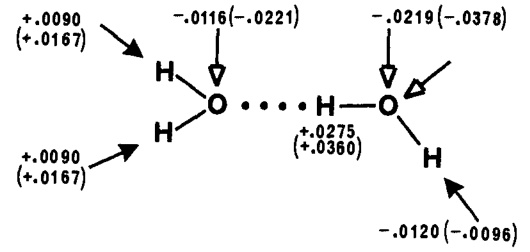

Figure 1. Changes in net atomic charges produced by dimerization.[3,4]

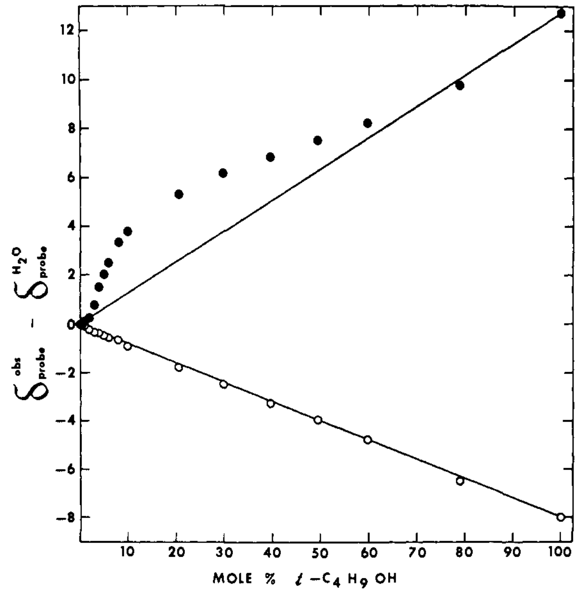

Figure 2. ^{1}H chemical shifts of $CHCl_3$ (●) and DMSO (○) *vs.* mole per cent *tert*-butyl alcohol in the system H_2O-*t*-BuOH at 37°. δ^{H_2O} is the shift at $X_{t\text{-BuOH}} = 0$. δ in hertz (at 60 MHz) downfield from external cyclohexane and corrected for bulk susceptibility differences. Precision: ±0.03 Hz. Original data tabulated in microfilm edition.[14]

but rather a maximum near 6 mol % *t*-BuOH, in the region of maximum water structuring. This is consistent with accompanying maximization of water's basicity.

δ_{DMSO} decreases linearly with X_{ROH} (Figure 2). The plot according to eq 4 is nearly linear and the data are consistent with $K \simeq 1.1$, at least down to *ca.* 5 mol % *t*-BuOH where the variable plotted loses precision rapidly. Thus eq 1 accounts for the observed shifts without considering water acidity changes. Whether this is due to low probe sensitivity or because the structural effect on water acidity is small must be investigated *via* better probes, probably using other nuclei.

The aqueous *t*-BuOH *OH* proton shifts[10,15] show an extra low-field shift in the 0–20 mol % *t*-BuOH region quite similar in direction and magnitude to δ_{CHCl_3} in Figure 2; but with the overall trend at higher *t*-BuOH concentration now upfield, the bulge of Figure 2 becomes a maximum at 6 mol % *t*-BuOH. If one hypothesizes that the dependence of H-bond stability on H-donor acidity is no less than that on acceptor basicity,[16] then the parallelism of δ_{OH} and δ_{CHCl_3} implies that the structure dependence of water acidity is small.

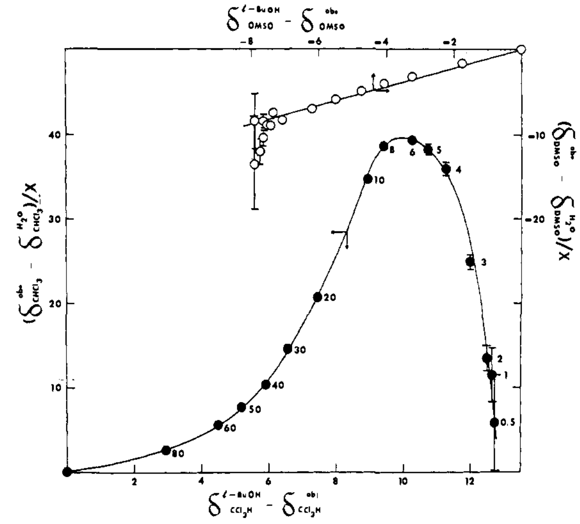

Figure 3. Chemical shift data for chloroform (●) and DMSO (○) plotted according to eq 4. Numbers near points are mole per cent *tert*-butyl alcohol.

