The Molecular Configuration of (Phenyltrimethylenemethane)tricarbonyliron

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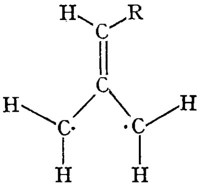
TRIMETHYLENEMETHANE (I; R = H) has long been of theoretical interest to chemists because its central carbon atom achieves the maximum total bond order possible for an sp^2 carbon atom.[1]



(I)

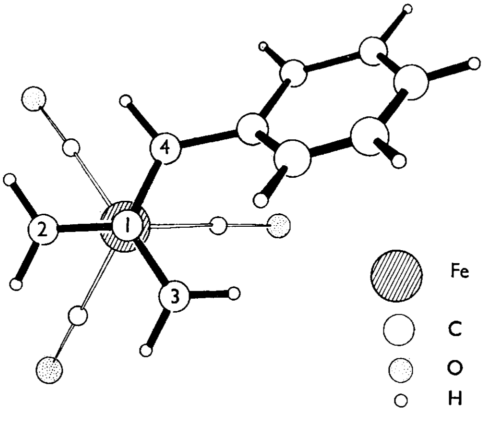
Recently, trimethylenemethane has been trapped at $-185°$ in a C_6F_6 matrix, and e.s.r. studies have shown that it has a triplet ground state (*i.e.* it is a diradical) which possesses three-fold (or higher) symmetry.[2] As with a number of other highly reactive, or intrinsically unstable, organic species, trimethylenemethane[3] [and also phenyltrimethylenemethane[4] (I; R = Ph)] may be stabilized in the form of a tricarbonyliron adduct. We report the preliminary results of a single-crystal *X*-ray diffraction study of (phenyltrimethylenemethane)-tricarbonyliron, $[(CH_2)_2C(CHPh)]Fe(CO)_3$.

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/a$ (C_{2h}^5; no. 14) with unit-cell parameters:

$$a = 16{\cdot}322 \pm 0{\cdot}012\ \text{Å},\ b = 6{\cdot}632 \pm 0{\cdot}005\text{Å},$$
$$c = 12{\cdot}542 \pm 0{\cdot}008\ \text{Å},\ \beta = 117{\cdot}18 \pm 0{\cdot}05°.$$

The observed density ($\rho_{\text{obs}} = 1{\cdot}33 \pm 0{\cdot}05$ g.cm.$^{-3}$) is in good agreement with the value calculated for $Z = 4$ ($\rho_{\text{calc}} = 1{\cdot}289$ g.cm.$^{-3}$). Complete three-dimensional diffraction data to $\sin\theta = 0{\cdot}42$ [Mo-K_α radiation] were collected with a 0·01° incrementing Buerger Automated Diffractometer, using the usual "stationary background, ω-scan, stationary background" counting sequence. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement procedures. All atoms (including hydrogens) have been located, the present discrepancy index being $R_F = 8·19\%$ for the 1475 independent non-zero reflections.

The overall geometry of the molecule is shown in the Figure. The iron atom is located directly beneath the central atom [C(1)] of the trimethylenemethane residue and is π-bonded to all four carbon atoms of this ligand, individual distances being Fe–C(1) = 1·929 ± 0·009, Fe–C(2) = 2·096 ± 0·010, Fe–C(3) = 2·119 ± 0·009, Fe–C(4) = 2·160 ± 0·008 Å. Values for the angles Fe–C(1)–C(2), Fe–C(1)–C(3), Fe–C(1)–C(4) are 76·1 ± 0·6, 77·1 ± 0·6, 78·4 ± 0·5°. As may be seen from the Figure, the trimethylenemethane ligand and the $Fe(CO)_3$ moiety adopt a mutually staggered conformation.



FIGURE

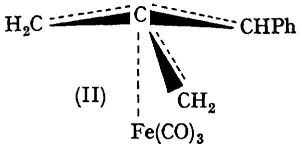
Carbon–carbon distances within the trimethylene methane residue are: C(1)–C(2) = 1·406 ± 0·014, C(1)–C(3) = 1·406 ± 0·013, C(1)–C(4) = 1·434 ± 0·012 Å. Interatomic angles are:

$$[C(2)–C(1)–C(3)] = 116·1 \pm 0·9,$$

$$[C(2)–C(1)–C(4)] = 114·3 \pm 0·8,$$

$$[C(3)–C(1)–C(4)] = 115·2 \pm 0·8°.$$

The carbon atom skeleton of the trimethylenemethane ligand is significantly nonplanar, with the central carbon atom [C(1)] being displaced 0·31 Å (away from the iron atom) relative to the plane defined by the terminal carbon atoms C(2), C(3), and C(4). The molecule may be formally represented by (II).



(II)

The carbon skeleton of the phenyl substituent has the expected D_{6h} symmetry. However, the plane of the phenyl ring makes an angle of *ca.* 59° with the plane defined by C(2), C(3), and C(4). This would appear to indicate that there is little conjugation between phenyl and trimethylenemethane systems in the present complex.

We thank the late Professor G. F. Emerson and the Advanced Research Projects Agency and the National Science Foundation for support.

(*Received, April 22nd,* 1968; *Com.* 490.)

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[1] J. D. Roberts, "Notes on Molecular Orbital Calculations", Benjamin, New York, 1961, p. 56.

[2] P. Dowd, *J. Amer. Chem. Soc.*, 1986, **88**, 2587; R. J. Crawford and D. M. Cameron, *ibid.*, p. 2589; P. Dowd and K. Sachdev, *ibid.*, 1967, **89**, 715; P. S. Skell and R. G. Doerr, *ibid.*, p. 3062; P. S. Skell and R. G. Doerr, *ibid.*, p. 4688; P. Dowd, A. Gold, and K. Sachdev, *ibid.*, in press.

[3] G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1966, **88**, 3172.

[4] G. F. Emerson, personal communication.