Heterocyclic Letters
Vol. 12| No.2|257-269|February -April|2022
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

SYNTHESIS, EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF N-(FERROCENYL METHYL) ORTHO, META AND PARA DIAMINE BENZENE PREPARED BY REDUCTION OF FERROCENYLMETHYL NITROANILINE WITH PHMS AS A SOURCE OF HYDROGEN AND TBAF AS CATALYST

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Abstract

A mild, environmentally friendly method for reduction of aromatic nitro compounds to the corresponding amines is reported, using polymethylhydrosiloxane (PMHS), in the presence of catalytic tetrabutylammonium fluoride (TBAF) in the THF medium at 60°C, with optimized operating conditions. Three aromatic nitro ferrocenic compounds; N-(ferrocenylmethyl)-2-nitroaniline (2-FcCH$_2$NHPhNO$_2$), N-(ferrocenylmethyl)-3-nitroaniline (3-FcCH$_2$NHPhNO$_2$) and N-(ferrocenylmethyl)-4-nitroaniline (4-FcCH$_2$NHPhNO$_2$) have been converted efficiently to the corresponding aromatic amines: N-(ferrocenyl methyl) 1,2-diamine benzene (2-FcCH$_2$NHPhNH$_2$), N-(ferrocenyl methyl) 1,3-diamine benzene (3-FcCH$_2$NHPhNH$_2$) and N-(ferrocenyl methyl) 1,4-diamine benzene (4-FcCH$_2$NHPhNH$_2$) with yield between 24%-65%. Some QSAR's Geometric parameters of the compounds; bond lengths in the studied compounds, angles between the bonds in the products and property of the synthesized compounds such us partition coefficient, hydration energy, molar; refractivity and polarizability, were calculated.

Key words : *N*itro, *A*mine, *P*MHS, *T*BAF, *R*eduction, *A*romatic *F*errocene *C*ompounds.

1. Introduction

Aromatic amines are an important class of compounds frequently used as key intermediates in the synthesis of pharmaceuticals, agrochemicals, dyes, pesticides and polymers. They are the precursors of many synthetic intermediates such as amides, imines, azo compounds, isocyanates and diazonium salts that could be converted into various other functional groups**[i]**. Various processes have been developed for the preparation of aromatic amines and are based on the hydrogenation of the corresponding aromatic nitro compounds**[ii]**. The different processes are classified according to the source of hydrogen used during the reduction and the mechanism involved in the reduction process; indeed, the selective reduction of nitro compounds to amines is one of the most important chemical reactions of synthetic organic chemistry[iii].

Reduction reactions are carried out by different methods, so each method has its advantages and disadvantages. We mention the reduction with complex hydrides and the most widespread and used is sodium borohydride ($NaBH_4$), which is known for its high selectivity, in the presence of iodine (I_2) it is possible to reduce esters, amides and amino acids[iv] and also in the presence of tetrachlorozirconium ($ZrCl_4$), reduce nitro aliphatic and aromatic function[v], and it has been reported that reactions of amino acids with $NaBH_4$ in the presence of $NiCl_2$ or MoO_3 in water gives high yield β-amino alcohols[vi]. Other reagents have been used to reduce amino acids like lithium hydride aluminum hydride $LiAlH_4$[vii] and Boran (BH_3)[viii].

Lithium aluminum hydride has also been used to reduce the carboxylic function, halogenated derivatives and esters in the presence of ether (OEt_2)[ix]. This type of metal hydride is very effective because it allows the reduction of most of the organic functions but is not selective. In addition, there is another method of reduction which is to add two hydrogen radicals, called reduction by hydrogenation, it's usually splits into two types, heterogeneous hydrogenation and homogeneous hydrogenation, where this method is often used to reduce double and triple bonds, but is sometimes considered dangerous[x]

Among the hydrides discovered recently (in 1946), polyethylhydrosloxane, which was initially used as a simple reagent in some organic preparations, and recently it has become used in reduction reactions with a wide range of catalysts. PMHS has been shown to be effective in reducing many organic functions with high efficiency.

In 1957, Wackerchemie Burghausen developed the first process using silanes as a hydride source to avoid the use of aluminum hydrides[xi]. PMHS has certain advantages because it is cheap, stable and can be considered a by-product of the silicone industry[xii]. In 1973, Lipowitz and Bowman published the catalytic reduction of nitrobenzene to aniline by Pd/C and PMHS in ethanol at 40−60°[xiii].

Several studies have been done on the reduction of nitro aromatic groups to amines, at room temperature, this reduction can be achieved with high yield and short reaction times (30 min) using a combination of palladium (II) acetate, aqueous potassium fluoride and polymethylhydrosiloxane. When they replaced PMHS/KF with triethylsilane, they were able to reduce the aliphatic nitro groups to their corresponding hydroxylamines[xiv]

A new methodology for the rapid and selective reduction of carbonyls in the solid phase has been published by Alain Y et al, it consists of using a silane as a source of green hydride, at low cost, non-toxic, and stable at l'air, polymethylhydrosiloxane (PMHS), they were able to reduce a variety of carbonyl compounds, with catalytic amounts of fluorides[xv]. Additionally, 5-hydroxymethylfurfural (5-HMF) can be reduced through this methodology to give 2,5-dimethylfuran (DMF) using commercial $PdCl_2$ as a catalyst and polymethylhydrosiloxane (PMHS), yielding the hydrodeoxygenation product. DMF as high as 89.7% was reached at room temperature (298 K) in 0.5 h[xvi]

A simple protocol for using inexpensive polymethylhydrosiloxane (PMHS), as a reducing agent for phosphine oxides to phosphines has been published by Xuan-Xuan Zhao et al. The reaction has been studied by following the effect of parameters, such that the substrate/reducing ratio, the temperature and the reaction time, obtaining good conversions and selectivities[xvii]

In 1997, Kobayashi et al. found that tetrabutylammonium fluorid (TBAF) could effectively promote the PMHS reduction of aldehydes and ketones to alcohols [xviii, xix]. Analogous fluoride-catalysed reduction of ketones by PMHS was also reported by Lawrence et al[xx, xxi].

