

X-ray diffraction lines were weak and diffuse. These properties suggest that these oxidation products are polymeric and this is supported by the fact that their infrared spectra were very similar to that of the bis-(cyclopentadienyl)titanoxane polymer  $[-Ti(C_5H_5)_2-O]_n$  prepared by Giddings.<sup>2</sup>

Work on the synthesis and characterization of other compounds of the type  $(C_5H_5)_2M$ , where M is a metal in the 4f or 5f transition series or a lanthanide, is in progress.

**Acknowledgment.** This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

(2) S. A. Giddings, *Inorg. Chem.*, **3**, 684 (1964).

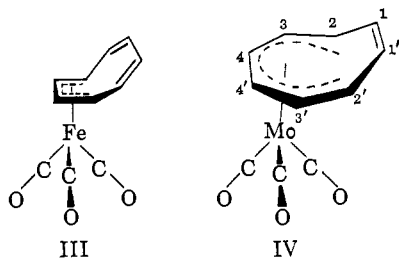
George W. Watt, Frank O. Drummond, Jr.  
Department of Chemistry, The University of Texas  
Austin, Texas 78712

Received September 12, 1966

### The Crystal Structure of Cyclooctatetraenemolybdenum Tricarbonyl<sup>1</sup>

Sir:

Cyclooctatetraenemolybdenum tricarbonyl,  $C_8H_8Mo(CO)_3$  (I),<sup>2</sup> is one of a class of  $\pi$ -bonded cyclic olefin-transition metal complexes where the olefin has more available  $\pi$  electrons than is required by the metal. The possible consequences of this situation on the geometry of the ligand have been examined with particular attention to I, the corresponding cyclooctatetraenochromium tricarbonyl (II), and  $C_8H_8Fe(CO)_3$  (III).<sup>3</sup> An nmr investigation<sup>3</sup> of I and II has eliminated the possibility that the "excess"  $\pi$  electrons might be involved in  $\sigma$  bonding resulting in the formation of bicyclic ligands. At 80°, the nmr of I exhibits a sharp singlet, which broadens as the temperature is lowered, and finally, at -30 to -40°, develops a complex multiplet pattern.<sup>2,3</sup> This behavior has been interpreted in terms of a "freezing" of a fixed configuration at lower temperatures, where the metal is involved in bonding with six  $\pi$  electrons, leaving one double bond unaffected. At higher temperatures, valency tautomerism takes place with a rapid rate of interconversion among the tautomers, resulting in all the protons in the molecule becoming equivalent on a time-average



basis.<sup>3</sup> We have investigated the crystal structure of I, presupposing that crystal forces are sufficient to "freeze" the lowest energy valence tautomer,<sup>4</sup> in order to examine the molecular geometry of the complex.

(1) This work was supported in part by the National Institutes of Health (GM 12470-02) and by the Hoffmann-LaRoche Foundation.

(2) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965).

(3) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

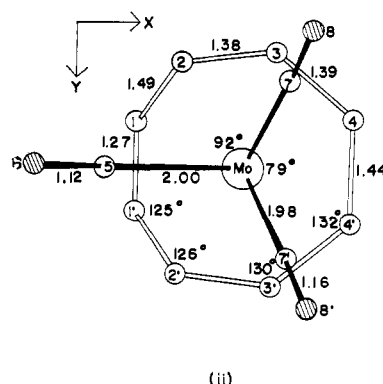
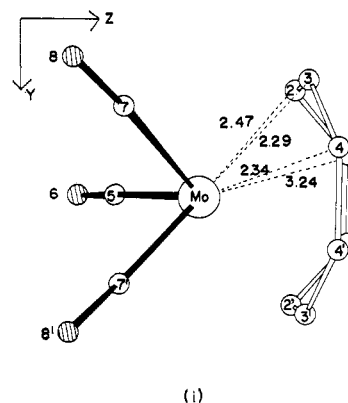


Figure 1. The complex viewed down (i) the  $a$  axis, and (ii) the  $c$  axis. Mo-C distances are  $\pm 0.02$  Å; C-C and C-O distances are  $\pm 0.03$  Å; C-Mo-C angles are  $\pm 1^\circ$ ; C-C-C angles are  $\pm 2^\circ$ .

