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Molecular geometry of *cis*-β-ferrocenylacrylonitrile

Z.V. Todres *, **A.I. Yanovsky, D.S. Ermekov and Yu.T. Struchkov**

A.N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St., Moscow, 117813 (U.S.S.R.)

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Abstract

An X-ray diffraction study of *cis*-β-ferrocenylacrylonitrile was carried out to reveal that the nitrile group is displaced from the plane of the cyclopentadienyl ring, to which it is bonded, in a direction away from the Fe atom. There was no evidence of any coordination of the acrylonitrile group to the metal atom. The dihedral angle formed by the planes of the π systems of the substituted cyclopentadienyl ligand and the double bond of the acrylonitrile group is 23.0°, which corresponds to a conjugation energy of ~85% of the maximum possible value for coplanar π systems.

Introduction

While studying the stereochemistry of one-electron oxidation of *cis*-β-ferrocenylacrylonitrile (I) in the liquid and gaseous phases [1,2], we found that the cation-radicals obtained retain the *cis* geometry of the parent compound, in contrast to other olefins (such as stilbene [3]) which undergo *cis/trans* isomerization in the course of oxidation. However, the one-electron reduction of the ferrocenyl derivative, I, initiates a *cis–trans* conversion [1].

The configurational stability of compound I as the cation-radical is probably attributable to (a) the localization of the spin-positive density on the Fe atom rather than on the ethylene bond and (b) the fixation of the *cis* configuration as a result of a specific interaction between the cyanovinyl group and the Fe atom carrying the positive charge.

In this connection, the determination of molecular geometry of the neutral parent compound (I), which has remained unclear up to now, seems to be of significant interest.

Experimental

Crystals of I are triclinic; at 20°C, $a = 10.430(1)$, $b = 7.574(1)$, $c = 27.083(3)$ Å, $\beta = 102.93(1)°$, $V = 2086.0$ Å^3, $d_{calc} = 1.51$ g/cm^3, space group $P2_1/n$, $Z = 8$, two

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Table 1

Atomic coordinates ($\times 10^4$; for Fe atom $\times 10^5$) and equivalent isotropic temperature factors ($Å^2$)

Atom	Molecule A				Molecule B			
	x	y	z	B_{eq}	x	y	z	B_{eq}
Fe	−8812(8)	67399(12)	34608(3)	2.35(2)	41629(8)	17171(2)	34479(3)	2.44(2)
C(1)	−1375(6)	4410(8)	3756(2)	2.8(2)	4999(5)	−558(8)	3780(2)	2.4(2)
C(2)	−1219(6)	4183(8)	3242(2)	3.0(2)	4331(5)	−862(8)	3265(2)	2.8(2)
C(3)	−2133(6)	5304(9)	2919(2)	3.3(2)	4906(6)	237(8)	2950(2)	2.8(2)
C(4)	−2863(6)	6245(9)	3218(3)	3.5(2)	5930(6)	1219(9)	3263(2)	3.1(2)
C(5)	−2395(6)	5701(8)	3736(2)	3.1(2)	5993(5)	753(8)	3781(2)	2.7(2)
C(6)	890(7)	7526(10)	3889(3)	3.9(2)	2677(10)	2505(12)	3769(4)	7.6(4)
C(7)	−95(7)	8778(10)	3932(2)	3.8(2)	3660(10)	3645(11)	3889(3)	6.4(3)
C(8)	−635(7)	9409(9)	3431(3)	3.9(2)	3879(7)	4353(9)	3446(4)	5.8(3)
C(9)	−7(6)	8550(9)	3082(2)	3.4(2)	2995(7)	3606(11)	3044(3)	4.5(2)
C(10)	958(6)	7416(10)	3378(3)	3.8(2)	2242(7)	2442(11)	3242(4)	6.0(3)
C(11)	−595(6)	3511(9)	4189(2)	3.3(2)	4680(6)	−1456(8)	4213(2)	3.1(2)
C(12)	−856(6)	3234(10)	4646(3)	3.8(2)	5427(7)	−1741(10)	4667(2)	3.8(2)
C(13)	−2042(7)	3829(10)	4783(2)	4.1(2)	6776(7)	−1210(10)	4814(2)	3.8(2)
N	−2971(7)	4208(10)	4909(2)	5.9(2)	7861(6)	−849(10)	4955(2)	5.9(2)

Table 2

Bond lengths (Å)