Drid et al obtained amino alcohols by reduction of α-amino acids such as Glycine, Valine, Methyonine, isoleucine, tyrosine and vinyl by PHMS in the presence of TBAF with yields ranging from 54% to 85%. They also reduced the amide function in some aromatic compounds, converting them into amines with a yield of about 75%. Finally, with the nitro compounds that required reduction at a temperature above 50 ° C, they obtained average results for the nitroaniline compounds in both meta- and para- positions with yields ranging from 40% - 50%**[xxii- xxiv]**.

In the light of all the previous studies and on the basis of studies by Sekhri in 1998 which concerns the reduction by PMHS in the presence of the tetra-butylammonium fluoride catalyst (TBAF) of several chemical functions**[xx]**, in this work, we have attempted to synthesize, characterize three amino ferrocenic compounds: N-(ferrocenylmethyl)-1,2-diamine benzene, N-(ferrocenylmethyl)-1,3-diamine benzene and N-(ferrocenylmethyl)-1,4-diamine benzene by reduction respectively of N-(ferrocenylmethyl)-2-nitroaniline, N-(ferrocenylmethyl)-3-nitroaniline and N-(ferrocenylmethyl)-4-nitroaniline and evaluate their QSAR's properties.

2. Experimental

2.1. Materials and instrumentation

- All chemicals were of reagent grade quality purchased from commercial sources and used as received. These included: polymethylhydrosiloxane (PMHS) 99% (Sigma-Aldrich), tetrabutylammonium fluoride (TBAF) 98% (Sigma-Aldrich), Tetrahydrofuran (THF) 99.9% (Sigma-Aldrich).
- N-(Ferrocenylmethyl) aniline (**$FcCH_2NHPh$**) and N-(ferrocenylmethyl) nitroaniline; (**2-$FcCH_2NHPhNO_2$, 3-$FcCH_2NHPhNO_2$ and 4-$FcCH_2NHPhNO_2$**) were synthesized by the coupling reaction between (ferrocenylmethyl) trimethyl ammonium iodide and the corresponding nitroaniline, as previously reported by our group**[xxv - xxvii]**.
- ^{1}H-and^{13}C-NMR spectra were recorded on BRUKER 400MHz spectrometer (AVANCEIII 400) in $CDCl_3$. Chemical shift values are reported in ppm and coupling constants in Hz. ^{1}H-NMR spectra were referenced internally using residual protons in the deuterated solvent ($CDCl_3$: δ (S) = 7.24 ppm) and values reported relative to tetramethylsilane (δ = 0.00 ppm). ^{13}C-NMR spectra were similarly referenced internally to the solvent resonance ($CDCl_3$: δ (t) = 77.0) with values reported relative to tetramethylsilane (δ =0.0ppm).The infrared spectra were recorded using Perkin Elmer spectrum 100 FT-IR spectrometer and the data are reported as percentage transmittances at given wave numbers
- All calculations relative to quantitative structure activity-relationship study (QSAR) done for the flavone and its derivate were performed by HyperChem 8.08 software**[xxviii]**.

2.2. General synthesis of amines

2.2.1. Synthesis of N-(ferrocenyl methyl) 1,2-diamine benzene (2-$FcCH_2NHPhNH_2$)

In a tricol flask, (0.2g, 0.57mmol) of the compound N-(ferrocenylmethyl)2-nitroaniline, which is reddish in color, was put in (0.2g, 0.57mmol) and 30ml of THF was added and the color became light yellow, then (0.00719g, 0.0228mmol) of TBAF was added, the coloring remains the same. After adding (0.386g, 0.0017mmol) of PMHS drop by drop to the reaction mixture, solidifications occurred and were destroyed by strong agitation. After stirring time, 50ml of 3N NaOH was added dropwise to the reaction mixture and left overnight. The mixture was then filtered and the solvent evaporated. Afterwards, a liquid-liquid extraction with CH_2Cl_2 was carried out once at pH= 8.5. Then the acidity of the medium was changed up to pH= 12, and extracted 4 times with CH_2Cl_2 (450ml). After drying and evaporation, a brown to orange-coloured solid product was obtained which is pure according to TLC analysis and yield R= 23.8%, m= 0.043g. IR: (KBr¸ ∂cm^{-1}): 3319.78-3400(F¸ ∂_{NH}), 3039.6(m¸ $\partial_{CH\ Ar}$), 2873.7(m¸ ∂_{CH}), 1681.8 (F¸ ∂_{N-H}), 1600.8(F¸ $\partial_{C=C}$), 1315.4(F¸ ∂_{C-N}), 1178.4(m¸ ∂_{C-C}), 752.3(∂ Aromatic Substituid), 450 (∂F_{C-CP}). RMN ^{1}H (400 MHz, $CDCl_3$) ; δ = 4.08(d, 2H, CH_2-NH), 4.14(s, 2H, $(CH_{Cp})_2$ or $(CH_{Cp})_3$), 4.19(s, 7H ; (5H) C_p and 2H, $(CH_{Cp})_3$ or $(CH_{Cp})_2$), 6.61(t, 1H, para CH-Ar), 6.84(d, 1H, ortho' CH-Ar), 7.19(s, 2H, NH_2), 7.39(t, 1H, meta' CH-Ar), 8.14(d, 1H, meta

