- species present, if any, since its esr spectrum would be similar to $^{16}O^{17}O^-$ or $^{18}O^{17}O^-$. Experiments with $Zn^{17}O$ (prepared by the oxidation of Zn dust in enriched oxygen) under conditions which lead to the exclusive formation of O^- ions at the surface are presently under way and could lead to an unambiguous identification of the species.

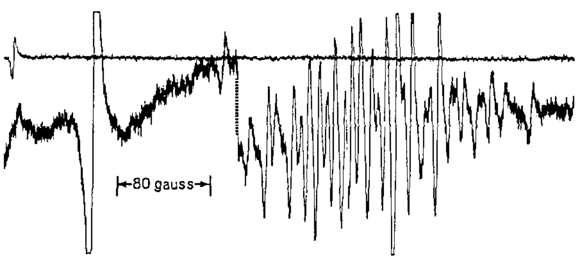

Figure 3. Esr spectrum of oxygen-17 at 15 mm, adsorbed on zinc oxide previously evacuated at room temperature. The center of the signal corresponds to a *g* value of 1.313. Spectrum recorded at −196°.

We also wish to report results on a series of experiments involving ZnO, TiO_2, MgO, and powdered porous glass, all outgassed at room temperature and treated with enriched oxygen at different pressures. A complex spectrum (Figure 3) was observed between 15 and 35 mm which was independent of the adsorbent used and appeared with identical *g* values in all cases. The spectrum was obtained at −196° but was not observable at room temperature. Its intensity increased slightly with microwave power in the range 20–200 mW. The characterization of the spectrum is not yet complete since it is obtained only with enriched oxygen. It seems that the spectrum arises from total spins of 5 and $^5/_2$ ($^{17}O^{17}O$ and $^{16}O^{17}O$). Further study of this phenomenon is presently in progress.

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Photochemistry of 5,8-Dihydro-5,8-bridged 1,4-Naphthalenediols. Structure of Photothebainehydroquinone

Sir:

As the dimeric structure suggested for photothebainehydroquinone (obtained by direct irradiation of thebainehydroquinone (**1**) with ultraviolet light[1]) did not account for its behavior with acid,[2] we examined crystals of photothebainehydroquinone hydrobromide (mp 255–257.5°. *Anal.* Calcd for $C_{25}H_{26}NO_5Br$: C, 60.01; H, 5.24; N, 2.80; Br, 15.97. Found: C, 59.81; H, 5.37; N, 2.81; Br, 16.16) by X-ray crystallography.

The crystals are orthorhombic, of space group $P2_12_12_1$, with cell dimensions $a = 10.67$, $b = 27.20$, and $c = 7.73$ Å. Since the crystal density is 1.46 g cm^{-3}, the alkaloid must be monomeric, and there are four molecules of $C_{25}H_{26}NO_5Br$ in the unit cell ($D_{\text{calcd}} = 1.48$ g cm^{-3}). The X-ray intensity data were collected by

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(5) I. D. Micheikin, A. I. Maschenko, and V. B. Kazanskii, *Kinetika i Kataliz*, **8**, 1363 (1967).

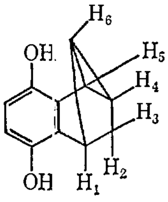
(1) Z. J. Barneis, D. M. S. Wheeler, and T. H. Kinstle, *Tetrahedron Lett.*, 275 (1965).

(2) Z. J. Barneis, R. J. Warnet, and D. M. S. Wheeler, unpublished work.

