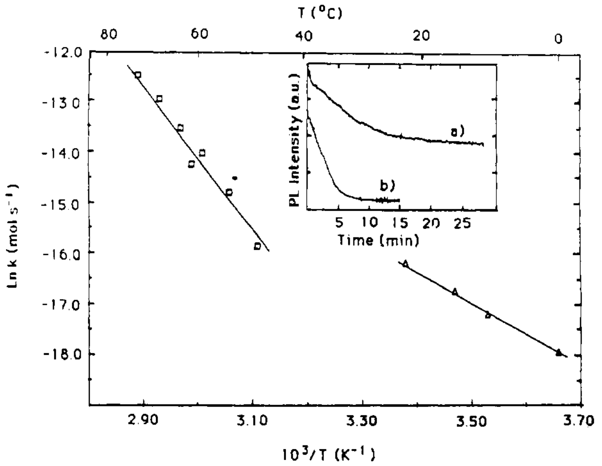


Figure 1. Arrhenius plots for the conversion of hydrogen uranyl phosphate to uranyl phosphate by thermal decomposition in water (squares) and by stirring with UO_2^{2+} ions (triangles). Decomposition experiments were conducted with 200 mg of HUP in 20 mL of triply distilled H_2O; for the intercalation reaction, 300 mg of HUP and a 0.5 M $UO_2(NO_3)_2$ solution were used. Each data point is the average of 2–4 runs. Slurries were stirred vigorously at temperatures maintained with an oil bath to ±0.5 °C. Inset: Representative PL decay curves for HUP decomposition at (a) 60 °C and (b) 70 °C. The initial PL intensities have been offset for clarity.

pitation of the solid. Alternatively, the reaction's reversibility suggests a "self-intercalation" mechanism, in which the elevated temperature increases the solubility of HUP. The uranyl ions thus liberated are then free to exchange with protons in undissolved HUP to give the observed products. The significance of the Arrhenius parameters is being assessed by characterization of related systems in our laboratories.

Acknowledgment. We thank Prof. Hyuk Yu, Dr. Hong Doo Kim, and Peter Dorhout for experimental assistance and Prof. S. H. Langer and a reviewer for helpful comments. We thank the Office of Naval Research for support of this research.

Registry No. HUO_2PO_4, 61156-01-2; $(UO_2)_3(PO_4)_2 \cdot 8H_2O$, 84934-15-6.

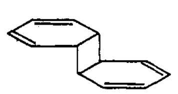
Chemistry of *cis,syn*-Tricyclo[6.4.0.$0^{2,7}$]dodeca-3,5,9,11-tetraene, a New 4n Dimer of Benzene

Nien-chu C. Yang,*[1] Bruce J. Hrnjez, and M. Glenn Horner

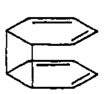
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received February 13, 1987

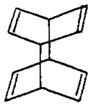
There is substantial theoretical interest[2] in the benzene 4n cyclodimer subset (**1**–**3**) of the $(CH)_{12}$ series of isomers. Among



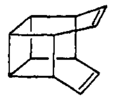
1



2



3



4

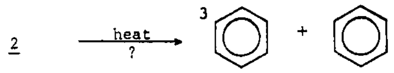
the three members of this subset, only the *anti-o,o'*-dibenzene (**1**) has been prepared.[3] We wish to report the synthesis and some novel chemical reactions of a new addition to this energy-rich class of molecules, *cis,syn*-tricyclo[6.4.0.$0^{2,7}$]dodeca-3,5,9,11-tetraene (**2**) or *cis,syn-o,o'*-dibenzene.

