

THEORETICAL STUDY OF TRICARBONYLIRON COMPLEXES OF *para*-QUINODIMETHANE AND RELATED CONJUGATED HYDROCARBONS

HELMUT VOGLER

*Max-Planck-Institut für medizinische Forschung, Abteilung Organische Chemie, Jahnstr. 29,
D-6900 Heidelberg (F.R.G.)*

(Received November 8th, 1985)

Summary

The tricarbonyliron complexes of *para*-quinodimethane and related conjugated hydrocarbons have been studied by semi-empirical methods. The observed geometrical structure for bis(tricarbonyliron)-*para*-quinodimethane is rationalized in terms of simple Hückel theory.

Introduction

There is considerable interest in the study of tricarbonyliron complexes of unsaturated hydrocarbons [1–4]. Except for the trimethylenemethane complex, **1** (see Fig. 1), the most studied systems are characterized by a mutual orientation of hydrocarbon and tricarbonyliron groups such as that in the cyclobutadiene complexes **2** and **3**.

Recently the syntheses of **4** and **5** were reported [5] and an X-ray study of **4** [5] revealed that it has the molecular structure **4a** in which the tricarbonyliron moieties are situated over the trimethylenemethane fragments of *para*-quinodimethane **6**, as in **1**. A similar structure **5a** can be assumed for **5**, since **4** and **5** show similar spectroscopic characteristics [5], including their EI mass spectra [6].

Stimulated by the synthesis of these first examples of *para*-quinodimethanes stabilized as transition metal complexes we performed molecular orbital calculations on **1**, **5** and the related systems **7–11** using extended Hückel theory (EHT) [1] and simple Hückel considerations. All conjugated systems were assumed to be planar, and the following standard bond lengths were used: 179 pm for the C...Fe bond,

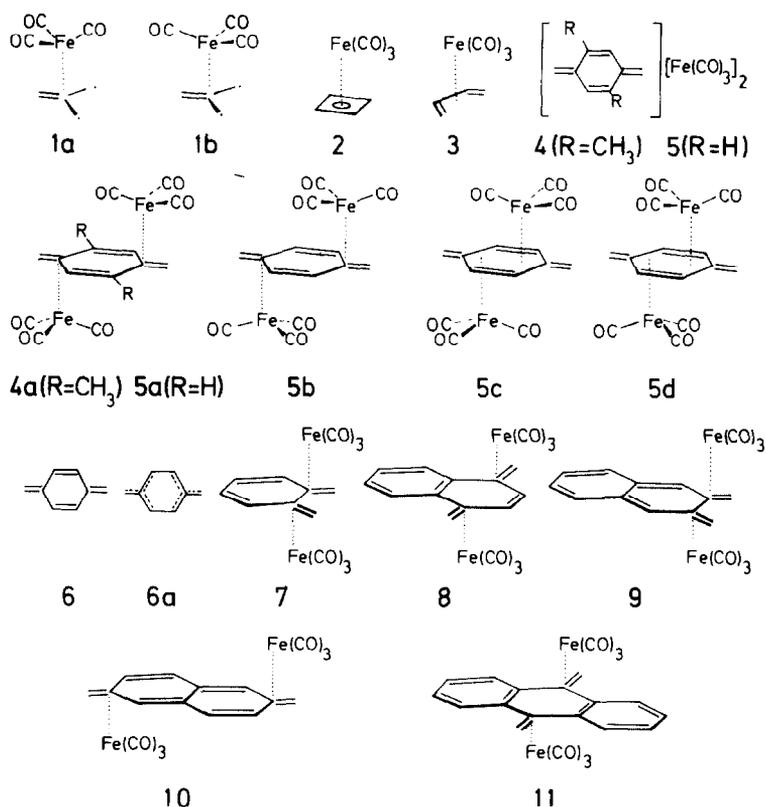


Fig. 1. The compounds studied.

146 pm for a quasi single CC bond (C–C), 141 pm for an aromatic CC bond (C=C), and 134 pm for a formal CC double bond (C=C).