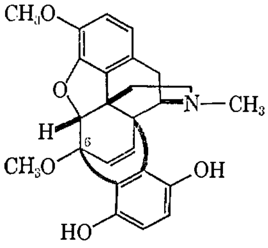
Table I. Calculated Nuclear Magnetic Resonance Shifts (60 Mc) and Coupling Constants of Alicyclic Protons in **4c**[a]

νH_1	213.3	νH_2	40.9	νH_3	167.5	νH_4	116.0	νH_5	161.5	νH_6	187.3
J_{12}	0.3	J_{23}	−8.6	J_{34}	3.4	J_{45}	5.4	J_{56}	5.0		
J_{13}	7.2	J_{24}	0.0	J_{35}	0.0	J_{46}	4.8				
J_{14}	2.4	J_{25}	0.0	J_{36}	0.0						
J_{15}	0.0	J_{26}	2.7								
J_{16}	2.9										

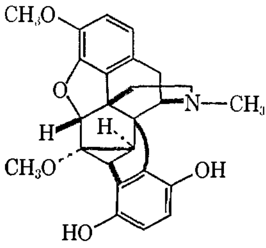
[a] Shifts given in hertz downfield from TMS. Protons numbered as indicated



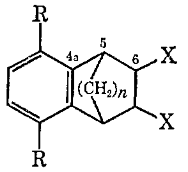
means of a Hilger and Watts' four-circle diffractometer controlled by a PDP-8 computer. Mo Kα radiation was employed and 1879 independent reflections were obtained with intensities significantly above background level. Preliminary coordinates for the bromide ion were derived from a Patterson synthesis, and the carbon, nitrogen, and oxygen atoms were then located in two successive three-dimensional electron-density distributions. The atomic coordinates and thermal parameters (anisotropic for the bromide ion, isotropic for the carbon, nitrogen, and oxygen atoms) were refined by full-matrix least-squares calculations incorporating corrections for anomalous dispersion, and the current value of R is 10.9%. The results of the analysis define the constitution and absolute stereochemistry of the photo compound to be **2**.

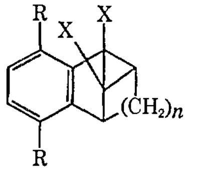


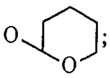
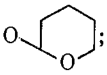
1



2





3a, R = H; X = H; n = 1
b, R = OAc; X = H; n = 1
c, R = OH; X = H; n = 1
d, R = OH; X = D; n = 1
e, R = ; X = H; n = 1
f, R = ; X = D; n = 1
g, R = OH; X = H; n = 2

4a, R = H; X = H; n = 1
b, R = OAc; X = H; n = 1
c, R = OH; X = H; n = 1
d, R = OH; X = D; n = 1
e, R = OH; X = H; n = 2
f, R = OAc; X = H; n = 2

The formation of **2** (a new type of morphine structure) involves a nonsensitized photorearrangement of a bicyclic di-π-methane to a vinylcyclopropane.[3,4] Usually such rearrangements of bicyclic systems take place only on sensitized irradiation.[5,6] We also find that other bicyclic di-π-methanes containing hydroquinone systems are converted by direct irradiation to the corresponding vinylcyclopropanes. Direct irradiation of **3c** and **3g** in ether for 2 hr with light from a 450-W medium pressure mercury lamp gave, respectively, **4c** [mp 167–169°; uv max (95% C_2H_5OH) 295 mμ (ϵ 3400); ir (KBr) 3250 (O–H), 1460 cm^{-1} (aromatic C=C); nmr (acetone-d_6) δ 7.48 (broad s, 2, OH), 6.49 (AB pattern, 2, aromatic), 3.55 (m, 1), 3.10 (m, 1), 2.77 (m, 1), 2.70 (t, 1, J = 5 Hz), 1.90 (m, 1), and 0.68 ppm (m, 1)] and **4e** [mp 147.5–149°; uv max (95% C_2H_5OH) 293 mμ (ϵ 2280); ir (KBr) 3300 (O–H), 1480 cm^{-1} (aromatic C=C); nmr (acetone-d_6) δ 7.22 (s, 1, OH), 7.10 (s, 1, OH), 6.31 (AB pattern, 2, aromatic), 3.57 (t, 1, J = 5 Hz), 2.61 (q, 1, J = 5.5 Hz), 2.39 (t, 1, J = 6.5 Hz), 1.74 (m, 4), and 1.15 ppm (m, 1)]. The structure of **4c** follows from its spectral properties and the identity of its acetate with authentic **4b**.[4a] The structure of **4e** is based on its spectral properties, those of its acetate **4f** [(mp 109–110°; nmr δ 6.75 (s, 2), 3.55 (t, 1, J = 5 Hz), 2.76 (m, 1), 2.26 (s, 3), 2.22 (s, 3), and 1.12–2.48 ppm (broad series of multiplets, 6). *Anal.* Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92; O, 23.50. Found: C, 70.72; H, 6.00; O, 23.28], and its relation to photothebainehydroquinone.