Recently, we had synthesized a pentacyclic dimer of benzene **4**[4] and found that **4** undergoes a facile thermal rearrangement at moderate temperature to **2** with the formation of benzene as the only other product. Thermolysis of **4** at 40 °C in pentane (6.4×10^{-3} M) under argon for 9.7 days, followed by flash chromatography over silica gel and cautious removal of the solvent, afforded **2** as colorless crystals with a characteristic camphor-like odor in 16% yield (isolated): mp 45–46 °C; MS found, m/z 156.0928; UV (C_6H_{12}) λ_{max} 240 nm (ϵ 4900); IR (C_6D_{12}) 3034, 2956, 2925, 2873, 2856, 1712 cm^{-1}; ^1H NMR (C_6D_{12}) δ 3.51 (br s, 4 H), 5.32 (br d, 4 H), 5.64 ppm (dd, J = 7.5 and 2.5 Hz); ^{13}C NMR (C_6D_{12}) δ 42.62, 123.85, 124.98.

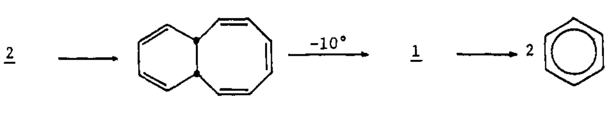
Since **1** is known to exhibit a half-life of 5.75 h at 40 °C,[3a] our results clearly indicate that **2** is thermally more stable than its cis,anti isomer **1**. It is surprising that, on the basis of thermochemical calculations,[5] **2** is the less stable isomer thermodynamically due to the unfavorable overlapping interactions between the two cyclohexadiene rings. However, Gleiter has shown that the through-bond interactions between the two isolated π-systems may be more important than their through-space interactions, suggesting that the HOMO of **1** may be actually higher than that of **2**.[2d,e] Our finding that the UV maximum of **2** (240 nm) is substantially blue-shifted from that of **1** (266 nm)[3a] is in agreement with his prediction. It is conceivable that the higher thermokinetic stability of **2** may be related to its lower HOMO level. The kinetics of thermolysis of **2** was then investigated in the temperature range 61.0–80.1 °C, and the following parameters were obtained: $\Delta H^{\ddagger} = 22.5 \pm 1.3$ kcal·M^{-1} and $\Delta S^{\ddagger} = -14.0 \pm 2.2$ eu.

Since the direct thermal dissociation of **2** into two molecules of benzene is highly exoergic but symmetry forbidden as a concerted process,[6] it is surprising that the reaction proceeds with such a highly negative activation entropy. The observation suggests that the reaction may proceed via a spin-forbidden transition state (pathway 1)[7,8] or via a metastable intermediate formed in a concerted process (pathway 2). The former pathway involves the formation of a molecule of benzene in its triplet state. The ΔG of the thermolysis of **2** may be estimated from thermochemical data to be approximately −73 kcal·M^{-1}.[5,9] This pathway is possible since the amount of energy available, the sum of ΔG and $\Delta G^{\ddagger}$, exceeds the triplet energy of benzene, 84.3 kcal·M^{-1}.[10] The latter pathway involves the disrotatory opening of the cyclobutane ring

Pathway 1



Pathway 2



---

[1] This work is dedicated to Professor George H. Büchi on his 65th birthday.

[2] (a) Engleke, R.; Hay, P. J.; Kleiner, D. A.; Wadt, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5439–5446. (b) Engleke, R. *J. Am. Chem. Soc.* **1986**, *108*, 5799–5803. (c) Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* **1978**, *34*, 1441–1447. (d) Gleiter, R.; Gubernator, K.; Zimmermann, H.; Fessner, W. D.; Prinzbach, H. *Chem. Ber.* **1985**, *118*, 3856–3860. (e) Gleiter, R.; Gubernator, K.; Grimme, W. *J. Org. Chem.* **1981**, *46*, 1247–1250.

[3] (a) Röttele, H.; Martin, W.; Oth, J. F. M.; Schroder, G. *Chem. Ber.* **1969**, *102*, 3985–3995. (b) Berson, J. A.; Davis, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 3658–3659. (c) Grimme, W.; Kosner, H. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 307–308.

[4] Yang, N. C.; Horner, M. G. *Tetrahedron Lett.* **1986**, *27*, 543–546.

