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Studies on the cyclomercuration of 1,1′-bis[(arylimino)phenylmethyl]ferrocenes

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Abstract

The reaction of bisferrocenylimines with mercuric acetate and subsequent treatment with LiCl lead to formation of mono (**9**) and double (**10**) cyclomercurated derivatives. The ^{1}H NMR and ^{199}Hg NMR spectra of the double cyclomercurated bisferrocenylimines show that compounds **10** exist as two isomers (*meso* and *dl*). The individual stereoisomers were isolated successfully by crystal picking. The structures of these new compounds have been confirmed by elemental analysis, IR and ^{1}H NMR spectroscopies, and further by X-ray crystal structure determination of *meso* [{HgCl(η^5-C_5H_3CPh=NAr)}$_2$Fe] (Ar=*m*-$CH_3C_6H_4$). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bisferrocenylimine; Mercury; Crystal structure

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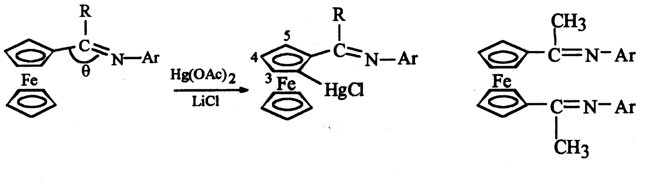
1. Introduction

We have demonstrated that the mercuration of ferrocenylimines **1**, **2** and **3** occur predominantly on the *ortho*-position of the substituted Cp ring (cyclopentadienyl ring), affording the cyclo-mercurated ferrocenylimines **4**, **5** and **6** [1–3], respectively. Such reactions are of interest in that they will provide a new route, after suitable functional group modification, to inherently chiral 1,2-disubstituted ferrocene. It has also been found that when R is a methyl group and Ar contains electron-donating group such as OCH_3 or CH_3 in the *para*-position, the yields of the *ortho*-mercurated products are very low, and it appears that the high electron density in the imino nitrogen is quite unfavorable to the mercuration on the *ortho*-position [2]. Double cyclomercuration of 1,1′-bis[1-(arylimino)ethyl]-ferrocenes **7** mainly produced the mono-*ortho*-mercurated products [4]. On the contrary, the acetoxymercuration of **3** followed by the treatment of the resulting products with lithium chloride produced *ortho*-chloromercurated ferrocenylimines **6** in higher yields in comparison with those of **1** and **2**, indicating the important role played by the C-phenyl. The effect of the phenyl can be due to the steric repulsion between the C-phenyl and the ferrocenyl moiety as well as the N-aryl leads to smaller angle θ than the normal 120° required for the sp^2 hybridization state and this facilitates the directing of mercury to the *ortho*-position by the nitrogen. This study is now extended to double cyclomercuration of 1,1′-bis[(arylimino)-phenylmethy]ferrocene, which can form both monocyclomercurated and double cyclomercurated products, with two isomers: *meso*- and *dl*-. We successfully separated the isomers and determined the structure of *meso* isomer by X-ray crystal analysis. This paper describes the experiment designed to gain further insight into the substitution effect and the relationship between the structure and property on the double mercuration of bisferrocenylimines, related stereochemistry and mechanism of the formation of stereoisomers of bis(mercury) complexes.



R=H(**1**), CH$_3$(**2**), Ph(**3**)　R=H(**4**), CH$_3$(**5**), Ph(**6**)　**7**

2. Results and discussion

The bisferrocenylimines [(η^5-C_5H_4CPh=NAr)$_2$Fe] des-

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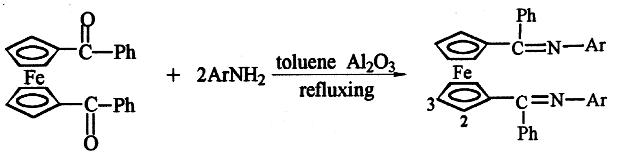
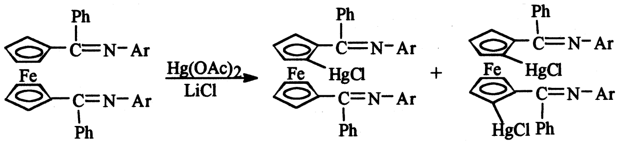
ignated as bis(FKB), were prepared by refluxing 1,1′-dibenzoylferrocene and the corresponding amines in the presence of freshly activated Al_2O_3 [5] in toluene for 3 d. Every day addition of small quantities of the amines and activated Al_2O_3 was needed to complete the reaction. Isolation of the pure bis(FKB) was achieved by chromatography of the reaction mixture on silica gel under reduced pressure; in each separation, the band possessing the highest R_f values contained the compound **8**.



