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Molecular properties of a bis(1,1-diphenylallenylidene)-octacarbonyltriiron complex obtained by symmetric cleavage from 1,1,6,6-tetraphenylhexapentaene. Idealized symmetry studied in *synperiplanar* and *synclinal* conformers by X-ray diffraction, NMR and density functional theory

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Abstract

Molecular deviations from symmetry of bis(1,1-diphenylallenylidene)-octacarbonyltriiron are compared in two distinct *synperiplanar* and *synclinal* conformers expressed as two polymorphic forms by the analysis of close contacts in crystals, quantum chemical DFT calculations for the isolated molecules and by ^{13}C-NMR in solution. © 2001 Published by Elsevier Science B.V.

Keywords: Iron complexes; Cumulenes; Bis(tricarbonyliron); Deviations from symmetry; Close contacts; NMR; DFT calculations; Bis(1,1-diphenylallenylidene)-octacarbonyltriiron

1. Introduction

In the reaction of tetraphenylhexapentaene $Ph_2C=C=C=C=C=CPh_2$ with iron dodecacarbonyl, a symmetrical cleavage of the organic molecule occurs[1] and a complex is formed in which two chemically identical allenylidene $Ph_2C=C=C$ ligands are bridged by the octacarbonyl-triiron core (synthesis first described in Ref. [1]). This central core consists of a Fe_3 triangle that includes a $Fe(CO)_2$ and two chemically equivalent $Fe(CO)_3$ groups (schematic structure is shown in Fig. 1). In the $[Fe(CO)_3]_2$ moiety, two different conformations were observed and expressed as two distinct polymorphs, *synperiplanar* [2] and *synclinal* [3], as determined by X-ray crystal structural studies.

In the crystalline state discernible molecular deviations from symmetry were noticed, different in each conformer. In the *synperiplanar* form the dislocation of the carbonyls towards each of diphenylallenylidene ligands is different, and this results in diversification of bonding forces for both ligands with the central core; however, the Fe_3 triangle remains nearly equilateral. In contrast, in the *synclinal* conformer the $Fe(CO)_2$ group

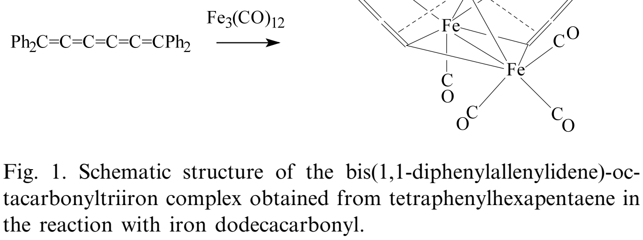

Fig. 1. Schematic structure of the bis(1,1-diphenylallenylidene)-octacarbonyltriiron complex obtained from tetraphenylhexapentaene in the reaction with iron dodecacarbonyl.

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[1] Similar symmetric incorporation was observed by us for acetophenone azine $Ph(CH_3)C=N–N=C(CH_3)Ph$ leading to *anti* and *syn* isomers of bis(μ^2-acetophenoniminato)-bis(tricarbonyliron). An article on deviations from symmetry in these complexes was accepted for publication in *J. Mol. Struct.*

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is deflected from its position by one of the carbonyls in the $Fe(CO)_3$ moiety and the Fe_3 ring shows clear deviations from equilateral behavior, but the carbonyl groups at each iron atom are arranged quasi-symmetrically with respect to both organic moieties. Nevertheless, both conformers reveal substantial molecular deviations from symmetry when examining the allenylidene ligands, mainly due to the twisting of benzene rings [3].

The main goal of the present work was an attempt to estimate quantitatively the deviations from symmetry in the conformers compared and to investigate the possibility of conformational transitions between both forms. The intra- and intermolecular close contacts and repulsive forces were analyzed in experimental and calculated structures obtained by X-ray analysis and by DFT optimization. In the case of strong intramolecular interactions, the resulting distortions could be possibly maintained in solution; hence, the conformational properties of the title compound were studied by ^{13}C-NMR.

2. Experimental and methods

Abbreviations used: NMR, nuclear magnetic resonance; d-chloroform, deuterated chloroform; DFT, density functional theory; BLYP, nonlocal correlation functional with gradient corrections to exchange; DNP, double numerical basis set with polarization functions; RMSD, root mean square displacement; CSD, Cambridge Structural Database; X-ray, crystallographic structural analysis; vdW, van der Waals; L-J, Lennard-Jones; r.t., room temperature. The *synperiplanar* conformer of bis(1,1-diphenylallenylidene)-octacarbonyltriiron is denoted as **I** and the *synclinal* conformer as **II**. The *anti* and *syn* locations of the phenyl rings are related to the $Fe(1)(CO)_2$ group.

The synthesis of **I** is described in Ref. [2], although the solvent used for recrystallization is not indicated. An analogous complexation procedure published by one of us in Ref. [1] has been applied in the synthesis of **II**: 1,1,6,6-tetraphenylhexapentaene (0.5 mmol) and triiron-dodecacarbonyl (3 mmol) were refluxed in isooctane under nitrogen, chromatographed on Kieselgel 60 and recrystallized from *n*-hexane. The synthesis of 1,1,6,6-tetraphenylhexapentaene is known [4].

The results of the X-ray structural analysis of **I** are described in Ref. [2], whereas the detailed crystallographic data for **II** were published by one of us in Ref. [3]. The structural parameters required in the present study have been obtained from the above sources; however, C–H bond lengths were normalized to the values typical for neutron diffraction, i.e. to 1.083 for C_{ar}–H in the phenyl rings (in Å) [5].

The ^{13}C-NMR spectrum was recorded with a Varian Unity+ 500 MHz instrument in d-chloroform at r.t. and at −70 °C.

The DFT calculations were carried out by using the DMOL program [6]. BLYP functional [7,8] was used in all calculations along with DNP basis. During optimization standard convergence criteria were used, i.e. 10^{-6} for density, 10^{-3} for gradient and 10^{-5} for energy change (in atomic units). Electron density was estimated by Hirshfeld charges [9]. The optimized structures and calculated parameters are marked by asterisks (*).