CH-Ar), 8.86(s, 1H, NH). RMN ^{13}C (100 MHz, $CDCl_3$; δ = 42.33(1C, Cp-CH_2- NH), 67 (2C, $(CH_{Cp})_3$ or $(CH_{Cp})_2$), 68.15(2C, $(CH_{Cp})_2$ or $(CH_{Cp})_3$), 68.82(5C, Cp), 84.57(1C, $C_{1;\ Ar}$), 114 (1C, ortho' $C_{6;\ Ar}$), 115.37(1C, para $C_{4;\ Ar}$), 126.97(1C, $C_{3;\ Ar}$), 132 (1C, $C_{3;\ Ar}$-NH_2) ; 136.32(1C, meta' $C_{5;\ Ar}$), 144.98(1C, HN-$C_{1;\ Ar}$).

2.2.2. Synthesis of N-(ferrocenyl methyl) 1,3-diamine benzene (3-$FcCH_2NHPhNH_2$)

A tricol flask was filled with (0.2g, 0.57mmol) of the compound N-(ferrocenylmethyl)3-nitroaniline and 30ml of THF, (0.00719g, 0.0228mmol) of TBAF and (0.386g, 0.0017mmol) of PMHS which showed a variety of colorations during addition and agitation. After stirring for 6 hours, 50ml of 3N NaOH was added dropwise to the mixture. The mixture was then filtered and the solvent evaporated, after which the mixture was extracted once with CH_2Cl_2 at pH=8.5, the organic phase was dried with $MgSO_4$ and the solvent evaporated to obtain a dark red solid with a yield of R =55.6%, m = 0.101g. IR: (KBr¸ cm^{-1}): 3400(F¸ ∂_{NH}), 2871.8-2956.7(m¸ ∂_{CH}), 1647.1(F¸ ∂_{N-H}), 1598.9 (F¸ $\partial_{C=C}$), 1300 (m¸ ∂_{C-N}), 1100(m¸ ∂_{C-C}), 800.8($\partial_{Aromatic\ Substituid}$), 420($\partial_{Fc-CP}$). RMN ^1H (400MHz, $CDCl_3$) ; δ=3.87 (d, 2H, CH_2-NH), 4.05(t, 2H, $(CH_{Cp})_2$ or $(CH_{Cp})_3$), 4.11(t, 2H, $(CH_{Cp})_3$ or $(CH_{Cp})_2$), 4.17 (s, 5H, C_p), 6.89 (t, 2H, NH_2), 7.11(s, 1H, ortho CH-Ar), 7.18 (t, 1H, ortho' CH-Ar), 7.37 (m, 1H, para CH-Ar), 7.49 (d, 1H, ortho CH-Ar), 7.54(t, 1H, NH). RMN ^{13}C (100 MHz, $CDCl_3$; δ = 31.02 (1C, Cp-CH_2-NH), 68.19 (2C, $(CH_{Cp})_3$ or $(CH_{Cp})_2$), 68.60 (2C, $(CH_{Cp})_2$ or $(CH_{Cp})_3$), 69.02 (5C, Cp), 111.96 (1C, $C_{1;\ Ar}$), 120 (1C, ortho' $C_{6;\ Ar}$), 125.83 (1C, para $C_{4;\ Ar}$), 128.75 (1C, ortho $C_{2;\ Ar}$), 147 (1C, $C_{3;\ Ar}$-NH_2), 152.71 (1C, meta $C_{5;\ Ar}$), 163.93 (1C, HN-$C_{1;\ Ar}$).

2.2.3. Synthesis of N-(ferrocenylmethyl) 1,4-Diamine benzene (4-$FcCH_2NHPhNH_2$)

In a tricol flask, N-(ferrocenyl methyl)3- nitroaniline compound (0.2g, 0.57mmol) was placed (0.2g, 0.57mmol) and 30ml of THF was added; the color turned yellow, then (0.386g, 0.0017mmol) of TBAF was added, the color was changed to black after a few minutes of stirring, then (0.386g, 0.0017mmol) of PMHS was added, of which we noticed the formation of a large quantity of solids and an increase in temperature, which forced us to increase the volume of solvent and with a quick stirring we were able to destroy the solids formed, the color turned yellowish green. After 6 hours of stirring, we added 50ml of 3N NaOH drop by drop and left the mixture under stirring for a complete night. After filtration of the mixture and evaporation of the solvent, it was extracted with CH_2Cl_2 once at pH 8.5. Then the organic phase was dried with $MgSO_4$ and evaporated once more. The acidity of the medium was changed to pH 12 and extracted 4 times with CH_2Cl_2 (450 ml).

