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Molecular properties of a bis(ketoiminato)-bis(tricarbonyliron) complex obtained by symmetric cleavage from acetophenone azine. Idealized symmetry in *anti* and *syn* isomers studied by X-ray diffraction, NMR and density functional theory

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Abstract

Distinct *anti* and *syn* isomers of the bis(μ_2-acetophenoniminato)-bis(tricarbonyliron) obtained from iron dodecacarbonyl and 1,4-dimethyl-1,4-diphenyl-2,3-diazabuta-1,3-diene by symmetric cleavage of the azine have been compared in terms of molecular deviations from symmetry. The study was carried out by the analysis of intra- and intermolecular close contacts in crystals, quantum chemical DFT calculations for the isolated molecules and by NMR in solution. In the crystalline state the intramolecular contacts and also the symmetry perturbations were more strongly expressed in the *syn* form as compared with *anti*, and the same relation was perceived in the DFT-optimized single molecules. However, in solution only symmetric conformations were observed for both isomers *anti* and *syn* by ^{1}H and ^{13}C NMR at room temperature and at −70°C.

Keywords: Iron complexes; Azines; Bis(tricarbonyliron); Structure; Symmetry; Close contacts; DFT calculations; NMR; Bis(μ_2-acetophenoniminato)-bis(tricarbonyliron)

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1. Introduction

In the reaction of iron dodecacarbonyl with ketazine $R^1R^2C{=}N-N{=}CR^1R^2$ system bis(μ_2-ketoiminato)-bis(tricarbonyliron) complexes are produced (schematic structure is shown in Fig. 1), formed by cleavage of the N–N bond. In contrast, in the complexation of similar benzaldazine system R(H)C=N–N=C(H)R, where R = Ph or *para*-substituted Ph, no cleavage of the molecule was observed, and the reaction proceeds with *ortho*-proton rearrangement to the azomethine carbon and the metallization of the phenyl ring [1,2].

In complexes obtained from ketazines (Fig. 1) the iron atoms form bridges between new chemically identical independent ligands, in which the C=N double bonds are not engaged in the complexation ([3], structure determination for $R^1 = R^2 = p\text{-}CH_3Ph$). In case when $R^1 \neq R^2$ structural isomers could be expected, but conformational selectivity has been reported for the complex when $R^1 = H$ and $R^2 = CH_3$, which was isolated only as isomer *syn* [4], however, this compound was not directly obtained from acetaldazine.

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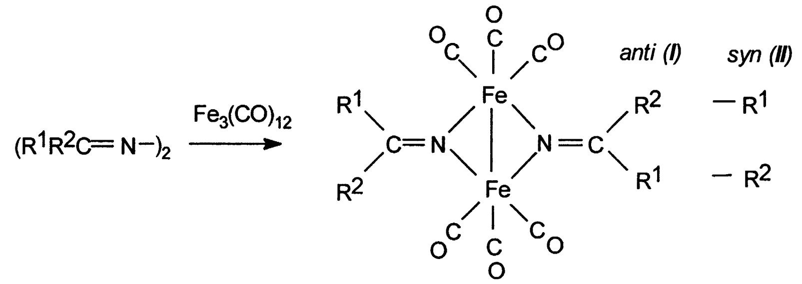

Fig. 1. Schematic structure of bis-iminato complexes obtained from azines in the reaction with iron dodecacarbonyl.

Nevertheless, from acetophenone azine where $R^1 = Ph$ and $R^2 = CH_3$, two distinct *anti* and *syn* structural isomers of the bis-ketoiminato complex were obtained by one of us [5], showing in the crystalline state deviations from symmetry different for each isomer.[1] For the form *anti*, a quasi-two-fold axis perpendicular to the Fe–Fe bond has been observed (C_2 symmetry point group), whereas the form *syn* shows a quasi-symmetry plane (C_s symmetry point group). The aim of the work presented was the quantitative estimation of deviations from symmetry in compared isomers, the analysis of close contacts, and the correlation of experimental and calculated molecular properties obtained by X-ray structural analysis and by DFT optimization, respectively. Furthermore, it was taken into consideration that the deviations from symmetry could be maintained in solutions, and this was examined by NMR.

2. Experimental and methods

Abbreviations used: NMR, nuclear magnetic resonance; d-chloroform, deuterated chloroform; X-ray, crystallographic structural analysis; 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; vdW, van der Waals; L–J, Lennard–Jones; rt, room temperature.

