Asymmetrical induction in the synthesis of ferrocenyl-substituted bicyclic pyrazolines. *E,Z*-Isomerization of the ferrocenylmethylidene fragment

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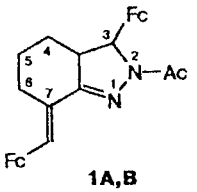
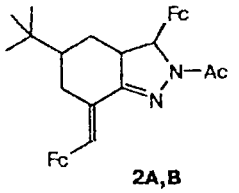
Asymmetrical induction in the synthesis of bicyclic ferrocenyl-substituted pyrazolines was studied. High diastereoselectivity of induction of the chiral center by the chiral center of the 1,2 type was observed. The *cis* diastereomer of 2-acetyl-3-ferrocenyl-7-ferrocenylmethylidene-2,3,3a,4,5,6,7-heptahydroindazole was studied by X-ray diffraction analysis. The *E,Z*-configurational isomerism of the ferrocenylmethylene fragment of pyrazolines in an acidic medium is described.

Key words: ferrocene, pyrazoline, asymmetrical induction, diastereoselectivity, isomerization, X-ray diffraction analysis.

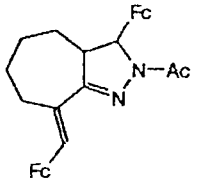
It is known that nine types of asymmetrical induction can occur in molecules of organic compounds depending on the nature of the chiral elements.[1] Asymmetrical inductions of the chiral center by the chiral plane or *vice versa* of the 1,3 and 1,1 types were reported[2] for the synthesis of 2-pyrazolines bearing ferrocenyl and phenylbutadienyltricarbonyliron substituents at positions 3 and 5 of the pyrazoline ring. It was mentioned[2] that this reaction proceeds with rather high diastereoselectivity in different synthetic procedures for the preparation of pyrazolines under study.



1A,B



2A,B



3A,B

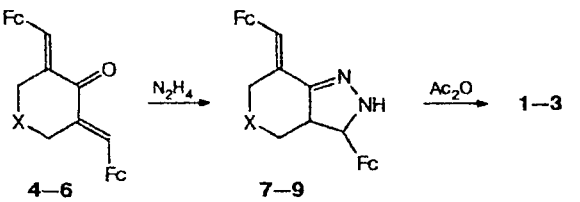
Fc = $C_5H_5FeC_5H_4$

In this work, we found 1,2-asymmetrical induction of the chiral center by the chiral center in the synthesis of bicyclic pyrazolines of the ferrocene series (**1**—**3**).

Results and Discussion

We used bis(ferrocenylmethylidene)cycloalkanones (**4**—**6**) with the "external" arrangement of a bulky ferrocenyl substituent with respect to the *s-cis*-triene systems[3,4] as starting compounds (Scheme 1).

Scheme 1



4—6 **7—9** **1—3**

X = CH_2 (**1**, **4**, **7**); $CHBu^t$ (**2**, **5**, **8**); $(CH_2)_2$ (**3**, **6**, **9**)

1-Acetyl-2-pyrazolines were prepared by the addition of hydrazine[2,5] to chalcones **4**—**6** followed by acylation of unstable products (**7**—**9**) containing no substituents at position 1.

In our opinion, pyrazolines **1**—**3**, like initial chalcones **4**—**6**, retain the *E* configuration of the ferrocenylmethylidene fragments.

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 765—770, April, 1999.
1066-5285/99/4804-0761 $22.00

