tetrahedral carbon might maintain degrees of configurational stability due to electrostatic inhibition of inversion. Electrostatic effects in the anion of sulfone I should be much greater than in the anions of either sulfoxide II or phosphine oxide III, and therefore the sulfone anion might exhibit configurational stability and the oxide anions lack of stability, as has been observed.

(2) When free from constrictions due to ring systems, carbanions stabilized by d-orbitals might provide better p-d overlap when trigonally hybridized. Several conditions would have to be fulfilled before stereospecificity for exchange reactions involving such species was observed. (a) The rotomer that gave the best p-d overlap would have to be asymmetric. (b) The rotomer would have to be formed and consumed through a *transition state that involved only one particular conformation.*[6] (c) The carbanion would have to undergo proton capture faster than the carbanion equilibrated (by rotation) with its enantiomer. These conditions might come closer to fulfillment with the sulfone than with the oxide anions. The d-orbitals of the sulfone group are more stabilizing than those of the oxide groups, and might impose more severe geometric requirements with respect to conformation than do the d-orbitals of the two oxides. Attempts are being made to test these notions in other systems that involve d-orbital-stabilizing groups.

[6] Application of the principle of microscopic reversibility indicates that if a carbanion is formed by loss of a proton from a particular side of the molecule, the same side will be involved when the proton is recaptured.

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THE MOLECULAR CONFIGURATION OF 2,4,6-TRIPHENYLTROPONE-IRON TRICARBONYL

Sir:

The recent syntheses of several cycloheptatrienone (tropone) complexes by Hübel and co-workers[1-4] have stimulated discussion about their molecular geometry and the type of bonding between the metal orbitals and the π-orbitals of the organic ring system. On the basis of simple molecular-orbital theory and the presumed similarity of these compounds to the cyclopentadienone-metal complexes, Brown[5] suggested a planar tropone ring with the iron bonding equally to all three double bonds of the ring. Hübel and co-workers[6] later found that one of the double bonds could be hydrogenated and this together with the existence of isomers for each tropone complex led them to postulate interaction of the iron atom with only two of the three double bonds.[4]

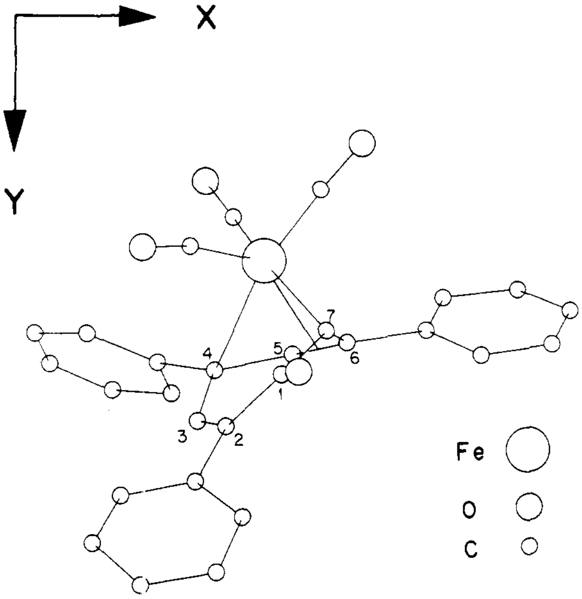

Fig. 1.—[001] Molecular projection of $[C_6H_3(C_6H_5)_3CO]$-$Fe(CO)_3$: bond distances for the tropone ring are 1.45 and 1.49 Å. for C_4–C_5 and C_6–C_7, respectively; 1.38 Å. for C_5–C_6, 1.34 Å. for the normal double bond C_2–C_3, 1.44 Å. (av.) for the other three bonds, and 1.26 Å. for C_1–O (all with e.s.d. ± 0.02 Å.). Fe–C distances are 2.17, 2.00, 2.09, and 2.13 Å. to carbon atoms $C_4 \ldots C_7$, respectively; iron distances to the midpoints of C_4–C_5, C_5–C_6 and C_6–C_7 are 1.96, 1.93 and 1.98 Å., respectively. Other non-bonding iron–tropone distances are $Fe \ldots C_1 = 2.97$ Å., $Fe \ldots C_2 = 3.46$ Å., and $Fe \ldots C_3 = 3.12$ Å. Fe–C (carbonyl) = 1.73 Å. (av.), C–O = 1.18 Å. (av.) (all with e.s.d. ± 0.02 Å). C–C bond lengths in phenyl rings range from 1.31 to 1.51 Å. (e.s.d. ± 0.03) with average length 1.40 Å.). Bond angles are (C_6H_5)–C_4–$C_5 = 118.2°$, (C_6H_5)–C_4–$C_3 = 112.2°$, C_3–C_4–$C_5 = 122.4°$, C_4–C_5–$C_6 = 124.3°$, C_5–C_6–$C_7 = 116.2°$, (C_6H_5)–C_6–$C_5 = 126.0°$, (C_6H_5)–C_6–$C_7 = 117.5°$, C_6–C_7–$C_1 = 129.5°$, C_7–C_1–$C_2 = 125.0°$, C_1–C_2–$C_3 = 121.8°$, (C_6H_5)–C_2–$C_1 = 117.3°$, (C_6H_5)–C_2–$C_3 = 119.9°$, C_2–C_3–$C_4 = 127.7°$ (all with e.s.d. $\pm 1.6°$). The dihedral angle between the two planes in the tropone ring is 139°.