Complexation reactions with iron dodecacarbonyl were carried out according to published methods. 1,4-Dimethyl-1,4-diphenyl-2,3-diazabuta-1,3-diene (synthesis described in Ref. [6]) (1 mmol) and triiron-dodecacarbonyl (3 mmol) were refluxed in isooctane under nitrogen, chromatographed on Kieselgel 60 and recrystallized from *n*-hexane [7]. The separation of *anti* and *syn* isomers of the bis-ketoiminato complex was accomplished by fractional recrystallization also from *n*-hexane. The reagents used were pure and have been purchased from Aldrich.

The X-ray data were collected on a Siemens P3 four-circle diffractometer at rt. The detailed crystallographic data, parameters for data collection, refinement procedures and parameters of molecular structures of bis-ketoiminato *anti* **I** and *syn* **II** isomers are described in Ref. [5]. The structural parameters needed were acquired from the above X-ray data, 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 and 1.059 for C_{sp^3}–H in the methyl groups (in Å) [8].

The ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini BB 200 MHz instrument in d-chloroform.

The DFT calculations have been carried out by use of DMOL program [9]. BLYP functional [10,11] was used in all the calculations along with DNP basis. Electron density was analyzed by using Hirshfeld charges [12]. The optimized structures and calculated parameters are marked by asterisks (*).

RMSD values were calculated for superimposed symmetrical moieties using standard equation [13]

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

where the superimposition is aimed at aligning N

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[1] Deviations from symmetry have been also studied by us in conformers of bis(1,1-diphenylallenylidene)-octacarbonyltriiron obtained by symmetric cleavage from tetraphenylhexapentaene $Ph_2C{=}C{=}C{=}C{=}C{=}CPh_2$ (will be published separately).

