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The solid state polymerization of diacetylenes. Crystal and molecular structure of 1,4-bis(1′-ethylferrocenyl)buta-1,3-diyne

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Abstract

An X-ray diffraction study of diacetylene having ethylferrocenyl substituents has been carried out ($R = 0.037$ for 1922 reflections). The molecule is in a special position at the symmetry centre, the ferrocenyl Cp-rings have eclipsed orientation, the planes of the ethyl groups and the Cp rings form the dihedral angles of 107°. The arrangement of adjacent diacetylene groups in the crystal does not satisfy the topochemical conditions for solid state di- or polymerization.

Introduction

An X-ray diffraction study of 1,4-bis(1′-ethylferrocenyl)buta-1,3-diyne (I) was carried out as a continuation of the systematic structural study of diacetylenes having various organic and organoelement terminal groups [1]. For the first time the terminal groups of this diacetylene are ferrocene moieties, which do not prevent the adjacent molecules from approaching to within ca. 4Å, the distance necessary for the topochemical reaction. However the actual situation is determined by the conformation of the molecules I in the crystal. To elucidate the conformation and the various features of the molecular arrangement in the crystal an X-ray diffraction study of I was carried out.

Results and discussion

In the crystal the molecule is in a special position at the symmetry centre and has a transoid conformation (Fig. 1), ethyl substituents in the ferrocenyl groups are in

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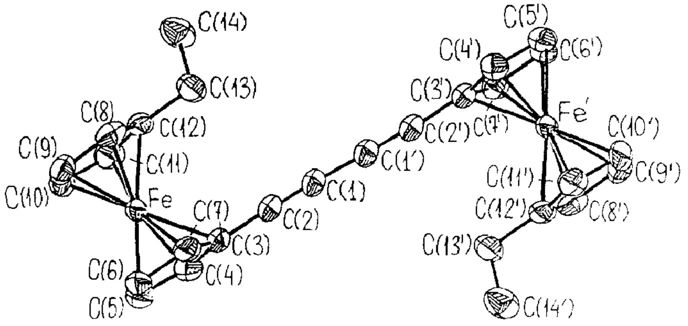

Fig. 1. General view of the centrosymmetric molecule I (projection on the mean plane of the molecule).

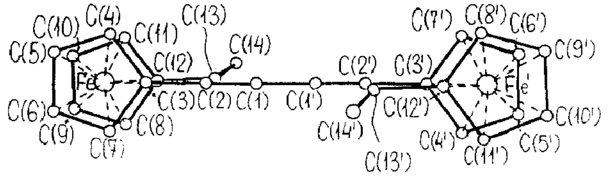

Fig. 2. Mutual orientation of cyclopentadienyl moieties (projection along the normal to the mean plane of the molecule)

eclipsed positions with respect to the diacetylene moiety (Fig. 2). The mutual arrangement of the cyclopentadienyl rings is also eclipsed, the ethyl planes C(12)C(13)C(14) and C(12′)C(13′)C(14′) together with the planes of the Cp rings form dihedral angles of 107°. These conformational features of the molecule 1 are not determined exclusively by intramolecular forces: rotation of the ferrocenyl groups around the C(Cp)–C≡ bonds is not hindered, the same is true for rotation of ferrocenyl Cp rings with substituents about their own C_5 axes [2,3]. Thus, the observed "compact" molecular configuration is most favourable in terms of the total intermolecular energy.

The mutually parallel diacetylene rods that are closest to each other, are related in the crystal I (Fig. 3) by the translation *b*, the distance between such adjacent

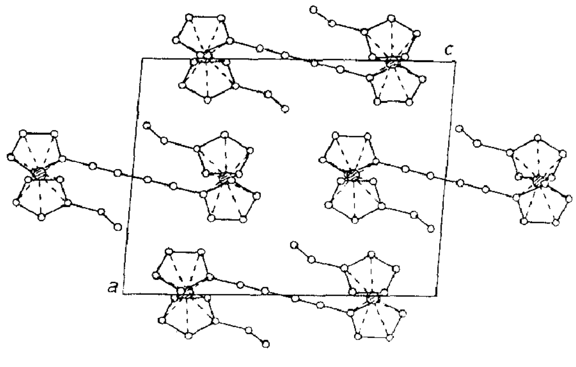

Fig. 3. The *ac* projection of the crystal structure I. The angle between a diacetylene rod and the *ac* plane is 19°.

