be useful. If the geometry of the CH framework in this compound is in any way indicative of geometry in the $(COT)^{-1}$ or $(COT)^{-2}$ 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 $a = 12.53$ Å. $b = 13.38$ Å., $c = 8.69$ Å., and $\beta = 111°$. 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 acknowledge[17] 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, C₄H₆Fe(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 $\rightleftarrows$ 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°, $[\alpha]^{20}D -13.3\pm 0.3°$ (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] $[\alpha]^{28}D -9.4°$ (neat), via the toluenesulfonate and phenyl thioether by oxidation of the latter with potassium permanganate in acetic acid–water (the racemic sulfone, m.p. 28–29°, was obtained by the same route). Racemization rates, measured polarimetrically at 5893 Å. 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 deuteroxide and sulfone.
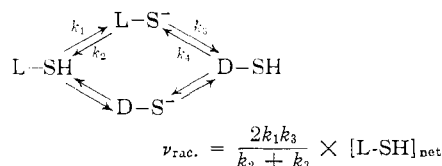
TABLE I
KINETIC STUDIES WITH PHENYL 2-OCTYL SULFONE

Entry	Temp., °C.	k_2(rac.) × 10⁴ M^{-1} min.⁻¹	k_2(exc.) × 10⁴ M^{-1} 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 kcal./mole and $\Delta S_0^* -25$ e.u. ^{b} This rate constant was measured for phenyl 2-deuterio-2-octyl sulfone in EtOD–D₂O (2:1).
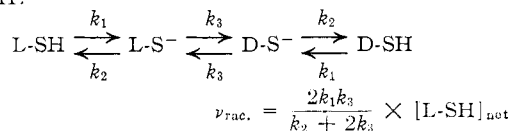
From the absence of a substantial kinetic effect on the racemization rate due to α-deuterium (Table I, B and D) we conclude[3] that racemization involves an anionic intermediate rather than a concerted proton exchange with hydroxide ion; further, it seems reasonable that concerted proton removal-addition is improbable for the deuterium–hydrogen exchange reaction, especially since the assistance of the sulfonyl group is not called upon for this pathway. Since $k_{exc}/k_{rac.} = 41$ (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:

$$v_{rac.} = \frac{2k_1k_3}{k_2 + k_3} \times [\text{L-SH}]_{net}$$

Scheme II:

$$\text{L-SH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{L-S}^- \underset{k_3}{\overset{k_3}{\rightleftharpoons}} \text{D-S}^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \text{D-SH}$$

$$v_{rac.} = \frac{2k_1k_3}{k_2 + 2k_3} \times [\text{L-SH}]_{net}$$

The ratio k_2/k_3 must be ~ 80 for both schemes; however, whereas a normal primary isotope effect (k_H/k_D at least 3) for racemization of the α-deuterated sulfone is predicted for Scheme I, essentially no isotope effect (k_H/k_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. Cordner, 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 (pKₐ 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.

II and consequently the latter is preferred (Table I cf. B and D.)[5]

Koch and Moffitt[6] have considered the problem of modes of conjugation between 2p (Cα) and 3d (SO₂) orbitals in terms of two extreme cases: Case I: axis of p (Cα) parallel to the sulfone O–O axis, and Case II: p (Cα) axis in Cα SCα plane. Our results exclude the Case I structure for the anion which is involved in proton transfer since this has a plane of symmetry, and indicate a Case II type structure for L-S⁻ and D-S⁻ (possibly interconverted via the optically inactive Case I anion). Whether the hybridization of C⁻α in the Case II anion is sp², sp³ or intermediate, cannot be decided at present, but experiments to settle this point are now in progress. Probable examples of Case II conjugation with Cα = sp² and Cα = sp³ have been recorded.[7,8] The fact that the ratio of D–H exchange rates in cyclopropyl- and isopropylphenyl sulfone are comparable provides evidence that the hybridization of C⁻α in Case II anions may be fairly close to sp³.[9]

The stereochemistry of anionic decarboxylation of optically active α-sulfonyl carboxylic acids,[10] the absence of an ortho effect in conjugation of aromatic π-electrons with the sulfonyl group,[11] and several other interesting observations are understandable in terms of Case II conjugation and the above findings.

Further studies on the stereoelectronic properties of d-orbital conjugation are in progress and will be reported in due course. We are indebted to the National Institutes of Health and the Higgins Fund of Harvard University for support of this work.[12]

(5) These predictions are based on the kinetic expressions for Scheme I and II with $k_2 + k_3 \cong k_2$ and with correction for the greater base strength of DO⁻ relative to HO⁻ and for a small medium effect.

(6) H. P. Koch and W. E. Moffitt, Trans. Far. Soc., **47**, 7 (1951).