When the deuterated compound **3d** (obtained *via* **3e** and **3f**) was irradiated under the same conditions as **3c**, product **4d** was obtained. The positions of the deuteriums in **4d** follow from an analysis of the nmr spectra of **4c** and **4d** by means of spin decoupling confirmed by theoretical simulation of the spectra. The best values of coupling constants and chemical shifts, which gave excellent agreement between the theoretical and actual spectra, are shown in Table I. The results of the deuterium labeling show that the conversion of **3c** to **4c** involves bridging between atoms 4a and 6 of **3** followed by bond breaking between 4a and 5. Similar bridging occurs in the sensitized irradiation of **3a**[4b] (*cf.* benzobarrellene[7]). Further the stereochemistry of **2** shows

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(3) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(4) (a) J. R. Edman, *ibid.*, **88**, 3454 (1966); (b) J. R. Edman, personal communication.

(5) For example, Edman[4a] reported that sensitized irradiation of **3a** and **3b** gave, respectively, **4a** and **4b**; nonsensitized irradiation of these compounds takes a different course.[4b]

(6) For exceptions see: (a) T. D. Walsh, *J. Amer. Chem. Soc.*, **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969); (b) R. C. Hahn and L. J. Rothman, *ibid.*, **91**, 2409 (1969). These authors attribute the course of their reaction to geometrical factors which inhibit a competitive singlet process.

(7) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

that, as expected,[3] the transformation of **1** into **2** involves an inversion of configuration at C_6.

The conversion of **3c** into **4c** is quenched by addition of isoprene. Our evidence suggests that the mechanism of the transformations of the hydroquinones parallels that of the hydrocarbons[7] with the difference that the hydroquinones do not need sensitizers to enter the triplet state.

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Correlation between Conformation and Pairwise Spin Exchange in Flexible Biradicals in Solution. Control of Conformation by pH-Dependent Ionic Forces

Sir:

Pairwise spin exchange between the free-radical subunits of *flexible* biradicals is manifest in the esr spectra of these molecules in dilute solutions.[1–10] The spin-containing subunits of the biradicals of interest here are attached *via* amide or ester bonds to the interconnecting *saturated* hydrocarbon chain. Two principal mechanisms enabling spin exchange have been discussed.[6] In the *indirect* process, spin density propagates through the molecular backbone. The alternative mechanism of spin exchange by the *direct* overlap of the singly occupied orbitals of the subunits requires the biradical to assume conformations favoring this overlap. Indirect exchange is expected to be no more sensitive to temperature or solvents than is the distribution of spin density.[6] The observations that exchange can be suppressed by cooling[6] or by the proper choice of solvents[2,10] have been interpreted to indicate the relative weakness of the indirect mechanism and the conformational parentage of the direct process.