Ar=m-CH$_3$C$_6$H$_4$ (**8a**)
m-BrC$_6$H$_4$ (**8b**)

The cyclomercuration reaction was carried out with bis(FKB) and two mole equivalents of mercuric acetate in methylene dichloride and methanol at ambient temperature for about 3.5 h, followed by the treatment with LiCl, gave mono (**9**) and double (**10**) cyclomercurated ferrocenylketimines. The isolation of pure compounds **9** and **10** was carried out by chromatography of the reaction mixture on silica gel, since the compound **10** exhibited higher R_f values than that of the compound **9**. The first band is for compound of **10**, second band is for compound **9** and third one is for the starting material. The yields of mono- and double-mercuration products are higher than those of **7** reported previously [4], indicating the important role played by the C-phenyl. The C-phenyl may also weaken the basicity of bisferrocenylimines **8**, which is favorable to the formation of the mercurated product. All the new compounds were characterized by elemental analysis, IR and ^{1}H NMR spectra.



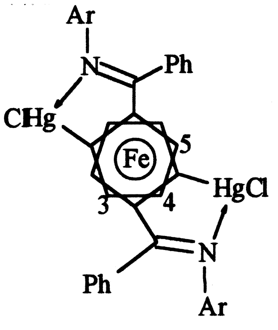
8 Ar=m-CH$_3$C$_6$H$_4$ (**9a**) **10a**
m-BrC$_6$H$_4$ (**9b**) **10b**

The IR spectra of compounds **8**–**10** showed no absorption band at 1000 and 1100 cm^{-1}, which indicated the presence of two substituted cyclopentadienyl rings [6]. In addition, the C=N IR absorptions of the compounds **9** and **10** shifted to lower energy by 29–38 cm^{-1} in comparison with the frequency of compounds **8**, which indicated that the imino nitrogen coordinated with mercury [6] in compounds **9** and **10**.

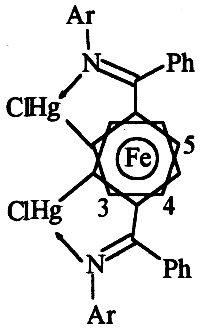
The ^{1}H NMR spectra of bisferrocenylimines were similar to those of mono ferrocenylimines [3], except for no signals of the unsubstituted Cp ring. For example, the ^{1}H NMR spectrum of **8a** exhibited two signals at δ 4.71 ppm and δ 4.50 ppm integrating for protons 2 and 3 respectively, and the signals at δ 6.33, δ 6.46, δ 6.65 and δ 6.91 ppm to the protons of N-phenyl ring. The multipet at δ 7.19 ppm was assigned to ten protons of the C-Ph rings.

The ^{1}H NMR spectra of compounds **9** indicated that the starting material converted to the corresponding mono mercurated products. The seven remaining protons in the ferrocenyl moiety behaved as if in seven different magnetic environments. The signals of the protons of the Cp ring can not be distinguished owing to the small chemical shift difference between them.

What is most interesting is that the ^{1}H NMR spectra of **10a**, **10b** exhibited two sets of signals and the ^{199}Hg NMR spectrum of **10a** also exhibited two signals at $\delta -760.96$ and $\delta -745.30$ ppm. Every compound exists as two isomers. We separated the different crystalline forms of compound **10a** by crystal picking. The major isomer was *meso*-**10a** and minor isomer was *dl*-**10a**. The pair of the proton signals for Cp ring for the individual stereoisomers, *meso*-**10a** and *dl*-**10a**, occur at δ 4.70, δ 4.59, δ 4.53 and δ 4.63, δ 4.59, δ 4.41 ppm, respectively. According to ^{1}H NMR study of the mercurated mono ferrocenylimines [3], the signals at δ 4.70, δ 4.59 and δ 4.53 ppm correspond to protons 4, 3 and 5 in *meso*-form, respectively. The signals at δ 4.63, δ 4.59 and δ 4.41 ppm correspond to protons 4, 3 and 5 in *dl*-form, respectively. In the meso configuration, the chemical shifts of the substituted Cp ring protons shift to downfield significantly in comparison with δ 4.57, δ 4.53, δ 4.40 ppm for the mono mercurated ferrocenylimines analogue compound **6**.