Table 1. ^{1}H NMR spectra of the compounds synthesized

Compound	δ, *J*/Hz				
	s, C_5H_5	m, C_5H_4	m, CH_2	CH	s, CH_3
1A	4.15, 4.17	4.16 (3 H); 4.30 (1 H); 4.32 (1 H); 4.35 (1 H); 4.40 (1 H); 4.43 (1 H)	1.66 (2 H); 2.20 (2 H); 3.00—3.15 (2 H)	3.40 (m, 1 H); 4.86 (d, 1 H, *J* = 6.2); 6.80 (d, 1 H, *J* = 1.8)	2.33 (3 H)
1B	4.148, 4.24	3.85—4.25 (8 H)	1.02 (2 H); 1.75 (2 H); 2.30 (2 H)	3.38 (m, 1 H); 5.53 (d, 1 H, *J* = 9.3); 7.12 (d. 1 H, *J* = 1.4)	2.46 (3 H)
1C	4.14, 4.18	3.92—4.50 (8 H)	1.42 (2 H); 2.05 (2 H); 2.96 (2 H)	3.42 (m, 1 H); 4.92 (d, 1 H, *J* = 6.0); 6.89 (d, 1 H, *J* = 1.5)	2.24 (3 H)
2A	4.14, 4.19	4.05—4.18 (3 H); 4.30—4.48 (5 H)	1.65 (2 H); 2.20 (2 H)	3.15 (m, 1 H); 3.44 (m, 1 H); 4.84 (d, 1 H, *J* = 6.4); 6.83 (d, 1 H, *J* = 2.4)	1.02 (9 H); 2.30 (3 H)
2B	4.15, 4.16	4.28 (1 H); 4.32 (1 H); 4.49 (1 H); 4.52 (2 H); 4.64 (1 H); 4.97 (2 H)	1.40—1.60 (2 H); 2.00—2.40 (1 H); 2.60—2.85 (1 H)	3.10 (m, 1 H); 3.55 (m, 1 H); 5.52 (d, 1 H, *J* = 9.3); 7.14 (d, 1 H, *J* = 2.7)	1.16 (9 H); 2.33 (3 H)
2C	4.15, 4.165	4.07—4.30 (8 H)	1.54 (2 H); 2.15 (2 H)	3.20 (m, 1 H); 3.50 (m, 1 H); 4.94, 7.09	0.99 (9 H); 2.34 (3 H)
3A	4.195, 4.199	4.00 (1 H); 4.15 (2 H); 4.36 (2 H); 4.46 (3 H)	1.20 (1 H); 1.72 (2 H); 2.15 (4 H); 3.32 (1 H)	3.49 (m, 1 H, *J* = 2.5, 9.60); 4.97 (d, 1 H, *J* = 2.5); 6.86 (d, 1 H, *J* = 1.6)	2.35 (3 H)
3B	4.20, 4.26	3.92 (2 H); 3.98 (2 H); 4.10 (2 H); 4.38 (2 H)	1.38 (1 H); 1.80 (2 H); 2.10 (4 H); 3.10 (1 H)	3.62 (m, 1 H); 5.44 (d, 1 H, *J* = 11.8); 7.19 (br.s, 1 H)	2.28 (3 H)
3C	4.14, 4.145	3.97 (2 H); 4.12 (2 H); 4.16 (2 H); 4.32 (2 H)	1.25 (1 H); 1.60 (2 H); 2.67 (4 H); 3.15 (1 H)	3.41 (m, 1 H); 4.99 (d, 1 H, *J* = 2.5); 6.34 (d, 1 H, *J* = 0.9)	2.31 (3 H)
5	4.148 (10 H)	4.39 (2 H); 4.43 (2 H); 4.51 (2 H); 4.56 (2 H)	1.56 (2 H); 2.16 (2 H, *J* = 1.1, 13.5)	3.06 (m, 1 H, *J* = 3.2, 13.5); 7.58 (d, 1 H, *J* = 2.3)	1.05 (9 H)
6	4.16 (10 H)	4.38 (4 H); 4.53 (4 H)	1.94 (4 H, *J* = 3.0); 2.60 (4 H)	7.14 (s, 1 H)	—

We found that pyrazolines **1—3** were formed as mixtures of two diastereomeric forms in various ratios. These forms differ in their physical parameters and are characterized by similar ^{1}H and ^{13}C NMR spectra (Tables 1 and 2). The diastereomeric form, which is present in a larger amount in all the cases, is denoted as **A** and the minor diastereomeric form is denoted as **B**.

We succeeded in separating diastereomers **A** and **B** of pyrazolines **1—3** by preparative TLC on SiO_2. The yields of compounds **1A—3A** and **1B—3B**, their melting points, and the data of elemental analysis are given in Table 3.

