

Structural studies of bis(μ_2 -acetophenoniminato)-bis(tricarbonyliron) by NMR and X-ray diffraction: deviations from symmetry in *anti* and *syn* isomers

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Abstract

Two distinct structural isomers obtained in the reaction of 1,4-dimethyl-1,4-diphenyl-2,3-diazabuta-1,3-diene ($(\text{CH}_3)_2(\text{Ph})_2\text{C}=\text{N}-$)₂ with triiron dodecacarbonyl were separated, characterized by NMR, and their molecular structures were determined by X-ray diffraction. Only idealized symmetry in both resolved *anti* and *syn* forms have been observed. Geometry analysis indicated in the *syn* form a substantial deviation from symmetry, especially in the peripheral region of the molecule. This deviation is preserved in solution, as demonstrated by ¹³C NMR.

Keywords: Iron complexes; Azines; Bis(tricarbonyl iron); Crystal structure; NMR; Bis(μ_2 -acetophenoniminato)-bis(tricarbonyliron)

1. Introduction

In the reaction of azines $(\text{R}^1\text{R}^2\text{C}=\text{N}-)$ ₂ with triiron dodecacarbonyl, complexes of the general formula $(\text{R}^1\text{R}^2\text{CN})_2\text{Fe}_2(\text{CO})_6$ have been obtained. A similar reaction with iron pentacarbonyl was described for 4,4'-dimethylbenzophenone azine [1]. When aldazines were used as substrates ($\text{R}^1 = \text{phenyl}$ or *p*-substituted phenyl; $\text{R}^2 = \text{H}$), deep red products were isolated, which could not be separated into isomers [2,3]. Complexes of ketazines have been described as orange compounds, substituted as follows: $\text{R}^1 = \text{R}^2 = p\text{-CH}_3\text{Ph}$ ([1], determination of structure) and $\text{R}^1 = \text{R}^2 = \text{CH}_3$ [4]. In the present work, a complex of this type with $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{CH}_3$ is reported for the first time in the form of two structural isomers.

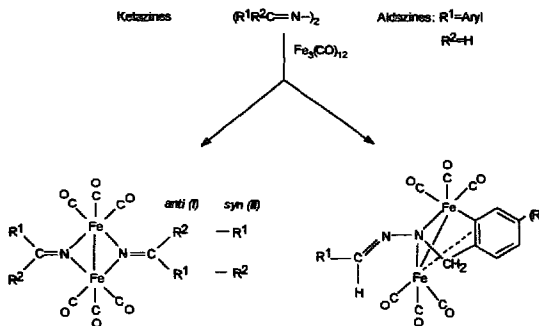
Thus, the type of substitution on the azine system is critical for the path of complexation. As found by us, ketazines and aldazines substituted by phenyl groups

yield complexes of the same composition but different structure. In the case of ketazines, the central N–N bond is cleaved and derivatives showing known di- μ -iminato structure occur [1] (Scheme 1).

In phenyl-substituted aldazines ($p\text{-RPhCH}=\text{N}-$)₂ ($\text{R} = \text{H, F, CH}_3, \text{OCH}_3$), according to our preliminary X-ray results (for $\text{R} = \text{CH}_3$), the backbone of the molecule remains intact. The reaction occurs with *ortho*-proton rearrangement to the azomethine carbon and the metallization of the phenyl ring; this structure resembles those found for complexes obtained from Schiff bases and diiron enneacarbonyl [5]. Our results demonstrate that, in the case of benzaldazines, only one of the nitrogen atoms is bonded to both irons, whereas the other $p\text{-RPhCH}=\text{N}-$ moiety remains unengaged in the complexation¹ (Scheme 1). In contrast, a complex of an aliphatic aldazine $(\text{CH}_3\text{CHN})_2\text{Fe}_2(\text{CO})_6$ has been reported as a typical di- μ -iminato system occurring in the *syn* form only [6]. A complex of a different substi-

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¹ Will be published separately.

Scheme 1. Complexation reactions of $Fe_3(CO)_{12}$ with ketazines and aldazines.

tuted aliphatic aldazine $[CH_3CH_2CHN]_2 \cdot Fe_2(CO)_6$ was formerly obtained by one of us [2].