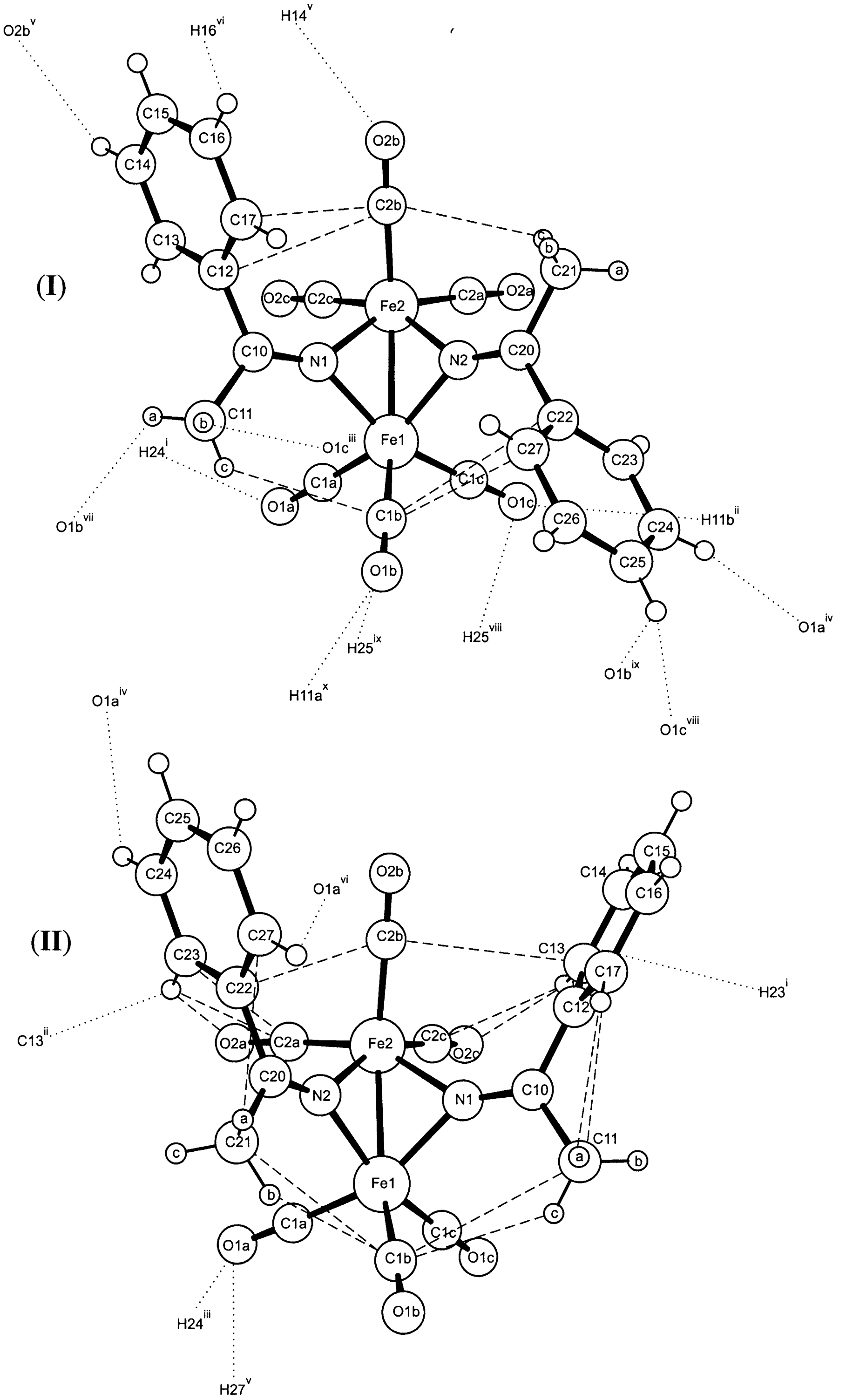

Fig. 2. View of the molecules **I** and **II** showing the atom numbering scheme. Close contacts are expressed as dashed and dotted lines, indicating intra- and intermolecular interactions, respectively. Symbols $^{i-x}$ distinguish external molecules.

atoms in two acetophenoniminato 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' reflected in the operation of symmetry (two-fold axis in **I** and symmetry plane in **II**) in the other ligand.

In the analysis of close contacts the van der Waals contact radii according to Bondi [14] have been accepted: (C) 1.70, (H) 1.20, (O) 1.52, (N) 1.55 (in Å). Distances between atoms separated by less than four bonds were neglected.

Van der Waals repulsive interactions have been approximated using Lennard–Jones (6–12) equation for nonbond potential E_{ij} [15]

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

where ϵ_{ij} is the potential well depth for pair of atoms i and j (equal to $\sqrt{\epsilon_{ii}\epsilon_{jj}}$), 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.

Parameters ϵ_{ii} and R_i for atoms C, N and O were taken directly from SYBYL force-field [16] (for these atoms SYBYL vdW radii are equal to Bondi's radii). For H atom parameter ϵ_H was also gained from SYBYL force-field whereas R_H 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 [17,18] based on accurate quantum mechanical calculations tend to lower its value down to the Bondi's standard.

3. Results and discussion

Intramolecular parameters taken into consideration in both *quasi*-symmetrical ligands have been reflected from one ligand to another according to the operation of symmetry appropriate to the geometry of each of compared isomers, i.e. two-fold axis was applied in **I** (*anti*) and a symmetry plane in **II** (*syn*), and the sum of the differences in values obtained in this manner for each isomer was analyzed. It should be stressed that the intra- and intermolecular contacts of the O···H type observed in isomers **I** and **II** cannot be classified as hydrogen bonds. Structures of **I** and **II** showing the atom numbering scheme are presented in Fig. 2.

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

The study has been accomplished by use of the structural X-ray data for **I** and **II** published earlier by one of us [5]. All positions of 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 experimental structures of compared isomers, the RMSD values have been calculated for superimposed molecular moieties in the appropriate operations of symmetry.

Respectively, for **I** and **II**, results for all atoms are 0.1774 and 0.3286, and in case when hydrogen atoms were omitted 0.1435 and 0.2228 (in Å). The values limited to the central region of the molecule, including carbonyliron moiety, C=N, methyl groups and quaternary aromatic carbons, are 0.0581 and 0.1022, accordingly. These results clearly point to lower symmetry of **II** with respect to **I**. Moreover, the RMSD values falling on one pair of atoms are nearly twice as high when all atoms are considered with respect to the data for the central region, i.e. 0.0341 and 0.0155 for **I**, whereas the values for **II** are 0.0632 and 0.0273, accordingly. Thus, as expected, the conformational irregularities are mainly placed in the peripheral areas of the molecule.

In the analysis of molecular spacing the contact was accepted as close when the interatomic distance was smaller than the sum of van der Waals radii according to Bondi [14] for the examined atoms (see Section 2 for details). Although there are no well-accepted values for atomic contact radii, the Bondi's values are acknowledged as one of the standards. 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 case when the difference between compared intramolecular distances in two ligands was smaller than the threefold 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 possibly are involved in the intramolecular contacts, such

Table 1

Intramolecular close contacts and respective repulsive forces for **I** and **II**. Atom numbering scheme is given in Fig. 2, respective locations in ligands 1 and 2 are reflected by molecular symmetry operations. Distances marked by ($*$) result from DFT-calculations.