RMSD values were calculated for superimposed quasi-symmetrical diphenylallenylidene ligands using the standard equation [10]:

$$\mathrm{RMSD} = \sqrt{\sum_{i=1}^{N} \frac{(x_i - x'_i)^2 + (y_i - y'_i)^2 + (z_i - z'_i)^2}{N}}$$

where the superimposition is aimed at aligning N pairs of atoms i–i' in two ligands of the same molecule of the complex and x_i, y_i, z_i represent the spatial coordinates of atom i in one ligand while x'_i, y'_i, z'_i represent the spatial coordinates of the atom i' from the other ligand reflected in the operation of symmetry (two-fold axis).

In the analysis of close contacts, the following van der Waals contact radii were accepted: C, 1.70; H, 1.20; O, 1.52 (in Å) [11]. Distances between atoms separated by less than four bonds were neglected.

Van der Waals repulsive interactions have been approximated using the Lennard-Jones (6–12) equation for nonbond potential E_{ij} [12]:

$$E_{ij} = \varepsilon_{ij}\left[\left(\frac{R_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{ij}}{r_{ij}}\right)^{6}\right]$$

where ε_{ij} is the potential well depth for the pair of atoms i and j (equal to $\sqrt{\varepsilon_{ii}\varepsilon_{jj}}$), R_{ij} is the sum of vdW radii ($R_{ij} = R_i + R_j$) and r_{ij} is the distance between atom i and atom j. The resulting forces were calculated using the negative gradient of E_{ij}.

Parameters ε_{ii} and R_i for atoms C and O were taken directly from the SYBYL force-field [13] (for these atoms SYBYL vdW radii are equal to Bondi's radii). For H atom parameter ε_H was gained also from the SYBYL force-field whereas R_H has been decreased from 1.5 to 1.2 Å, which is a value suggested by Bondi. This modification results from an observation that the value for R_H in many force fields seems to be overestimated. Recent reparameterizations [14,15] based on accurate quantum mechanical calculations tend to lower its value down to Bondi's standard.

3. Results and discussion

In the comparative study of symmetry only the diphenylallenylidene ligands were considered, the octacarbonyltriiron moiety for simplification was excluded from the investigation. Intramolecular parameters of both compared conformers **I** (*synperiplanar*) and **II** (*synclinal*), taken into account in both quasi-symmetrical ligands, have been reflected from one ligand to another according to the operation of symmetry, and the sum of differences in values obtained in this manner for each conformer was analyzed. Regarding the geometry and the structural irregularities of the ligands two symmetry point groups could be alternatively applied: two-fold axis (C_2) passing through iron atom Fe(1) perpendicular to the bond Fe(2)–Fe(3) or the symmetry plane (C_s) on which lay all three iron atoms Fe(1), Fe(2) and Fe(3). After mathematical superimposition of ligands according to the C_2 or C_s symmetry, the RMSD values for the carbon atoms were calculated for each conformer. The results for **I** are 0.2683 and 0.4150, respectively, for C_2 and C_s, while the relevant data for **II** are 0.2327 and 0.5473 (in Å). Thus, the two-fold axis (C_2) was preferably accepted for both conformers. The structures of **I** and **II**, showing the atom-numbering scheme, are presented in Fig. 2, and projections of conformations are shown in Fig. 3.

3.1. Deviations from symmetry, close contacts and repulsive forces in the solid state

The analysis has been performed using published structural X-ray data. The data required for **I** were taken from Ref. [2] and from CSD [16], whereas the crystal structure of **II** was published earlier by one of us [3]. All positions of the atoms considered were refined and the distances are given with the proper margins of error.

In order to relate quantitatively the deviations from symmetry in the X-ray structures of the compared conformers, the RMSD values have been calculated for **I** and **II** after superimposition of the diphenylallenylidene ligands applying the two-fold axis in an operation of symmetry. For **I** and **II** the results for all atoms are 0.3535 and 0.3461, respectively; in the case when hydrogen atoms were omitted the values for **I** and **II** are 0.2683 and 0.2327, respectively (in Å). The values limited to the central regions of each ligand, including allenylidene chains and quaternary aromatic carbons, are 0.1138 and 0.0834, respectively, for **I** and **II**. These results point to the comparable extent of deviations from symmetry in both conformers, especially when all atoms are considered, whereas for the central regions of ligands the deviations are somewhat lower for **II**. This could be explained by the effective unsymmetrical location of the central carbonyliron core towards allenylidene ligands in **I**. Moreover, as expected, the conformational irregularities are mainly placed in the peripheral areas of the molecule.

In the analysis of molecular spacing, the contact for the examined atoms was accepted as close when the interatomic distance was smaller than the sum of van der Waals radii according to Bondi [11] (see Section 2). Although there are no well-accepted values for atomic contact radii, Bondi's values are acknowledged as standard. It should be stressed that in this work most critical is the estimation of differences between two quasi-symmetric ligands and not the determination of absolute values.

In the specification of intramolecular contacts several restrictions have been imposed. In the case when the difference between compared intramolecular distances located in the two ligands was smaller than the 2.5-fold value of maximal error, this result was omitted. Such limitation was essential for C–H bond lengths bearing relatively high errors of 0.03–0.04 Å, while errors of C–C bonds lengths usually did not exceed 0.004 Å. Moreover, though iron atoms are possibly involved in the intramolecular contacts, such interactions were neglected because the vdW radius of six-coordinated iron is not precisely determined. Intramolecular short contacts for both conformers meeting the above requirements are listed in Table 1.

In this study not only distances expressing close contacts were analyzed but primarily the resulting repulsive forces have been considered, calculated according to the L-J potential [12]. As one can see from Table 1, in particular cases, only one of the two compared distances, quasi-symmetrically located in different ligands, was identified as short contact, while the other in the pair exceeded the sum of vdW radii. In such instances, both distances were analyzed, but the repulsive force corresponding to the latter interaction was assumed to be zero.

No intramolecular interactions were noted between both diphenylallenylidene ligands, except of C(1)–C(4) which corresponds to the distance 2.560 in **I** and 2.576 in **II** (in Å). However, in **I** altogether six pairs of intramolecular contacts have been perceived, explicit short ones between the geminal phenyl rings at the carbon C(3) and, accordingly, at C(6), and also between the allenylidene chains and the *ortho* carbons and hydrogens in the phenyl rings located in the positions *anti* with respect to the Fe(1)$(CO)_2$ moiety. Intramolecular contacts for both conformers are shown in Fig. 2, while distances and repulsive forces are listed in Table 1.