2. Results and discussion

In a reaction of acetophenone azine $\{(CH_3)(Ph)C=N\}_2$ with triiron dodecacarbonyl, a yellow complex was obtained in good yield which could be separated chromatographically into two isomers (I and II) according to Ref. [7]. In the work described in the present paper, the structure of these isomeric complexation products was studied by NMR and by single crystal X-ray diffraction. According to the structure described for the benzophenone system [1], it was theoretically possible that both *anti* and *syn* forms of the bis(μ_2 -acetophenoniminato)-bis(tricarbonyliron) would be obtained. However, the possibility of a conformational selectivity for this type of complexation product has been reported previously [6].

2.1. Discussion of the NMR data

In 1H NMR, the analysis confirmed the conformational homogeneity of the starting azine. The methyl groups gave one sharp singlet at 2.32 ppm. In the spec-

Table 1
 ^{13}C NMR shifts for complexes obtained from acetophenone azine in parts per million (δ), measured in $CDCl_3$

Isomer	$CH_3C=N$	Aromatic CH	Aromatic C_{IV}	$C=N$
I <i>anti</i>	32.87	125.59 128.41	145.65	177.32
II <i>syn</i>	32.83	125.32 128.30 128.41	145.77	177.69

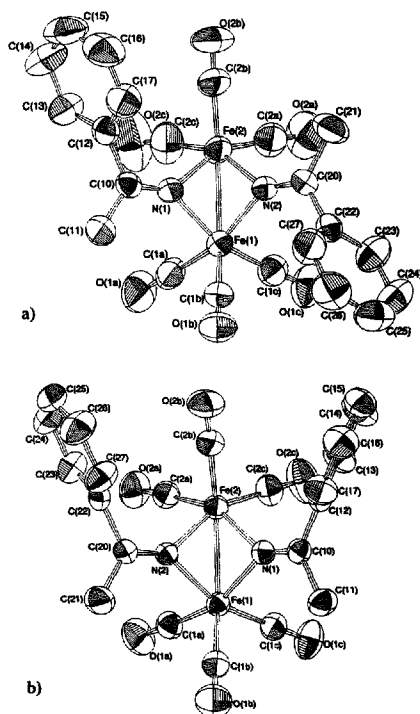


Fig. 1. ORTEP diagram of (a) *anti* and (b) *syn* isomers of $\{(CH_3)(Ph)CN\}_2Fe_3(CO)_6$, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

tra of complexes I and II the methyl groups appeared as sharp singlets at 2.40 and 2.50 ppm respectively. These results could signify a high symmetry of both isomeric molecules. However, the multiplets in the aromatic region were not regular for both I and II, and no distinct differentiation in symmetry could be assumed.

The ^{13}C NMR spectra (listed in Table 1) confirm the general symmetric structure for both isomers, although in the aromatic CH region three signals are observed for II, and only two signals for I. This rather indicates the possibility of perturbation in symmetry of the phenyl ring area in II compared with I, although a simple coincidence of resonances in I cannot be excluded.

2.2. Molecular structure

As found by X-ray crystallographic studies, the weak N–N bond in acetophenone azine is cleaved during the complexation and two iron atoms are incorporated into

the center of the molecule forming equivalent bridges between new independent and identical ligands, in analogy to 4,4'-dimethylbenzophenone azine described in Ref. [1]. Two possible conformations at the C=N double bond give rise to two isomeric forms: *anti* (I) and *syn* (II). Molecular structures of I and II are shown in Fig. 1, and selected bond lengths and angles are listed in Table 2. To illustrate the structural differences between isomers, least-squares planes passing through selected groups of atoms have been defined and the respective dihedral angles have been calculated (discussion in the text).