Location in ligand 1	Distance $D1$ (Å) from X-ray	Force $F1$ (kJ/mol Å)	Distance $D1^*$ (Å) calc.	Location in ligand 2	Distance $D2$ (Å) from X-ray	Force $F2$ (kJ/mol Å)	Distance $D2^*$ (Å) calc.	$\lvert D1^* - D2^* \rvert$ (Å) calc.	$\lvert D1 - D2 \rvert$ (Å)	$\lvert F1 - F2 \rvert$ (kJ/mol Å)
I										
C(1b)–C(27)	3.269 (12)	0.553	3.332	C(2b)–C(17)	3.346 (17)	0.178	3.416	0.084	0.077	0.375
C(1b)–C(22)	3.355 (3)	0.144	3.415	C(2b)–C(12)	3.285 (22)	0.461	3.356	0.059	0.070	0.317
C(2b)–H(21c)	2.697 (35)	Omitted[a]	2.745	C(1b)–H(11c)	2.698 (32)	Omitted[a]	2.704	–	–	–
								$\sum \lvert D1^* - D2^* \rvert = 0.143$	$\sum \lvert D1 - D2 \rvert = 0.147$	$\sum \lvert F1 - F2 \rvert = 0.692$
II										
C(1b)–C(21)	3.379 (4)	0.062	3.449	C(1b)–C(11)	3.305 (4)	0.358	3.422	0.027	0.074	0.296
C(1b)–H(21b)	2.472 (20)	5.706	2.537	C(1b)–H(11c)	2.558 (30)	3.139	2.672	0.135	0.086	2.567
C(2a)–C(23)	3.330 (4)	0.243	3.412	C(2c)–C(13)	3.431 (4)	No repulsion[b]	3.481	0.069	0.101	0.243
C(2a)–H(23)	2.710 (30)	0.936	2.792	C(2c)–H(13)	2.566 (30)	2.964	2.639	0.153	0.144	2.028
C(2b)–C(22)	3.238 (4)	0.757	3.351	C(2b)–C(12)	3.407 (4)	No repulsion[b]	3.493	0.142	0.169	0.757
C(2b)–C(23)	3.437 (4)	No repulsion[b]	3.521	C(2b)–C(13)	3.290 (4)	0.434	3.354	0.167	0.147	0.434
C(21)–H(27)	3.088 (30)	No repulsion[b]	3.127	C(11)–H(17)	2.826 (30)	0.234	2.835	0.292	0.262	0.234
H(27)–H(21a)	2.519 (40)	No repulsion[b]	2.551	H(17)–H(11a)	2.341 (40)	0.166	2.328	0.223	0.178	0.166
O(2a)–H(23)	2.667 (30)	Omitted[a]	2.770	O(2c)–H(13)	2.708 (30)	Omitted[a]	2.752	–	–	–
C(27)–H(21a)	2.881 (30)	Omitted[a]	2.917	C(17)–H(11a)	2.928 (30)	Omitted[a,b]	2.938	–	–	–
								$\sum \lvert D1^* - D2^* \rvert = 1.208$	$\sum \lvert D1 - D2 \rvert = 1.161$	$\sum \lvert F1 - F2 \rvert = 6.725$

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

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

interactions were neglected because the vdW radii of six-coordinated iron atoms are not determined. Intramolecular short distances for both isomers meeting above requirements are listed in Table 1.

In the present analysis not only distances expressing close contacts have been considered but also the resulting repulsive forces were calculated according to the L–J potential [15]. 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 as zero.

In **I** only two pairs of symmetrically arranged close intramolecular contacts were considered, located between carbonyl groups and adjacent phenyl rings (Fig. 2). Carbonyl carbon atoms and also the quaternary and *ortho* aromatic carbons are engaged into this interactions. In contrast, in the molecule of **II** altogether 14 interactions were noted, situated between following groups: carbonyl–methyl, carbonyl–phenyl and methyl–phenyl. Involved are carbon atoms from carbonyls located between the phenyl rings or between the methyl groups, quaternary carbon of the phenyl ring, protons and carbons in positions *ortho*, and also protons and carbons of the methyl substituents. As shown in Table 1, where all contacts are specified, the sum of differences (absolute values) between accordingly located analyzed distances $\sum|D1 - D2|$ is 0.147 in **I**, whereas in **II** it increases by nearly an order of magnitude to 1.161 (inÅ).

More adequate extent of steric crowding than only close contacts are the resulting repulsive forces (Table 1). Outstanding strong interactions of this type were noted in **II** between the following atoms: C(1b)–H(11c), C(1b)–H(21b) and C(2c)–H(13). The absolute values of differences of respective forces localized in both ligands were summarized giving $\sum|F1 - F2|$ 0.692 in **I**, whereas in **II** the result was 10-fold as high reaching 6.725 (in kJ/mol Å). Similar difference was observed for close contacts. The noted inequality in distribution of internal stresses in **II** could be considered as one of the possible reasons of deviations from symmetry.