Results and discussion

Experimental data show that the two rotors in **1** prefer a staggered conformation **1a** [7]. This is correctly reproduced by the EHT energies, see Table 1, since **1b** is less stable than **1a** if the geometrical model *A* with aromatic CC bonds is used. The stability of **1a** with respect to **1b** can readily be understood by means of simple Hückel theory. The valence orbitals of the tricarbonyliron fragment are shown in Fig. 2. The interaction between the $1e$ tricarbonyliron fragment orbitals and the $2p_{\pi}$ functions of the conjugated system is insignificant [1]. Therefore only the $1a_1$ and $2e$ orbitals need to be taken into consideration. Following Mingos [4] we use the Hückel Coulomb integrals $\alpha = \alpha_C := 0$ for the $1a_1$ and $\alpha = -\beta$ for the $2e$ functions, where β denotes the negative Hückel resonance integral. The resonance integrals between the $1a_1$ and $2e$ orbitals and the $2p_{\pi}$ functions of the trimethylenemethane moiety are taken to be $\pm\beta$, where the sign depends on the nodal properties of the tricarbonyliron valence orbitals. The resulting interaction pattern for **1a** and **1b** is schematically displayed in Fig. 3. The simple Hückel energies E and stabilization energies S with respect to infinitely separated hydrocarbon and tricarbonyliron correctly favour **1a** over **1b** (see Table 1).

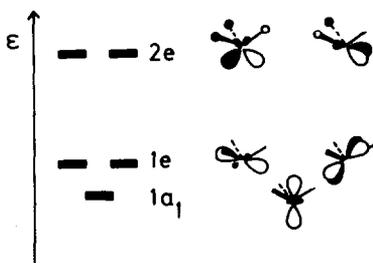


Fig. 2. Schematic representation of the valence orbitals of tricarbonyliron.

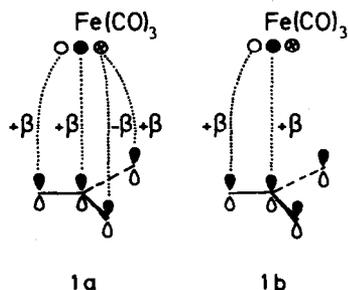


Fig. 3. Schematic drawing of the interaction pattern between trimethylenemethane and tricarbonyliron $\text{Fe}(\text{CO})_3$. Circles denote the valence orbitals $1a_1$ (\bullet) and $2e$ (\circ and \otimes).

The conjugated network of trimethylenemethane or butadiene forms part of *para*-quinodimethane, **6**. Therefore we studied the structures **5a–5d** for the complex **5**, since they correspond to those in **1** (**5a**, **5b**) and **3** (**5c**, **5d**). In addition to the geometrical model *A* two further bond lengths pattern for the hydrocarbon were examined, viz. model *B*, with alternating formal double and single bonds, as indicated in form **6**, and model *C*, with aromatic CC bonds in the trimethylene-

TABLE I

EHT TOTAL ENERGIES (in eV) FOR TRICARBONYLIRON COMPLEXES **1** AND **5** WITH GEOMETRIES *A*, *B*, AND *C*. ALONG WITH THE HÜCKEL ENERGIES, E , AND STABILIZATION ENERGIES, S , (both in units of β) FOR **1**, **5** AND **7–11**

Complex	<i>A</i>	<i>B</i>	<i>C</i>	E	S
1a	-1088.9			7.08	5.62
1b	-1088.4			5.08	3.62
5a	-2106.7	-2106.0	-2107.1	14.82	4.45
5b	-2106.0	-2105.3	-2106.4		
5c	-2105.2	-2104.8			
5d	-2105.3	-2104.9			
7				14.02	4.04
8				20.27	4.24
9				20.02	4.25
10				20.42	4.48
11				25.71	4.02

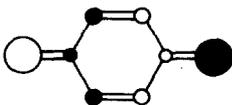


Fig. 4. Hückel lowest virtual orbital of *para*-quinodimethane (**6**).

methane fragments which are connected by quasi single bonds, as in form **6a**. Table 1 reveals that complexes **5a** and **5b** are more stable than **5c** and **5d** for a given geometrical model. Furthermore **5a** with geometry *C* represents the most stable arrangement for complex **5**. This finding is in agreement with the X-ray data for **4**, which reveal for **4a** a structure with bond lengths similar to those assumed in geometrical model *C*. Thus experiment and EHT calculations indicate that **5** can be regarded as involving two weakly coupled trimethylenemethane units.