The nitrogen and iron atoms form an almost symmetric tetrahedron, typical for this type of compound. Also, in the case where the nitrogens show sp^3 hybridization, the same symmetry of the core $\text{Fe}_2(\text{CO})_6\text{N}_2$ occurs [8]. The geometry observed by us for I and II is in agreement with the literature data [6,8]. In both isomers I and II the N–Fe bonds show full equivalency, are of σ

Table 2
Selected interatomic distances (Å) and bond angles [°] for I and II

I		II	
Fe(1) – Fe(2)	2.4137(7)	Fe(1) – Fe(2)	2.3990(6)
Fe(1) – C(1A)	1.784(3)	Fe(1) – C(1A)	1.790(3)
Fe(1) – C(1B)	1.805(3)	Fe(1) – C(1B)	1.804(3)
Fe(1) – C(1C)	1.780(3)	Fe(1) – C(1C)	1.786(3)
Fe(2) – C(2A)	1.784(3)	Fe(2) – C(2A)	1.783(3)
Fe(2) – C(2B)	1.800(3)	Fe(2) – C(2B)	1.828(3)
Fe(2) – C(2C)	1.791(4)	Fe(2) – C(2C)	1.778(3)
Fe(1) – N(1)	1.918(2)	Fe(1) – N(1)	1.924(2)
Fe(1) – N(2)	1.925(2)	Fe(1) – N(2)	1.919(2)
Fe(2) – N(1)	1.918(2)	Fe(2) – N(1)	1.924(2)
Fe(2) – N(2)	1.915(2)	Fe(2) – N(2)	1.925(2)
N(1) – C(10)	1.256(3)	N(1) – C(10)	1.263(3)
N(2) – C(20)	1.256(3)	N(2) – C(20)	1.254(3)
C(10) – C(11)	1.500(3)	C(10) – C(11)	1.501(3)
C(10) – C(12)	1.489(3)	C(10) – C(12)	1.491(3)
C(20) – C(21)	1.503(4)	C(20) – C(21)	1.499(3)
C(20) – C(22)	1.491(3)	C(20) – C(22)	1.491(3)
N(1) – Fe(1) – N(2)	76.48(8)	N(1) – Fe(1) – N(2)	76.23(8)
N(1) – Fe(2) – N(2)	76.71(7)	N(1) – Fe(2) – N(2)	76.10(8)
N(1) – Fe(1) – Fe(2)	51.01(5)	N(1) – Fe(1) – Fe(2)	51.42(5)
N(2) – Fe(1) – Fe(2)	50.88(5)	N(2) – Fe(1) – Fe(2)	51.50(5)
N(1) – Fe(2) – Fe(1)	51.02(5)	N(1) – Fe(2) – Fe(1)	51.44(5)
N(2) – Fe(2) – Fe(1)	51.23(5)	N(2) – Fe(2) – Fe(1)	51.28(5)
Fe(1) – N(1) – Fe(2)	77.98(7)	Fe(1) – N(1) – Fe(2)	77.14(7)
Fe(1) – N(2) – Fe(2)	77.89(7)	Fe(1) – N(2) – Fe(2)	77.22(7)
C(10) – N(1) – Fe(1)	141.6(2)	C(10) – N(1) – Fe(1)	139.2(2)
C(10) – N(1) – Fe(2)	140.4(2)	C(10) – N(1) – Fe(2)	143.3(2)
C(20) – N(2) – Fe(1)	140.4(2)	C(20) – N(2) – Fe(1)	142.4(2)
C(20) – N(2) – Fe(2)	141.6(2)	C(20) – N(2) – Fe(2)	140.3(2)
N(1) – C(10) – C(11)	122.7(2)	N(1) – C(10) – C(11)	121.3(2)
N(1) – C(10) – C(12)	120.8(2)	N(1) – C(10) – C(12)	122.3(2)
C(11) – C(10) – C(12)	116.5(2)	C(11) – C(10) – C(12)	116.5(2)
N(2) – C(20) – C(21)	122.5(3)	N(2) – C(20) – C(21)	122.7(2)
N(2) – C(20) – C(22)	120.9(2)	N(2) – C(20) – C(22)	121.1(2)
C(21) – C(20) – C(22)	116.5(2)	C(21) – C(20) – C(22)	116.2(2)