Cyclooctatetraenemolybdenum tricarbonyl crystallizes in the form of thick red plates belonging to the monoclinic system, with  $a = 7.33 \pm 0.02$ ,  $b = 10.43 \pm 0.03$ ,  $c = 7.16 \pm 0.02$  Å, and  $\beta = 107^\circ 15' \pm 20'$ , as determined on a precession camera with Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å). There are two molecules of  $C_8H_8Mo(CO)_3$  in the unit cell. Systematic absences indicate that the space group is either  $P2_1$  or  $P2_1/m$ . A total of 1046 independent structure amplitudes was obtained by visual estimation of equiinclination Weissenberg photographs (Mo  $K\alpha$  radiation) at 25°. The structure analysis followed the usual heavy atom method,<sup>5</sup> and full-matrix, least-squares refinement incorporating anisotropic temperature factors has given an  $R$  factor of 0.13 on the 1046 observed reflections.

The molecular structure is shown in Figure 1. With-in the accuracy of our analysis, the space group is  $P2_1/m$ ,<sup>7</sup> which requires the molecule to have mirror symmetry with the molybdenum atom and one carbonyl group lying in the reflection plane. The Mo atom is closely, but not equally, associated with C(2), C(3),

(4) A recent X-ray study on the geometry of bullvalene, another olefin exhibiting rapid tautomerism, has indicated that at temperatures where rearrangement normally occurs in solution,  $Ag^+$  complexation and crystal forces are sufficient to stabilize one tautomer: M. G. Newton and I. C. Paul, *ibid.*, **88**, 3161 (1966). The crystallographic study<sup>8</sup> on cyclooctatetraeneiron tricarbonyl shows no evidence for disorder which would indicate coexistence of valence tautomers in the crystal.

(5) B. Dickens and W. N. Lipscomb, *ibid.*, **83**, 4862 (1961); *J. Chem. Phys.*, **37**, 2084 (1962).

(6) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

(7) After initial attempts to refine the structure in each of the two possible space groups, a decision was made in favor of  $P2_1/m$  and the final refinements were based on this group.

and C(4) and their symmetry equivalent atoms (the Mo-C(2) distance of 2.47 Å is definitely longer than the Mo-C(3) and Mo-C(4) distances, where the difference of 0.05 Å is not significant based on our present analysis), while the Mo-C(1) distance is very much greater. The C(1)-C(1') link appears to be almost a pure double bond, while C(1)-C(2) has a very high degree of single-bond character; the distances in this portion of the molecule are similar to those found in free cyclooctatetraene in the gas phase.<sup>8</sup> The bond angles, C(2)-C(3)-C(4) and C(3)-C(4)-C(4'), approach the ideal value for a regular octagon (135°). The group of six atoms C(2), C(2'), C(3), C(3'), C(4), and C(4') is significantly nonplanar with C(3) and C(3') deviating by 0.16 Å from the best plane through the other four atoms. The angle between the plane through C(1), C(1'), C(2), C(2') and that through C(2), C(2'), C(3), C(3') is 130°. The wide variation in the C(5)-Mo-C(7) and C(7)-Mo-C(7') angles was also a feature of the analysis of cycloheptatrienemolybdenum tricarbonyl.<sup>9</sup> We consider that structure IV, as proposed by Winstein and co-workers,<sup>3</sup> is a good representation of the geometry, providing it does not imply that the Mo is equally associated with six carbon atoms.

There is no evidence for crystallographic disorder which could be indicative of valency tautomerism occurring in the crystal at 25°. This structure is an interesting contrast to that of cyclooctatetraeneiron tricarbonyl (III),<sup>5</sup> where the iron atom is bonded to a butadiene-like residue in the cyclooctatetraene ring, and where valency tautomerism has been detected in solution at temperatures as low as -100°; but at -140 to -150° the spectrum corresponding to a frozen complex is observed.<sup>3</sup>

**Acknowledgment.** We wish to thank Professor S. Winstein and Professor H. D. Kaesz for kindly supplying us with crystals of C<sub>8</sub>H<sub>8</sub>Mo(CO)<sub>3</sub>. We have benefited from discussions with Dr. M. Gary Newton, while Miss Jeannie Herrin assisted in the data estimation.