In **II**, nine pairs of close contacts were observed generally in the same locations as in **I**, and additionally substantial interactions occurred in the region of the Fe(1)$(CO)_2$ group. This is assumed to be due to repulsive interaction between atoms C(1b) and O(3b) belonging to carbonyls at Fe(1) and Fe(3), respectively, and results in crowding out of the carbonyl groups at Fe(1) from their positions. Also, explicit twisting of the *syn* phenyl rings was observed; hence, the least-squares

Table 1
Intramolecular close contacts obtained from X-ray analysis (normalized) and resulting repulsive forces calculated according to L-J potentials for allenylidene ligands 1 and 2 in conformers **I** and **II**

Location in ligand 1	Dist. $D1$ (Å) from X-ray	Force $F1$ (kJ mol^{-1} $Å^{-1}$)	Dist. $D1^*$ (Å) calc.	Location in ligand 2	Dist. $D2$ (Å) from X-ray	Force $F2$ (kJ mol^{-1} $Å^{-1}$)	Dist. $D2^*$ (Å) calc.	$\|D1^*-D2^*\|$ (Å) calc.	$\|D1-D2\|$ (Å) from X-ray	$\|F1-F2\|$ (kJ mol^{-1} $Å^{-1}$)
I										
C(1)–C(12)	3.390(4)	0.029	3.435	C(4)–C(32)	3.270(4)	0.547	3.474	0.039	0.120	0.518
C(1)–H(12)	2.662(30)	1.420	2.695	C(4)–H(32)	2.552(30)	3.277	2.746	0.051	0.110	1.857
C(1b)–C(22)	3.327(5)	0.256	3.560	C(1a)–C(46)	3.835(5)	No repulsion [a]	3.595	0.035	0.508	0.256
C(2)–H(12)	2.595(30)	Omitted [b]	2.628	C(5)–H(32)	2.636(30)	Omitted [b]	2.667	–	–	–
C(21)–H(16)	2.461(30)	Omitted [b]	2.551	C(41)–H(36)	2.482(30)	Omitted [b]	2.522	–	–	–
C(22)–H(16)	2.904(30)	Omitted [a,b]	3.037	C(46)–H(36)	2.874(30)	Omitted [b]	2.997	–	–	–
								$\Sigma\|D1^*-D2^*\|$	$\Sigma\|D1-D2\|$	$\Sigma\|F1-F2\|$
								$=0.125$	$=0.738$	$=2.631$
II										
C(1)–C(12)	3.369(3)	0.095	3.422	C(4)–C(32)	3.383(3)	0.050	3.477	0.055	0.014	0.045
C(1)–H(12)	2.623(30)	Omitted [b]	2.680	C(4)–H(32)	2.668(30)	Omitted [b]	2.777	–	–	–
C(1a)–C(21)	3.614(4)	No repulsion [a]	3.742	C(1b)–C(41)	3.288(4)	0.445	3.409	0.333	0.326	0.445
C(1b)–C(22)	3.248(4)	0.687	3.380	C(1a)–C(46)	3.360(4)	0.126	3.375	0.005	0.112	0.561
C(1b)–H(22)	3.067(30)	No repulsion [a]	3.199	C(1a)–H(46)	2.755(30)	0.600	2.825	0.374	0.312	0.600
C(2)–H(12)	2.609(30)	Omitted [b]	2.629	C(5)–H(32)	2.631(30)	Omitted [b]	2.657	–	–	–
C(16)–C(26)	3.271(4)	0.540	3.320	C(36)–C(42)	3.254(4)	0.648	3.341	0.021	0.017	0.108
C(21)–H(16)	2.511(30)	Omitted [b]	2.556	C(41)–H(36)	2.559(30)	Omitted [b]	2.603	–	–	–
C(26)–H(16)	2.689(30)	1.130	2.766	C(42)–H(36)	2.813(30)	0.288	3.341	0.575	0.124	0.842
								$\Sigma\|D1^*-D2^*\|$	$\Sigma\|D1-D2\|$	$\Sigma\|F1-F2\|$
								$=1.363$	$=0.905$	$=2.601$

Atom numbering scheme is given in Fig. 2, respective locations are reflected by molecular symmetry operations. Distances resulting from DFT calculations shown for comparison are marked by (*).

[a] This distance exceeds the sum of vdW radii.

[b] The difference between corresponding distances in compared ligands was smaller than 2.5-fold maximal error.