meso-**10a**



dl-**10a**

The X-ray crystal structure of *meso*-**10a** was determined and a perspective view of its molecular structure is shown in Fig. 1, which has been supported by the spectral data. Selected bond lengths and angles are listed in Tables 1 and 2, respectively. It confirms that in the compound the Fe atom of the double mercurated bisferrocenylimine is situated on a crystallographic center of symmetry. This configuration is identified as the *meso* isomer. The com-

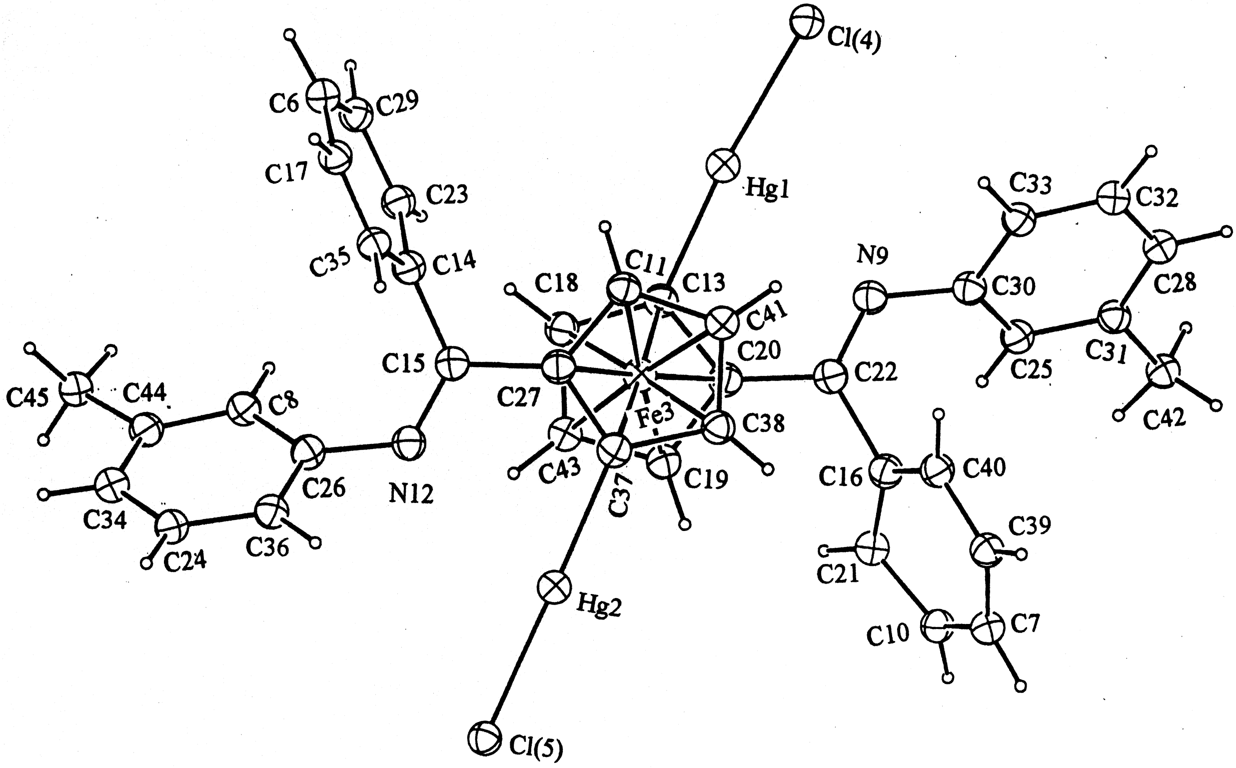


Fig. 1. Structure of *meso*-**10a**.