In the dislocation of intermolecular close contacts, as expected, no symmetry was observed, thus, the calculated repulsive forces were summarized separately for each moiety, including acetophenoniminato ligand and the carbonyl groups, reflected by appropriate operation of symmetry, and excluding the chain O(1b)–C(1b)–Fe(1)–Fe(2)–C(2b)–O(2b) parting the molecule (results are shown in Table 2). In rough estimation, these values can be assumed as the extent of deformation of each ligand caused by external repulsions. For **I** the results for moieties 1 and 2 are as follows (quantities representing intermolecular interactions are marked by primes): $\sum F1'$ 3.306 (five contacts), $\sum F2'$ 1.660 (five contacts) and the difference $|\sum F1' - \sum F2'|$ is 1.646 (in kJ/mol Å). The respective values for **II** are: $\sum F1'$ 0.597 (five contacts), $\sum F2'$ 0.017 (one contact), and $|\sum F1' - \sum F2'|$ is 0.580. Thus, the external repulsive forces are definitely more strongly expressed in **I** as compared with **II** and also the difference in strength of deforming interactions acting on each moiety is considerably higher in **I**.

Based on the above results one can conclude that from among repulsive interactions rather the intramolecular repulsions than the network stresses contribute to higher deviations from symmetry, observed in the molecule of **II** as compared with **I**.

3.2. DFT calculations

Full geometry optimization by the DFT method has been performed in order to compare the electronic energies for the isolated molecules of isomers **I** and **II** and to note the differences between experimental and theoretical conformations, which to some extent could arise from the absence of the network intermolecular contacts in the calculated structures. To start conformations those known from the X-ray analysis were used [5].

The energies for $\mathbf{I}^*$ and $\mathbf{II}^*$ (symbols related to the calculated quantities are marked by asterisks) are practically equal, differing by 3.8 kJ/mol. As effect of optimization no substantial changes in the overall molecular geometry of **I** and **II** have been observed (selected bond lengths, valence and dihedral angles of experimental and theoretical structures are compared in Table 3). Contrarily, only limited modifications in conformations were noted, e.g. after mathematical superimposition of the structures determined by X-ray and the calculated ones the positions of

Table 2
Intermolecular and respective intermolecular repulsive forces for **I** and **II**. The O–H distances are given with maximal errors of 0.04 Å. Close contacts were analyzed separately for each quasi-symmetric moiety of the molecule exclusive of interactions with atoms O(1b)–C(1b)–Fe(1)–Fe(2)–C(2b)–O(2b) laying on an idealized symmetry plane in **II** and with respective atoms in **I**. (Following contacts in **I** were excluded: O(1b)–H(11a)^{x}, 2.714; O(1b)–H(25)^{ix}, 2.715; O(2b)–H(14)^{v}, 2.663 (in Å). No intermolecular contacts with atoms laying on symmetry plane were found in **II**.) Symbols $^{i-x}$ distinguish external molecules.

Locations in moiety 1	Dist. (Å) from X-ray	Forces $F1'$ (kJ/mol Å)	Locations in moiety 2	Dist. (Å) from X-ray	Forces $F2'$ (kJ/mol Å)
I					
O(1a)–H(24)^{i}	2.550	0.958	O(1c)–H(11b)^{ii}	2.582	0.681
H(11a)–O(1b)^{vii}	2.714	0.018	O(1c)–H(25)^{viii}	2.719	0.003
H(11b)–O(1c)^{iii}	2.582	0.681	H(24)–O(1a)^{iv}	2.550	0.958
H(14)–O(2b)^{v}	2.663	0.203	H(25)–O(1b)^{iv}	2.715	0.015
H(16)–H(16)^{vi}	2.172	1.446	H(25)–O(1c)^{viii}	2.719	0.003
		$\sum F1' = 3.306$			$\sum F2' = 1.660$
					$\lvert\sum F1' - \sum F2'\rvert = 1.646$
II					
O(1a)–H(24)^{iii}	2.649	0.267	C(13)–H(23)^{i}	2.893	0.017
O(1a)–H(27)^{v}	2.712	0.023			
H(23)–C(13)^{ii}	2.893	0.017			
H(24)–O(1a)^{iv}	2.649	0.267			
H(27)–O(1a)^{vi}	2.712	0.023			
		$\sum F1' = 0.597$			$\sum F2' = 0.017$
					$\lvert\sum F1' - \sum F2'\rvert = 0.580$

Table 3
Selected bond lengths (Å), valence and dihedral angles (°). Experimental data (X-ray [5]) are given for **I** and **II**, theoretical for **I*** and **II***. The DFT-optimized structures are marked by ($*$)