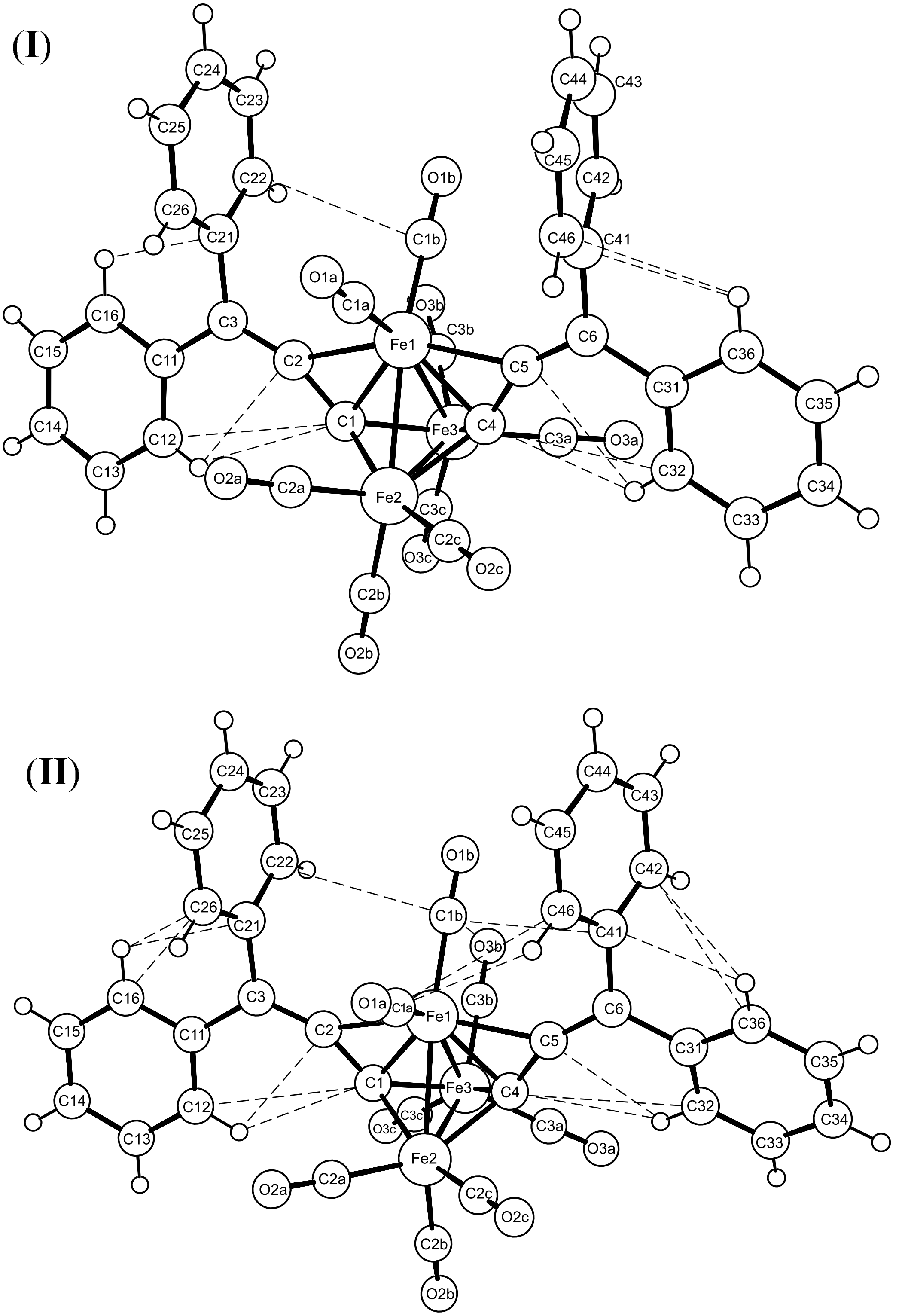

Fig. 2. View of the molecules **I** and **II**. Intramolecular close contacts are expressed as dashed lines.

planes of these rings are turned towards the plane of the central Fe_3 triangle by 13.8 and 24.8° in **II**, whereas the respective values for **I** are 4.1 and $-9.8°$. Moreover, close contacts were noted between carbon C(1a) and both atoms H(46) and C(46) in the *ortho* position of one of the *syn* phenyl rings, and between the carbon C(1b) and both *syn* phenyl rings. In both **I** and **II** the phenyl substituents in the location *anti* are involved in a number of intramolecular contacts, but the formation of such strong repulsions is energetically counterbalanced by favorable coupling of these rings with the allenic double bonds C(2)=C(3) and C(5)=C(6).

As one can see from Table 1, the sum of differences (absolute values) between accordingly located analyzed short distances $\Sigma|D1-D2|$ is 0.738 in **I**, and 0.905 in **II** (in Å). However, more adequate extents of steric crowding than only close contacts are the resulting repulsive forces (specified in Table 1). The strongest from among the compared interactions were observed in **I** between atoms C(1)–H(12) and C(4)–H(32), i.e. terminal carbons in the allenylidene chain and *ortho* hydrogen atoms in the *anti* benzene rings. A similar strength of repulsion was noted in **II** between atoms C(26)–H(16), belonging to geminal benzene rings attached to carbon C(3). The latter interaction results from mutual twisting of both rings. The absolute values of differences of respective forces localized in both ligands were summarized giving $\Sigma|F1-F2|$ of 2.631 for **I**, and a very similar value 2.601 for **II** (in kJ mol^{-1} Å^{-1}). Thus, as a result of the described quantitative assessment no significant differences in deviations from symmetry were noted between conformers **I** and **II**. Moreover, the inequality in distribution of internal stresses, which could be considered as one of the possible reasons of deviations from symmetry, is not essential.

In the dislocation of intermolecular close contacts, as expected, no symmetry was observed; thus, the calculated repulsive forces were summarized separately for each diphenylallenylidene ligand (results are shown in Table 2). In a rough estimation, these values can be assumed as the extent of deformation of a particular ligand caused by external repulsions. For **I** 19 contacts with seven external molecules have been noted, and the results for ligands 1 and 2 are as follows (quantities representing intermolecular interactions are marked by primes): $\Sigma F1'$ 3.685 (14 contacts), $\Sigma F2'$ 2.896 (five contacts) and the difference $|\Sigma F1'-\Sigma F2'|$ is 0.789 (in kJ mol^{-1} Å^{-1}). The respective values for **II** considering 13 contacts with seven molecules are: $\Sigma F1'$ 3.080 (eight contacts), $\Sigma F2'$ 2.218 (five contacts) and $|\Sigma F1'-\Sigma F2'|$ is 0.862. Based on the above results, one can conclude that the external deforming forces act similarly on ligands in both conformers.

It should be stressed that intramolecular contacts of the O···H type have been observed neither in **I** nor in **II**,