Bergen and Long[17] (BL) showed that neutral salts of large organic ions (relative to KCl) provoke an exalted salting in of acidic (relative to neutral) nonelectrolytes. This is consistent with enhancement of water basicity by the structure-making ions, and BL in fact hinted at this explanation. Basic nonelectrolytes show *diminished* salting in by the R_4NX but not by the $ArSO_3Na$.

The weight of available evidence thus points strongly to enhanced water basicity as a consequence of enhanced water structure, but the effect (if any) on water acidity is ambiguous. These phenomena doubtless affect many common systems. Changing alkyl substitution or hydrocarbon-like cosolutes should alter the solvation of acidic and basic species and hence activity coefficients, and rate and equilibrium constants. In most cases, however, such effects are difficult to separate from other influences.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to Dr. S. Castellano (Mellon Institute) for kindly providing access to nmr equipment.

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(14) Original data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(15) N. N. Ugarova, L. Radič, and I. Nemes, *Russ. J. Phys. Chem.*, **41**, 835 (1967).

(16) J. E. Gordon, *J. Phys. Chem.*, **67**, 19 (1963).

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Received August 13, 1971

Light-Induced Bond Switching in Oxygen and Nitrogen Analogs of Thiathiophthenes[1]

Sir:

An extended Hückel[2] calculation carried out on unsubstituted thiathiophthene (I), varying the angle α,

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(1) The electronic structure of thiathiophthenes. IV. Part III: R. Gleiter, D. Schmidt, and H. Behringer, *Chem. Comm.*, 525 (1971).

(2) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).

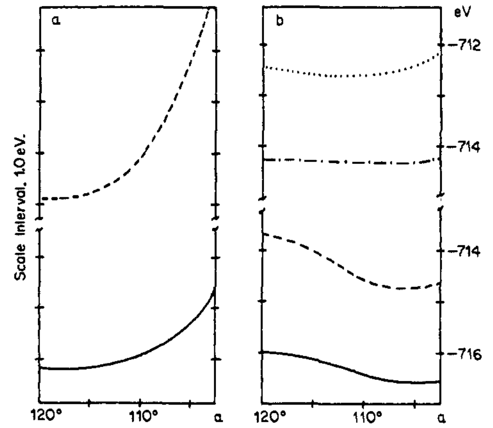


Figure 1. (a) Potential energy of the ground state of I as a function of α with (——) and without (- - -) participation of 3d orbitals on sulfur, using a CNDO/2 model. (b) Potential energy of I as a function of α, using an EHT model. The two top curves represent the first excited state without (· · ·) and with (-·-·) participation of 3d orbitals on sulfur. The two lower ones show the ground state without (- - -) and with (——) participation of 3d orbitals on sulfur.

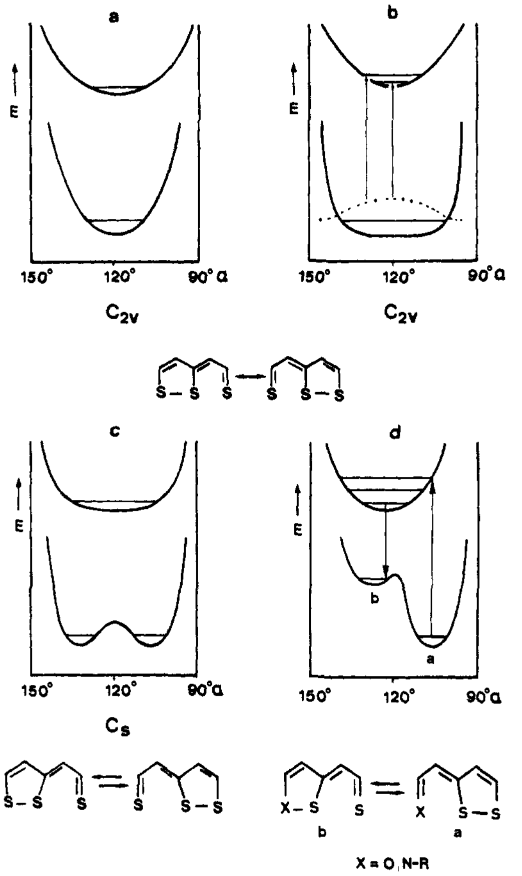


Figure 2. Schematic representation of the potential curves of the ground and first excited states of I as a function of α for a single (a) and a double minimum (c) potential. In b, a situation with a U-shaped potential curve in the ground state is shown together with the Franck-Condon transitions. In d, a photochemical process from isomer a to isomer b is indicated.