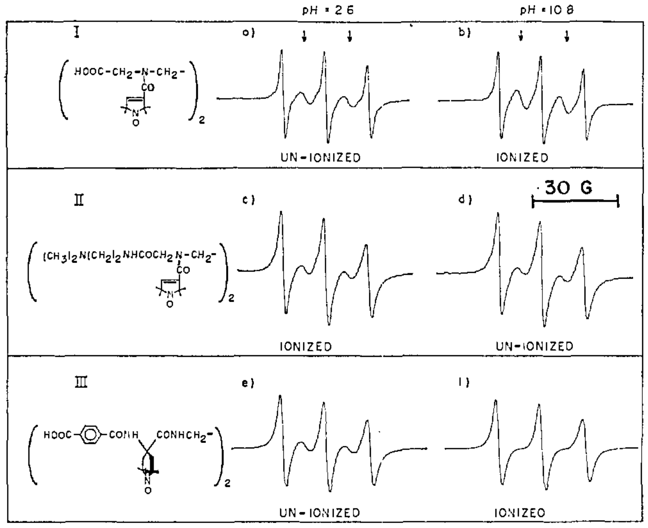

Figure 1. The formulas of the three flexible bielectrolyte biradical molecules (I–III) and their respective esr spectra in $\sim 10^{-4}\ M$ aqueous solutions at pH values of 2.6 and 10.8, at 24°. The spectra are distinguished by the presence of the two interpolating lines (marked by arrows at the top), the intensities of which are a measure of the intramolecular spin exchange. The molecules stretch at pH values in which fully ionized $-COO^-$ or $-NH^+(CH_3)_2$ groups are formed. Under similar conditions the behavior of III is opposite to that of I.

Lack of methods for the on–off switching of the interaction other than by solvent or thermal treatment[2–10] has precluded the conclusive verification of the plausible direct exchange model.

We report here the introduction of a switchable ionic interaction between the biradical subunits. This has been achieved in three biradical molecules[11] (Figure 1, I–III) in which each subunit contains a nitroxide radical and an ionizable functional group. Electrostatic repulsion between the subunits, and hence conformational modification, can be turned on and off by ionizing or neutralizing the polar groups *without necessitating a change of solvent or temperature.*

Each of the biradicals[11] (Figure 1) (the preparation and characterization of which will be reported elsewhere[12,13]) consists of two identical subunits connected by a flexible hydrocarbon chain. The subunit contains one heterocycle ring which incorporates a nitroxide group[14–17] and one ionizable function, *e.g.*, $-COOH$ or $-N(CH_3)_2$. The bonding of the radical-carrying rings in I and II has much in common with the majority of nitroxide biradicals under study, whereas the spirane-

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(1) R. Briere, R. M. Duperyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

(2) E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 559 (1965).

(3) A. L. Buchachenko, V. A. Golubev, A. A. Medzhidov, and E. G. Rozantsev, *Teor. Eksp. Khim.*, **1**, 249 (1965).

(4) H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, *Mol. Phys.*, **11**, 49 (1966).

(5) G. R. Luckhurst, *ibid.*, **10**, 543 (1966).

(6) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

(7) H. Lemaire, *J. Chim. Phys.*, **64**, 559 (1967).

(8) H. Lemaire, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 886 (1968).

(9) H. Lemaire, A. Rassat, P. Rey, and G. R. Luckhurst, *Mol. Phys.*, **14**, 441 (1968).

(10) M. Calvin, H. H. Wang, G. Entine, D. Gill, P. Ferruti, M. A. Harpold, and M. P. Klein, *Proc. Nat. Acad. Sci. U. S.*, **63**, 1 (1969).

(11) The compounds are I, N,N′-bis(1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxy)ethylenediamine-N,N′-diacetic acid; II, N,N′ bis(2-dimethylamino)ethyldiamide of I; III, N,N′-bis[2,2,6,6-tetramethyl-4-(*p*-carboxybenzoyl)amino-4-carboxypiperidine]ethylenediamine.

(12) P. Ferruti, M. Calvin, D. Gill, M. P. Klein, and H. H. Wang, manuscript in preparation.

(13) G. Havach, P. Ferruti, D. Gill, M. P. Klein, and M. Calvin, manuscript in preparation.

(14) E. G. Rozantsev, *Usp. Khim.*, **35**, 1549 (1966); *Russ. Chem. Rev.*, 658 (1966).

(15) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 233.

(16) C. L. Hamilton and H. M. McConnell, in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Company, San Francisco, Calif., 1968, p 115.

(17) O. H. Griffith and A. S. Waggoner, *Accounts Chem. Res.*, **2**, 17 (1969).