After drying and evaporation of the solvent, a solid product with a brown to orange color was obtained. The yield R was 64.89%, m= 0.118g. IR: (KBr¸ ∂cm^{-1}): 3300-3500(F¸ ∂_{NH}), 2871.8-2956.7(m¸ ∂_{CH}), 1598.9(m¸ ∂_{N-H}), 1473.5(F¸ $\partial_{C=C}$), 1300(m¸ ∂_{C-N}), 1109.0(m¸ ∂_{C-C}), 894.9($\partial_{Aromatic\ Substituid}$), 420 ($\partial_{FC-CP}$). RMN ^1H (400MHz, $CDCl_3$) ; δ=2.54 (m, 4H, CH_2-NH and $(CH_{Cp})_2$ or $(CH_{Cp})_3$), 3.18(d, J=8.4Hz, 2H, $(CH_{Cp})_3$ or $(CH_{Cp})_2$), 3.32 (s, 5H, C_p), 6.51- 6.89 (m, 3H, NH and meta, meta' CH-Ar), 7.85-8.14 (m, 2H, ortho, ortho' CH-Ar). RMN ^{13}C (100 MHz, $CDCl_3$; δ = 39.32- 40.92 (11C, Cp-CH_2-NH and Cp_{sub}, Cp), 57.31 (1C, HN- $C_{4;\ Ar}$), 112.57 (2C, meta $C_{3;\ Ar}$ and meta' $C_{5;\ Ar}$), 126.58 (2C, ortho $C_{2;\ Ar}$ and ortho' $C_{6;\ Ar}$), 155.92 (1C, HN-$C_{1;\ Ar}$).

2.3. Geometry optimization (Theoretical characterization) of N-(ferrocenyl methyl) ortho, meta and para diamine benzene and QSAR's properties study

The four prepared molecules have been pre-optimized using the Molecular Mechanics (MM^+) force field included in HyperChem version 8.0.3 with a partition coefficient Rms = 0.1 Kcal/mol. Geometrical parameters, link length, valence angle and dihedral angle are optimized. HyperChem's QSAR property module was used to calculate: molar weight (MW), molar polarisability (Pol), molar refractivity (MR), octanol/water partition coefficient (logP), hydration energy (HE), molar volume (MV), surface grid (SAG) and Surface Area Approx (SAA).

N-(Ferrocenylmethyl) aniline (**$FcCH_2NHPh$**) constitutes the mother structure, while the other compounds of identical structure identical to that of the mother structure and has a single active center which is the primary amine function, for this reason, we will study the influence of the position of the active center in ortho, meta and para on the coordinates, total energy (minimum molecule stability energy) and the QSAR structure and properties of N-(ferrocenylmethyl)1,2-diamine benzene **(2-$FcCH_2NHPhNH_2$)**, N-(ferrocenylmethyl) 1,3-diamine benzene (**3-$FcCH_2NHPhNH_2$**) and N-(ferrocenylmethyl) 1,4-diamine benzene (**4- $FcCH_2NHPhNH_2$**)
In order to compare the effect of active sites (NH for $FcCH_2NHPh$, both NH and NH_2 for 2-$FcCH_2NHPhNH_2$, 3-$FcCH_2NHPhNH_2$, and 4-$FcCH_2NHPhNH_2$) and to validate the results of the geometric optimization measurements and their crystal structures **[xxviii]**

3. Results and discussion :

3.1. Synthesis

After optimization of the operating conditions, all reactions are carried out at 60 °C in THF solvent and the reducing system TBAF/PMHS.
Figure (01) presents optimized geometrical structure of N-(Ferrocenylmethyl) aniline ($FcCH_2NHPhNH_2$) by Hyperchem.

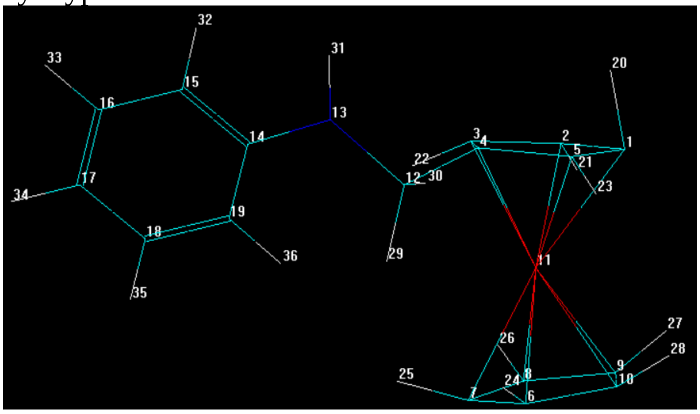


Figure (01) : Optimized geometrical structure of $FcCH_2NHPh$

3.1.1. Reduction of N-(ferrocenylmethyl) 2-nitroaniline ($FcCH_2NHPhNO_2$)

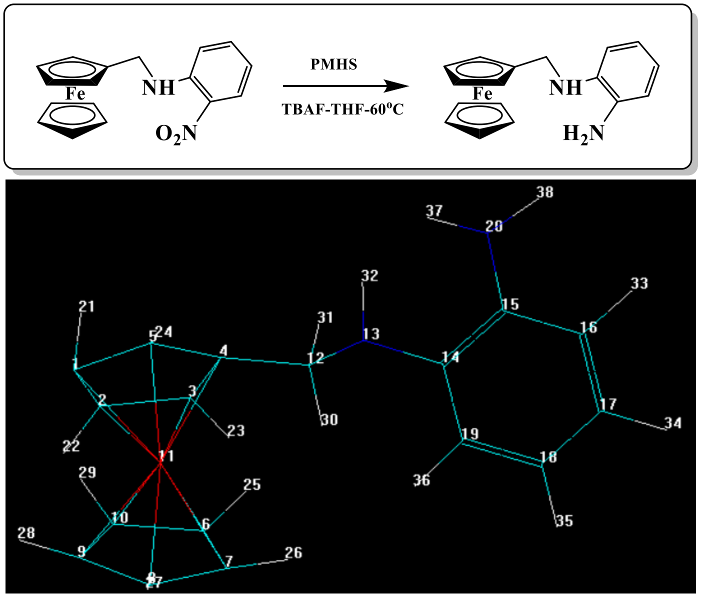


Figure (02) : Reduction reaction of 2-$FcCH_2NHPhNO_2$ by (TBAF-PMHS) and Optimized geometrical structure of 2-$FcCH_2NHPhNH_2$