predicts a double minimum for the ground state (Figure 1b). The energy barrrier between the two minima is reduced by including 3d orbitals on sulfur in the calculation.[3–5] This is mainly due to considerable interaction between the in-plane 3p and 3d combinations of appropriate symmetry. The calculations also show

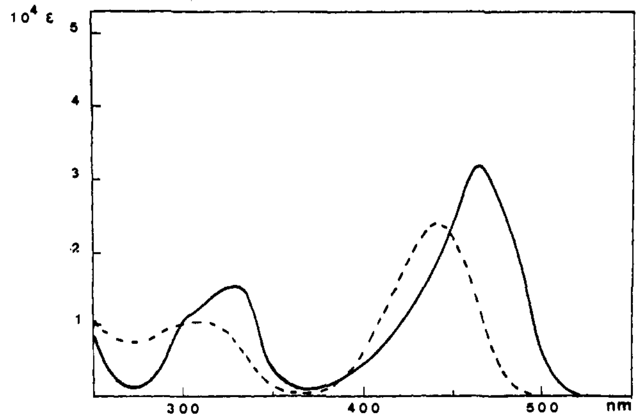
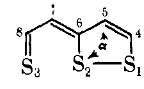


Figure 3. Electronic spectra of IIa (- - -) and its longest lived photoproduct (——) in ethanol at room temperature. The ε values have qualitative character.



I

that the first electronically excited state should have a single minimum potential (Figure 1b). A CNDO/2[6] calculation, on the other hand, yields a single minimum potential already without the 3d orbitals on sulfur (Figure 1a). It seemed of interest to check these predictions made by the model calculations for two reasons.

(1) The shape of the potential curve in the ground state and the excited state may be the reason for the discrepancy in the interpretation of uv measurements[1] and X-ray data.[7] This is elaborated in Figure 2. The situations in Figures 2a and 2c are clear cut. Figure 2a corresponds to a situation in which the molecule is best described by the no-bond resonance model[8] and Figure 2c corresponds to the other extreme, a valence tautomerism.[9] In Figure 2a, uv and X-ray measurements would be compatible with a structure with C_{2v} symmetry. In Figure 2c, the X-ray analysis would yield a Fourier map, suggesting C_{2v} symmetry, but with an exceptionally high temperature factor. For the situation shown in Figure 2b,[10] where the potential curve in the ground state has a flat bottom or has a small barrier on the order of kT, both methods may very well "see" different things. The electronic spectrum may be compatible with an unsymmetric species since the Franck–Condon principle holds, while an

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(3) The assumed geometry of I (C_{2v}) was S_1–S_2 = 2.35, S_1–C_4 = 1.7, S_2–C_6 = 1.75 Å; all C–C distances = 1.40 Å, all C–H distances = 1.10 Å.

(4) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(5) The parameters used for the calculation were those given in ref 4 except for the Slater exponent of the 3d orbitals on sulfur for which we used 1.6. A related calculation is given in ref 4. However, a more realistic geometry is used in the present potential surface.

(6) (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, and references cited therein; (b) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(7) Most recent X-ray data are given in A. Hordvik and L. J. Saethre, *Acta Chem. Scand.*, **24**, 2261 (1970).

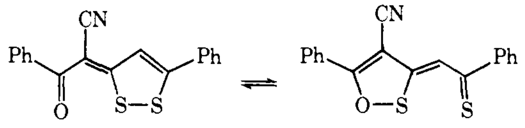
(8) E. Klingsberg, *Quart. Rev., Chem. Soc.*, 537 (1969).

(9) D. Leaver and D. M. McKinnon, *Chem. Ind.* (London), 461 (1964).

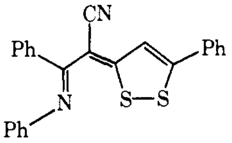
(10) A similar situation is discussed by H. H. Jaffé, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962; E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

X-ray measurement will still yield a symmetric density map with a reduced temperature factor compared with that of the situation in Figure 2c.