	I	**I***	**II**	**II***
Bond lengths				
Fe(1)–Fe(2)	2.4137 (7)	2.5014	2.3990 (6)	2.4810
Fe(1)–C(1a)	1.784 (3)	1.812	1.790 (3)	1.814
Fe(1)–C(1b)	1.805 (3)	1.813	1.804 (3)	1.809
Fe(1)–C(1c)	1.780 (3)	1.818	1.786 (3)	1.815
Fe(2)–C(2a)	1.784 (3)	1.814	1.783 (3)	1.809
Fe(2)–C(2b)	1.800 (3)	1.817	1.828 (3)	1.818
Fe(2)–C(2c)	1.791 (4)	1.818	1.778 (3)	1.807
Fe(1)–N(1)	1.918 (2)	1.962	1.924 (2)	1.989
Fe(1)–N(2)	1.925 (2)	1.984	2.919 (2)	1.978
Fe(2)–N(1)	1.918 (2)	1.976	1.924 (2)	1.982
Fe(2)–N(2)	1.915 (2)	1.961	1.925 (2)	1.974
N(1)–C(10)	1.256 (3)	1.282	1.263 (3)	1.287
N(2)–C(20)	1.256 (3)	1.282	1.254 (3)	1.285
C(10)–C(11)	1.500 (3)	1.517	1.501 (3)	1.523
C(10)–C(12)	1.489 (3)	1.505	1.491 (3)	1.505
C(20)–C(21)	1.503 (4)	1.517	1.499 (3)	1.520
C(20)–C(22)	1.491 (3)	1.504	1.491 (3)	1.507
Bond angles				
N(1)–Fe(1)–N(2)	76.48 (8)	75.93	76.23 (8)	75.63
N(1)–Fe(2)–N(2)	76.71 (7)	76.16	76.10 (8)	75.87
N(1)–Fe(1)–Fe(2)	51.01 (5)	50.80	51.42 (5)	51.21
N(2)–Fe(1)–Fe(2)	50.88 (5)	50.24	51.50 (5)	51.05
N(1)–Fe(2)–Fe(1)	51.02 (5)	50.32	51.44 (5)	51.47
N(2)–Fe(2)–Fe(1)	51.23 (5)	51.07	51.28 (5)	51.18
Fe(1)–N(1)–Fe(2)	77.98 (7)	78.88	77.14 (7)	77.38
Fe(1)–N(2)–Fe(2)	77.89 (7)	78.69	77.22 (7)	77.76
C(10)–N(1)–Fe(1)	141.6 (2)	141.2	139.2 (2)	139.5
C(10)–N(1)–Fe(2)	140.4 (2)	139.9	143.3 (2)	142.9
C(20)–N(2)–Fe(1)	140.4 (2)	140.0	142.4 (2)	141.6
C(20)–N(2)–Fe(2)	141.6 (2)	141.2	140.3 (2)	140.6
N(1)–C(10)–C(11)	122.7 (2)	123.2	121.3 (2)	121.9
N(1)–C(10)–C(12)	120.8 (2)	120.5	122.3 (2)	122.8
C(11)–C(10)–C(12)	116.5 (2)	116.3	116.5 (2)	115.3
N(2)–C(20)–C(21)	122.5 (3)	123.4	122.7 (2)	122.8
N(2)–C(20)–C(22)	120.9 (2)	120.4	121.1 (2)	121.3
C(21)–C(20)–C(22)	116.5 (2)	116.3	116.2 (2)	115.9
C(1)–Fe(1)–Fe(2)–C(2)[a]	0.6 (2)	0.5	0.8 (2)	0.5
N(1)–C(10)–C(12)–C(17)	− 85.6 (2)	− 86.4	128.2 (3)	128.1
N(2)–C(20)–C(22)–C(27)	− 81.2 (3)	− 83.4	− 112.0 (3)	− 113.3

[a] Average calculated from sum of absolute values of dihedral angles defined by the carbonyls in facing (*syn*-periplanar) locations.

according atoms in the central core nearly overlapped. Thus, for isomer *anti* the angle between the bonds (Fe–CO) and respective (Fe–CO)* was 0.9° (average for three results), whereas analogous value for the isomer *syn* was 2.1°. Similarly, the difference between experimental and calculated dihedral angles C(11)–C(10)–C(12)–C(13) (for numbering of atoms see Fig. 2) was 0.2° for *anti*, and 0.6° for *syn*.