The course of the reaction was followed by thin layer chromatography, a new product with a retention factor $R_f = 0.73$ which is different from that of the reagent of $R_f = 0.81$, the product is a red solid. The IR spectrum of the product was compared with that of the reagent, the disappearance of the characteristic band of the NO_2 function in the reagent spectrum at $1508.2 cm^{-1}$ and $1325.9 cm^{-1}$, the disappearance of the characteristic absorption bands of N-O in the reagent spectrum at $825.5 cm^{-1}$ and $808.1 cm^{-1}$, and the appearance of the characteristic band of NH_2 at $3350 cm^{-1}$. In addition, the melting point of the product was determined and found to be 98°C while the melting point of the reagent is 110°C. A nuclear magnetic resonance spectrophotometric analysis was performed, the ^{13}C NMR spectrum showed that the compound contains 17 carbon atoms as shown in the above structural formula and the ^{1}H NMR spectrum showed that the compound contains 18 hydrogens

3.1.2. Reduction of N-(ferrocenylmethyl)-3-nitroaniline (3-$FcCH_2NHPhNO_2$):

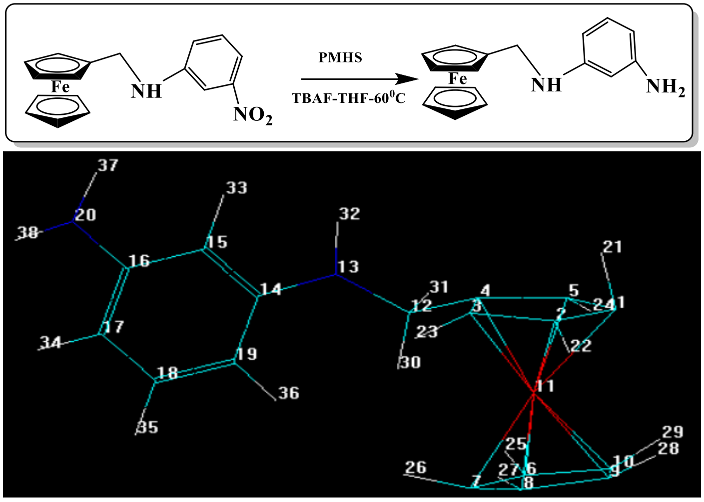
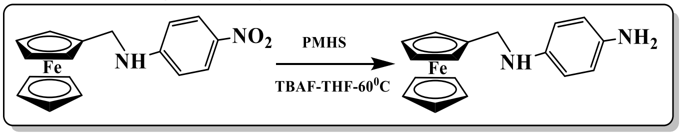


Figure (03) : Reduction reaction of 3-$FcCH_2NHPhNO_2$ by (TBAF-PMHS) and Optimized geometrical structure of 3-$FcCH_2NHPhNH_2$

N-(ferrocenylmethyl)3-nitroaniline has been reduced to N-(ferrocenylmethyl)1,3-diaminobenzene of which The progress of the reaction was always monitored by TLC, where it showed the appearance of a new compound with a retention factor $R_f= 0.58$ different from the reagent of $R_f= 0.87$. The product was analyzed by IR spectrophotometry and the two characteristic bands of NO_2 in the reagent spectrum at $1521.7 cm^{-1}$ and $1340.4 cm^{-1}$ disappeared and a characteristic band of NH_2 appeared at $3400 cm^{-1}$. The melting point of the product $m_P= 108°C$ was determined to be different from that of the reagent $m_P= 120°C$.

3.1.3. Reduction of N-(ferrocenylmethyl)-4-nitroaniline (4-$FcCH_2NHPhNO_2$)



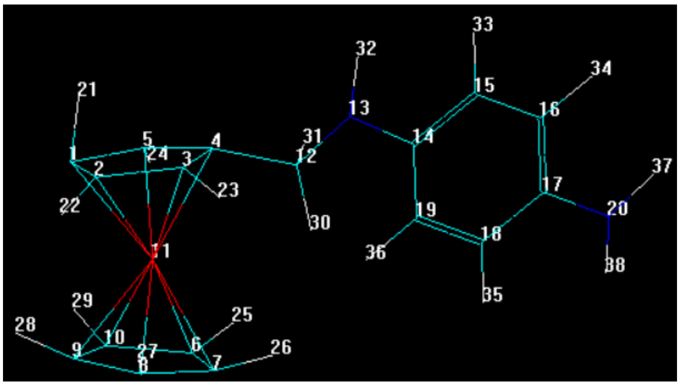


Figure (04) : Reduction reaction of 4- $FcCH_2NHPhNO_2$ by (TBAF-PMHS) and Optimized geometrical structure of 4- $FcCH_2NHPhNH_2$

The progress of the reaction was always monitored by TLC, where it showed the appearance of a new compound of retention factor R_f= 0.74 different from the reagent of R_f= 0.58. The product was analyzed by IR spectrophotometry, and the disappearance of the characteristic NO_2 band in the starting reagent spectrum at 1521.7cm^{-1} and 1344.3cm^{-1}, the disappearance also of the absorption band characteristic of the N-O function at 823.5cm^{-1} and the appearance of a new band at 3400cm^{-1} and 3380cm^{-1} characteristic of the NH_2 function. The melting points of reagent and product were determined to be 115°C and 124°C, respectively.

