

activity. The peptide migrated at a rate somewhat slower than histidine in 24 hour Partridge paper chromatograms³ and Stein-Moore analysis¹⁴ of an acid hydrolysate gave the following amino acid ratios: ser_{1.7}tyr_{1.8}met_{0.8}glu_{0.9}his_{0.8}phe_{0.9}arg_{3.1}gly_{2.0}lys_{4.3}pro_{2.3}val_{3.4}. The average recovery of individual amino acids was 95%.

This first synthesis of a peptide which possesses essentially the full *in vivo* ascorbic acid depleting and plasma corticosterone elevating activity of the natural corticotropins opens the way to systematic investigations relating peptide structure to this important physiological activity.

(14) S. Moore, D. H. Spackman and W. H. Stein, *Anal. Chem.*, **30**, 1185 (1958).

(15) The skillful technical assistance of Mrs. Chizuko Yanaihara and Mr. John L. Humes is gratefully acknowledged.

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STRUCTURE OF $(OC)_3Fe(COT)Fe(CO)_3$

Sir:

The cyclooctatetraene (COT) ring has the tub form in COT itself^{1,2} and in the $AgC_8H_8^+$ ion.³ Electron transfer to the ring to form⁴ (COT)⁻ and (COT)⁻² changes the geometry of the original molecule to a new form, suggested⁴ to be the planar form. The many suggestions^{5,6,7,8,9,10} concerning the geometry of the $(OC)_3Fe(COT)Fe(CO)_3$ molecule include the tub and planar forms of the (COT) ring, with mention⁶ of a ring of D_4 symmetry. The puckered ring of D_{4d} symmetry, which has similar molecular orbital degeneracies to those of the planar ring, and less strain, but poorer π - π overlap, has not been included in these discussions.

We have completed a determination of the structure of a single crystal of $(OC)_3Fe(COT)Fe(CO)_3$, which shows a geometry of the COT residue different from any of the above proposals. The ring (Fig. 1) is oval, but with little residual bonding expected across the closest "non-bonded" C...C distance of 2.85 Å. The form is approximately an eight membered "chair" form, neither tub nor crown. Each $Fe(CO)_3$ is associated with four CH groups, with each set of 4C forming a planar or nearly planar group, somewhat suggestive of butadiene. Assuming very approximate sp^2 hybrids in the various C-C-C planes, the π ... π overlap integral is 0.25 between C₂-C₃, but only 0.11 between C₁-C₂ or C₃-C₄. All of these π orbitals are fairly well

(1) H. S. Kaufman, H. Mark and I. Fankuchen, *Nature*, **161**, 165 (1948).

(2) J. Bregman, private communication.

(3) F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959); also *J. Am. Chem. Soc.*, **80**, 4745 (1958).

(4) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

(5) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959).

(6) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 336 (1960).

(7) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(8) D. A. Brown, *J. Inorg. and Nuclear Chem.*, **10**, 39 (1959); **10**, 49 (1959).

(9) F. A. Cotton, *J. Chem. Soc. (London)*, 400 (1960).

(10) P. L. Pauson, *Proc. Chem. Soc. (London)*, 297 (1960).

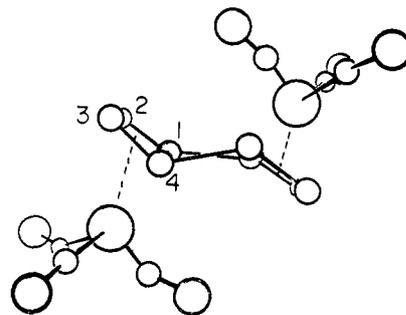


Fig. 1.—The $(OC)_3Fe(COT)Fe(CO)_3$ molecule: bond distances average to 1.39 Å. for the two distances at the ends of the COT residue, 1.49 Å. for the two central bonds, and 1.44 Å. for the other four C—C bonds, all ± 0.03 Å. Fe...C distances are 2.06 Å. to the end carbon atoms (bonded together) and 2.15 Å. to the central four carbon atoms, to be compared with 2.05 Å. for Fe...C in ferrocene.¹⁶ The average Fe—C and C≡O distances are 1.76 Å. and 1.15 Å., respectively, in the Fe—C≡O groups.