The RMSD values, reflecting well the extent of deviations from symmetry, were calculated for the optimized molecules. Results for isomer *anti* and *syn* are, respectively, as follows (for comparison, in

Table 4
Comparison of Hirshfeld charges (in e) for pairs of atoms defined by the operations of symmetry in optimized isomers $\mathbf{I}^*$ and $\mathbf{II}^*$. Charges on atoms O(1b)–C(1b)–Fe(1)–Fe(2)–C(2b)–O(2b) laying on an idealized symmetry plane in $\mathbf{II}^*$ and respective atoms in $\mathbf{I}^*$ were omitted

Pairs of atoms	Charges in $\mathbf{I}^*$		$\|\Delta\|_{(\mathbf{I}^*)}$	Charges in $\mathbf{II}^*$		$\|\Delta\|_{(\mathbf{I}^*)}$
N(1–2)	−0.1251	−0.1253	0.0002	−0.1263	−0.1256	0.0007
C(1a–2a)	0.0978	0.0979	0.0001			
O(1a–2a)	−0.1112	−0.1110	0.0002			
C(1c–2c)	0.0999	0.1000	0.0001			
O(1c–2c)	−0.1078	−0.1081	0.0003			
C(1a–1c)				0.0995	0.0991	0.0004
O(1a–1c)				−0.1090	−0.1094	0.0004
C(2a–2c)				0.0991	0.1002	0.0011
O(2a–2c)				−0.1080	−0.1088	0.0008
C(10–20)	0.0850	0.0848	0.0002	0.0848	0.0858	0.0010
C(11–21)	−0.0949	−0.0949	0.0000	−0.0961	−0.0949	0.0012
C(12–22)	0.0000	0.0001	0.0001	0.0004	0.0003	0.0001
C(13–23)	−0.0412	−0.0406	0.0006	−0.0372	−0.0386	0.0014
H(13–23)	0.0434	0.0440	0.0006	0.0364	0.0387	0.0023
C(14–24)	−0.0377	−0.0377	0.0000	−0.0357	−0.0363	0.0006
H(14–24)	0.0466	0.0466	0.0000	0.0493	0.0487	0.0006
C(15–25)	−0.0385	−0.0379	0.0006	−0.0365	−0.0366	0.0001
H(15–25)	0.0473	0.0476	0.0003	0.0476	0.0476	0.0000
C(16–26)	−0.0373	−0.0368	0.0005	−0.0393	−0.0376	0.0017
H(16–26)	0.0475	0.0479	0.0004	0.0461	0.0469	0.0008
C(17–27)	−0.0392	0.0391	0.0001	−0.0393	−0.0388	0.0005
H(17–27)	0.0456	0.0451	0.0005	0.0426	0.0445	0.0019
H(11a–21a)				0.0475	0.0511	0.0036
H(11b–21c)				0.0471	0.0461	0.0010
H(11c–21b)				0.0381	0.0351	0.0030
H(11b–21b)	0.0485	0.0496	0.0011			
H(11a–21a)	0.0492	0.0478	0.0014			
H(11c–21c)	0.0382	0.0394	0.0012			
			$\sum \|\Delta\|_{(\mathbf{I}^*)}$ $= 0.0085$			$\sum \|\Delta\|_{(\mathbf{II}^*)}$ $= 0.0232$

brackets the appropriate RMSD values for X-ray experimentally determined structures are given): for all atoms 0.1712^* (0.1774) and 0.3235^* (0.3286); after excluding the hydrogen atoms 0.1411^* (0.1435) and 0.2087^* (0.2228); and for the central region including $Fe_2(CO)_6$, C=N, CH_3 and aromatic C_{IV} carbons 0.0604^* (0.0581) and 0.0703^* (0.1022) (in Å). These results confirm, that the symmerization of the molecule as a result of optimization was observed neither for *anti* nor for *syn*, moreover, the magnitude of the deviations from symmetry remained practically unchanged after calculations. In fact, the lower symmetry of **II** as compared with **I** was maintained in the optimized isolated molecule. In both experimental and calculated structures the conformational irregularities are mainly placed in the peripheral molecular regions.

Furthermore, the results related to calculated and experimental short contacts, given by expressions $\sum|D1^* - D2^*|$ and $\sum|D1 - D2|$ (data is given in Table 1, explanations of symbols see pt. 1.3.) are 0.143^* and 0.147 for *anti*, respectively, and 1.208^* and 1.161 for *syn*. In general, most of the close contacts observed by X-ray maintained after optimization their shorter distances than the sum of vdW radii, although elongation also has been noted (Table 1). Since the calculations have been accomplished for isolated molecules, these results confirm the earlier statement that the contribution of intramolecular repulsions to the observed deviations from symmetry is more significant as compared with intermolecular forces.

Quasi-symmetrical ligands might be also compared in terms of charges localized on respective atoms.