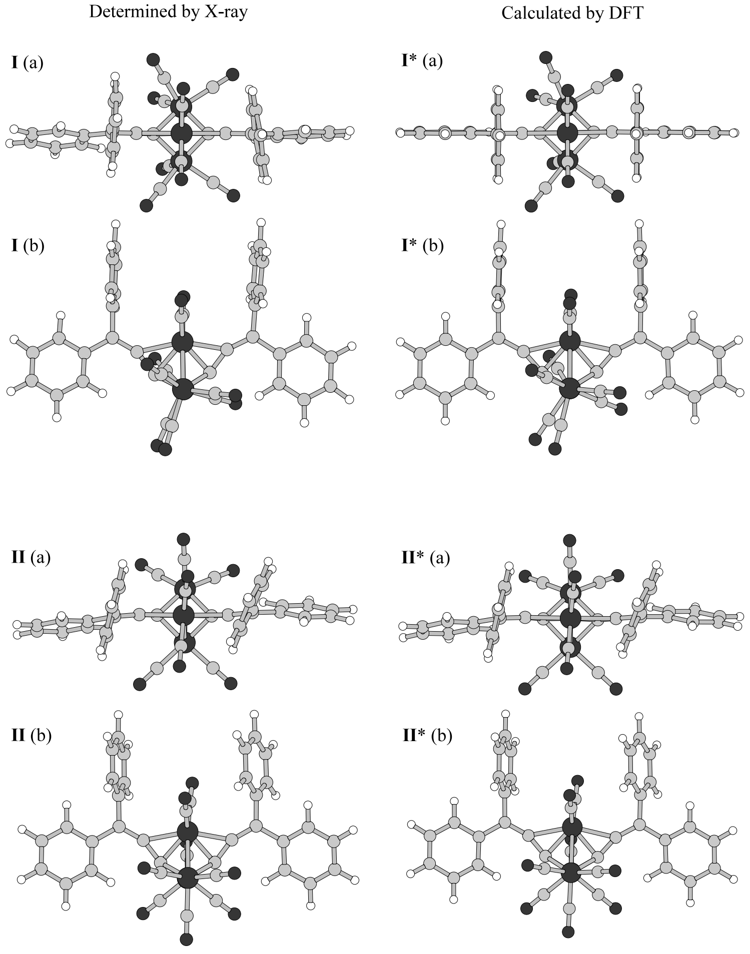

Fig. 3. View of conformers investigated: (a) projection exposing Fe(1) (in the center of the structure); (b) view along the Fe(2)–Fe(3) axis.

Table 2
Intermolecular close contacts and respective repulsive forces for **I** and **II**

Locations in ligand 1	Dist. (Å) from X-ray	Forces $F1'$ (kJ mol^{-1} Å^{-1})	Locations in ligand 2	Dist. (Å) from X-ray	Forces $F2'$ (kJ mol^{-1} Å^{-1})
I					
C(12)–H(24)$^{\mathrm{i}}$	2.872	0.074	H(32)–H(44)$^{\mathrm{i}}$	2.200	1.104
C(12)–H(25)$^{\mathrm{ii}}$	2.881	0.049	C(34)–H(42)$^{\mathrm{vi}}$	2.863	0.102
C(13)–H(25)$^{\mathrm{ii}}$	2.801	0.343	C(35)–H(42)$^{\mathrm{vi}}$	2.836	0.194
H(12)–H(24)$^{\mathrm{i}}$	2.321	0.244	H(44)–H(32)$^{\mathrm{v}}$	2.200	1.104
H(13)–H(24)$^{\mathrm{i}}$	2.383	0.038	H(46)–C(2c)$^{\mathrm{vii}}$	2.791	0.392
H(22)–O(3c)$^{\mathrm{iii}}$	2.536	1.099			$\Sigma F2' = 2.896$
H(23)–O(1b)$^{\mathrm{iv}}$	2.568	0.794			
H(24)–C(12)$^{\mathrm{v}}$	2.872	0.074			
H(24)–C(34)$^{\mathrm{vi}}$	2.863	0.102			
H(24)–C(35)$^{\mathrm{vi}}$	2.836	0.194			
H(24)–H(12)$^{\mathrm{v}}$	2.321	0.244			
H(24)–H(13)$^{\mathrm{v}}$	2.383	0.038			
H(25)–C(12)$^{\mathrm{ii}}$	2.881	0.049			
H(25)–C(13)$^{\mathrm{ii}}$	2.801	0.343			
		$\Sigma F1' = 3.685$			$\lvert\Sigma F1' - \Sigma F2'\rvert = 0.789$
II					
C(13)–H(25)$^{\mathrm{i}}$	2.844	0.165	C(35)–H(42)$^{\mathrm{v}}$	2.816	0.275
H(13)–C(44)$^{\mathrm{ii}}$	2.895	0.012	H(42)–C(35)$^{\mathrm{vi}}$	2.816	0.275
H(22)–H(24)$^{\mathrm{iii}}$	2.369	0.076	H(43)–C(3c)$^{\mathrm{vii}}$	2.880	0.052
C(24)–H(45)$^{\mathrm{iii}}$	2.647	1.604	C(44)–H(13)$^{\mathrm{vii}}$	2.895	0.012
H(24)–O(3b)$^{\mathrm{iv}}$	2.636	0.332	H(45)–C(24)$^{\mathrm{iv}}$	2.647	1.604
H(24)–H(22)$^{\mathrm{iv}}$	2.369	0.076			$\Sigma F2' = 2.218$
H(25)–O(1b)$^{\mathrm{iv}}$	2.586	0.650			
H(25)–C(13)$^{\mathrm{i}}$	2.844	0.165			
		$\Sigma F1' = 3.080$			$\lvert\Sigma F1' - \Sigma F2'\rvert = 0.862$

The distances are given with maximal errors of 0.04 Å. Close contacts were analyzed separately for each diphenylallenylidene ligand, symbols$^{\mathrm{i–vii}}$ distinguish external molecules.

whereas in the crystal lattice of both conformers four intermolecular interactions of the type CO···H$_{\mathrm{ar}}$ occur, but they were not classified as hydrogen bonds.

3.2. DFT calculations

Full geometry optimizations have been performed for both conformers starting with structures known from the X-ray analysis, **I** [2] and **II** [3], in order to compare the energies of **I** and **II** and also to note the differences between experimental and theoretical conformations, which to some extent could arise from the absence of the network intermolecular interactions. The calculated electronic energies for optimized structures **I*** and **II*** (symbols related to the calculated quantities are marked by asterisks) are practically equal, differing by 0.59 kJ mol^{-1}, and the dipole moments are 2.22 and 2.46 D, respectively.

As an effect of optimization in **I*** an almost perfect symmetrization of allenylidene ligands have been observed, whereas in **II*** minor conformational changes were introduced as compared with the starting structure **II**, and the deviations from symmetry have been generally maintained (projections of X-ray and optimized conformations are shown in Fig. 3). This result is well illustrated by RMSD values, which are 0.0417 for **I*** and 0.3351 for **II*** (in Å) in the case when all atoms are considered, 0.0377 and 0.2279, respectively, for carbon atoms only, and 0.0243 and 0.0625, respectively, for allenylidene chains and quaternary aromatic carbons. As one can see from Table 3, where RMSD data for **I**, **I***, **II** and **II*** are collected, in both experimental and calculated structures the conformational irregularities, as expected, are mainly placed in the peripheral molecular regions.

