lack of orbital following, types of neighboring bonds), other than those included in the simple model, are important in determining the extent of the deviation from perfect pairing that occurs in a given system. Confirmation of these suggestions will have to await experimental measurements corresponding to those outlined here, as well as applications of the theory to more refined molecular wave functions.

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RECEIVED APRIL 12, 1962

ORGANOSULFUR DERIVATIVES OF METAL CARBONYLS. I. THE ISOLATION OF TWO ISOMERIC PRODUCTS IN THE REACTION OF TRIIRON DODECACARBONYL WITH DIMETHYL DISULFIDE

Sir:

Compounds of the general formula $[Fe(CO)_3SR]_2$ have been isolated in the reaction of triiron dodecacarbonyl with dialkyl sulfides, alkyl mercaptans, and dialkyl disulfides.[1-3] I wish to report the separation of the methyl derivative into two isomeric compounds.

A mixture of 84 g. (0.167 mole) of triiron dodecacarbonyl, 150 ml. of dimethyl disulfide, and 1 liter of thiophene-free benzene was refluxed for 6 hr. under nitrogen with magnetic stirring. After cooling to room temperature, the reaction mixture was filtered giving a red filtrate and a black pyrophoric residue. Solvent was removed from the red filtrate at 30 mm. leaving about 28 g. (27% yield) of red crystals which may be purified either by recrystallization from pentane or by sublimation at 50° (0.1 mm.).

Samples of either recrystallized or resublimed $[Fe(CO)_3SCH_3]_2$ prepared in the above manner showed in the proton n.m.r. three methyl resonances at 2.13, 2.07 and 1.62 p.p.m.[4] of varying intensities suggesting that the product was a mixture of isomers. It was found possible to separate the product into two isomers by chromatography in pentane solution on a 2 × 110 cm. alumina column. This gave rise to two very distinct bands on the column, a large red band followed by a smaller orange band. Each band was eluted with pentane and the air-stable eluates were evaporated to dryness. From 3 g. of the original mixture about 2.4 g. of red crystals, m.p. 65–67.5°, hereafter designated as Isomer A, was isolated from the first red band and about 0.2 g. of orange crystals, m.p. 101.5–103.5°, hereafter designated as Isomer B, was isolated from the orange band.

Analyses showed Isomers A and B to have the same composition (Calcd. for $C_8H_6O_6S_2Fe_2$: C, 25.7; H, 1.6; S, 17.1; Fe, 29.9. Found on Isomer A: C, 25.4; H, 1.8; S, 17.2; Fe, 29.0. Found on Isomer B: C, 26.1; H, 1.9). The infrared spectra also were quite similar although not identical (Isomer A: 2085 (s), 2050 (vs), 2000 (vs), 1428 (sh), 1420 (w), 1310 (sh), 1303 (w), 1260 (vvw), 967 (w), 964 (m) and 710 (vw) cm.$^{-1}$; Isomer B: 2075 (s), 2040 (vs), 2000 (vs), 1995 (sh), 1430 (m), 1318 (m), 1260 (vw), 966 (w), 959 (w) and 703 (vw) cm.$^{-1}$). The proton magnetic resonance spectra provide information as to the nature of these isomers. Isomer A was found to exhibit two methyl peaks at 2.13 and 1.62 p.p.m.[4] in a 1:1 intensity ratio indicating each of the two methyl groups to be different. However, Isomer B was found to exhibit a single methyl peak at 2.07 p.p.m. indicating both methyl groups to be identical.

The absence of carbonyl bands in the 1700–1850 cm.$^{-1}$ region of the infrared spectrum indicates the absence of carbonyl bridging in each of the two isomers. In view of this and in view of the diamagnetism of each isomer as evidenced by the ability to obtain high resolution n.m.r. spectra, the most reasonable structure for each of the two isomers contains an iron–iron bond and two RS-bridges. The two isomers differ therefore only in the relative orientations of the methyl groups attached to the sulfur atoms. From the n.m.r. data it is apparent that the two methyl groups of Isomer A are in different positions but that the two methyl groups of Isomer B are in identical positions. However, on the basis of the presently available information on these compounds, the exact locations of the methyl groups and the nature of the iron-iron bonds in each of the isomers are still uncertain.

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RECEIVED MAY 2, 1962

THE SYNTHESIS OF A HEPTADECAPEPTIDE POSSESSING ADRENOCORTICOTROPIC, MELANOTROPIC AND LIPOLYTIC ACTIVITIES

Sir:

Adrenocorticotropins (ACTH) isolated from pituitaries of various species[1,2,3,4] are polypeptides consisting of 39 amino acids. Since the first synthesis of a biologically active nonadecapeptide corresponding to the first 19 amino acid residues of the hormone was published,[5] two other laboratories[6,7,8] have described the synthesis of ACTH analogs with chain lengths of 19, 20, 23 and 24

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