Table 1
Selected bond distances (Å) for *meso*-**10a**

Hg(1)-Cl(4)	2.31(1)	Fe(3)-C(41)	2.11(4)
Hg(1)-N(9)	2.78(3)	Fe(3)-C(43)	2.08(4)
Hg(1)-C(13)	2.06(3)	N(9)-C(22)	1.26(4)
Hg(2)-Cl(5)	2.32(1)	N(9)-C(30)	1.41(4)
Hg(2)-N(12)	2.84(1)	N(12)-C(15)	1.28(4)
Hg(2)-C(37)	2.09(3)	N(12)-C(26)	1.40(4)
Fe(3)-C(11)	2.04(3)	Fe(3)-C(20)	2.06(3)
Fe(3)-C(13)	2.06(3)	Fe(3)-C(27)	2.06(3)
Fe(3)-C(18)	2.07(3)	Fe(3)-C(37)	2.06(3)
Fe(3)-C(19)	2.06(3)	Fe(3)-C(38)	2.06(3)

pound *meso*-**10a** has two chloromercurio groups directly linked to the 2-position of the two Cp rings. The N(9)-Hg(1) and N(12)-Hg(2) distances are 2.78 Å and 2.84 Å respectively, shorter than the sum of Van der Waals radii of N and Hg (3.05–3.15 Å) [7–9] and indicate the presence of intramolecular coordination between N and Hg. The bond angles Cl(4)-Hg(1)-C(13) and Cl(5)-Hg(2)-C(37) are 172.9° and 178.0°, close to the ideal value of 180° in organic derivatives of mercury [7]. The chelate cycles Hg(1)-C(13)-C(20)-C(22)-N(9) and Hg(2)-C(37)-C(27)-C(15)-N(12) are nearly planar. The dihedral angle between the two substituted Cp rings and the two chelate cycles are 176.4° and 173.2°, respectively. The interangles between the two C-phenyl rings and the two substituted Cp rings are 70.49° and 62.91° respectively, less than that in compound **6** (81.98°) [10]. As a result, the protons for the Cp ring in *meso*-**10a** appear at downfield when compared to those for compound **6**. This can be interpreted in terms of the interplanar angle θ between the C-phenyl and substituted Cp rings, since the anisotropy of the phenyl ring varies as a $\cos^2\theta$ function of the interplanar angle (the larger θ, the lower the deshielding) [11]. The Fe-C(Cp) bond distance ranges from 2.04 Å to 2.11 Å. The average C-C bond length in the Cp ring is 1.435 Å. The two Cp rings are parallel with interplanar angle 1.72°.

Table 2
Selected bond angles (°) for *meso*-**10a**

Cl(4)-Hg(1)-C(13)	172.9(8)	N(9)-C(22)-C(16)	125.8(8)
Cl(4)-Hg(2)-C(37)	178.0(8)	C(14)-C(15)-N(12)	124.8(8)
Hg(1)-C(13)-C(18)	130.1(22)	N(12)-C(15)-C(27)	117.7(9)
Hg(1)-C(13)-C(20)	117.2(21)	N(9)-C(30)-C(25)	122.3(8)
Hg(2)-C(37)-C(27)	122.5(22)	N(9)-C(30)-C(33)	118.3(8)
Hg(2)-C(37)-C(38)	125.9(21)	N(12)-C(26)-C(8)	122.7(8)
C(22)-N(9)-C(30)	123.9(8)	C(26)-N(12)-C(15)	122.7(7)
N(12)-C(26)-C(36)	118.0(7)	N(9)-C(22)-C(20)	117.1(9)

It was established that the mercuration involved the initial coordination of the mercury to the imino nitrogen and subsequent electrophilic attack at the 2-carbon atom [1–3], which lead us to find proposed explanation for the formation of stereoisomers in double cyclomercuration (Scheme 1). Once one chelate ring is formed through the cyclomercuration reaction, the orientation of the other Cp ring during the second mercuration step determines the stereochemistry. In case of formation of *meso*-product the second electrophilic position is at C-5′ whereas electrophilic attack on the C-2′ leads to the *dl*-form. After the two chelate rings are formed, the interconversion of the two stereoisomers is not possible without breaking the Hg-C bond. The *meso*-isomer produced as the major product is due to the difficult rotation about C-C bond caused by the presence of C-phenyl ring.