Based on the reduction reactions of the three (ferrocenylmethyl)nitroaniline compounds under the above experimental conditions and in the three positions; ortho, meta and para and as shown in table (01), it was found that the position which gives a better reduction efficiency R= 65.89% is the para position, followed by the meta position with an efficiency equal to 55.6% and finally the ortho position with a relatively low efficiency equal to 23.8%, This is linked to the simplicity of their molecular structure characterized by the presence of a "nitro" group ($-NO_2$) in the ortho, meta and para position of an electron-donating group (hydroxyl or amino groups), this can be explained in general by the electronic nitroaniline effect bat in these results the steric hindrance caused by ferrocene and phenyl.

Table (01) : results of reduction reactions by (TBAF- PMHS)

The efficiency of the reduction%	**The resulting compounds**	**Reactive compounds**
64.89	4- $FcCH_2NHPhNH_2$	4-$FcCH_2NHPhNO_2$
55.6	3- $FcCH_2NHPhNH_2$	3- $FcCH_2NHPhNH_2$
23.8	2- $FcCH_2NHPhNH_2$	2- $FcCH_2NHPhNH_2$

The reduction of nitro aromatic compounds for the preparation of aromatic amines is generally carried out either by catalytic hydrogenation in the presence of a catalyst such as nickel or palladium, or by the use of metals such as iron or tin in presence of an acid, in addition, these reactions take place under difficult experimental conditions and can give a mixture of compounds in addition to the amines, which are nitroazo compounds and hydroxylamine’s (figure 05). Therefore, the search for safe, clean and selective reduction systems remains a concern for chemical researchers.

Figure (05) shows the different products resulting from the reduction of nitro aromatic compounds.

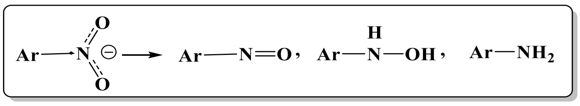


Figure (05) : The different products resulting from the reduction of aromatic nitro compounds

Based on reference [xxix, xxx], the following mechanism for the reduction of the nitro group to the amine group can be proposed ; This process is called “Zipper” catalysis, in detail **Figure (06)**.

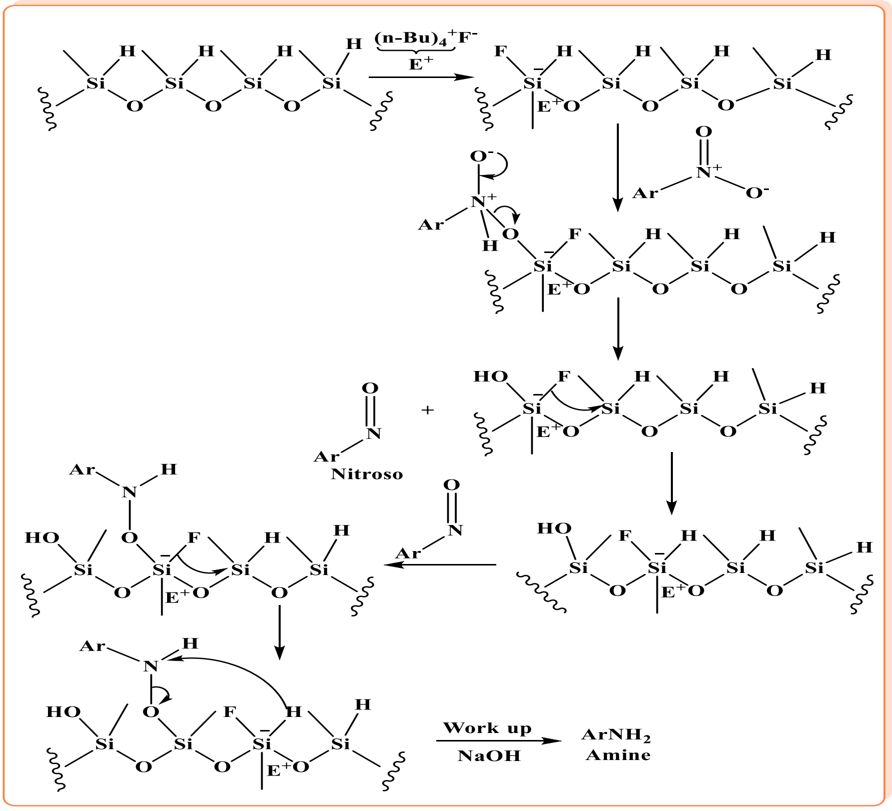


Figure (06) : Proposed mechanism of the nitro group reduction by TBAF- PMHS

3.2. Stabilization energy

Table (02) gathers the values of the stabilization energy of the compounds $FcCH_2NHPh$, 2-$FcCH_2NHPhNH_2$, 3-$FcCH_2NHPhNH_2$ and 4$FcCH_2NHPhNH_2$.