According to the data of ^{1}H NMR spectroscopy, the chemical shifts of the H(5)* protons at the C(3) atoms of the pyrazoline fragments in the resulting bicyclic pyrazolines of type **A** (**1A—3A**) (see Table 1) have close values (δ 4.86, 4.84, and 4.97, respectively), and $^3J_{H(4),H(5)}$ are 6.2, 6.4, and 2.5 Hz, respectively. The chemical shifts of the analogous protons in the diastereomers of type **B** (**1B—3B**) are observed at lower fields (δ 5.53, 5.52, and 5.44, respectively) and are characterized by larger values of the spin-spin coupling constants ($^3J_{H(4),H(5)}$ are 9.3, 9.3, and 11.8 Hz, respectively). Identification of 3-aryl-5-ferrocenyl- and 5-aryl-3-ferrocenyl-substituted pyrazolines by ^{1}H NMR spectroscopy has been described previously.[5] It was demonstrated that the positions of substituents in the five-membered ring can be determined from the values of the chemical shifts and spin-spin coupling constants of the H(4) and H(5) protons of the pyrazoline ring. However, in our case these data did not allow us to draw a conclusion about the *trans* or *cis* orientations of the H(4) and H(5) protons at the C(3a) and C(3) atoms, respectively, in the pyrazoline rings of isomers **A** and **B**.

With the aim of unambiguously establishing the structures of diastereomers **A** and **B**, we performed X-ray diffraction study of a single crystal of pyrazoline **1A**. The overall view of molecule **1A** is shown in Fig. 1. The positional parameters of the atoms and their isotropic thermal parameters are given in Table 4. The principal geometric parameters, namely, the bond lengths and bond angles, are listed in Tables 5 and 6, respectively.

The central bicyclic framework is the key fragment in structure **1A**. The six-membered ring is fused with the five-membered ring. The latter adopts a flattened envelope conformation. The ferrocenyl substituent is in the pseudoaxial orientation. The H(4) and H(5) atoms at the C(3a) and C(3) atoms, respectively, are in *cis* positions. The N(1)=C(7a) bond in the pyrazoline ring is somewhat longer, while the N(1)—N(2) bond is somewhat shorter, than the standard bonds (C=N, 1.23 Å[6]; and N—N, 1.45 Å [7]). The ferrocenylmethylidene fragment in the pyrazoline molecule has the *E*-configuration. The Fe—C and C—C bond lengths

* The atomic numbering scheme is given in Fig. 1.

Table 2. ^{13}C NMR spectra of compounds **1A,B—3A,B**

Compound	δ										
	C_5H_5	C_5H_4	$C_{ipso}Fc$	CH=	CH_3	CH_2	CH—Fc	CH	C	C=O	C=N
1A	68.25, 69.22	66.48, 67.96, 68.07, 69.26, 69.42, 69.72, 69.73, 70.55	80.40, 88.67	125.93	31.29	22.32, 24.57, 27.82	61.14	55.12	127.20	170.15	159.46
1B	69.25, 69.37	65.43, 66.52, 67.07, 67.38, 67.86, 69.27, 69.50, 70.84	80.23, 85.99	126.20	29.22	21.95, 23.45, 24.64	58.76	50.24	127.95	167.75	159.69
2A	68.20, 69.22	66.32, 67.12, 67.45, 68.15, 68.25, 69.50, 70.13, 70.50	80.12, 85.63	125.85	27.56, 32.63	32.88, 45.43	61.40	32.58, 50.59	127.18	170.09	159.52
2B	69.20, 69.29	65.55, 66.46, 67.97, 69.10, 69.46, 69.66, 69.84, 70.29	80.32, 88.44	128.28	27.53, 30.82	29.37, 46.87	59.01	33.09, 55.51	126.62	167.69	159.89
3A	68.30, 69.22	65.78, 68.78, 68.15, 69.34, 69.40, 69.81, 69.93, 69.98	80.93, 87.44	127.45	30.50	21.84, 28.76, 29.92, 35.70	62.94	54.84	130.34	168.57	161.40
3B	69.30, 69.75	64.67, 65.83, 66.24, 68.30, 69.11, 69.48, 71.04, 72.01	79.96, 91.19	128.02	29.00	21.80, 26.12, 28.83, 34.78	62.98	54.42	130.27	169.24	161.43

Table 3. Yields, melting points, and the data of elemental analysis of the synthesized compounds