directed toward the corresponding Fe atoms, which are actually closer to the bond centers than to the C atoms themselves. A comparison of distances in a butadiene type of complex^{11,12,13} is not yet available, but would be of interest. Little π ... π interaction between the two halves of the COT complex is probable, because of the 96° to 101° angle between π orbitals as inferred from the assumption of sp^2 hybrids in planes defined by C-C-C. Also, the average C-C distance of 1.49 Å. joining the two nearly planar C₄ groups seems reasonable for little more than a single bond in view of the immediate strong-bonding coordination numbers,^{14,15} but we do not eliminate a very small π ... π interaction between the C₄ halves. The distortion of sp^2 bond angles of C₈H₈ in this complex occurs almost entirely in the central four C-C-C angles, which average to 130°. As usual, the most naive way of counting electrons around Fe is unbelievably satisfactory. Each C₄ group can be thought of as donating four electrons to its Fe, which already has eight, and receives six more from its three C≡O groups. Octahedral coordination is apparent around the Fe, as the three C—C bonds are staggered with respect to the three C≡O groups around each corresponding Fe. However, a more detailed description of the bonding and back coordination will be deferred until completion of our study of the (COT)Fe(CO)₃ structure, presently in progress.

The equivalence of the H¹ nuclear magnetic resonances^{5,6} is suggestive of a dynamical effect, of negligible relative chemical shifts of the C-H groups, or of different geometries in the solid and solution. A study of the n.m.r. spectrum of $(OC)_3Fe(COT)Fe(CO)_3$ as a function of temperature may

(11) H. Rheilin, A. Gruhl, G. Hessling and O. Pfrangle, *Annalen*, **482**, 161 (1930).

(12) B. F. Hallam and P. L. Pauson, *J. Chem. Soc. (London)*, 646 (1958).

(13) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. and Nucl. Chem.*, in press.

(14) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

(15) Values of 1.50 Å. (C. A. Coulson, "V. Henri Memorial Lectures," Desoer, Liege, 1948, p. 25) and 1.48 Å. (D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., London*, **A258**, 270 (1960)) have been suggested for a single bond between two sp^2 carbon atoms.

be useful. If the geometry of the CH framework in this compound is in any way indicative of geometry in the $(\text{COT})^{-1}$ or $(\text{COT})^{-2}$ ions, a dynamical effect producing proton equivalence may also be suggested as a possibility here, as well as a tendency toward the crown form. A study of the electron spin resonance at various temperatures may be of interest in this system of equilibria among ions.

The crystals are monoclinic with four molecules in a unit cell of parameters $a = 12.53 \text{ \AA}$, $b = 13.38 \text{ \AA}$, $c = 8.69 \text{ \AA}$, and $\beta = 111^\circ$. The structure was solved by analysis of the three dimensional Patterson function, and refined by least squares procedures. The present agreement factor $R = \Sigma[F_0] - [F_c]/\Sigma[F_0]$ is 0.10 for the 978 observed reflections.¹⁶

We wish to acknowledge¹⁷ the courtesy of Dr. T. A. Manuel and Dr. F. G. A. Stone for supplying us with samples, and the Office of Naval Research for support.

(16) J. D. Dunitz and L. E. Orgel, *Proc. Roy. Soc. London*, **23**, 954 (1955).

(17) We also acknowledge receipt of a very recent private communication from O. S. Mills and G. Robinson, who have in press in the *Chem. Soc. Proc.*, a communication on the structure of the butadiene complex, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$.

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STEREOCHEMISTRY OF ELECTRON DELOCALIZATION INVOLVING d -ORBITALS: α -SULFONYL CARBANIONS

Sir:

The traditional analogy between sulfonyl and carbonyl functions which depends on the common property of facilitating proton transfer from an adjacent carbon atom by anion stabilization, cannot be extended to the manner in which these groups effect electron delocalization in α -carbanions. Nor does the much-studied enolate structure contribute to the understanding of α -sulfonyl carbanions since the latter uniquely involve the $3d$ -orbitals of sulfur. We present herein a preliminary report of a study aimed at revealing the stereochemical characteristics of this d -orbital interaction which in measure can be explored using the techniques of the classical ketone \rightleftharpoons enolate researches.¹

In Table I appear kinetic data which have been obtained for hydroxide ion catalyzed racemization and deuterium-hydrogen exchange with phenyl 2-octyl sulfone in ethanol-water (2:1 vol.). The optically active sulfone, m.p. $44-45^\circ$, $[\alpha]^{20}_{\text{D}} -13.3 \pm 0.3^\circ$ (c , 0.7 to 1.9 in 2:1 ethanol-water), (C, 65.98; H, 8.61) was prepared from optically active $(-)$ -2-octanol,² $[\alpha]^{25}_{\text{D}} -9.4^\circ$ (neat), *via* the toluene-sulfonate and phenyl thioether by oxidation of the latter with potassium permanganate in acetic acid-water (the racemic sulfone, m.p. $28-29^\circ$, was obtained by the same route). Racemization rates, measured polarimetrically at 5893 \AA , were found to be first order in sulfone and in hydroxide ion. Deuterium exchange rates in O -deuterioethanol-deuterium oxide (2:1) were measured by infrared intensity analysis (at 10.88μ) and by mass spectro-

(1) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 10.