Idealized symmetry of the investigated structures of conformers, determined by X-ray and optimization, can also be compared in terms of experimental and calculated short contacts given by expressions $\Sigma\lvert D1 - D2\rvert$ and $\Sigma\lvert D1^{*} - D2^{*}\rvert$ (data are collected in Table 1), respectively, which equal 0.738 and 0.125* for the *synperiplanar* form, whereas for the *synclinal* form the values are 0.905 and 1.363*. One can notice that as a result of DFT calculations concerning **I** the mutual arrangement of ligands becomes definitely more symmetric, in contrast to the optimization of **II**, which resulted in preservation or decrease of symmetry. This result was confirmed by other data, e.g. the torsion angle C(2)–C(3)–C(21)–C(22) in the X-ray structure of **I** is 83.6° and after optimization in **I*** 89.6°, whereas for

Table 3
Selected experimental (X-ray [2,3]) and calculated (DFT) bond lengths (Å), valence and torsion angles (°), and RMSD values (Å) for **I**, **I***, **II** and **II***

	I	**I***	**II**	**II***
Bond lengths				
Fe(1)–Fe(2)	2.534(1)	2.6082	2.5266(6)	2.6112
Fe(1)–Fe(3)	2.537(1)	2.6237	2.5437(5)	2.6212
Fe(2)–Fe(3)	2.537(1)	2.6246	2.5271(6)	2.5118
Fe(1)–C(1a)	1.793(5)	1.795	1.780(3)	1.787
Fe(1)–C(1b)	1.805(4)	1.814	1.821(3)	1.818
Fe(2)–C(2a)	1.790(5)	1.810	1.809(3)	1.822
Fe(2)–C(2b)	1.802(5)	1.810	1.807(3)	1.802
Fe(2)–C(2c)	1.805(4)	1.822	1.802(3)	1.821
Fe(3)–C(3a)	1.797(5)	1.831	1.820(3)	1.830
Fe(3)–C(3b)	1.783(5)	1.796	1.767(3)	1.796
Fe(3)–C(3c)	1.801(4)	1.828	1.821(3)	1.832
Fe(1)–C(1)	1.989(3)	2.012	1.947(2)	1.974
Fe(1)–C(2)	2.157(4)	2.263	2.139(2)	2.231
Fe(1)–C(4)	1.900(3)	1.947	1.939(2)	1.966
Fe(1)–C(5)	2.098(4)	2.206	2.127(2)	2.222
Fe(2)–C(1)	1.948(4)	2.018	1.960(2)	2.013
Fe(2)–C(4)	1.941(4)	1.999	1.945(2)	2.001
Fe(3)–C(1)	1.955(4)	2.003	1.946(2)	1.987
Fe(3)–C(4)	1.935(4)	1.992	1.954(2)	2.015
C(1)–C(2)	1.334(5)	1.331	1.341(3)	1.332
C(2)–C(3)	1.325(5)	1.352	1.331(3)	1.352
C(4)–C(5)	1.337(5)	1.337	1.336(3)	1.334
C(5)–C(6)	1.333(5)	1.352	1.338(3)	1.354
Bond angles				
Fe(2)–Fe(1)–Fe(3)	60.05(3)	60.22	59.78(2)	59.38
Fe(1)–Fe(2)–Fe(3)	60.04(3)	60.18	60.44(1)	60.50
Fe(1)–Fe(3)–Fe(2)	59.91(3)	59.60	59.77(2)	60.12
C(1)–Fe(1)–C(4)	82.30(17)	82.21	83.02(9)	82.99
C(2)–Fe(1)–C(5)	158.20(15)	154.76	158.91(8)	155.71
C(1)–Fe(1)–C(2)	37.26(17)	35.67	37.95(8)	36.29
C(4)–Fe(1)–C(5)	38.65(15)	36.88	38.02(9)	36.51
C(1a)–Fe(1)–C(1b)	93.5(2)	95.80	94.64(12)	96.77
C(1a)–Fe(1)–Fe(2)	101.42(16)	97.37	93.85(8)	93.46
C(1b)–Fe(1)–Fe(3)	105.07(13)	106.61	111.83(9)	110.48
Fe(2)–C(1)–Fe(3)	81.1(1)	81.49	80.65(8)	80.75
Fe(2)–C(4)–Fe(3)	81.8(1)	82.23	80.81(7)	80.33
C(1)–C(2)–C(3)	157.7(4)	159.39	156.2(2)	158.34
C(4)–C(5)–C(6)	152.8(4)	158.84	156.2(2)	160.10
C(2a)–Fe(2)–Fe(3)–C(3b)	12.2(3)	33.66	78.26(19)	80.16
C(2b)–Fe(2)–Fe(3)–C(3c)	7.9(2)	20.46	49.39(13)	48.55
C(2c)–Fe(2)–Fe(3)–C(3a)	8.2(2)	16.88	42.93(16)	41.37
C(2)–C(3)–C(21)–C(22)	83.6(5)	89.56	68.2(3)	71.29
C(5)–C(6)–C(41)–C(46)	98.8(5)	89.37	61.5(3)	63.93
C(2)–C(3)–C(11)–C(12)	12.1(6)	−0.64	6.9(3)	5.42
C(5)–C(6)–C(31)–C(32)	−5.8(6)	−0.32	17.3(3)	16.46
RMSD values [a]				
All C and H	0.3535	0.0417	0.3461	0.3351
All C	0.2683	0.0377	0.2327	0.2279
C=C=C and C_{IVar}	0.1138	0.0243	0.0834	0.0625

The optimized structures are marked by (*).

[a] For diphenylallenylidene ligands superimposed in an operation of symmetry (C_2).

II and **II*** the corresponding values are 61.5 and 71.3°. For the angle C(5)–C(6)–C(41)–C(46) the values for **I** and **I*** are 98.8 and 89.4°, respectively, and for **II** and **II*** 68.1 and 63.9° (in Å). A selection of basic geometric parameters characterizing determined and calculated structures is shown in Table 3.

