lustrated[8] by combining a "wolf and lamb" reaction, as described above, with a third polymeric reagent, situated in a different vessel. The reaction is described in Scheme VI.

The product of the "wolf and lamb" acylation of acetophenone, dibenzoylmethane anion, was passed without isolation into Amberlyst 15 resin (a macroporous sulfonic acid resin) loaded with hydrazine. A 91% yield of 3,5-diphenylpyrazole (based on acetophenone) was obtained upon filtration of the latter polymer.

Other examples of multipolymer reactions, using additional advantages of these reactions, are being studied at present.

Acknowledgment. The authors wish to thank the Camille and Henry Dreyfus Foundation for financial support.

References and Notes

(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.
(2) A preliminary account of part of this work was presented at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976. See A. Patchornik, *Polym. Prepr., Am. Chem. Soc., Div. Polym.*, **17**, 213 (1976).
(3) C. G. Overberger and K. N. Sannes, *Angew. Chem., Int. Ed. Engl.*, **13**, 99 (1974).
(4) C. C. Leznoff, *Chem. Soc. Rev.*, **3**, 65 (1974).
(5) A. Patchornik and M. A. Kraus, *Pure Appl. Chem.*, **43**, 503 (1975).
(6) M. A. Kraus and A. Patchornik, *J. Am. Chem. Soc.*, **93**, 7325 (1971).
(7) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, **97**, 3453 (1975).
(8) C. U. Pittman and L. R. Smith, *J. Am. Chem. Soc.*, **97**, 1749 (1975).
(9) Isaiah 11:6, "And the wolf shall dwell with the lamb . . .".
(10) A. Patchornik and M. A. Kraus, *J. Am. Chem. Soc.*, **92**, 7587 (1970).
(11) Macroreticular XE-305 "Rohm and Haas" polystyrene was used. The commercial polymer was ground to particles of 100–150 mesh size.
(12) For Friedel–Crafts alkylations of polystyrene, see A. Patchornik, R. Kalir, M. Fridkin, and A. Warshawsky, U.S. Patent 3 974 110 (Aug 10, 1976).
(13) R. Kalir, M. Fridkin, and A. Patchornik, *Eur. J. Biochem.*, **42**, 151 (1974).

B. J. Cohen,* M. A. Kraus, A. Patchornik
Department of Organic Chemistry
Weizmann Institute of Science, Rehovot, Israel
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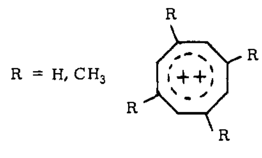
Protonated Cycloocta[*def*]fluorenone Dication. A New 14π-Electron Aromatic System

Sir:

The validity of Huckel's ($4n + 2$) π electron rule for aromaticity[1] has been extensively tested during the past 20 years.[2] Early attempts to prepare the cyclooctatetraenylium dication **1** (R = H) failed, and only very recently has Olah succeeded in oxidizing 1,3,5,7-tetramethylcyclooctatetraene, thus obtaining the diatropic aromatic dication **1** (R = CH_3).[3] One of the difficulties in obtaining **1** is the ready formation of the stable homotropylium ion.[3] We wish to report the preparation and characterization of the protonated cycloocta[*def*]fluorenone dication 2(vide supra), a benzannelated derivative of **1** which is stable at room temperature.[4] The formation of **2** is not accompanied by the formation of any discernible amount of a homotropylium type cation.

Oxidation of cycloocta[*def*]fluorene[5] with oxygen in the presence of "Triton B" or in air in the presence of KOH and 18-crown-6 afforded after chromatography **3** (90% yield, mp 126 °C),[6,7] ν_{max}^{Nujol} (cm^{-1}) 1710 (C=O stretching); *m/e* 231 (M + 1, 19%), 230 (M, 74%), 202 (M − CO, 100%); λ_{max}^{EtOH} 237 (ε 42 000), 295 (12 000), 350 (s) (1050), 430 nm (640); $\lambda_{max}^{H_2SO_4}$ 267 (ε 20 000), 300 (s) (7200), 415 (6200), 500 (s) nm (1000) with tailing to longer wavelengths. ^{1}H NMR ($CDCl_3$)[8] δ ppm 5.79 (s, 4 H, H_4–H_7), 6.90–7.44 (m, 6 H, H_1–H_3 and H_8–H_{10}). Treatment of **3** at −40 °C with "magic acid" (1:1 M FSO_3H-SbF_5) in SO_2 produced a dark red solution. Its ^{1}H NMR spectrum showed the following bands:[8]



