

illustrated 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.

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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).
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- (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).

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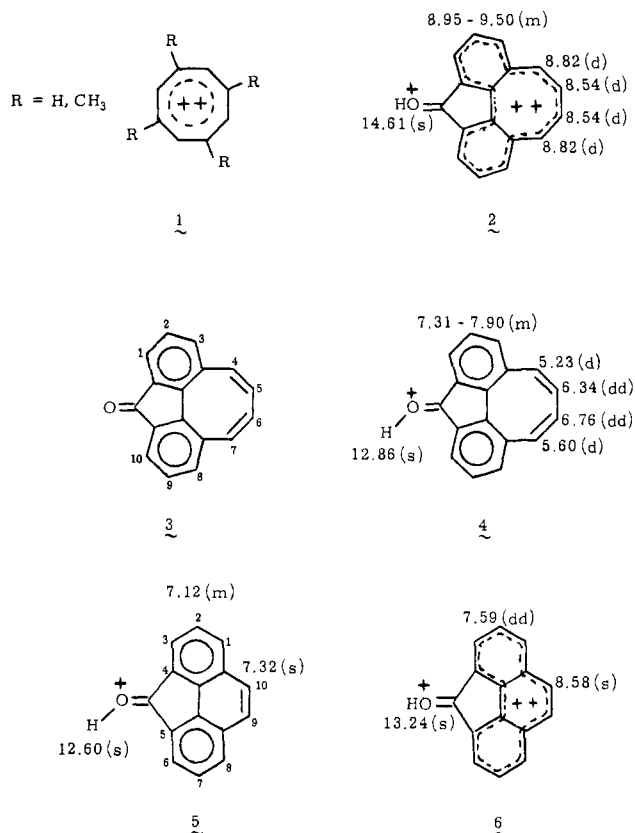
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Protonated Cycloocta[def]fluorenone Dication. A New 14 π -Electron Aromatic System

Sir:

The validity of Huckel's $(4n + 2)$ π electron rule for aromaticity¹ has been extensively tested during the past 20 years.² Early attempts to prepare the cyclooctatetraenylum 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]fluorene⁵ 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} $\nu_{\max}^{\text{Nujol}}$ 1710 (C=O stretching); m/e 231 ($M + 1$, 19%), 230 (M , 74%), 202 ($M - CO$, 100%); $\lambda_{\max}^{\text{EtOH}}$ 237 (ϵ 42 000), 295 (12 000), 350 (s) (1050), 430 nm (640); $\lambda_{\max}^{\text{EtOH}}$ 267 (ϵ 20 000), 300 (s) (7200), 415 (6200), 500 (s) nm (1000) with tailing to longer wavelengths. ¹H 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 ¹H NMR spectrum showed the following bands:⁸



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 ¹H 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 ¹³C NMR spectrum⁸ 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 $4 \rightarrow 2$ is 402 ppm or 201 ppm/e. This value is very near that observed for other dicationizations.⁹ It should be noted the observed difference in ¹H 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., $5 \rightarrow 6$ affords a probe for the estimation of charge deshielding in **6** vs. charge deshielding and diamagnetic ring current in **2**. Treatment of 4,5-methylenphenanthrene ketone at –40 °C with "magic acid" (1:1 M FSO_3H – SbF_5) in SO_2 produced **5**, ¹H 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 ¹H 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, H₉, H₁₀), 13.24 (s, 1 H, OH). The change in chemical shift, $\Delta\delta$, in the reaction **5** $\rightarrow$ **6** is 1.26 ppm for H₉ and H₁₀ and 0.48 ppm for the aromatic protons.¹¹ The ¹H NMR as well as ¹³C 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** $\rightarrow$ **2** as compared with that of **5** $\rightarrow$ **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 ¹³C 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 14 π -electron aromatic system.

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- (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.
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- (7) All new compounds gave satisfactory C, H analyses.
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- (9) D. A. Forsyth and G. A. Olah, *J. Am. Chem. Soc.*, **98**, 4086 (1976).
- (10) Prepared from 4,5-methylenphenanthrene.⁶
- (11) The ¹³C 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

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Molybdenum Complexes of Aliphatic Thiols. Isolation and Characterization of Two Isomeric Forms of the Redox Active Binuclear Mo(V) Anion, [Mo₂S₄(S₂C₂H₄)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 ge-

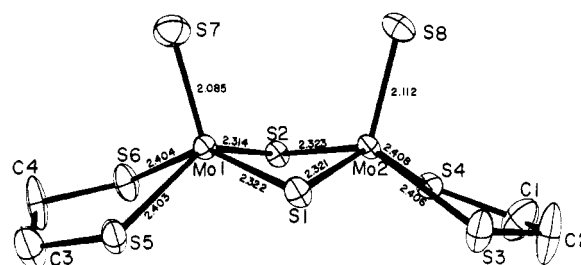


Figure 1. Perspective view of the anion of **1**. The estimated standard deviations of Mo-S bonds are 0.003 Å. Other distances and angles follow: Mo...Mo = 2.863 (2) Å; S1-Mo1-S2 = 99.9 (1), S1-Mo2-S2 = 99.7 (1), Mo1-S1-Mo2 = 76.2 (1), Mo1-S2-Mo2 = 76.3 (1)°. Exclusive of the CH₂ groups the anion has approximate C_{2v} symmetry.

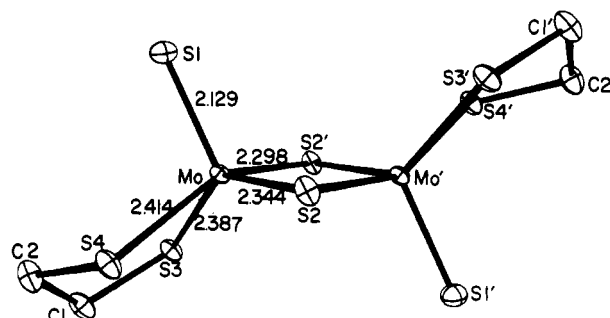
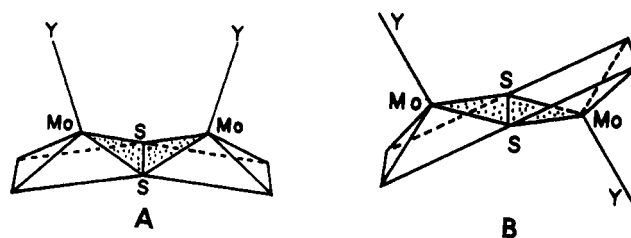


Figure 2. Perspective view of the anion of **2**. Primed atoms are related to unprimed atoms by a center of symmetry. The estimated standard deviations of Mo-S bonds are 0.002 Å. Other distances and angles follow: Mo...Mo = 2.878 (2) Å; S2-Mo-S2' = 103.38 (7); Mo-S2-Mo' = 76.62 (7)°. The space group imposes $\bar{1}$ symmetry on the anion. Exclusive of the CH₂ groups the approximate symmetry is C_{2h}.

ometry about each Mo atom. Two structures (A and B) are possible for two tetragonal pyramids sharing a basal edge.



Structure A has a bent Mo₂S₂ moiety with a dihedral angle between the two Mo₂ planes of ~150°; structure B has a planar Mo₂S₂ 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(CH₃)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 MoCl₃, NaHS, NaOCH₃, 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(C₂H₅)₄]₂[Mo₂S₄(S₂C₂H₄)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