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)				Molecular formula
			C	H	Fe	N	
1A	68	187—188	65.73 65.96	5.33 5.53	20.57 20.45	5.28 5.13	$C_{30}H_{30}Fe_2N_2O$
1B	12	197—198	66.11 65.96	5.27 5.53	20.63 20.45	5.01 5.13	$C_{30}H_{30}Fe_2N_2O$
1C	21	173—174	65.68 65.96	5.64 5.53	20.29 20.45	4.96 5.13	$C_{30}H_{30}Fe_2N_2O$
2A	54	188—189	67.64 67.79	6.41 6.36	18.72 18.54	4.51 4.65	$C_{34}H_{38}Fe_2N_2O$
2B	29	203—204	67.96 67.79	6.17 6.36	18.42 18.54	4.70 4.65	$C_{34}H_{38}Fe_2N_2O$
2C	18.7	184—185	67.99 67.79	6.52 6.36	18.71 18.54	4.43 4.65	$C_{34}H_{38}Fe_2N_2O$
3A	72	209—210	66.63 66.45	5.57 5.76	19.73 19.94	4.71 5.00	$C_{31}H_{32}Fe_2N_2O$
3B	12	186—187	66.27 66.45	5.92 5.76	20.10 19.94	5.03 5.00	$C_{31}H_{32}Fe_2N_2O$
3C	19.8	214—215	66.57 66.45	5.61 5.76	20.07 19.94	4.85 5.00	$C_{31}H_{32}Fe_2N_2O$
6	46	177—178	68.87 69.08	5.73 5.60	22.31 22.15	— —	$C_{29}H_{28}Fe_2O$

and the geometric parameters of the ferrocenyl sandwiches in isomer **1A** have standard values.

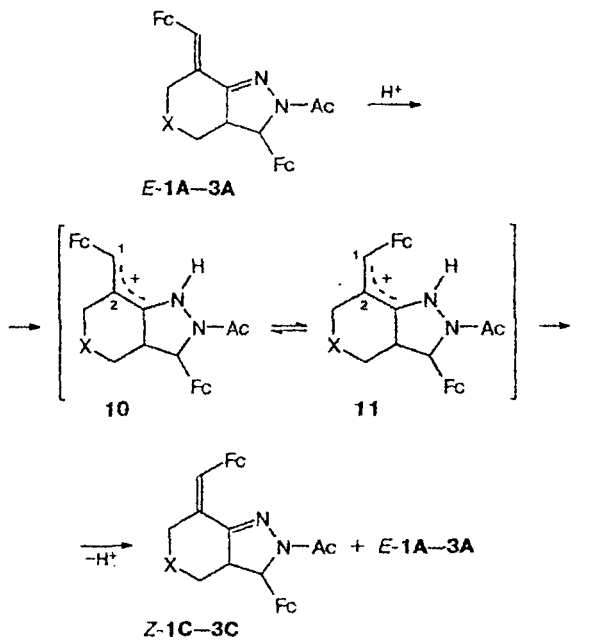
Based on the X-ray diffraction data for pyrazoline **1A** and the ^1H NMR spectra of diastereomeric compounds **1A—3A** and **1B—3B**, a structure, in which the H(4) and H(5) atoms of the pyrazoline ring are in the pseudoequatorial orientations and the ferrocenyl fragment is in the pseudoaxial position, was assigned to the isomers of type **A**. In the diastereomers of type **B**, the ferrocenyl fragment and the H(4) atom are apparently in

pseudoequatorial orientations and the H(5) atom is in the pseudoaxial position. In our opinion, the *E*-configuration of the ferrocenylmethylidene fragment remains unchanged.

The ratio between isomers **A** and **B** was determined more accurately from the ^{1}H NMR spectra of specimens isolated from the reaction mixtures. These data are listed in Table 7, which gives an idea of the effect of the chiral elements on the diastereoselectivity of formation of pyrazolines **1**—**3**.

