

atoms resulted in an  $R$  factor of 11% for 325 independent data.

The interatomic distances and angles are shown in Table II. Nearest approaches between molecules are  $C(1) \cdots C(31'')$  at 4.14 Å, and  $C(1) \cdots C(23'')$  at 4.52 Å.

It is seen that all the bonded C–C distances are near 1.54 Å., the diamond value, and all the angles are near the tetrahedral value. Adamantane,<sup>4</sup> the single cage structure related to congressane, also crystallizes in the cubic system and has C–C bond distances of 1.54 Å. and tetrahedral bond angles. It is of interest that the nearest approach between molecules of adamantane is the same as that for congressane. Both substances have unusually high densities for hydrocarbons, namely, 1.07 g./cm.<sup>3</sup> for adamantane and 1.21 g./cm.<sup>3</sup> for congressane.

*Acknowledgment.* We wish to thank Dr. P. Schleyer for suggesting that we investigate the structure of congressane, Dr. Schleyer and Mr. C. Cupas for furnishing us with the crystal, and Mr. S. Brenner for performing the calculations.

(4) W. Nowacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

I. L. Karle, J. Karle

U. S. Naval Research Laboratory  
Washington, D. C.

Received January 7, 1965

## The Inductive Effect in the Toluene Anion Radical

Sir:

The general agreement found between the aromatic ion-radical spin densities calculated by molecular orbital theory and estimated from electron spin resonance hyperfine splittings is considered an important experimental confirmation of  $\pi$ -electron theory.<sup>1</sup> A prime example of this type of comparison is provided by the toluene anion.<sup>2</sup> For this radical a simple, yet relatively accurate, description of the measured ring hyperfine splittings is obtained by assuming that the double degeneracy of the benzene anion ground state is lifted by the presence of the methyl group and that the unpaired electron is in the lower energy orbital, which is the one that is "antisymmetric" with respect to the perpendicular plane through the substituted carbon ( $C_1$ ) and the *para* carbon ( $C_4$ ). This orbital (often designated as  $\Psi_5$ ) has the form

$$\Psi_5 = \frac{1}{\sqrt{4}}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \quad (1)$$

where the  $\phi_i$  are atomic  $\pi$ -orbitals associated with carbon  $C_i$ . Equation 1 yields spin densities of  $1/4$  in the 2-, 3-, 5-, and 6-positions and zero in the 1- and 4-positions in correspondence with the e.s.r. result that there are four large hyperfine constants of nearly equal magnitude ( $|a^H| \cong 5.3$  gauss) due to the 2-, 3-, 5-, and 6-ring protons and very small splitting constants from the ring proton in the 4-position and from the methyl group protons. Although this interpretation is almost certainly correct, we wish to point out that it is not consistent with a calculation based on the most common model for the methyl group

(1) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 6.

(2) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

ring interaction; that is, if a Hückel molecular orbital (HMO) treatment with the Mulliken hyperconjugative model<sup>3</sup> and Coulson–Crawford parameters<sup>4</sup> for the methyl group is performed, it is found that the *symmetric* member of the degenerate benzene orbitals has a lower energy. Since this orbital ( $\Psi_4$ ) has the form

$$\Psi_4 = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \quad (2)$$

it yields two large spin densities ( $1/3$ ) in the 1- and 4-positions and four small ones ( $1/12$ ) in the 2-, 3-, 5-, and 6-positions. Thus, the result that  $\Psi_4$  is more stable in the toluene anion and, therefore, is occupied by the unpaired electron is clearly in disagreement with the e.s.r. spectrum.

The difficulty with the Coulson–Crawford model can be described in a simple manner. Since the antisymmetric orbital ( $\Psi_5$ ) has no contribution from the atomic orbital  $\phi_1$  at the methyl-substituted position, it has exactly the HMO energy that it would have in the benzene anion. Only the energy of the symmetric orbital ( $\Psi_4$ ) is altered by the substitution and a *stabilization* is produced by conjugation with the methyl group. To consider this effect in more detail, we number the significant positions  $C_1$ ,  $C_7$ , and  $X_8$ , where  $C_1$  is the benzene carbon,  $C_7$  is the methyl group carbon, and  $X_8$  is the hydrogen group pseudo-atom. The essential parameters for the interacting methyl group are

$$\begin{aligned} \alpha_7 &= \alpha_0 + h_7\beta_0 & \beta_{17} &= k_{17}\beta_0 \\ \alpha_8 &= \alpha_0 + h_8\beta_0 & \beta_{78} &= k_{78}\beta_0 \end{aligned}$$