Table 5
NMR shifts (in ppm, δ, spectra taken in d-chloroform) for **I** and **II** at different temperatures. Sharp singlets have been observed, unless otherwise noted

Isomer/nuclei	CH$_3$		Aromatic CH		Aromatic C$_{IV}$		C=N	
I/^{13}C	32.87[a]	33.30[b]	125.59[a] 128.41[a]	125.30[b] 128.32[b]	145.65[a]	144.96[b]	177.32[a]	176.68[b]
I/^{1}H	2.40[a]	2.38[b]	Multiplet	Multiplet				
II/^{13}C	32.83[a]	33.22[b]	125.32[a] 128.30[a] 128.41[a]	125.82[b] 128.32[b] 128.32[b]	145.77[a]	145.25[b]	177.69[a]	177.42[b]
II/^{1}H	2.50[a]	2.46[b]	Multiplet	Multiplet				

[a] At 25°C.
[b] At −70°C.

Hirshfeld charges calculated for **I*** and **II*** are collected in Table 4 (atoms laying on the idealized mirror plane of isomer *syn* and respective atoms in *anti* were omitted). The absolute values of differences in charges for atoms reflected in appropriate operation of symmetry were summarized, giving 0.0085 for *anti* and 0.0232 (in e) for *syn*, what points on perceptibly less regular dislocation of electron density in the isomer *syn*. The differences in respective charges also testify a relevant perturbations in symmetry in the regions of methyl groups in both isomers, and around the *ortho* positions in the phenyl rings in isomer *syn*.

3.3. NMR investigation

Considering results obtained in the analysis of close contacts an attempt to distinguish the ketoiminato ligands by the NMR techniques in solution seemed promising, especially regarding to more spatially crowded isomer *syn*. As observed earlier [5], the methyl groups of isomers **I** and **II** give at room temperature in ^{1}H NMR sharp singlets at 2.40 and 2.50 ppm, respectively, thus, no differentiation of ligands was noted.

In this work the ^{13}C resonances of the methyl groups at rt were obtained at 32.87 and 32.83 ppm for **I** and **II**, accordingly. Furthermore, the low-temperature ^{1}H and ^{13}C NMR study was performed at −70°C, but neither the splitting nor broadening of the signals occurred, and the chemical shifts remained nearly unchanged (the data is given in Table 5).

According to the NMR analysis, both isomers **I** and **II** generally preserved high symmetry in solution, although the multiplets of aromatic protons were not regular in the spectra of both compounds. The simplification of the sequence of aromatic carbon signals was higher in **I** as compared with **II**, but in general no spectral differentiation of ketoiminato ligands was observed in both isomers. One can conclude, that in the range of temperature from 25 to −70°C fast conformational transitions resulted in symmetrization of ligands and this was perceived in both isomers *anti* and *syn*.

4. Conclusions

From among the two structural isomers of bis(μ_2-acetophenoniminato)-bis(tricarbonyliron), the *syn* form discloses in the solid state definitely higher deviations from symmetry, as observed in comparison with several experimental and calculated molecular parameters. Moreover, in *syn* the repulsing forces originating from intramolecular close contacts are substantially higher and their distribution in related ligands is less symmetric, whereas the intermolecular repulsions are generally weaker in *syn* and also the difference in their strength regarding each quasi-symmetric part of the molecule is lower with respect to *anti*. Thus, it might be supposed that the intramolecular repulsive interactions contribute more to the deviations from symmetry in investigated isomers with reference to similar intermolecular effects.

The latter assumption was confirmed by the DFT-optimization of the isolated molecules. The overall conformations of theoretical and X-ray crystal structures remained analogous and also the deviations from symmetry were in general maintained in both isomers. These differences could be quantitatively estimated by root mean square displacement method and also by comparison of calculated Hirshfeld charges in both twin-ligands. Despite of higher steric crowding in *syn* the calculated energies of both isomers are practically equal, which allows the conclusion that the intramolecular repulsing forces are generally weak.

An approach to distinguish the quasi-symmetric ketoiminato ligands have been accomplished by ^{1}H and ^{13}C NMR in solution at room temperature and also at −70°C, but the differentiation could be observed neither in *anti* nor in *syn*, thus, a perfect molecular symmetrization of each isomer proceeds as effect of fast conformational transitions, taking place also in *syn* despite the close molecular packing.

Conclusion can be made that in the studied complex the deviations from symmetry originating primarily from the intramolecular interactions are stabilized by the network in solids and can also be analyzed by quantum chemical calculations. Moreover, the conformational analogy of structures determined experimentally and optimized validates the adequacy of the DFT method for structural analysis of this type of organoiron compounds.

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