(8) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(9) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

James S. McKechnie, Iain C. Paul

Noyes Chemical Laboratory, University of Illinois  
Urbana, Illinois 61801

Received September 19, 1966

### Evidence for the Dipolar Field Effect<sup>1</sup>

Sir:

Attempts to distinguish between inductive and field propagation models for the transmission of polar effects have not been entirely successful. The problem persists because, in most instances, molecular structure requires that the low dielectric cavity of the field effect model<sup>2</sup> be occupied by the chemical bonds important in the inductive effect model.<sup>3</sup> If a small

(1) Chemistry of the Bicyclo[2.2.2]octanes. VII. This research was supported by a grant from the National Science Foundation.

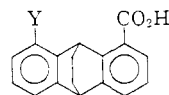
(2) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(3) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, Chapter 6.

attenuation factor is adopted for through-bond transmission of the polar effect, both models predict similar results.<sup>4</sup> However, these limiting models predict quite different results when the angle between a dipolar substituent and the reaction site is varied.<sup>5</sup> Roberts and Carboni point out that, although *o*-chlorophenylpropionic acid is somewhat stronger than phenylpropionic acid, it is weaker than expected on the basis of an inductive model.<sup>5</sup> Wells and Adcock note that the lessened acidities of 7-chloro-1-naphthoic and 8-chloro-2-naphthoic acids, for example, are compatible with the angular dependence implicit in the field effect model.<sup>6</sup> We now report the first example of a reversed substituent effect supporting these interpretations and offering secure evidence for the importance of dipolar field effects.

The ethano-bridged anthracenes I-IV were selected for investigation because simple electrostatic considerations indicated that substituent effects would be reversed. Moreover, resonance contributions are excluded and hydrogen bonding is unlikely.

The acids were prepared by the addition of ethylene to the corresponding anthroic acids which were obtained from benzanthrone or 1,8-dichloroanthraquinone by conventional methods.<sup>7</sup> The dissociation constants were determined in 50% ethanol-water (w/w) at 25°.<sup>8</sup>



I, Y = H;  $pK_{\text{H}} = 6.04 \pm 0.03$

II, Y = Cl;  $pK_{\text{Cl}} = 6.25 \pm 0.02$

III, Y = CO<sub>2</sub>CH<sub>3</sub>;  $pK_{\text{CO}_2\text{CH}_3} = 6.20 \pm 0.02$

IV, Y = CO<sub>2</sub>H;  $pK_1 = 5.67 \pm 0.03$ ; statistical correction =  $5.97 \pm 0.03$

Y = CO<sub>2</sub><sup>-</sup>;  $pK_2 = 7.19 \pm 0.02$ ; statistical correction =  $6.89 \pm 0.02$

Two lines of evidence point to the importance of the field effect model. First and most pertinent,  $pK_{\text{Cl}}$  and  $pK_{\text{CO}_2\text{CH}_3}$  are larger than  $pK_{\text{H}}$ . This reversal in normal substituent effects is cogent evidence for the angular dependence of the polar effect. As noted, electrostatic considerations predict  $\log(K_{\text{Cl}}/K_{\text{H}}) = -2.4/D_{\text{E}}$ . The effective dielectric constant,  $D_{\text{E}}$ , may not be defined with complete confidence for these acids, but a value near 10 is not unreasonable.

Second,  $\log(K_2/K_{\text{H}})$  is unusually small, -0.85. This ratio is generally larger (less negative), since, in most compounds, the influence of the charge and the carboxylate dipole act in opposition.<sup>9</sup> For IV, however, the predicted contribution of the carboxylate dipole is near zero. The reduction in  $\log(K_2/K_{\text{H}})$  is therefore also predicted by the angular dependence implicit in the field effect model.

The similar values of  $pK_{\text{Cl}}$  and  $pK_{\text{CO}_2\text{CH}_3}$  and the normal value of  $\log(K_1/4K_2)$  exclude an interpretation based on hydrogen bonding.<sup>10</sup>

(4) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

(5) J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955).

(6) P. R. Wells and W. Adcock, *Australian J. Chem.*, **18**, 1365 (1965).

(7) Satisfactory microanalyses were obtained for all unknown compounds. The substances exhibited spectroscopic properties compatible with the assigned structures.

(8) The differential potentiometric method (A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955)) or the potentiometric titration method (J. C. Speakman, *J. Chem. Soc.*, 855 (1940)) was used for the determination of  $pK$ .

(9) C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, **30**, 777 (1965).

(10) For IV,  $\log(K_1/4K_2) = 0.92$ . This result is comparable to that for glutaric and succinic acids, 0.73 and 1.30, respectively, in 52.3%