where  $\alpha_0$  and  $\beta_0$  are the ring-carbon atomic integral and resonance integral, respectively; and  $h_7$ ,  $h_8$ ,  $k_{17}$ , and  $k_{78}$  are proportionality constants selected by some fitting procedure.<sup>1,4</sup> With the Coulson–Crawford values  $h_7 = -0.1$ ,  $h_8 = -0.5$ ,  $k_{17} = 0.7$ , and  $k_{78} = 2.5$ , one finds for the symmetric orbital energy  $\epsilon_4 = \alpha_0 - 0.986\beta_0$ , while for the antisymmetric orbital has the unperturbed energy  $\epsilon_5 = \alpha_0 - \beta_0$ . Variation of the methyl group parameters, ( $h_7$ ,  $h_8$ ;  $k_{17}$ ,  $k_{78}$ ) within reasonable ranges does not alter the order of the energy levels. Independent of  $k_{17}$  and  $k_{18}$ ,  $\alpha_8$  has to be increased to  $\alpha_0 - 1.0\beta_0$  to make  $\epsilon_4$  and  $\epsilon_5$  degenerate, while a still larger value of  $\alpha_8$  is needed to make the energy level differences ( $\epsilon_4 - \epsilon_5$ ) have the required positive sign.

The paradox that emerges from the above calculation can be solved by introducing an additional parameter corresponding to the inductive effect<sup>5</sup> of the methyl group on the ring carbon atoms, in particular on the substituted position  $C_1$ . Writing  $\alpha_1 = \alpha_0 + h_1\beta_0$ , and using the previously listed values for the methyl group, one finds that  $\epsilon_4 - \epsilon_5 \cong (1/3)h_1\beta_0$ . Thus, a "chemically" reasonable negative  $h_1$  can produce the correct ordering of the energy levels; a value on the order of  $-0.1$  seems to be needed to produce the proper energy level splitting. Such a value for  $h_1$  is not out of line with estimates based on other molecular properties. What is important about the e.s.r. data is that their "all or nothing?" character seems to

(3) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(5) See ref. 1, Section 5.7. The simple inductive model [G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935)] yields the correct order for the energy levels but no methyl group hyperfine splittings.

provide essentially unequivocal evidence for the presence of an inductive contribution to the methyl-group aromatic-ring interaction in the toluene anion.<sup>6</sup> A subsequent paper will present a more detailed description of the HMO results and their confirmation by an ASMO-CI (Pariser-Parr) treatment.

*Acknowledgment.*—One of the authors (M. K.) wishes to thank Dr. J. M. Parks and Dr. G. K. Fraenkel for helpful discussions of the hyperconjugation problem.

(6) The conclusion of J. R. Bolton, A. Carrington, and A. D. McLachlan [*Mol. Phys.*, **5**, 31 (1962)] that hyperconjugation and induction can result in equivalent energy changes appears to be incorrect; the difficulty arises from their neglect of the methyl group antibonding orbital. See, also, J. P. Colpa and E. de Boer, *ibid.*, **7**, 333 (1964).

D. Lazdins, M. Karplus

Department of Chemistry and IBM Watson Laboratory  
Columbia University, New York, New York

Received December 29, 1964

## A Multiple Bond between Technetium Atoms in an Octachloroditechnetate Ion<sup>1</sup>

Sir:

We wish to present a preliminary account of the results of an X-ray diffraction study of the compound  $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$  recently reported by Eakins, Humphreys, and Mellish.<sup>2</sup> The compound was prepared as directed by these authors. The unit cell has trigonal symmetry with the dimensions  $a = 13.03 \pm 0.02$  and  $c = 8.40 \pm 0.01$  Å. With three of the above formula units per cell, the calculated density is  $2.31 \text{ g. cm.}^{-3}$  ( $d_{\text{exptl}} 2.4 \text{ g. cm.}^{-3}$ ). From systematic extinctions and the three-dimensional Patterson function, the space group was found to be  $P3_121$ .

The salient feature of the structure (for which the usual reliability index now stands at 15% for 412 reflections) is the occurrence of  $\text{Tc}_2\text{Cl}_8$  groups which are essentially isostructural with the  $[\text{Re}_2\text{Cl}_8]^{2-}$  group.<sup>3,4</sup> Their virtual symmetry is  $D_{4h}$ , although, crystallographically, they possess only a single  $C_2$  axis bisecting the Tc-Tc bond. The four crystallographically independent Tc-Cl bonds have lengths of 2.34, 2.35, 2.35, and 2.36 Å., each with a standard deviation of 0.03 Å., while the Tc-Tc distance is  $2.13 \pm 0.01$  Å. Two-thirds of the ammonium ions have been located on the sixfold equipoint, lying between the  $\text{Tc}_2\text{Cl}_8$  groups, with  $\text{N} \cdots \text{Cl}$  distances of 3.04 to 3.37 Å., while the remaining ammonium ions are on a threefold equipoint.

