Vitamin-A Aldehyde Iron Tricarbonyl

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VITAMIN-A ALDEHYDE reacts with $Fe_3(CO)_{12}$ in benzene to yield in 45% a mono-adduct $C_{20}H_{28}OFe(CO)_3$, m.p. 142°. From spectral evidence, this seemed to have the structure (I). There are three bands in the region ν_{max} 2000 cm.$^{-1}$ [$Fe(CO)_3$] and one at ν_{max} 1680 cm.$^{-1}$ (CHO), while absorption at λ_{max} 287 and 357 mμ indicates lower conjugation than in the original aldehyde, approximately equivalent to loss of one double bond. The n.m.r. spectra of such complexes show "inner" and "outer" protons, that of the adduct according with (I); τ 9·00 (6H)Me_2; 8·34 (3H) cyclic MeC=C; 8·05 (3H) in-chain Me; 7·50 (3H) terminal acyclic Me; 7·3 (1H) inner proton; 4·75 (2H) outer protons; 4·0 other C=CH; thus only the terminal acyclic Me is deshielded as would be expected for (I).

A major problem with adducts of this type is the nature of the bonding between the metal and diene systems—proposals, which represent extreme canonical structures, being of type (II) and (III). Partly to confirm the structure (I) and more particularly to elucidate the last point, an *X*-ray examination has been carried out.

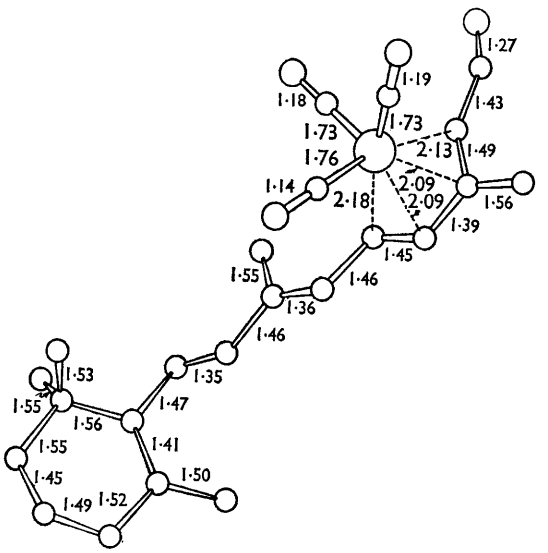
The molecular geometry, determined by Patterson, Fourier, and least-squares methods, is shown in the Figure.

The discrepancy index for 1250 independent reflexions, integrated intensities of which were measured on a "Pailred" automatic diffractometer, is, at present, 0·09; the average estimated standard deviations, derived by inversion of the block-diagonal least-squares matrix, in the bond-lengths are Fe–C 0·02 Å, C–C and C–O 0·03 Å.

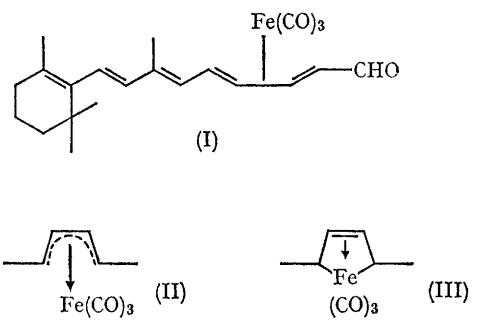
The structure suggested by the spectroscopic

data is confirmed, the bonding of the iron tricarbonyl fragment to the polyene chain being very similar to that observed in a number of butadiene– and substituted-butadiene–metal complexes.[1] The carbon–carbon bond lengths of 1·45, 1·39, and 1·49 Å in the co-ordinated "butadiene" portion of the chain illustrate, once more, the need to include the σ–π structure (III) in a valence-bond description of the molecule. The formal differences between structures (II) and (III) must not, however, be emphasised; in molecular-orbital terms, these bond lengths prove the involvement of the lowest antibonding molecular orbital of the butadiene fragment in the bonding scheme.[2] The effect of bonding the iron to the polyene is to perturb the strict bond alternation found in the ligand itself and, indeed, in the unco-ordinated section of the chain in the present structure.

The low discrepancy index and molecular geometry may be taken as a clear indication of the general correctness of our results, although high temperature factors of several atoms and residual electron density in the terminal difference-density synthesis indicate that the molecule is disordered to some extent in the crystal. The mechanism of molecular disordering has not, as yet, been determined.



FIGURE



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[1] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, in the press.
[2] S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, 1966, **5**, 97.