We examined the possibility of the synthesis of configurational isomers using pyrazolines of diastereomeric type **A**, *viz.*, *E*-**1A**, *E*-**2A**, and *E*-**3A**, as examples. It appeared that pyrazolines with the *Z*-configuration of the ferrocenylmethylidene substituent can be prepared from the corresponding *E*-isomers under the action of strong acids (HBF_4 or $HBPh_4$) (Scheme 2) in satisfactory yields (~20%). In our opinion, the formation of *Z*-diastereomers **1C**—**3C** proceeds *via* intermediate ferrocenylallyl carbocations (**10** and **11**) due to rotation about the C(1)—C(2) bond is spite of the rather high energy barrier.[8—11]

Scheme 2



Previously, we have observed this type of isomerization in the case of ferrocenylmethylidene-substituted

Table 4. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) in molecule **1A**

Atom	*x*	*y*	*z*	$U_{eq} \cdot 10^3$/Å^2
Fe(1)	3216(1)	8554(1)	933(1)	41(1)
Fe(2)	−2009(1)	8349(1)	−4224(1)	40(1)
O(1)	3154(5)	10536(3)	589(5)	54(2)
N(1)	1362(5)	9920(3)	−1810(5)	36(1)
N(2)	2336(5)	9997(3)	−957(5)	36(1)
C(1)	2255(7)	10444(3)	−109(6)	37(2)
C(2)	1013(8)	10804(4)	−26(8)	56(2)
C(3)	3471(6)	9586(3)	−1225(6)	35(2)
C(3a)	3340(6)	9570(3)	−2564(6)	32(2)
C(4)	3486(7)	9000(4)	−3236(6)	45(2)
C(5)	3375(7)	9061(4)	−4499(6)	47(2)
C(6)	1924(7)	9001(4)	−4585(6)	47(2)
C(7)	1171(7)	9393(3)	−3707(6)	34(2)
C(7a)	1893(6)	9644(3)	−2700(6)	32(2)
C(8)	3357(6)	8922(3)	−724(6)	33(2)
C(9)	2207(7)	8545(4)	−601(6)	37(2)
C(10)	2547(8)	7907(4)	−260(6)	47(2)
C(11)	3910(8)	7878(4)	−186(6)	48(2)
C(12)	4400(7)	8495(4)	−460(5)	41(2)
C(13)	3476(13)	9279(5)	2112(7)	75(3)
C(14)	2236(12)	9038(7)	2171(8)	80(3)
C(15)	2316(13)	8365(7)	2452(9)	92(4)
C(16)	3643(15)	8227(6)	2549(7)	88(4)
C(17)	4290(14)	8791(7)	2355(9)	98(4)
C(18)	−102(7)	9460(3)	−3725(6)	35(2)
C(19)	−1038(7)	9199(4)	−4552(6)	39(2)
C(20)	−2376(7)	9306(4)	−4427(7)	46(2)
C(21)	−3068(8)	8951(4)	−5284(7)	55(2)
C(22)	−2171(8)	8609(5)	−5950(7)	59(2)
C(23)	−924(8)	8752(4)	−5505(6)	51(2)
C(24)	−2434(9)	8121(4)	−2539(7)	59(2)
C(25)	−1149(9)	7947(4)	−2791(8)	60(2)
C(26)	−1154(9)	7501(4)	−3706(10)	71(3)
C(27)	−2462(9)	7390(4)	−4033(8)	66(3)
C(28)	−3225(8)	7766(4)	−3318(8)	61(2)

Table 5. Principal bond lengths (*d*) in molecule **1A**

Bond	*d*/Å	Bond	*d*/Å
N(1)—N(2)	1.412(7)	N(1)—C(7a)	1.298(8)
N(2)—C(1)	1.344(8)	N(2)—C(3)	1.487(8)
C(1)—C(2)	1.495(10)	C(3)—C(3a)	1.544(9)
C(3)—C(8)	1.490(10)	C(3a)—C(4)	1.503(9)
C(3a)—C(7a)	1.520(9)	C(5)—C(6)	1.517(10)
C(6)—C(7)	1.517(9)	C(7)—C(7a)	1.468(9)
C(7)—C(18)	1.331(10)		