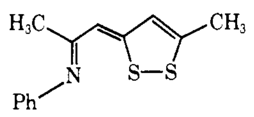
(2) For an unsymmetric molecule, *e.g.*, IIa, one should be able to obtain the valence tautomer in a photochemical reaction (see Figure 2d). To test this latter prediction, we have carried out a flash experiment with IIa, III, IV, and V. We used a 900-J flash (30 kV, 2μF), with WG1 and GG455 Schott filters. The measurements were done in cyclohexane and ethanol at room temperature in the presence and absence of air.



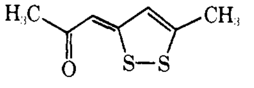
IIa IIb



III



IV

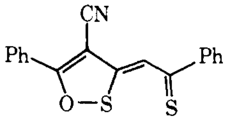


V

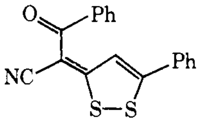
Irradiation of IIa yields two products in cyclohexane. In Figure 3, we show the electronic spectrum of IIa and the spectrum of the second longer lived product, which reverts in a dark reaction. The change in optical density which accompanies the reaction at wavelengths from 300 to 500 nm obeys first-order kinetics. No stable products were detected under these conditions. In cyclohexane, the electronic spectrum of the photoproduct of IIa is similar to that in ethanol: maxima at 470 and 305 nm, isosbestic points at 455, 415, and 350 nm. The relaxation time at room temperature is 300 sec in cyclohexane and 0.1 sec in ethanol.

Compounds III, IV, and V show behavior similar to that of IIa. The decay of the longest lived product obeys first-order kinetics. The relaxation times for the different compounds in cyclohexane are 350 sec for III, 240 sec for IV, and 670 sec for V. The estimated standard error is about 15%, taken from six measurements. The measurements also show that there is a similar bathochromic shift of the first band in the electronic spectrum as observed for IIa.

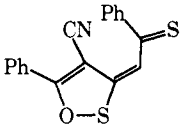
From the facts that the long-lived product reverts into the starting material according to a first-order kinetics, that there is a bathochromic shift of the first $\pi^* \leftarrow \pi$ band relative to that of the starting product, and that air does not influence the lifetime of the product, we conclude that this species is a singlet isomer of the starting material. For IIa we have taken into consideration three isomers, IIb, c, d. As was pointed out previously,[1] the position of the band which corresponds to a $\pi^* \leftarrow \pi$ transition of lowest energy allows one to discriminate between the structures of different isomers like IIa–IId. We have carried out PPP calculations[11] on the four unsubstituted isomers a–d corresponding to IIa–IId. We obtained a shift of the long-wavelength band relative to the position of a as follows: b = +48, c = −51, and d = −16 nm. It is obvious that only isomer b is compatible with the bathochromic shift as observed in our measurements. The size of this calculated shift corresponds to the measured one of 30 nm for the photoproduct of IIa in cyclohexane. This result is supported by the observation that the known trans isomers[12] corresponding to structure c show a hypsochromic shift of the first $\pi^* \leftarrow \pi$ band of about 50–60 nm relative to the a isomer. The observed solvent shift is also in agreement with isomer b. Hydrogen bonding in ethanol should lower the stability of the S–O bond, and thus the lifetime of the tautomer IIb should be smaller than in cyclohexane, which is observed.



IIb



IIc



IId

We conclude that the longest lived product encountered in our experiments is in each case the valence tautomer of the starting material.

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Molecular Oxygen Binding in a Monomeric Cobalt Complex. The Crystal and Molecular Structure of Dioxygen–Bis[*cis*-1,2-bis(diphenylphosphino)ethylene]cobalt Tetrafluoroborate

Sir:

We report the structure of the title compound $[O_2Co(2{=}phos)_2]BF_4$ where (2=phos) is *cis*-$[(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$ containing two benzene molecules of solvation. This represents the first announcement of a structure determination of a synthetic monomeric O_2 complex with a metal of the iron triad. Several structure investigations of oxygenated Co complexes have been reported;[1-3] these have all been O_2 bridged dimers, which are well-known oxygen carriers.[4]

The oxygen adduct is prepared by exposing either the crystalline material or solutions of the planar Co(I) chelate, $[Co(2{=}phos)_2]^+BF_4^-$,[5] to atmospheric oxygen.

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(5) L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, **93**, 6671 (1971).