Bond	Molecule A	Molecule B	Bond	Molecule A	Molecule B
Fe–C(1)	2.050(6)	2.046(6)	C(1)–C(11)	1.440(9)	1.459(9)
Fe–C(2)	2.032(6)	2.033(6)	C(2)–C(3)	1.422(9)	1.418(9)
Fe–C(3)	2.045(7)	2.036(6)	C(3)–C(4)	1.421(9)	1.417(9)
Fe–C(4)	2.058(7)	2.051(6)	C(4)–C(5)	1.440(9)	1.435(9)
Fe–C(5)	2.048(6)	2.054(6)	C(6)–C(7)	1.42(1)	1.32(1)
Fe–C(6)	2.038(7)	2.03(1)	C(6)–C(10)	1.405(9)	1.40(1)
Fe–C(7)	2.053(7)	2.029(9)	C(7)–C(8)	1.429(9)	1.38(1)
Fe–C(8)	2.042(7)	2.018(7)	C(8)–C(9)	1.423(9)	1.38(1)
Fe–C(9)	2.045(7)	2.033(8)	C(9)–C(10)	1.426(9)	1.37(1)
Fe–C(10)	2.046(7)	2.031(8)	C(11)–C(12)	1.344(9)	1.319(9)
C(1)–C(2)	1.448(9)	1.432(8)	C(12)–C(13)	1.44(1)	1.43(1)
C(1)–C(5)	1.437(9)	1.435(8)	C(13)–N	1.13(1)	1.143(9)

independent molecules. The unit cell parameters and intensities of 1839 reflections with $F^2 \geqslant 3\sigma$ were measured by use of an automated 4-circle "Hilger & Watts" diffractometer at 20 °C (λMo-K_α, graphite monochromator, $\theta/2\theta$-scan, $\theta \leqslant 26°$).

The structure was solved by the heavy atom method. The coordinates of the two independent Fe atoms * were determined from the Patterson synthesis, all other non-hydrogen atoms were located in subsequent electron density syntheses. The structure was refined first in the isotropic and then in the anisotropic approxima-

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* These atoms are related by the diagonal translation (0.5, 0.5, 0) which does not belong to the space group symmetry elements and does not hold for light atoms. Consequently, in the experimental set of intensities pseudo-symmetry is observed, which is manifested in the considerable difference in the intensities of reflections with even and odd $h+k$ sums.

Table 3

Relevant bond angles (°)

Angle	Molecule A	Molecule B	Angle	Molecule A	Molecule B
C(2)C(1)C(5)	106.6(5)	107.9(5)	C(6)C(7)C(8)	106.5(6)	108.0(8)
C(2)C(1)C(11)	124.2(6)	124.1(5)	C(7)C(8)C(9)	109.6(5)	108.4(7)
C(5)C(1)C(11)	129.1(6)	128.0(5)	C(8)C(9)C(10)	105.9(6)	107.1(7)
C(1)C(2)C(3)	108.5(5)	108.2(5)	C(6)C(10)C(9)	109.5(6)	107.1(8)
C(2)C(3)C(4)	108.6(6)	108.2(5)	C(1)C(11)C(12)	129.1(6)	129.3(6)
C(3)C(4)C(5)	107.7(6)	108.6(5)	C(11)C(12)C(13)	123.4(7)	123.6(7)
C(1)C(5)C(4)	108.5(6)	107.1(5)	C(12)C(13)N	175.8(8)	176.1(8)
C(7)C(6)C(10)	108.5(6)	109.2(9)			

tions. All H atoms were located in the difference Fourier synthesis and their contributions to F_{calc} were taken into account in the final cycles of refinement; but their positional and thermal parameters ($B_{iso} = 4.5$ Å^2) were not refined. The final discrepancy factors R and R_w are 0.042 and 0.046, respectively. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [4]. Atomic coordinates and temperature factors are listed in Table 1. Bond lengths and relevant bond angles for the two independent molecules (A and B) of structure I are given in Tables 2 and 3, respectively. The structure of molecule IA is depicted in Figure 1.

The sample for an X-ray study was prepared by separating the mixture of *cis*- and *trans*-β-ferrocenylacrylonitriles by TLC on silica gel L40/100 (eluent: hexane-benzene, 1 : 3). The crystals of the *cis* form were obtained by slow cooling of a hexane-THF solution with an initial concentration of 0.1 *M*.