Table 6. Principal bond angles (ω) in molecule **1A**

Angle	ω/deg	Angle	ω/deg
C(7a)—N(1)—N(2)	106.8(5)	C(1)—N(2)—N(1)	122.1(6)
C(1)—N(2)—C(3)	126.6(6)	N(1)—N(2)—C(3)	110.9(5)
O(1)—C(1)—N(2)	121.5(7)	N(2)—C(3)—C(8)	112.2(6)
N(2)—C(1)—C(2)	116.5(6)	C(8)—C(3)—C(3a)	111.0(6)
N(2)—C(3)—C(3a)	99.0(5)	C(4)—C(3a)—C(3)	120.1(6)
C(4)—C(3a)—C(7a)	112.2(6)	C(3a)—C(4)—C(5)	108.3(6)
C(7a)—C(3a)—C(3)	100.3(5)	C(5)—C(6)—C(7)	115.7(6)
C(6)—C(5)—C(4)	111.4(6)	C(18)—C(7)—C(6)	124.4(6)
C(18)—C(7)—C(7a)	118.5(6)	N(1)—C(7a)—C(7)	123.9(6)
C(7a)—C(7)—C(6)	116.6(6)	C(7)—C(7a)—C(3a)	123.0(6)
N(1)—C(7a)—C(3a)	113.0(6)	O(1)—C(1)—C(2)	122.0(7)
C(12)—C(8)—C(3)	125.8(6)		

Table 7. Degree of asymmetrical induction in the synthesis of ferrocenylpyrazolines

Direction of induction	Induction variant	Induction type	Yield of diastereomers(%) A	B	Diastereoselectivity (%)
4→1	center→center	1,2	80	20	60
5→2	center→center	1,2	60	25	35
6→3	center→center	1,2	90	10	80

derivatives of camphor, quinuclidone,[12] menthone,[13] *etc.* The extension of this procedure to isomerization of pyrazoline systems is reported for the first time.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 and 50 MHz) in $CDCl_3$ solutions with $SiMe_4$ as the internal standard.

The unit cell parameters and intensities of reflections were measured on a Siemens P4/PC diffractometer at 293 K. The crystallographic data and characteristics of X-ray diffraction data collection and refinement are given in Table 8.

Chalcones **4** and **5** were synthesized from cyclohexanone or 4-*tert*-butylcyclohexanone and ferrocenecarbaldehyde in an aqueous-ethanolic alkali.[5] Bis(ferrocenylmethylidene)cycloheptanone **6** was prepared by boiling the corresponding reagents in PhMe in the presence of Bu^tOK.[12,13]

Pyrazolines **7**—**9** were synthesized according to a standard procedure[5] from chalcones **4**—**6** and hydrazine hydrate in ethanol. Treatment of dry compounds **7**—**9** with Ac_2O afforded 1-acetyl-substituted derivatives **1**—**3**.

E,Z*-Isomerization of pyrazolines 1A—3A.** ***A. HBF_4 etherate (2 mL) was added dropwise to a solution of pyrazoline **1A**—**3A** (1 mmol) in CH_2Cl_2 (50 mL). The bright-green mixture was stirred at 20 °C for 1 h under a dry inert atmosphere. Then $PhNMe_2$ (2 mL) was added dropwise and the mixture was stirred for ~30 min until the color of the solution changed from green to brown. The reaction mixture was washed with water, 1% HCl, and again with water. The solvent was distilled off and the residue was washed with EtOH.

B. Pyrazoline **1A**—**3A** (1 mmol) was added to a solution of a 120% excess of $NaBPh_4$ in glacial AcOH. The mixture was stirred at 70—80 °C for 5 h, cooled to 20 °C, and mixed with benzene (100 mL) and water (100 mL). The organic layer was separated and washed with a 5% $NaHCO_3$ solution and water. The solvent was distilled off *in vacuo* and the residue was washed with *n*-heptane and EtOH.

Chromatographic separation of isomers A and B was carried out by TLC on SiO_2 (hexane—benzene, 1 : 1). The