3. Experimental section

3.1. Materials and intruments

Melting points were measured on a WC-1 apparatus and uncorrected. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. ^{1}H NMR spectra were recorded on a Bruker DPX-400, using $CDCl_3$ as the solvent and TMS as an internal standard. ^{199}Hg NMR was recorded on a Bruker DPX-400 spectrometer in $CHCl_3$ at 25°C. The operating frequency was 71.6 MHz. The routine acquisition parameters used were as follows: pulse width 15.0 μs, acquisition time 1.1 s, spectral width 28571 Hz, number of scans 28889. A solution of $HgCl_2$ in DMSO-d_6 was used as external reference. IR spectra were recorded on a Perkin Elmer FTIR 1750 spectrophotometer. Chromatography was carried out on a short column packed with dry silica gel under reduced pressure.

3.2. Synthesis of the ferrocenylketimines

1,1′-dibenzoylferrocene (1.0 g, 2.5 mmol) was dissolved in toluene (30 ml) at room temperature. Once the starting material had dissolved completely, the corresponding amine (8.9 mmol) was added. The red solution was refluxed for three days. Every day addition of small quantities of the amines and activated Al_2O_3 was needed to complete the reaction. The hot solution was carefully filtered and the filtrate reduced to dryness on a rotary evaporator. Isolation of the pure compound **8** was carried out on silica gel under reduced pressure, the band possessing the highest R_f values contained the compound **8**. They are new ferrocenylketimine and were characterized as following:

3.3. 1,1′-bis[(3-methylphenylimino)phenylmethyl]ferrocene ***(8a)***

Orange crystals, yields 55.9%, m.p. 164–164.5°C, IR KBr (pellet): 3020, 2919, 1618, 1596, 1578, 1456, 901, 793, 708 cm^{-1}. ^{1}H NMR: 2.16 (s, 6H, CH_3); 4.51 (t, 4H, $J=1.9$ Hz, H-3); 4.71 (t, 4H, $J=1.9$ Hz, H-2); 6.33 (d, 2H, $J=7.8$ Hz, N-Ph-H); 6.46 (s, 2H, N-Ph-H); 6.66 (d, 2H, $J=7.9$ Hz, N-Ph-H); 6.91 (m, 2H, N-Ph-H); 7.19 m (10H, C-Ph-H). Found: C, 79.82; H, 5.67; N, 4.84. Calc. for $C_{38}H_{32}FeN_2$: C, 79.69; H, 5.69; N, 4.84%.

3.4. 1,1′-bis[(3-bromophenylimino)phenylmethyl]ferrocene ***(8b)***

Brown-red crystals, yields 16.7%, m.p. 180–180.5°C, IR KBr(pellet): 3021, 1617, 1586, 1553, 1455, 890, 791, 705 cm^{-1}, ^{1}H NMR: 4.52 (t, 4H, $J=1.9$ Hz, H-3); 4.69 (t, 4H, $J=1.9$ Hz, H-2); 6.45 (d, 2H, $J=7.6$ Hz, N-Ph-H); 6.76 (s, 2H, N-Ph-H); 6.88 (d, 2H, $J=7.9$ Hz, N-Ph-H); 6.96 (m, 2H, N-Ph-H); 7.17 m (10H, C-Ph-H). Found: C, 61.97; H, 3.65; N, 3.87. Calc. for $C_{36}H_{26}Br_2FeN_2$: C, 61.57; H, 3.73; N, 3.99%.

3.5. Mercuration of bisferrocenylimines

A solution of compound **8** (0.5 mmol) in methylene dichloride (10 ml) was added into a 50 ml flask equipped with a magnetic stirrer and an equilibrated addition funnel. Meanwhile, 1 mmol of mercuric acetate was dissolved in a sufficient amount of methanol. This solution was then added dropwise to the flask over a period of 30 min. Subsequently, 1.5 mmol of lithium chloride dissolved in methanol was added, and then the mixture stirred for 30 min. The contents of the flask were transferred to a separatory funnel, and an additional 20 ml of methylene dichloride was added. The solution was washed with two 30 ml portions of water, and then dried over Na_2SO_4. The resulting solution was evaporated *in vacuo* to a minimum amount and subjected to a dry column of silica gel, eluted with methylene dichloride. The first band is for compound **10**, second band is for compound **9**.