Table 1

Coordinates ($\times 10^5$ for Fe, $\times 10^4$ for C) and thermal parameters B_{eq} (Å^2) of nonhydrogen atoms

Atom	x	y	z	B_{eq}
Fe	−809(5)	13713(6)	20273(4)	2.58(1)
C(1)	−148(4)	4713(4)	4519(3)	3.44(9)
C(2)	−405(3)	4193(5)	3697(3)	3.50(9)
C(3)	−745(3)	3591(5)	2707(3)	3.26(8)
C(4)	−1766(3)	2399(5)	2390(3)	3.7(1)
C(5)	−1784(3)	2210(5)	1351(3)	3.9(1)
C(6)	−778(4)	3217(5)	1005(3)	3.7(1)
C(7)	−132(3)	4078(4)	1839(3)	3.50(9)
C(8)	1767(3)	573(5)	2186(3)	3.7(1)
C(9)	1136(4)	−197(5)	1327(3)	4.2(1)
C(10)	141(4)	−1219(5)	1635(3)	4.6(1)
C(11)	130(4)	−1080(4)	2692(3)	3.7(1)
C(12)	1166(3)	55(4)	3032(3)	3.34(9)
C(13)	1525(4)	515(5)	4100(3)	4.5(1)
C(14)	2126(4)	−1030(6)	4690(3)	4.9(1)

Table 2

Bond lengths d (Å)

Fe–C(3)	2.057(3)	C(3)–C(4)	1.441(5)
Fe–C(4)	2.041(4)	C(3)–C(7)	1.434(5)
Fe–C(5)	2.050(4)	C(4)–C(5)	1.409(5)
Fe–C(6)	2.050(4)	C(5)–C(6)	1.418(5)
Fe–C(7)	2.050(3)	C(6)–C(7)	1.422(5)
Fe–C(8)	2.039(4)	C(8)–C(9)	1.413(5)
Fe–C(9)	2.037(4)	C(8)–C(12)	1.408(5)
Fe–C(10)	2.036(4)	C(9)–C(10)	1.395(6)
Fe–C(11)	2.053(3)	C(10)–C(11)	1.432(5)
Fe–C(12)	2.064(4)	C(11)–C(12)	1.434(5)
C(1)–C(1′)	1.378(5)	C(12)–C(13)	1.499(5)
C(1)–C(2)	1.187(5)	C(13)–C(14)	1.517(6)
C(2)–C(3)	1.428(5)		

Table 3

Bond angles ω (Å)

C(1′)C(1)C(2)	179.0(4)	C(9)C(8)C(12)	109.8(3)
C(1)C(2)C(3)	178.5(4)	C(8)C(9)C(10)	107.3(3)
C(2)C(3)C(4)	126.8(3)	C(9)C(10)C(11)	109.1(3)
C(2)C(3)C(7)	126.0(3)	C(10)C(11)C(12)	107.0(3)
C(4)C(3)C(7)	107.2(3)	C(11)C(12)C(8)	106.9(3)
C(3)C(4)C(5)	107.8(3)	C(8)C(12)C(13)	128.4(3)
C(4)C(5)C(6)	109.1(3)	C(11)C(12)C(13)	124.7(3)
C(5)C(6)C(7)	107.9(3)	C(12)C(13)C(14)	112.9(3)
C(6)C(7)C(3)	108.1(3)		

moieties is ca. 6 Å, which is much farther than the ca. 4 Å required for the realization of topochemical reactions [4], including the topochemical polymerization of diacetylenes by the shearing mechanism [5]. Indeed, the crystal I are quite stable to γ or UV radiation, heating and visible light.

The geometrical parameters of ethylferrocenyl and diacetylene groups (Tables 2 and 3) are unexceptional. The mean lengths of the C–C bonds in the ethyl-substituted Cp rings is ca. 0.01 Å less than in the rings bonded to the diacetylene moiety; moreover, of the C–C bonds occupying equivalent positions (such as C(3)–C(4) and C(8)–C(12)) the longer ones, as a rule, are found in the C(3)...C(7) cycle. The differences mentioned are probably caused by the differing induction effects by the ethyl and the diacetylene moieties. This supposition is consistent with exceeding the maximum atomic deviation from the mean plane in the C(3)...(7) cycle over such deviation in the C(8)...C(12) cycle (viz., 0.009(4) vs. 0.004(4) Å respectively), though these deviations are rather negligible. The planes of the Cp-rings are almost parallel, the corresponding dihedral angle is 1.6°.

Thus, our X-ray diffraction study has shown that the topochemical reaction in crystal I cannot proceed by the shearing mechanism.

Experimental

Yellow crystals I are monoclinic, a 10.5832(8), b 7.5163(5), c 13.4996(8) Å, β 94.837(5)°, V 1070(1) Å^3, d_{calc} 1.472g cm^{-3}, $Z = 2$. $C_{28}H_{26}Fe_2$, space group $P2_1/n$.

The unit cell parameters and intensities of 2258 reflections were measured with an automated Hilger & Watts diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 60°$). The structure was solved by MULTAN [6] and refined anisotropically by block-diagonal least squares for the nonhydrogen atoms. The H atoms that were located in the difference Fourier synthesis were refined isotropically. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. No absorption and secondary extinction corrections were applied. Final discrepancy factors are $R = 0.037$, $R_w = 0.038$ for 1922 reflections with $I > 25(I)$. The coordinates of the nonhydrogen atoms are given in Table 1.

Supplementary material. The coordinates of H atoms, anisotropic temperature factors and structure factors are available from the authors. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [7].

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