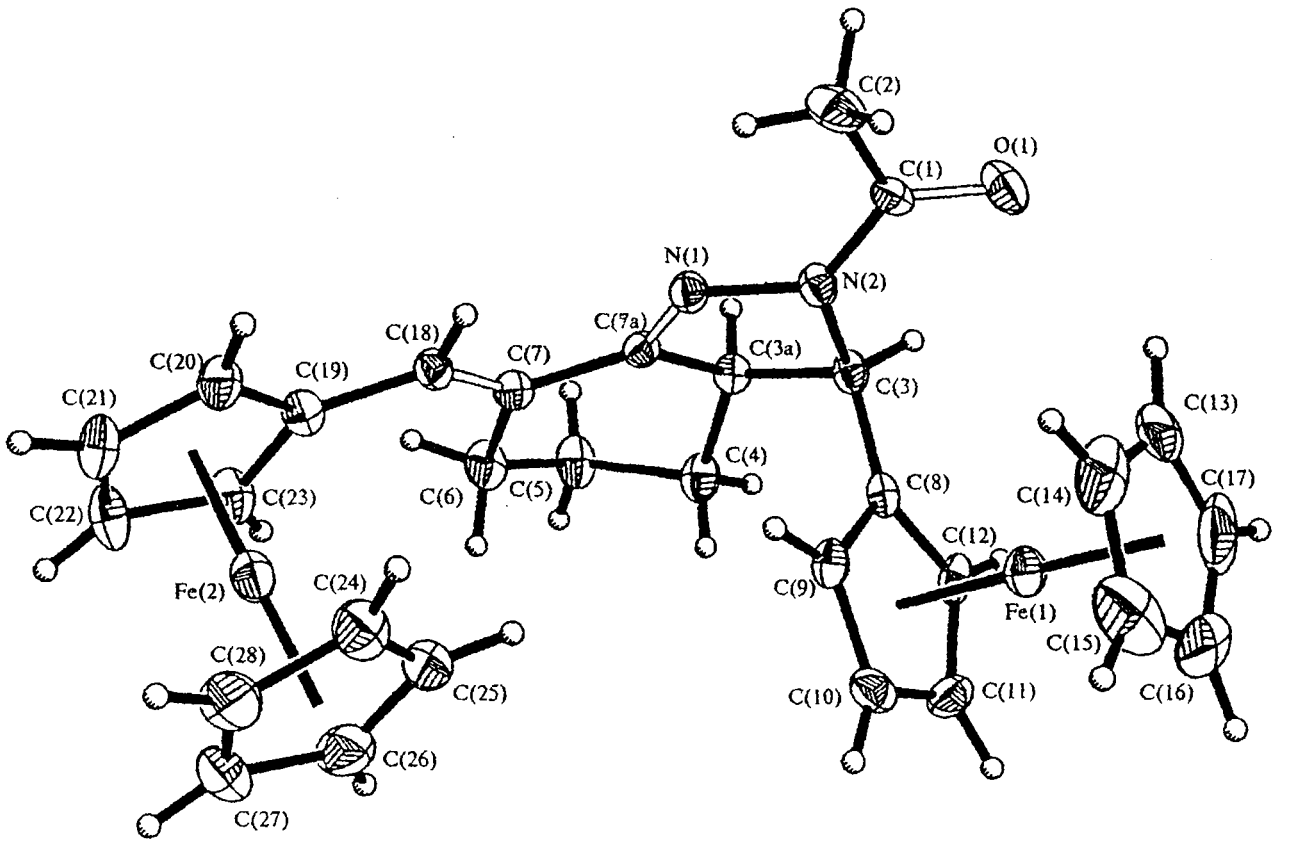


Fig 1. Molecular structure of compound **1A**.

Table 8. Crystallographic data and characteristics of X-ray data study of structure **1A**

Parameter	Value
Molecular formula	$C_{30}H_{30}Fe_2N_2O$
Molecular weight	546.26
Crystal system	Monoclinic
Space group	$P2_1/C$
a/Å	10.403(1)
b/Å	20.605(1)
c/Å	11.494(1)
α/deg	90.0
β/deg	90.55(1)
γ/deg	90.0
V/Å^3	2463.7(3)
Z	4
ρ_{calc}/g cm^{-3}	1.473
$F(000)$	1136
Absorption coefficient/mm^{-1}	9.639
λ/Å (Cu-Kα radiation)	1.54178
2θ scanning range/deg	$3.0 < 2\theta < 113.50$
Total number of reflections	4195
Number of independent reflections	3289
R_{int}	0.0630
Number of refinable parameters	317
Goodness of fit	1.007 (full-matrix least-squares refinement on F^2)
Residual electron density/e · Å^{-3}, ρ_{min}/ρ_{max}	−0.403/0.646
Scanning mode	psi
Temperature/K	293
Monochromator	Graphite
Weighting scheme	$w = [\sigma^2(F_0^2 + (0.0605P)^2 + 3.8592P)]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$

isomers of types **A**, **B**, and **C** are characterized by R_f of 0.56—0.65, 0.60—0.75, and 0.3—0.45, respectively.

The NMR spectra were recorded immediately after isolation of mixed samples from the reaction mixtures and chromatographic separation of isomers.

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Received July 14, 1998