[5] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

[6] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1971.

[7] Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091–7092.

[8] Turro, N. J.; Lechtken, P. *Pure Appl. Chem.* **1973**, *33*, 363–388.

[9] A value for ΔH of −63.8 kcal/mol was obtained from an optimized molecular mechanics calculation (MM-2).

[10] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1971; p 3.

0002-7863/87/1509-3158$01.50/0

to form *cis*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**5**) as the rate-determining step. Pentaene **5** is known to undergo a disrotatory ring closure below −10 °C to **1**, which dissociates to two molecules of benzene in situ.[3a,11]

Triplet benzene has been detected in the thermolysis of Dewar benzene by using 9,10-dibromoanthracene as the energy acceptor;[12] however, no triplet benzene was detected in the thermolysis of **2** under the same conditions. Although pathway 1 cannot be excluded at this moment, we favor the alternate pathway for the thermolysis of **2** under our experimental conditions. The detailed mechanisms of thermolysis of **1** and **2** are currently under investigation in our laboratory.

Acknowledgment. We thank the National Institutes of General Medical Sciences and the National Science Foundation for their generous support of this work. The partial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is also acknowledged. We also appreciate the cooperation of Professor Jerome Berson in providing us with some of his unpublished information, and the assistance of Professor Gerhard Closs in carrying out the MM-2 calculations.

---

(11) Grimme, W.; Mauer, M.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 224–225.

(12) Lechtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3025–3027.

NMR Determination of Rates of Electron Pair Transfer through Bridges to or between Heteropoly Complex Centers. Enthalpy and Entropy Contributions to Activation. Evaluation of Equilibrium Constant for the Disproportionation Reaction

Mariusz Kozik and Louis C. W. Baker*

Department of Chemistry, Georgetown University
Washington, DC 20057

Received January 26, 1987

Substantial interest centers on electron transfer in polynuclear bridged complexes. Numerous heteropoly structures may be bridged by a variety of MO_n polyhedra and/or by organic bridging groups coordinated to transition metals that are integral parts of heteropoly structures.[1-4] Organic conducting groups are significant biochemically, and heretofore-little-investigated oxometalate bridges have importance for catalysis. Both have potential significance for investigation of electronic materials.

NMR studies of heteropoly blues[5,6] lead to an elegant method for elucidating activation energies and rates of electron transfer among heteropoly and other structures through a variety of bridges. The method is illustrated here with the $[P_2W_{15}O_{49}–Zn_4O_{14}(H_2O)_2–O_{49}W_{15}P_2]^{16-}$ complex,[7] Figure 1. The two $P_2W_{15}O_{49}$ heteropolytungstate portions are bridged by a layer of four edge-sharing $Zn^{2+}O_6$ octahedra. Analogous complexes are obtained[7] by replacing Zn^{2+} by Co^{2+} or Cu^{2+}. Ongoing investigations compare (1) abilities to transmit electrons and (2) relative equilibrium electron populations in the respective bridged heteropoly or other reducible moieties.

The ^{31}P NMR spectrum of $Na_{16}[P_2W_{15}O_{49}–Zn_4O_{14}(H_2O)_2–O_{49}W_{15}P_2]$ solution consists of two sharp ($\Delta\nu_{1/2} < 1.5$ Hz) lines, one from each pair of structurally identical P atoms.[7] The complex's first reduction wave represents a reversible four-electron process at a single cathodic potential (−0.50 V vs. SCE). The complex was reduced by just four electrons by constant potential electrolysis. This places two spin-coupled electrons in each heteropolytungstate end of the complex, forming a typical heteropoly blue.[5,6] The added electrons, delocalized on the NMR time scale, are rapidly hopping among the 12 "belt" W atoms in each polytungstate portion.[5] This diamagnetic 4e-reduced product also exhibits two narrow ^{31}P NMR lines, the signal from the inner pair of P atoms having been shifted to lower frequency by ~128 Hz (−1.05 ppm) and that from the outer pair to higher frequency by ~98 Hz (+0.81 ppm).