To resolve this conflict we have carried out an X-ray structural analysis of one isomer of a substituted tropone, 2,4,6-triphenylcycloheptatrienone-iron tricarbonyl, $[C_6H_3(C_6H_5)_3CO]Fe(CO)_3$. The dark red crystals[3] are orthorhombic with lattice parameters $a = 19.53$ Å., $b = 7.62$ Å., and $c = 15.03$ Å. Systematic absences show $P2_12_12_1$ as the probable space group. For four molecules per unit cell the calculated density is 1.41 g./cc. in agreement with the density, 1.41 g./cc., measured by the flotation method.

X-Ray intensity data obtained with MoKα radiation by the usual equi-inclination Weissenberg techniques were estimated visually. A three dimensional structural analysis of the data including isotropic least squares refinement[7] and error analysis[8] has yielded the molecular configuration

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[7] W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," ORXLS, 1959.

[8] W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," ORXFE, 1959.

for $[C_6H_3(C_6H_5)_3CO]Fe(CO)_3$ shown in Fig. 1. The present reliability index, R_1, is 9.4% for 970 independent, observed reflections.

In agreement with the chemical evidence, the intramolecular distances clearly indicate bonding of the $Fe(CO)_3$ fragment with only two of the three double bonds of the ring. This organometallic interaction results in a bending of the tropone ring (Fig. 1) at atoms C_4 and C_7 into two approximate planes—one plane comprising the diene-type carbon atoms C_4, C_5, C_6 and C_7; and the other plane containing the remaining ring atoms. A similar molecular configuration has been found by Dodge and Schomaker[9] in tropone-iron tricarbonyl; the (*syn*-butadiene)-$Fe(CO)_3$ residue also is embodied in $C_4H_6Fe(CO)_3$,[10] $Fe_2(CO)_6(COH)_2(CH_3C_2CH_3)$,[11] $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$,[12] $(OC)_3Fe(COT)Fe(CO)_3$,[13] and $(COT)Fe(CO)_3$.[14]

The molecular geometry of the triphenyltropone–$Fe(CO)_3$ complex provides an explanation for the non-planarity of the tropone ring. The phenyl groups attached to ring atoms C_2 and C_6 are twisted out of the mean planes of the ring carbon atoms; the phenyl bonded to the terminal diene atom, C_4, however, is not only twisted but bent out of the mean diene plane such that the bonding orbital of C_4 is directed more nearly toward the iron resulting in better metal–ligand overlap. Presumably, the local environment at the other terminal C_7 atom to which a hydrogen is bonded in place of a phenyl group is analogous to that of C_4. To the extent that each of the terminal carbon atoms and its three attached neighbors are planar, the bending of the phenyl group (and the hydrogen) from the mean diene plane represent rotations about the C_4-C_5 and C_6-C_7 axes, respectively.

Further analysis, however, shows that the C_4 atom does *not* lie in the localized plane of its three bonded carbons; C_4 is located approximately 0.22 Å. above this plane (almost one-half of the distance for a normal tetrahedral configuration). The *central* diene atoms, C_6 (and presumably C_5), are planar with their immediate neighbors. The combination of these rotations and deformations produces the dihedral angle at C_4 and C_7. This dihedral angle also has been observed in the unsubstituted tropone-$Fe(CO)_3$[9] and in both COT-$Fe(CO)_3$[13,14] complexes for which the stereochemical disposition of the $Fe(CO)_3$ fragment is similar.

The detailed representation of the bonding of the *syn*-butadiene group as a four-electron donor system to the metal has been the subject of much speculation. Hallam and Pauson[15] first formulated the widely-held view that the basic structure is a π-complex in which the conjugated diene system remains essentially unaltered and in which the four π-electrons utilized in bonding are delocalized. The three CO's and the midpoints of the two double bonds of the diene group then would form a distorted tetragonal pyramidal configuration about a five-coördinated iron. Another formal representation proposed by Wilkinson and co-workers[16–18] from n.m.r. studies (but found by them to be in conflict with the infrared data) involves a Diels–Alder type addition of the diene system to the iron atom with the central two carbon atoms, C_5 and C_6, forming a coördinate double bond. This latter structural representation based on a three-point attachment of the butadiene residue to the iron atom *via* the two σ-alkyl bonds and the bond to the central olefinic group would lead to an approximately octahedrally coördinated iron atom.

We strongly favor the latter description of bonding primarily on the basis of distortion of the *terminal* C_4 (and presumably C_7) atoms toward sp^3 hybridization. Of course, the actual electron-density distribution will involve contributions from both formal structures. A number of other closely related conjugated diene-transition metal complexes[17,19] should possess similarly deformed configurations.

We gratefully thank Dr. Hübel and co-workers for supplying us with a sample of the compound. We wish to acknowledge the use of the computing facilities of NAL and MURA and the financial support of this research by both the National Science Foundation (Grant No. 86-3474) and the Atomic Energy Commission (Contract No. AT-(11-1)-1121).

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INSERTION OF DICHLOROCARBENE INTO AROMATIC HYDROCARBONS

Sir:

Although methylene, CH_2, is sufficiently reactive to insert in hydrocarbons,[1] dichlorocarbene has not previously been known to react in this manner. A recent review[2] states that halogen-substituted carbenes do not attack C–H bonds. 2H-1-Benzothiopyrone reacts with dichlorocarbene[3] to give isomeric products that apparently were formed by insertion; here the sulfur atom probably acted as an electron donor to the electrophilic carbene and played an important role in the formation of the final products.

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