type, and deviate only slightly from the mean value of 1.92 Å. The distance of 2.38 Å between nitrogen atoms rules out the existence of the bond. The iron atoms are linked and the lengths of the bonds are 2.4137(7) and 2.3990(6) Å respectively for I and II. The dihedral angle between planes Fe(1)Fe(2)N(1) and Fe(1)Fe(2)N(2) is 74.29(8)° and 75.80(6)° for *anti* and *syn* respectively. The atoms of the double bonds C₃C=N are located approximately in the planes of the heterocyclic three-membered rings Fe(1)Fe(2)N. Some distortion of the plane defined by the Fe(1)Fe(2)N atoms with respect to the above-mentioned N=CC₂ planes has been observed. The dihedral angles between these planes are 4.9(2)° and 2.9(1)° for the isomer *anti*, and 5.2(2)° and 1.9(2)° for *syn*. The π orbitals of the double bonds C(10)=N(1) and C(20)=N(2) are not engaged in the binding of iron; the lengths of these bonds are 1.256(3), 1.256(3) Å for I and 1.263(3), 1.254(3) Å for II. The central core Fe₂(N=C)₂ in both isomers is almost identical. Significant structural differences between isomers are detectable in the regions of methyl and phenyl groups, and the carbonyl ligands. Thus, the angles between planes of both double bonds (N=CC_{methyl}C_{phenyl}) are 71.2(1)° for I and 82.3(1)° for II. For the *anti* form I, a quasi-two-fold axis perpendicular to the Fe–Fe bond has been observed (C₂ symmetry point group). In the *syn* form II, both phenyl rings are located close to one of the iron atoms. The molecule shows a quasi-symmetry plane (C_s symmetry point group) which runs through both iron atoms.

Deviation from symmetry in each isomer can be roughly estimated by comparison of dihedral angles formed by the planes of the phenyl rings and the planes of the double bonds, different for both parts of the molecule. Their values are 86.5(1)° and 81.7(1)° in *anti*, and 51.8(1)° and 68.3(1)° in *syn*. Thus, the non-equality for *syn* is remarkably higher than that for *anti*. These values also show that in both isomers the coupling of the double bonds with the aromatic rings is only partial.

Thus, for the *syn* isomer, the highest value of deflection has been observed for the phenyl rings. The central system containing the iron bridge and nitrogen atoms shows a relatively high symmetry compared with peripheral parts of the molecule. In the *anti* isomer, the deviation from symmetry is similar in all regions of the molecule.

The above data in general confirm a higher symmetry of the *anti* isomer in relation to *syn*, although both isomers show attributes of only a quasi- (idealized) symmetry. Both NMR and X-ray experiments reveal a distinct non-equivalence of the phenyl rings in the *syn* form, presumably because of higher spatial crowding. For comparison [6], in the case of *syn* bis(μ -ethylideneamido)-bis(tricarbonyliron), substituted by relatively small methyl groups, the molecule lies on the crystallographic mirror plane and shows C_s symmetry.

In contrast, the molecule of bis(μ -cyclohexylideneimino)-bis(tricarbonyliron) with bulkier substituents exhibits in the solid state only idealized symmetry [9].

It should be emphasized that the differences in symmetry observed in this study for solid state structures (X-ray results) are preserved in solution (NMR), indicating that the impact of intramolecular interactions on the geometry of the molecules is more pronounced than the effect of external factors, e.g. solvation.

3. Experimental

Complexation reactions with iron dodecacarbonyl and the separation of isomers were carried out according to published methods [7]. 1,4-Dimethyl-1,4-diphenyl-2,3-diazabuta-1,3-diene (1 mmol) and triiron dodecacarbonyl (3 mmol) were refluxed in isooctane under nitrogen. For the chromatographic purification on Kieselgel 60 (Merck), chloroform-*n*-hexane (1:5) was used as the solvent. The products were recrystallized from *n*-hexane. ¹H NMR in CDCl₃: δ *anti* isomer I 2.40 (s, 6H), 7.07–7.38 (m, 10H); *syn* isomer II 2.50 (s, 6H), 6.99–7.38 (m, 10H). All reagents and solvents used were pure or analytically pure. The synthesis of 1,4-dimethyl-1,4-diphenyl-2,3-diazabuta-1,3-diene is described in Ref. [10]. The NMR spectra were recorded with a Varian XL-200 instrument, the chemical shift values are given in parts per million (δ).