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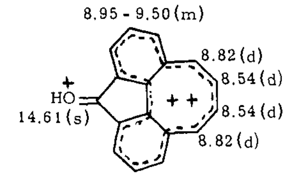

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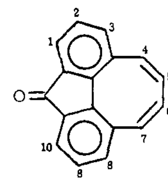

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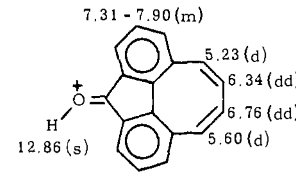

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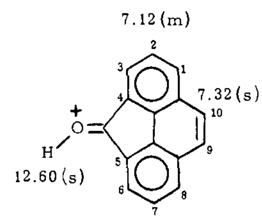

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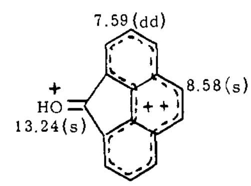

6

δ (ppm) 5.23 (d, 1 H, J = 8.0 Hz, H_4), 5.60 (d, 1 H, J = 6.0 Hz, H_7), 6.34 (dd, 1 H, J_1 = 11.0, J_2 = 8.0 Hz, H_5), 6.76 (dd, 1 H, J_1 = 11.0, J_2 = 6.0 Hz, H_6), 7.31–7.90 (m, 6 H, aromatic), 12.86 (s, 1 H, OH). The spectrum of this species has been assigned to **4**, formed by the protonation of the carbonyl group of **3**. It should be noted that the vinylic protons H_4–H_7 exhibit an ABCD pattern. Elevation of the sample temperature to +31 °C evoked a dramatic change of the ^{1}H NMR spectrum as follows:[8] δ (ppm) 8.54 (d, 2 H, J = 8.0 Hz, H_5 and H_6), 8.82 (d, 2 H, J = 8.0 Hz, H_4 and H_7), 8.95–9.50 (m, 6 H, aromatic), 14.61 (s, 1 H, OH). This spectrum did not show any changes within a temperature range of +30 to −50 °C. Neither was it altered after a prolonged stay at room temperature. We attribute the spectrum to **2**, a two-electron oxidation product of **4**. The presence of the OH proton clearly indicates that the oxidation product **2** did not lose its proton at the carbonyl function. The ^{13}C NMR spectrum[8] of **2** supports this assignment. Although the carbon spectrum of **4** showed 17 bands due to its nonsymmetric configuration, oxidation to **2** resulted in a significant downfield shift and in a much simpler spectrum (nine bands). The total change in carbon chemical shift δC for all 17 carbon atoms in the reaction **4** → **2** is 402 ppm or 201 ppm/e. This value is very near that observed for other dications.[9] It should be noted the observed difference in ^{1}H chemical shift between **4** and **2** is 2.6 ppm for the vinylic protons and 1.7 ppm for the aromatic protons. A similar oxidation of the closely related protonated 4,5-methylenphenanthrene ketone, **5**,[7,10] should yield the nonaromatic protonated doubly charged species **6**. This reaction, viz., **5** → **6** affords a probe for the estimation of charge deshielding in **6** vs. charge deshielding and diamagnetic ring current in **2**. Treatment of 4,5-methylenephenanthrene ketone at −40 °C with "magic acid" (1:1 M FSO_3H-SbF_5) in SO_2 produced **5**, ^{1}H NMR, δ[8] ppm 7.12 (m, 2 H, aromatic), 7.32 (broad singlet, 2 H, H_9, H_{10}), 7.62 (m, 4 H, aromatic), 12.60 (s, 1 H, OH). Oxidation to the dication occurred upon elevation of the temperature to +31 °C and the following ^{1}H NMR was observed: δ[8] (ppm) 7.59 (dd, 2 H, J_1 = 7.0, J_2 = 4.0 Hz, H_2, H_7), 8.1 (m, 4 H, aromatic), 8.58 (s, 2 H, H_9, H_{10}), 13.24 (s, 1 H, OH). The change in chemical shift, $\Delta\delta$, in the reaction **5** → **6** is 1.26 ppm for H_9 and H_{10} and 0.48 ppm for the aromatic protons.[11] The ^{1}H NMR as well as ^{13}C NMR of the ions **2** and **6** reveal that a plane of symmetry exists in these protonated dicationic molecules while their precursors **4** and **5** lack this property. The large proton downfield shift in the process **4** → **2** as compared with that of **5** → **6** is attributable to the generation of a diamagnetic ring current in **2** due to its aromatic character. Formally, **2** and **6** may be regarded as trications. However, the slow exchange with the environment of the proton at the carbonyl group even at a relatively high temperature as well as the downfield ^{13}C chemical shift of the carbonyl carbon support the assigned structures. In these structures two positive charges are delocalized and the third charge is localized at the carbonyl function. Transformation of **4** to the protonated cycloocta[*def*] fluorenone dication **2**, at room temperature represents the formation of a polycyclic dication containing the cyclooctatetraene moiety—a 14π-electron aromatic system.