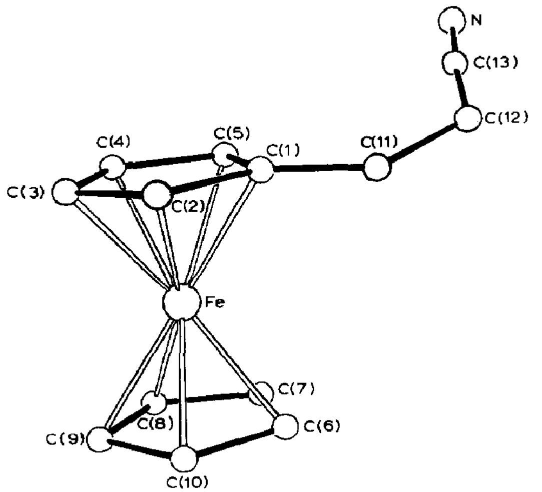

Fig. 1. Structure of IA.

Results and discussion

The difference in the geometric parameters of two independent molecules in the structure of I involve mainly a consistent shortening of the bond lengths in the unsubstituted Cp ligand of molecule B as compared with molecule A. This shortening is probably due to the more intense thermal motion of the Cp ring in molecule B, which is reflected in the high values of equivalent isotropic temperature factors of the relevant atoms listed in Table 1.

The geometric parameters of I which are of particular interest, viz. the parameters of the substituted Cp-ring and the acrylonitrile group, show no substantial differences between molecules A and B. Therefore, in the following text we mention only average geometric parameters.

In the structural study of *trans*-β-ferrocenylacrylonitrile published almost 20 years ago [5] it was shown that owing to steric hindrance the acrylonitrile substituent in the *cis* isomer cannot entirely become coplanar with the Cp ligand, bonded to it. The results presented here confirm this assumption. In analogy to other derivatives of α-alkenylferrocenes having a non-hydrogen substituent in the position cis to the ferrocenylcarbon atom, such as 2,2-dicyano [6], 2-nitro-2-phenyl [7] and 1-methyl-2,2-dicyanovinylferrocene [8], in molecule I the plane of the double bond which is defined by atoms C(1), C(11), C(12), C(13) (coplanar to within 0.006 Å) does not coincide with the Cp ligand plane: the acrylonitrile group is displaced from the Cp ligand plane because of rotation around the C(1)–C(11) single bond away from the Fe atom. Thus in molecule I no additional coordination of the Fe atom either by the double bond or by the acrylonitrile substituent is observed. At the same time, the dihedral angle of 23.0° formed by the C(1)C(11)C(12)C(13) and C(1)C(2)C(3)C(4)C(5) planes and the C(5)C(1)C(11)C(12) torsion angle of 23.2(8)° indicate that the conjugation of the π system of the Cp ligand and the double bond of the acrylonitrile group remains substantial. As is generally accepted the conjugation energy is proportional to $\cos^2\psi$ (ψ is the dihedral angle formed by the planes of the π systems). Therefore the conjugation energy in molecule I amounts to ~ 85% of the maximum possible value (corresponding to the coplanarity of the π systems). It should be noted, however, that neither loss of coplanarity nor distortions of bond angles (inequality of the C(2)C(1)C(11) (124.2(5)°) and C(5)C(1)C(11) (128.5(6)°) bond angles, and widening of the C(1)C(11)C(12) angle to 129.2(6)°) characteristic for the cis-alkenylferrocenyl systems [5–8], can completely remove steric hindrance: the non-bonded intramolecular C(5) · · · C(12) distance 3.217(8) Å in molecule I is still substantially less than double the Van der Waals radius (3.6 Å [9]) of the carbon atom.

The planes of the Cp ligands are at a dihedral angle of 1.0°; the Cp-rings are almost in the eclipsed conformation: the C(1) Cp(1) * Cp(2) * C(6) torsion angle is 8.9(9)°. The Fe–C(Cp) distances of 2.018–2.058 Å are typical for ferrocene derivatives, the bond lengths C(1)–C(11) 1.450(9), C(11)=C(12) 1.332(9), C(12)–C(13) 1.435(9), C(13)≡N 1.138(9) Å are likewise close to the standard values [10] of C(sp^2)–C(sp^2) 1.460, C(sp^2)=C(sp^2) 1.326, C(sp^2)–C(sp) 1.431, C≡N 1.136 Å, respectively. Other geometric parameters of molecule I are unexceptional.

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* Cp(1) and Cp(2) are the centroids of the Cp-rings C(1)–C(5) and C(6)–C(10), respectively.

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