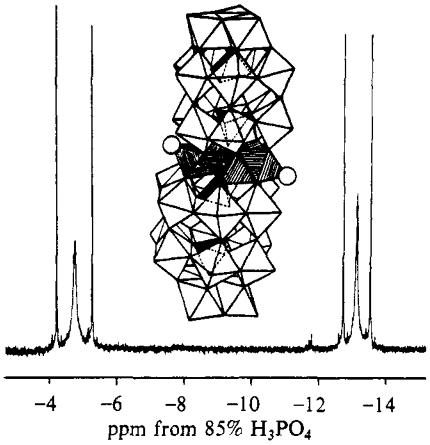


Figure 1. Inset: Structure[7] of $[P_2W_{15}O_{49}–M_4^{2+}O_{14}(H_2O)_2–O_{49}W_{15}P_2]^{16-}$, $M^{2+} = Zn^{2+}$, Co^{2+}, or Cu^{2+}. Each vertex of an octahedron locates the center of an oxygen atom. Each white octahedron contains a W atom. Each hatched octahedron contains a M^{2+} atom. The four interior PO_4 tetrahedra are shown in black and by dotted outlines. The locations of the two H_2O molecules coordinated to M^{2+} are circled. **Spectrum**: ^{31}P NMR spectrum, taken on a Bruker AM-300WB spectrometer at 300 K, of mixture made by reduction, by two electrons per complex, of a 5 mM solution of $Na_{16}[P_2W_{15}O_{49}–Zn_4O_{14}(H_2O)_2–O_{49}W_{15}P_2]$ in 0.5 M lithium acetate buffer, pH 4.3, 20% D_2O. Outer pair of lines, oxidized complex; inner pair of lines, 4e-reduced complex; central lines in each group, 2e-reduced complex. The downfield set of three lines is for the P's nearer the $Zn_4O_{14}(H_2O)_2$ bridge.

A reduction that involves only half as many Coulombs per mole of complex as does the 4e reduction produces a solution that contains a mixture of complexes: unreduced, 4e-reduced, and 2e-reduced. This is shown by its ^{31}P NMR spectrum (Figure 1), which consists of six base-line-resolved lines: two sharp lines coinciding exactly with those from the unreduced species, two sharp lines coinciding exactly with those from the 4e-reduced species, and two much broader lines (one for each structural type of P). Each of the latter lines centers exactly midway between the pair of sharp lines for its kind of P. Neither chemical shifts nor line widths for any of these signals change with concentration or with proportion of the complex reduced. The widths of the central broader lines decrease with increasing temperature while the widths of the sharp lines remain constant. All the systems are always perfectly diamagnetic, as shown by the Evans NMR method for susceptibility.[8] Thus the added electrons' spins are always paired by multiroute superexchange.[5]

The broad NMR lines are therefore assigned to complexes which have two added electrons on one side of the $Zn_4O_{16}H_4$ bridge and none on the other. The electrons are exchanging, with spins paired, between the two heteropoly ends of the complex via concerted penetration through the $Zn_4O_{16}H_4$ bridge. The single broad peak, for each structurally similar pair of P's, results from coalescence of the signals from the two nonidentical ends of the 2e-reduced complex, the electron exchange rate being in the NMR intermediate/fast exchange time scale region.[9] The P's envi-

---

(1) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794.

(2) Figgis, J. S. Doctoral Dissertation, Georgetown University, 1970.

(3) Landis, A. M. Doctoral Dissertation, Georgetown University, 1977.

(4) Weakley, T. J. R.; Evans, H. T., Jr.; Showell, J. F.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139.

(5) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2748.

(6) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(7) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006.

(8) Evans, D. F. *J. Chem. Soc.* **1959**, 2005.

(9) (a) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Heyden and Son: London, 1980; p 301. (b) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, 1977; p 256.

0002-7863/87/1509-3159$01.50/0