Table (02) : stabilization energy values of the compound $FcCH_2NHPh$, 2-$FcCH_2NHPhNH_2$, 3-$FcCH_2NHPhNH_2$ and 4-$FcCH_2NHPhNH_2$

Compound	**$FcCH_2NHPh$**	**2-$FcCH_2NHPhNH_2$**	**3-$FcCH_2NHPhNH_2$**	**4-$FcCH_2NHPhNH_2$**
S.E(Kcal/mol)	677.75	684.27	682.86	682.73

*S.E (Stabilization energy)

According to table (02), we notice that the highest energy of stability was recorded with the compound **2-$FcCH_2NHPhNH_2$** and the lowest energy is recorded with the compound **$FcCH_2NHPh$**, also, we noticed that there is not a large energy difference of compounds 3-**$FcCH_2NHPhNH_2$**, and 4-**$FcCH_2NHPhNH_2$**

3.3. Geometric parameters of the compounds :

Bond lengths in the studied compounds, angles between the bonds in the products. Table (03) presents the bond length between atoms of molecules FcCH$_2$NHPh, 2-FcCH$_2$NHPhNH$_2$, 3-FcCH$_2$NHPhNH$_2$ and 4-FcCH$_2$NHPhNH$_2$.

Table (03) : Bond lengths of the products

Bond	**FcCH$_2$NH Ph**	**4-FcCH$_2$NH PhNH$_2$**	**3-FcCH$_2$NH PhNH$_2$**	**2-FcCH$_2$NH PhNH$_2$**
C(15)-N(20)		1.3448	1.345	1.346
N(20)-H(38)		1.0182	1.0176	1.0181
N(20)-H(37)		1.0179	1.0179	1.0168
C(18)-C(19)	1.3426	1.3427	1.3429	1.3423
C(17)-C(18)	1.3417	1.3416	1.3419	1.3413
C(16)-C(17)	1.3416	1.3417	1.3417	1.3417
C(15)-C(16)	1.3424	1.3425	1.3425	1.3432
C(14)-C(19)	1.3445	1.3444	1.3443	1.3449
C(14)-C(15)	1.3443	1.3443	1.3440	1.3466
N(13)-C(14)	1.3508	1.3511	1.3517	1.3524
C(12)-N(13)	1.4484	1.449	1.4527	1.4537
C(10)-Fe(11)	2.1205	2.1194	2.1200	2.1195
C(9)-Fe(11)	2.1210	2.1201	2.1205	2.1203
C(9)-C(10)	1.4789	1.4790	1.479	1.4789
C(8)-Fe(11)	2.1198	2.1190	2.1196	2.1193
C(8)-C(9)	1.479	1.4792	1.4794	1.4792
C(7)-Fe(11)	2.1195	2.1190	2.1191	2.1190
C(7)-C(8)	1.4785	1.4787	1.4788	1.4787
C(6)-Fe(11)	2.1196	2.1185	2.1192	2.1188
C(6)-C(10)	1.4788	1.479	1.4789	1.4789
C(6)-C(7)	1.4792	1.4796	1.4796	1.4796
C(5)-Fe(11)	2.0856	2.0853	2.0853	2.0856
C(4)-C(12)	1.5178	1.5175	1.5181	1.5182
C(4)-Fe(11)	2.0963	2.0959	2.0968	2.0968
C(4)-C(5)	1.4826	1.4823	1.4825	1.4824
C(3)-Fe(11)	2.0926	2.0922	2.092	2.0915
C(3)-C(4)	1.4810	1.4808	1.4813	1.4813
C(2)-Fe(11)	2.0873	2.0868	2.0869	2.0868
C(2)-C(3)	1.4828	1.4828	1.4825	1.4827
C(1)-Fe(11)	2.1312	2.1304	2.1307	2.1306
C(1)-C(5)	1.4982	1.4984	1.4985	1.4987
C(1)-C(2)	1.4991	1.4994	1.4992	1.4994

In Table (03), it is noted that the lengths of the bonds of the four compounds are very close Table (04) gathers the values of the tri-angles of the studied compounds (amine part)

Table (04): measurements of the tri-angles of the compounds studied (amine part)

Angle	**$FcCH_2NHPh$**	**4-$FcCH_2NHPhNH_2$**	**3-$FcCH_2NHPhNH_2$**	**2-$FcCH_2NHPhNH_2$**
H(38)-N(20)-H(37)		130.1318	130.1748	129.5907
H(38)-N(20)-C(15)		114.8933	114.884	114.6002
H(37)-N(20)-C(15)		114.9748	114.9412	115.8003
N(20)-C(15)-C(16)		119.8846	119.748	117.8623
N(20)-C(15)-C(14)		119.9095	119.8075	121.7420
C(18)-C(19)-C(14)	120.2668	120.2967	120.2301	120.513
C(19)-C(18)-C(17)	120.21	119.8825	120.2249	120.0886
C(18)-C(17)-C(16)	119.7394	120.2052	119.5172	119.7768
C(17)-C(16)-C(15)	120.0223	119.717	120.4445	120.1127
C(16)-C(15)-C(14)	120.4687	120.4743	120.0428	120.3935
C(19)-C(14)-C(15)	119.2826	119.4153	119.5333	119.1109
C(19)-C(14)-N(13)	123.2969	123.0660	122.3963	120.8634
C(15)-C(14)-N(13)	117.4117	117.5104	118.0615	120.0131
C(14)-N(13)-C(12)	126.037	125.6144	122.7711	122.1214
N(13)-C(12)-C(4)	108.7858	108.7549	108.3677	108.2393

From table (04), we notice that the angles are very close to each other except the angle N (20) -C (15) -C (14) which is equal to 121.742 in the compound 2-$FcCH_2NHPhNH_2$ which is greater than that in the other compounds and this results in the repulsion between the amine groups because of their coming together, and the angle C (19) -C (14) -N (13) of compound $FcCH_2NHPh$ is less than C (15) - C (14) -N (13) of the same compound because the amine group is a donor group, also we can notice the angle measurements of the compounds $FcCH_2NHPh$ and 4-$FcCH_2NHPhNH_2$ are close because the amine group in the para position, the repulsion between the grouping decreases and the structure of the compound becomes close to that of the parent compound.