3.6. 2-Chloromercurio-1,1′-bis[(3-methylphenylimino)phenylmethyl]ferrocene ***(9a)***

Orange crystal, yields 19.8%. m.p. 145–146°C, IR KBr(pellet): 3055, 2918, 1592, 1485, 1445, 783, 706 cm^{-1}. ^{1}H NMR: 2.17 s, 2.15 s (6H, 2CH_3); 4.49–4.76 (7H, Cp-H); 6.31–6.93 (8H, N-Ph-H); 7.14 m, 7.23 m (10H, C-Ph-H). Found: C, 56.60; H, 5.67; N, 4.84. Calc. for $C_{38}H_{31}ClFeHgN_2$: C, 56.51; H, 5.59; N, 4.84%.

3.7. 2-chloromercurio-1,1′-bis[(3-bromophenylimino)phenylmethyl]ferrocene ***(9b)***

Brown-red crystals, yields 48.1%, m.p. 144–145°C. IR KBr(pellet): 3058, 1576, 1456, 1444, 894, 782, 709 cm^{-1}. ^{1}H NMR: 4.49–4.76 (7H, Cp-H); 6.32–6.95 (8H, N-Ph-H); 7.11 m, 7.25 m (10H, C-Ph-H). Found: C, 45.78; H, 2.63; N, 3.04. Calc. for $C_{36}H_{25}Br_2ClFeHgN_2$: C, 46.05; H, 2.67; N, 2.99%.

3.8. 2,2′-bis(chloromercurio)-1,1′-bis[(3-methylphenylimino)phenylmethylferrocene ***(10a)***

Orange crystals, total yields 41.7%, m.p. >250°C (dec.).

IR KBr(pellet): 3057, 2920, 1589, 1486, 1426, 784, 706 cm^{-1}. ^{1}H NMR: 2.15 s, 2.17 s (6H, 2CH$_3$); (*meso*): 4.71 (t, 2H, $J=2.5$ Hz, H-4), 4.59 m (2H, H-3); 4.53 (d, 2H, $J=1.5$ Hz, H-5); (*dl*): 4.63 (bs, 2H, H-4); 4.59 m (2H, H-3); 4.42 (bs, 2H, H-5): 6.38–6.94 (8H, N-Ph-H); 7.18 m, 7.33 m (10H, C-Ph-H). Found: C, 44.05; H, 2.90; N, 2.91. Calc. for $C_{38}H_{30}Cl_2FeHgN_2$: C, 43.74; H, 2.88; N, 2.69%.

*3.9. 2,2′-bis(chloromercurio)-1,1′-bis[(3-bromophenylimino)phenylmethyl]ferrocene (**10b**)*

Brown-red crystals, total yields 34.9%. m.p. >250°C (dec.). IR KBr(pellet): 3077, 1579, 1490, 1465, 901, 780, 706 cm^{-1}. ^{1}H NMR: (*meso*): 4.73 t (2H, $J=2.5$ Hz, H-4); 4.61 m (2H, H-3); 4.56 m (2H, H-5). (*dl*): 4.65 bs (2H, H-4); 4.61 m (2H, H-3); 4.45 bs (2H, H-3). 6.36–7.06 (8H, N-Ph-H); 7.16 m, 7.33 m (10H, C-Ph-H). Found: C, 36.61; H, 2.05; N, 2.56. Calc. for $C_{36}H_{24}Br_2Cl_2FeHgN_2$: C, 36.85; H, 2.05; N, 2.39%.

*3.10. X-ray crystal structure determination for meso-**10a***

Crystal data: $(C_{19}H_{15}NHgCl)_2Fe$, Mr=1044.2, triclinic, P-1, $a=7.745(3)$, $b=14.761(5)$, $c=15.657(5)$ Å, $\alpha=98.14(7)$, $\beta=97.16(8)$, $\gamma=99.85(8)$°, $V=1725.36$ Å^3, $Z=2$, Dc=2.0086 g/cm^3, $\sigma=0.71073$ Å.

An orange crystal of *meso*-**10a** measuring 0.80*0.20*0.10 mm^3 was mounted on a MAC Science DIP-2000. Data for crystal were collected with MoKa radiation using the MAC Research Image Plate System. The crystal was positioned at 90 mm from the Image Plate. Forty five frames were measured at 4° intervals. Total of 5385 reflections were measured, 3903 reflections were considered with I $>3\sigma$(I). The data were corrected for Lorentz and polarization effects. The structure was solved by using MAC Science CryatanG. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were refined isotropically, final $R=0.0740$, Rw=0.0856.

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