As an effect of optimization of **I**, in the $Fe_2(CO)_6$ moiety the conformation was modified; however, it could be still defined as *synperiplanar* (compare projections in Fig. 3). The dihedral angles between the carbonyl ligands have been changed, i.e. the angle C(2b)–Fe(2)–Fe(3)–C(3c) is 7.9° in **I**, whereas it is 20.4° in **I***. The average values of all three OC–Fe(2)–Fe(3)–CO angles are 9.4 and 23.6° for **I** and **I***, respectively. The corresponding average values for **II** and **II*** are 56.9 and 56.7°.

Deviations from symmetry might be also discussed in terms of charges localized on respective atoms in both twin-ligands. Selected atomic Hirshfeld charges calculated for **I*** and **II*** are specified in Table 4. The absolute values of differences in charges for atoms reflected in operation of symmetry (two-fold axis) were summarized, giving $\Sigma|\Delta|_{(\mathbf{I}^*)}$ 0.0186 for **I*** and $\Sigma|\Delta|_{(\mathbf{II}^*)}$ 0.0234 for **II***. This result confirms higher symmetry of **I*** as related with **II***. The differences in respective charges also testify relevant irregularities in the regions of aromatic *ortho* hydrogens H(12), H(22), H(32) and H(46) in conformer **II***.

In general, after optimization of isolated molecules both forms revealed no tendency to adopt one most advantageous conformation; contrarily, in the *synclinal* form **II*** the basic structural differences between diphenylallenylidene ligands and arrangements in the $Fe_2(CO)_6$ moiety were practically maintained, whereas in the *synperiplanar* form **I*** far-reaching symmetrization of ligands has been observed, but not of the carbonyliron moiety.

In order to examine the possibility of conformational transition between *synperiplanar* and *synclinal* forms a energy scan in such a simulated process has been accomplished. The angle C(2b)–Fe(2)–Fe(3)–C(3c) in the optimized structure **I*** was changed from 10 to 60° basically in steps of every 10° and for these constrained conformations in the $[Fe(CO)_3]_2$ moiety the entire molecule was re-optimized every time. The minima were found at about 20 and 53°, the maximum at 33°, and the accuracy of the scanning turned out to be satisfactory to estimate the height of the barrier, which is about 10 kJ mol^{-1} (the energy profile is shown in Fig. 4). It is known that density functionals tend to underestimate barrier heights [17,18]; therefore, experimental verification of this result has been performed using ^{13}C-NMR spectrometry.

3.3. NMR investigation in solution

The differentiation of the conformers in solution by the ^{13}C-NMR technique could be achieved provided that the barrier of conformational transition is ade-

Table 4
Comparison of Hirshfeld charges for pairs of atoms defined by the operations of symmetry (C_2) in optimized conformers **I*** and **II***

Pairs of atoms	Charges in **I***		$\lvert\Delta\rvert_{(\mathbf{I^*})}$	Charges in **II***		$\lvert\Delta\rvert_{(\mathbf{II^*})}$
C(1–4)	−0.0971	−0.0989	0.0018	−0.0975	−0.0956	0.0019
C(2–5)	−0.0114	−0.0136	0.0022	−0.0131	−0.0115	0.0016
C(3–6)	0.0093	0.0122	0.0029	0.0108	0.0116	0.0008
C(21–41)	0.0022	0.0025	0.0003	0.0025	0.0024	0.0001
C(22–46)	−0.0400	−0.0397	0.0003	−0.0408	−0.0409	0.0001
H(22–46)	0.0441	0.0442	0.0001	0.0426	0.0381	0.0045
C(23–45)	−0.0386	−0.0385	0.0001	−0.0384	−0.0385	0.0001
H(23–45)	0.0467	0.0467	0.0000	0.0471	0.0479	0.0008
C(24–44)	−0.0406	−0.0404	0.0002	−0.0402	−0.0386	0.0016
H(24–44)	0.0457	0.0461	0.0004	0.0456	0.0461	0.0005
C(25–43)	−0.0387	−0.0385	0.0002	−0.0393	−0.0381	0.0012
H(25–43)	0.0466	0.0471	0.0005	0.0465	0.0458	0.0007
C(26–42)	−0.0401	−0.0399	0.0002	−0.0378	−0.0374	0.0004
H(26–42)	0.0436	0.0448	0.0012	0.0456	0.0453	0.0003
C(11–31)	0.0015	0.0016	0.0001	0.0017	0.0020	0.0003
C(12–32)	−0.0405	−0.0394	0.0011	−0.0400	−0.0407	0.0007
H(12–32)	0.0356	0.0343	0.0013	0.0342	0.0301	0.0041
C(13–33)	−0.0391	−0.0379	0.0012	−0.0382	−0.0385	0.0003
H(13–33)	0.0466	0.0471	0.0005	0.0477	0.0471	0.0006
C(14–34)	−0.0384	−0.0366	0.0018	−0.0373	−0.0373	0.0000
H(14–34)	0.0458	0.0460	0.0002	0.0467	0.0464	0.0003
C(15–35)	−0.0403	−0.0397	0.0006	−0.0400	−0.0399	0.0001
H(15–35)	0.0466	0.0467	0.0001	0.0466	0.0469	0.0003
C(16–36)	−0.0400	−0.0390	0.0010	−0.0393	−0.0385	0.0008
H(16–36)	0.0388	0.0391	0.0003	0.0389	0.0402	0.0013
$\Sigma\lvert\Delta\rvert$			$\Sigma\lvert\Delta\rvert_{(\mathbf{I^*})} = 0.0186$			$\Sigma\lvert\Delta\rvert_{(\mathbf{II^*})} = 0.0234$