Complex **5a** belongs to space point group C_{2h} , and it is straightforward to show that the symmetry-adapted linear combinations of the valence orbitals in Fig. 2 of the two tricarbonyliron fragments can interact with all occupied π -orbitals of the *para*-quinodimethane moiety. These interactions cause an electron transfer from the tricarbonyliron fragments to the conjugated system of about 1.3 electrons according to the EHT calculations. Thus the lowest virtual orbital of the isolated *para*-quinodimethane π -system becomes occupied in the complex **5a**, causing changes in the π -bond orders. These are given simply by the products of the orbital coefficients at the bonds. In conjugated hydrocarbons CC bond lengths depend linearly on the π -bond order [8]. Consequently the interaction between the hydrocarbon **6** and the tricarbonyliron groups in **5a** leads to an increase (decrease) of the length of those bonds with orbital coefficient pairs of equal (opposite) sign. It is obvious from Fig. 4 that all the formal double bonds are lengthened whereas the opposite applies to all the quasi single bonds. This rationalizes pattern of the bond length in **4a** and **5a** revealed by our EHT calculations and X-ray analysis.

Since **4** and **5** represent the first known examples of tricarbonyliron complexes of quinodimethane it was of interest to find out whether the other complexes **7–11** are stabilized equally well by the complexation. For **7–11** we assumed a staggered arrangement of the tricarbonyliron moieties with respect to the carbon skeleton of the hydrocarbon, as in **1a**, **4a** and **5a**. According to Hückel theory *ortho*-quinodimethane is slightly more stable than its *para*-isomer, but the order of stability might be inverted for steric reasons, leading to a nonplanar geometry [9,10]. Our Hückel results listed in Table 1 reveal that the complex **7** is both less stable and less stabilized by the complexation than **5a**. Slightly larger stabilization energies *S*, are calculated for the isomeric compounds **8–10**, whereas *S* for **11** is as low as that of **7**. Thus our simple Hückel calculations indicate that **10** could represent another stable tricarbonyliron complex of a highly unstable hydrocarbon.

Acknowledgement

The author thanks Dr. A.R. Koray for stimulating discussions. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were performed in the Universitätsrechenzentrum Heidelberg on the IBM 3081D computer.

References

- 1 T.A. Albright, P. Hofmann and R. Hoffmann, *J. Am. Chem. Soc.*, 99 (1977) 7546.
- 2 B.J. Nicolson, *J. Am. Chem. Soc.*, 88 (1966) 5156.
- 3 J.M. Landesberg, in E.A. Koerner von Gustorf, F.-W. Grevels and I. Fischler (Eds.), *The Organic Chemistry of Iron*, Vol. 1, Academic Press, London, 1978, p. 627; J. Aihara, *Bull. Chem. Soc. Jpn.*, 51 (1978) 1541; W.C. Herndon, *Isr. J. Chem.*, 20 (1980) 276; M.C. Böhm and R. Gleiter, *J. Comp. Chem.*, 1 (1980) 407.
- 4 D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1977) 20, 26, 31.
- 5 A.R. Koray, C. Krieger and H.A. Staab, *Angew. Chem.*, 97 (1985) 513; *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 521.
- 6 M. Rentzea, A.R. Koray and H.A. Staab, *Tetrahedron Lett.*, (1985) 2563.
- 7 A. Almenningen, A. Haaland and K. Wahl, *J. Chem. Soc., Chem. Commun.*, (1968) 1027.
- 8 G. Ege and H. Fischer, *Tetrahedron*, 23 (1967) 149.
- 9 T.-K. Ha, *Theor. Chim. Acta*, 66 (1984) 111 and references therein.
- 10 P. Karafiloglou, *Int. J. Quant. Chem.*, 25 (1984) 293.