3.1. X-ray structure determination

X-ray data were collected on a Siemens P3 four-circle diffractometer at room temperature. Crystals of isomeric complexes I and II were grown from *n*-hexane. The crystallographic data, parameters for data collection, and refinement procedure are presented in Table 3. A well-shaped yellow crystal of I was mounted directly on a glass pin attached to the goniometer head. An automatic search routine was used to locate up to 26 reflections in the range 15.7° < 2 θ < 33.0°, which were used for determination and least-squares refinement of the unit cell parameters. Intensity data were recorded using the ω -2 θ scan technique. No crystal decay was noticed. The data were corrected for Lorentz and polarization effects. Since the absorption coefficient was comparatively high ($\mu = 1.28 \text{ cm}^{-1}$) a numerical correction based on a well-defined crystal shape (nine faces) was applied. The structure was solved in C₂/c space group by direct methods using the SHELXS-86 program [11], which revealed the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located using difference Fourier maps and isotropically refined.

General procedures used for data collection of compound II were as for I. A suitable, well-shaped yellow

Table 3
Crystal data and structure refinement for I and II

Empirical formula	<i>anti</i> -C ₂₂ H ₁₆ Fe ₂ N ₂ O ₆ (I)	<i>sym</i> -C ₂₂ H ₁₆ Fe ₂ N ₂ O ₆ (II)
Formula weight	516.07	516.07
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pbca
Unit cell dimensions		
<i>a</i> (Å)	31.389(8)	14.838(3)
<i>b</i> (Å)	10.476(3)	16.522(4)
<i>c</i> (Å)	14.304(4)	18.608(5)
β (°)	95.68(2)	
Volume (Å ³)	4681(2)	4562(2)
Z	8	8
Density (calc.) (Mg m ⁻³)	1.465	1.503
Absorption coefficient (mm ⁻¹)	1.278	1.311
<i>F</i> (000)	2096	2096
Crystal size (mm ³)	0.64 × 0.58 × 0.36	0.87 × 0.74 × 0.15
2 θ range for data collection (°)	4.0 to 50.0	4.0 to 50.0
Reflections collected	4157	3992
Independent reflections	4079	3990
<i>R</i> _{int}	0.0196	0.0277
Absorption correction	Analytical from crystal shape	Analytical from crystal shape
Max. and min. transmission	0.6954 and 0.5847	0.8226 and 0.4330
Data/restraints/parameters	4077/0/353	3989/0/303
Goodness-of-fit on <i>F</i> ²	1.033	0.974
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ 0.0292	0.0298
	<i>wR</i> ₂ 0.0725	0.0683
<i>R</i> indices (all data)	<i>R</i> ₁ 0.0419	0.0468
	<i>wR</i> ₂ 0.0809	0.0732
Largest difference peak/hole (e ² Å ⁻³)	+0.23/-0.14	+0.31/-0.18

crystal of II was selected for all X-ray measurements. 26 reflections in the range $15.8^\circ < 2\theta < 34.3^\circ$ were used for least-squares refinement of the unit cell parameters. Two check reflections (314, 144) repeated every 70 reflections showed a decay of 1.3%, and the intensities were adjusted accordingly. A numerical absorption correction was applied on the basis of the crystal shape. The observed systematic absences indicated that the space group was *Pbca*. The phase problem was solved by direct methods using the SHELXS-86 program [11]. The Fe, O and N atoms and part of the C atoms were found on the *E*-map. The remaining non-hydrogen atoms were located using difference Fourier maps and refined with anisotropic thermal parameters. Positions of hydrogen atoms of the phenyl groups were generated and allowed to ride on the appropriate carbon. Hydrogens of the methyl groups were refined as disordered groups with two positions rotated about the C–C bond by 60° [$U_{10} = 1.2U_{eq}(C)$].

Both structures were refined using a full-matrix least-squares method against *F*² values (SHELXL-93 program [12]). The final weighting schemes for I and II were $w^{-1} = \sigma^2(F_o^2) + (0.0424P)^2$, and $w^{-1} = \sigma^2(F_o^2) + (0.0456P)^2 + 0.3350P$ respectively, where $P = 1/3(F_o^2 + 2F_c^2)$. In both cases the largest positive and

negative peaks on a final difference Fourier map have no significant chemical meaning, and the maximum shift/error ratios in final cycles of refinement were less than 0.001. Tables of atomic coordinates and anisotropic thermal parameters, hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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