(2) "Organic Syntheses," John Wiley and Sons, New York, N. Y., 2nd Edition, 1941, 418.

metric and combustion methods with satisfactory agreement. The exchange rate is also first order both in deuterioxide and sulfone.

TABLE I
KINETIC STUDIES WITH PHENYL 2-OCTYL SULFONE

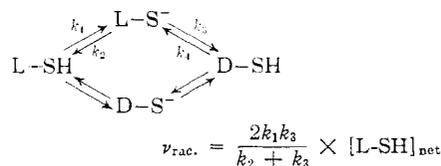
Entry	Temp., °C.	$k_2(\text{rac.}) \times 10^4$ $M^{-1} \text{ min.}^{-1}$	$k_2(\text{exc.}) \times 10^4$ $M^{-1} \text{ min.}^{-1}$
A ^a	72.0	4.6	190
B ^a	80.1	7.4	...
C ^a	96.6	33.0	...
D ^b	80.1	7.6	...

^a These values lead to $\Delta H^* 20 \text{ kcal./mole}$ and $\Delta S_0^* -25 \text{ e.u.}$ ^b This rate constant was measured for phenyl 2-deuterio-2-octyl sulfone in EtOD- D_2O (2:1).

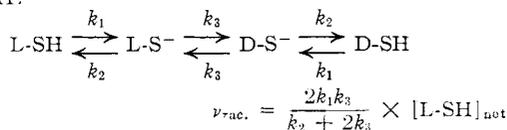
From the absence of a substantial kinetic effect on the racemization rate due to α -deuterium (Table I, B and D) we conclude³ that racemization involves an anionic intermediate rather than a concerted proton exchange with hydroxide ion; further, it seems reasonable that concerted proton removal-addition is improbable for the deuterium-hydrogen exchange reaction, especially since the assistance of the sulfonyl group is not called upon for this pathway. Since $k_{\text{exc.}}/k_{\text{rac.}} = 41$ (Table I, A) it appears that the α -sulfonyl carbanion is optically active and its racemization is much slower than protonation.⁴

Kinetic analysis permits distinction between the two reasonable anionic pathways for sulfone (SH) racemization-exchange: Scheme I for a single asymmetric anion which can be protonated with either retention or inversion, and Scheme II involving interconversion between two antipodal asymmetric anions which are protonated stereospecifically.

Scheme I:



Scheme II:



The ratio k_2/k_3 must be ~ 80 for both schemes; however, whereas a normal primary isotope effect ($k_{\text{H}}/k_{\text{D}}$ at least 3) for racemization of the α -deuterated sulfone is predicted for Scheme I, essentially no isotope effect ($k_{\text{H}}/k_{\text{D}}$ not far from, and probably somewhat less than, unity) is expected for Scheme

(3) The kinetic effect of isotropic change of medium clearly is small compared to that for isotopic bond-breaking. See: (a) C. G. Swain, A. J. DiMilo and J. P. Corder, *J. Am. Chem. Soc.*, **80**, 5983 (1958); (b) K. Wiberg, *Chem. Rev.*, **55**, 713 (1955); (c) O. Reitz, *Z. physik. Chem.*, **A175**, 257 (1936).

(4) D. J. Cram, C. C. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **81**, 5835 (1959), have observed that D-H exchange proceeds more rapidly than racemization with optically active 2-phenylbutane and methyl α -phenylethyl ether in *tert*-butyl alcohol-potassium *tert*-butoxide (ratios ca. 9 and 4). This effect, which disappears with dimethyl sulfoxide as solvent, has been ascribed to asymmetric solvation of a planar ion. The assumption of an asymmetric environment for non-asymmetric α -sulfonyl carbanions (suggested to us by Professor D. J. Cram) is not a tenable explanation of the above results, since it is intrinsically unlikely for relatively stable anions (pK_{a} for sulfones ≈ 23) and totally unsatisfactory for aqueous media in which changes in the shape of the solvation shell to fit a symmetric ion should be unimpeded structurally and hence exceedingly rapid.