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References and Notes

(1) E. Huckel, *Z. Phys.*, **70**, 204 (1931).
(2) For reviews see I. Agranat, *MTP Int. Rev. Sci.: Aromatic Compounds*, **3**, 139 (1973); F. Sondheimer, *Chimia*, **28**, 163 (1974).
(3) G. A. Olah, J. S. Staral, and L. A. Paquette, *J. Am. Chem. Soc.*, **98**, 1267 (1976). Upon warming of **1** (R = CH_3), isomerization to a bicyclic dication was observed. The formation of **1** (R = CH_3) is accompanied by varying amounts of the corresponding homotropylium ion.
(4) For cyclooctatetraene dications, cf. G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Carmody, *J. Am. Chem. Soc.* in press, personal communication.
(5) I. Willner and M. Rabinovitz, *Tetrahedron Lett.*, 1223 (1976).
(6) (a) Y. Sprintzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958); (b) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976); (c) J. Michl, R. Zahradnik, and P. Hochmann, *J. Phys. Chem.*, **70**, 1732 (1966).
(7) All new compounds gave satisfactory C, H analyses.
(8) The ^{1}H NMR spectra were recorded at 100 MHz in SO_2–magic acid. A Me_4Si capillary was used for locking the instrument. Decoupling experiments assisted the assignments and were carried out on a Model 4204 A Hewlett Packard oscillator. ^{13}C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer. Acetone-d_6 in a capillary was used for locking and as a reference.
(9) D. A. Forsyth and G. A. Olah, *J. Am. Chem. Soc.*, **98**, 4086 (1976).
(10) Prepared from 4,5-methylenphenanthrene.[6]
(11) The ^{13}C NMR spectrum of **5** showed 15 bands pointing to a nonsymmetrical configuration while **6** showed only 8 bands. A total downfield shift of 422 ppm was observed in agreement with a doubly charged species.[9]

Itamar Willner, Arie L. Gutman, Mordecai Rabinovitz*
Department of Organic Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel
Received January 31, 1977

Molybdenum Complexes of Aliphatic Thiols. Isolation and Characterization of Two Isomeric Forms of the Redox Active Binuclear Mo(V) Anion, $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$

Sir:

Research on the coordination chemistry of molybdenum-sulfur compounds has been stimulated by evidence that oxidation-reduction reactions which are catalyzed by molybdoenzymes occur at sites where the molybdenum is coordinated by one or more S atoms.[1] A variety of reactions are now known to produce stable diamagnetic binuclear di-μ-sulfido bridged Mo(V) species in which each Mo atom also is strongly bound to a terminal oxo or sulfido group.[2] As emphasized previously,[3] additional ligands lead to pseudotetragonal coordination geometry about each Mo atom. Two structures (A and B) are possible for two tetragonal pyramids sharing a basal edge.