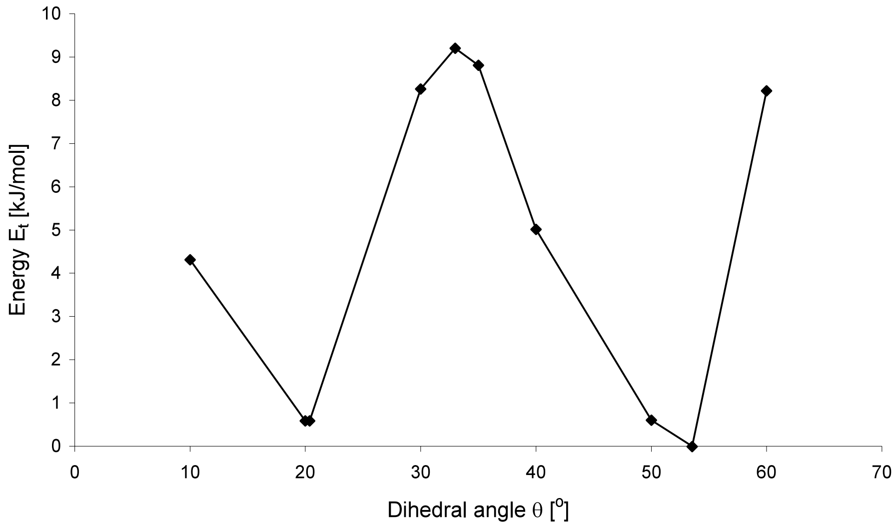

Fig. 4. Scan of energy for conformational transition between **I*** and **II*** simulated by rotation around the Fe(2)–Fe(3) axis. Dihedral angle θ is defined by the sequence C(2b)–Fe(2)–Fe(3)–C(3c), the energy E_t is given as an excessive value of lowest energy calculated for *synclinal* form **II***.

quately high. The published chemical shifts for **I** [2] consider only the allenylidene carbon skeleton and are consistent with our results (data are specified in Table 5). Also, the general remarks [2] about the occurrence of signals indicating two different aromatic rings and the presence of only two signals of terminal carbonyls are in agreement with our observations.

In the ^{13}C-NMR spectrum **II*** performed at r.t. in solution a typical peak pattern of two magnetically nonequivalent phenyl substituents (*anti* and *syn*) and one set of signals for both allenylidene chains were observed. After lowering the temperature down to −70 °C practically no changes in the spectrum have been noted, except for insignificant alteration of chemical

Table 5
^{13}C-NMR shifts for bis(1,1-diphenylallenylidene)-octacarbonyltriiron in (ppm, δ), measured in $CDCl_3$ at r.t.

Allenylidene chains			Phenyl rings			Carbonyls
$=CPh_2$	$=C=$	$=CFe_2$	C_{IV}	*o,m*-CH	*p*-CH	C≡O
124.15	159.57	293.16	139.58	128.22	126.97	207.60
			139.73	128.68	127.74	209.72
				128.81		
				129.25		

The literature data are limited to the allenylidene chain: 124.3, 160.0, 293.2 (not assigned) [2].

shifts of carbons in the aromatic rings. Thus, the differentiation of diphenylallenylidene ligands was not observed in the above conditions, and these results indicate easy conformational transitions in the applied temperature range. Moreover, the consistency of spectral data for **I** [2] and **II** (this work) proves the formation of one final conformation detectable by NMR beyond the crystal network in solution.

The direct assignment of signals using the chemical shift values and intensities turned out to be satisfactory. All aromatic carbon signals appear in pairs of equal intensity, and the most intense four peaks are located in the typical region from 128.22 to 129.25 (resonances are given in ppm, δ) representing the *ortho* and *meta* CH carbon atoms in both nonequivalent phenyl substituents (the signals were not assigned to the rings in positions *anti* or *syn*). Next, two singlets of about 50% of the major intensity at 126.97 and 127.74 arise from the *para* CH carbons, whereas only about 6% of this intensity disclose two close resonances of the quaternary carbon atoms in the benzene rings (139.58 and 139.73). The signal at 124.15 was assigned to the $=CPh_2$ carbon in the allene chain. The shift calculated from increments [19] for analogous carbon in non-complexed 1,1-diphenylallene was 110.76; thus, moderate deshielding (-13) took place. Somewhat similar γ-Fe effect in $(\pi\text{-}C_5H_5)Fe(CO)_2\text{–}(\sigma\text{-}CH_2\text{–}CH{=}CH_2)$ was comparable (-18) [20]. It is known that the metal σ-bonded carbon atoms undergo strong downfield shift; hence, the signal at 293.16 can be assigned to the terminal =CFe(2)Fe(3) carbon.

The calculated chemical shift for the central carbon in 1,1-diphenylallene was 210.92; however, in π-complexes a strong diamagnetic upfield shift is generally observed [21] and this could explain the appearance of the =C= carbon signal at 159.88 ($+51$). This value is in good agreement with published upfield shifts for butadiene–tricarbonyliron which are ($+52$) for carbon atoms C-2 and C-3, whereas ($+76$) for C-1 and C-4.

4. Conclusions

Quantitative estimation of the deviations from symmetry for organic ligands in two *synperiplanar* and *synclinal* conformers of bis(1,1-diphenylallenylidene)-octacarbonyltriiron, expressed as distinct polymorphs in the crystalline state, has been accomplished by comparative analysis of differences in close contacts, repulsive forces and Hirshfeld charges, reflected between diphenylallenylidene ligands by the C_2 operation of symmetry, and by examination of RMSD values obtained by superimposition of these ligands.

Molecular structures of both conformers remain distinct after optimization of single molecules by DFT and their electronic energies are practically equal. The calculated barrier of simulated transition between both forms is low (10 kJ mol^{-1}), and this finding was confirmed by experimental ^{13}C-NMR investigation performed in solution at room temperature and at -70 °C. No differentiation of diphenylallenylidene ligands was observed in these conditions; moreover, the spectra of both conformers appeared identical.

It should be stressed that the conformational analysis presented should be recognized as approximate, especially in the case of DFT calculations, where the potential energy surface is relatively flat; thus, the results should be treated with caution. Nevertheless, in this study, the differences between the series of respective molecular properties and the resulting tendencies were regarded as important, rather than the absolute values. In general, the calculated features are in good agreement with experimental results.

One can conclude that for the investigated conformers compared in the solid state the quantitatively estimated deviations from symmetry for diphenylallenylidene ligands differ by arrangement but are much the same by values. Two distinct conformers are stabilized only in the crystal network, whereas in solution in the temperature range from 25 to -70 °C distortions observed in solids are not maintained and the fluxionality of the carbonyl–iron core is expressed by easy conformational transitions.

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