Recent studies in this laboratory of metal atom cluster compounds,<sup>5</sup> especially those of rhenium,<sup>3</sup> have led to the preparation<sup>6</sup> and characterization<sup>4,6</sup> of the  $[\text{Re}_2\text{X}_8]^{2-}$  ions, in which there is an extremely short Re-Re bond (2.24 Å.). On the basis of the bond length and the eclipsed structure of the  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion, as well as for some other reasons, it has been proposed that the Re-Re

bond is quadruple,<sup>3,7</sup> consisting of a  $\sigma$ -bond, two  $\pi$ -bonds, and a  $\delta$ -bond. It has also been suggested<sup>7</sup> that the carboxylate-bridged dimers,<sup>8</sup>  $[\text{Re}(\text{O}_2\text{CR})_2\text{X}]_2$ , have quadruple bonds; X-ray studies are in progress to test this suggestion.

The charge of  $-3$  on the  $\text{Tc}_2\text{Cl}_8$  group is somewhat surprising. However, in addition to the X-ray evidence, our own analytical data confirm the formula, and magnetic susceptibility data are consistent with the presence of one unpaired electron per  $\text{Tc}_2\text{Cl}_8$  unit.

It is of interest to compare our results for the  $\text{Tc}_2\text{Cl}_8$  group with those which have been obtained by Lawton and Mason<sup>9</sup> for Wilkinson's Mo(II) acetate.<sup>10</sup> These workers find that the compound is a centrosymmetric dimer with the acetate groups acting as bridges between the metal atoms in the same general manner as in the Cu(II) carboxylate dimers. There is a square-planar set of oxygen atoms about each Mo atom, and the Mo-Mo distance is 2.10 Å. This distance is practically the same as the Tc-Tc distance we have found in the  $\text{Tc}_2\text{Cl}_8$  ion. It appears that the formation of extremely short, presumably quadruple, bonds between  $d^4$ -ions of the second- and third-row transition elements may be quite general. Chemical and structural studies of these and related compounds are being continued.

(7) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(8) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(9) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(10) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

F. A. Cotton, W. K. Bratton

Department of Chemistry, Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received November 30, 1964

## The Molecular Structure of Molybdenum(II) Acetate

Sir:

We have completed an X-ray analysis of the crystal structure of molybdenum(II) acetate.<sup>1,2</sup> The crystals are triclinic, space group  $P\bar{1}$ , with  $a = 8.35$ ,  $b = 5.46$ , and  $c = 7.50$  Å.,  $\alpha = 82.9^\circ$ ,  $\beta = 105.1^\circ$ ,  $\gamma = 105.1^\circ$ ; with  $\rho_{\text{obsd}} = 2.10 \text{ g./cc.}$ ,  $Z = 1$  for  $[\text{Mo}(\text{O}_2\text{CCH}_3)_2]_2$ . The molecule is strictly centrosymmetric in the crystal, its stereochemistry being shown in Figure 1; the observed molecular dimensions are the result of a least-squares analysis of 393 reflections ( $R = 0.071$ ), average e.s.d.'s of bond lengths being 0.003 (Mo-Mo), 0.025 (Mo-O), and 0.04 Å. (C-C and C-O).

With the exception of the remarkably short metal-metal bond, the structure is similar to that of the copper acetate dimer structure,<sup>3</sup> the four bridging acetate groups establishing a slightly distorted planar configuration of each molybdenum ion. The covalent radius of the metal can be estimated from the observed mean Mo-O bond length of 2.10 Å. as 1.45 Å.,<sup>4</sup> and a metal-metal bond length of *ca.* 2.9 Å. would therefore be

(1) E. Bannister and G. Wilkinson, *Chem. Ind. (London)*, 319 (1960).

(2) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

(3) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(4) The covalent radius of oxygen is given a value of 0.65 Å. as judged from the available accurately determined carbon-oxygen bond lengths.<sup>5</sup>

(5) "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

(1) Supported by the U. S. Atomic Energy Commission.

(2) J. D. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 6012 (1963).

(3) F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, **145**, 1305 (1964).

(4) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(5) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

(6) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *ibid.*, **4**, 326 (1965).