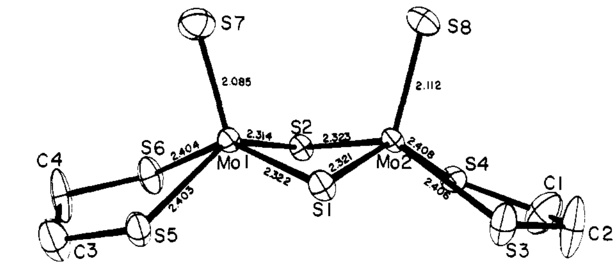


Figure 1. Perspective view of the anion of **1**. The estimated standard deviations of Mo–S bonds are 0.003 Å. Other distances and angles follow: Mo···Mo = 2.863 (2)Å; S1–Mo1–S2 = 99.9 (1), S1–Mo2–S2 = 99.7 (1), Mo1–S1–Mo2 = 76.2 (1), Mo1–S2–Mo2 = 76.3 (1)°. Exclusive of the CH_2 groups the anion has approximate C_{2v} symmetry.

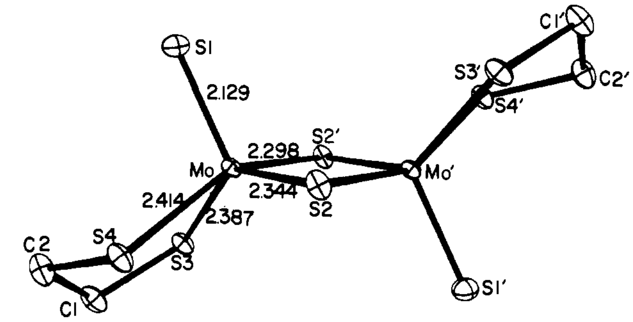
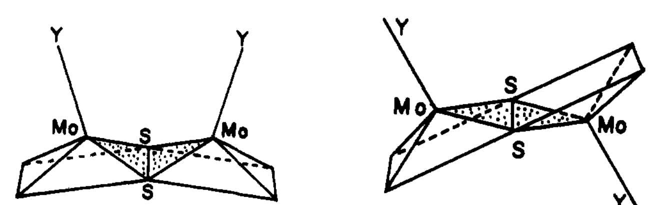


Figure 2. Perspective view of the anion of **2**. Primed atoms are related to unprimed atoms by a center of symmetry. The estimated standard deviations of Mo–S bonds are 0.002 Å. Other distances and angles follow: Mo···Mo = 2.878 (2) Å; S2–Mo–S2′ = 103.38 (7); Mo–S2–Mo′ = 76.62 (7)°. The space group imposes $\bar{1}$ symmetry on the anion. Exclusive of the CH_2 groups the approximate symmetry is C_{2h}.



A B

Structure A has a bent Mo_2S_2 moiety with a dihedral angle between the two Mo_2 planes of ~150°; structure B has a planar Mo_2S_2 moiety.[4] Several compounds of structure A with Y = S or O are known,[2,3,5] and three cyclopentadienyl derivatives related to B (Y = O,[6] S,[7] and $NC(CH_3)_3$)[8] have been reported. However, there is no prior example of structures A and B both being observed with the same ligands. Herein we describe redox active binuclear Mo(V) complexes of both geometries with Y = S and one 1,2-dimercaptoethanato (dme) ligand per Mo.

Refluxing mixtures of $MoCl_3$, NaHS, $NaOCH_3$, and 1,2-dimercaptoethane in anhydrous oxygen-free methanol produces intractable black solids and dark red solutions. Two forms of diamagnetic crystals of what proved to be tetraethylammonium di-μ-sulfidobis(sulfido-1,2-dimercaptoethanato)molybdate(V)), $[N(C_2H_5)_4]_2[Mo_2S_4(S_2C_2H_4)_2]$, have been isolated from the intensely colored filtrates by adding a saturated methanolic solution of tetraethylammonium bromide. Form **1** has been obtained as red-violet prisms from a 1:2:2:1 molar ratio of the refluxed reagents, and form **2** as small red-violet rhombohedral plates from a 1:1:3:2.25 ratio of reagents. The yields of both reactions are low, 6 and 3%, respectively.[9] Infrared spectra of the two samples (KBr) are similar, but not identical. The strongest bands for **1** and **2** occur