(7) J. Toussaint, Bull. soc. chim. Belg., **54**, 319 (1954).

(8) W. E. Doering and L. K. Levy, J. Am. Chem. Soc., **77**, 509 (1955).

(9) H. E. Zimmermann and B. S. Thyagarajan, ibid., **82**, 2505 (1960).

(10) J. E. Taylor and F. H. Verhoek, ibid., **81**, 4537 (1959).

(11) H. Kloosterziel and H. J. Baker, Rec. trav. chim., **72**, 185 (1953).

(12) Prof. D. J. Cram has kindly informed us of studies in his Laboratory which are in part parallel to those reported here.

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THE MOLECULAR STRUCTURE OF B₉H₁₃NCCH₃

Sir:

The structure of B₉H₁₃NCCH₃ (Fig. 1b) has been established from a complete three dimensional X-ray diffraction study of a single crystal. This compound has only recently been first isolated and characterized,[1] although previous indications of its existence were known.[2,3] Its heavy atom arrangement as a fragment of decaborane was deduced by Hawthorne[4]; its correct geometrical and valence

(1) M. F. Hawthorne, B. M. Graybill and A. R. Pitochelli, paper 45-N, Abstracts 138th Meeting, American Chemical Society, September 11–16, 1960, New York, N. Y.

(2) S. J. Fitch and A. W. Laubengayer, J. Am. Chem. Soc., **80**, 5911 (1958).

(3) R. Schaeffer, private communication, December, 1958; see R. Schaeffer, ibid., **79**, 1006 (1957).
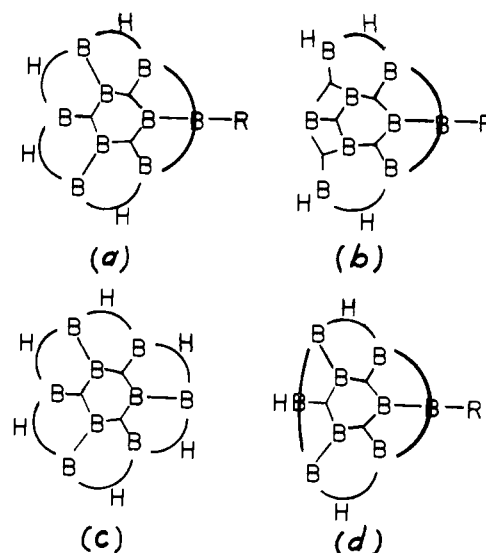
(4) M. F. Hawthorne, private communication, 1960.

FIG. 1.—One terminal H has been omitted from each B atom in these drawings: (a) starting structure for the final Fourier and least squares refinement; (b) final structure after refinement; (c) hypothetical B₉H₁₅, which violates a topological rule, as does the starting structure (a related B₉H₁₂⁻³ of symmetry C₃ᵥ and topology[5] 0633 does not); (d) a probable B₉H₁₂R⁻ structure. A transformation of the (a) → (b) type or some intermediate structure involving a very unsymmetrical B—H—B bond is possible here.

structure was deduced by Lipscomb on the basis of the topological theory and the high field doublet of the B¹¹ nuclear magnetic resonance spectrum[4] which indicated three B atoms in apex environments. In the course of the three dimensional refinement Structure (a) of Fig. 1 refined to Structure (b), hitherto unreported, which definitely has two BH₂ groups to help absorb the extra electrons contributed by the Lewis base, acetonitrile. We suggest that an intermediate type of structure between (a) and (b) might possibly occur when the donating power of the Lewis base is not so large. Even though Structure (a) and its parent hypothetical hydride,[5] B₉H₁₅ of C₃ᵥ symmetry (Structure (c)), both violate the weakest topological rule,[5] concerning the improbability of finding two bridge H atoms to a B connected to four other B atoms, we find it useful to think of these structures as related to the most nearly correct form, Structure (b). These relations lead us to consider Structure (d) as a safe prediction for the B₉H₁₂R⁻ ion, recently isolated,[1] but we are quite uncertain about the structure of the unstable, and even possibly dimerized, B₉H₁₂⁻ ion: topology[5] 2621 is chnceivable.

The unit cell of the crystal is monoclinic with $a = 5.64$ Å., $b = 9.22$ Å., $c = 9.81$ Å., and $\beta = 90°$, and contains two molecules. Extinction of 0k0 when k is odd leads to either P2₁ or P2₁/m as possible space groups, but very clear indication of the linear B—N≡C—CH₃ groups in the three dimensional Patterson function immediately suggested that the space group is P2₁/m, later confirmed. All H atoms including H's on the methyl group have been located by three dimensional difference syntheses.

(5) R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys., **27**, 212 (1957).