Table (05) gathers the dihedral angles of studied compounds.

Table (05) : Dihedral angles of the products

Angle	**$FcCH_2NHPh$**	**4-$FcCH_2NHPhNH_2$**	**3-$FcCH_2NHPhNH_2$**	**2-$FcCH_2NHPhNH_2$**
N(13)-C(14)-C(15)-N(20)				-1.124
N(20)-C(15)-C(16)-C(17)		-179.9422		-179.6899
C(14)-C(15)-N(20)-H(37)		-0.2046	-0.1043	-0.7936
C(14)-C(15)-N(20)-H(38)		179.9127	179.9739	-179.8218
C(16)-C(15)-N(20)-H(37)		-179.9	179.9598	178.6705
C(16)-C(15)-N(20)-H(38)		0.2172	0.038	-0.3577
C(19)-C(14)-C(15)-N(20)		179.9875	179.6028	-179.8452
C(17)-C(18)-C(19)-C(14)	0.2467	0.3074	0.2869	0.3596
C(16)-C(17)-C(18)-C(19)	0.4157	0.3633	0.2469	0.1362
C(15)-C(16)-C(17)-C(18)	-0.2913	-0.3181	-0.1595	-0.206
C(14)-C(15)-C(16)-C(17)	-0.4968	-0.3984	-0.4618	-0.2183
N(13)-C(14)-C(19)-C(18)	-179.9184	-179.9419	-179.7994	-179.485
C(15)-C(14)-C(19)-C(18)	-1.0235	-1.0129	-0.9038	-0.7751
N(13)-C(14)-C(15)-C(16)	-179.8907	-179.9522	179.9328	179.4252
C(19)-C(14)-C(15)-C(16)	1.1498	1.0598	0.9895	0.7041
C(12)-N(13)-C(14)-C(15)	151.8125	148.1399	134.3181	130.2898

C(12)-N(13)-C(14)-C(19)	-29.2733	-32.9119	-46.7709	-51.0119
C(4)-C(12)-N(13)-C(14)	124.8839	128.384	151.3947	157.1333

Through table (06), we notice that the angles are very close except the angles C (12) -N (13) -C (14) -C (15), C (12) -N (13) -C (14) -C (19) have an inversely proportional relationship and this results in the influence of amine group on the angle at C (15). The closer the amine group, the smaller the angle. In addition to the angle C (4) -C (12) -N (13) -C (14), we note that the closer the group of amines is to the carbon atom C (14), the more the angle measurement is high.

3.4. QSAR's study

Table (06) : QSAR properties of compounds $FcCH_2NHPh$, 2-$FcCH_2NHPhNH_2$, 3-$FcCH_2NHPhNH_2$ and 4-$FcCH_2NHPhNH_2$

compound	**SAG [A^2]**	**MV [A^3]**	**HE [Kcal/mol]**	**Log P**	**MR [A^3]**	**Pol [A^3]**	**MW [am]**
$FcCH_2NHPh$	460.205	778.75	-1.49	-2.02	71.18	27.34	291.18
4-$FcCH_2NHPhNH_2$	476.27	812.05	-6.61	-3.74	74.73	28.69	306.19
3-$FcCH_2NHPh$ NH_2	479.58	815.21	-6.34	-3.74	74.73	28.69	306.19
2-$FcCH_2NHPhNH_2$	476.98	809.26	-5.17	-3.74	74.73	28.69	306.19

From Table (06), it can be seen that the addition of the amine group caused a considerable increase in the QSAR properties except in compound $FcCH_2NHPh$, the partition coefficient and the hydration energy were lowered in addition one has noticed an equivalence in the values of the partition coefficients, refraction, polarizability and mass in compounds 2-$FcCH_2NHPhNH_2$, 3-$FcCH_2NHPhNH_2$ and 4-$FcCH_2NHPhNH_2$ while the highest surface area and volumes were recorded in compound 3-$FcCH_2NHPhNH_2$.

4. Conclusion

The objective of this study was to prepare three ferrocene compounds; N- (ferrocenylmethyl) 1,2-diamine benzene, N-(ferrocenylmethyl) 1,3-diamine benzene and N-(ferrocenylmethyl) 1,4-diamine benzene by reduction respectively of N-(ferrocenylmethyl) 2-nitroaniline, N-(ferrocenylmethyl) 3-nitroaniline and N- (ferrocenylmethyl) 4-nitroaniline by polyhydromethylsiloxane (PHMS) as a source of hydrogen in the presence of TBAF. These obtained products were identified and characterized by NMR and IR. A theoretical characterization of these compounds is also performed in this manuscript by the Hyperchem program; these are the lengths of the bonds between the atoms of molecules, the tri and dihedral angles as well as the QSAR properties (SAG, MV, HE, logP, MR, Pol and MW).

5. Acknowledgments: The authors would like to thank to Algerian Ministry of Higher Education and Scientific Research and General Directorate of Scientific Research and Technological Development (DGRSDT) for their support and providing the necessary facilities to carry out this research.

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Received on February 3, 2022.