RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 2954

# Microwave-assisted synthesis of fulleropyrazolines/fulleroisoxazolines mediated by (diacetoxyiodo)benzene: a rapid and green procedure

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Received 21st August 2013
Accepted 21st October 2013

DOI: 10.1039/c3ra44567d

www.rsc.org/advances

Microwave as a green, rapid and effective procedure has been applied to the synthesis of fulleropyrazolines/fulleroisoxazolines. The reaction mixtures containing substituted phenylhydrazones/oximes, $C_{60}$ and $PhI(OAc)_2$ allowed to achieve products at room temperature in a good yield and short time without any side product.

## 1. Introduction

Since the discovery of fullerenes[1] and isolation in bulk,[2] the research of appropriate procedures for their functionalization has become one of the main challenges in organic chemistry.[3] In particular, the most numerous member of the fullerene family, $C_{60}$, has obtained the highest interest as $C_{60}$-based molecules exhibit a broad range of interesting features, biological fields such as anti-HIV activity and ability to inhibit enzymes, DNA cleavage, neuroprotective, antioxidant, antimicrobial activities.[4] In addition, fullerene derivatives have wide applications in biomedicine including radiotracers,[5] magnetic resonance imaging (MRI) contrast agents for metallo-fullerenols[6] and drug delivery system.[7] The double bonds between two hexagons in $C_{60}$ structure are dienophilic, which enables the molecule to undergo a variety of cycloaddition reactions including cycloadditions,[8] cyclopropanation,[9] addition organometallic reagents,[10] and photo-induced electron transfer reactions.[11] Among the different types of cycloaddition reactions[12] available for the preparation of fullerene derivatives, 1,3-dipolar cycloadditions demonstrate a powerful tool due to the fact that $C_{60}$ behaves as an electron-deficient olefin. Different types of fullerene derivatives such as fullerene-fused pentagonal heterocyclic rings, such as fulleropyrolidines,[13] fulleroindolines,[14] fullerene fused lactones,[15] pyrazolo- and oxazolo-fullerenes[16] have been reported in the literature. Fullerene-fused pentagonal heterocyclic rings, such as fulleroisoxazolines or fulleropyrazolines, which is known to show attractive chemical, electrochemical, and photophysical properties have been made through 1,3-dipolar cycloadditions like fulleropyrrolidines. The electrochemical properties of the fulleroisoxazoline and fulleropyrazoline compounds in which a heteroatom is directly attached to the $C_{60}$ cage were studied to indicate the same or better acceptor character than $C_{60}$. It is different from fulleropyrrolidines which usually show a decline in electron affinity with respect to the parent $C_{60}$.[17] Fulleroisoxazolines or fulleropyrazolines can be readily synthesized through several methods such as addition of nitrilimine or nitrile oxide to $C_{60}$. For the first time, the addition reaction of $C_{60}$ with nitrile oxides was reported by Meier.[18] The most commonly used strategy for the synthesis of fulleroisoxazolines and fulleropyrazolines include two steps: first synthesis of hydroximinoyl halides or hydrazonoyl halides resulted from reaction of aldoxime or hydrazone with NCS or NBS, then reacting with $C_{60}$ in the presence of organic base.[19] Also isoxazoline-fused fullerenes can also be obtained from the reaction of $C_{60}$ and nitrile oxide.[20] Also synthesis of fulleroisoxazolines through the reaction of $C_{60}$ with *N*-silyloxynitrones, formed from nitroalkene and $Me_3SiCl/Et_3N$ was reported.[21] Recently, one-step synthesis of several fullerene derivatives was reported at room temperature by Yang's group.[22]

In the recent years, the synthetic utility of microwave irradiation has appeared as a very efficient and clean alternative to conventional heating for introducing energy in organic reactions has considerably been increased. Microwave includes an electric and magnetic field and thus specifies electromagnetic energy which can act as a non-ionising energy. This energy causes molecular movements of ions and rotation of the dipoles, but does not affect the molecular structure. Under microwaves, the energy transfer is produced by dielectric loss not by conduction or convection.[23]

This methodology is applied in cycloaddition reactions of compounds that are sensitive and/or have low reactivity such as heterocycles, natural products and fullerene derivatives. Examples of this technology in organic synthesis are numerous.[24] Furthermore, the related literatures on microwave-assisted synthesized fullerene derivatives have been reported.

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In 1999 Cruz *et al.*, synthesized the 3-(*N*-phenylpyrazol-4-yl) isoxazolo[60]fullerene dyad through a microwave induced 1,3-dipolar cycloaddition between the pyrazole nitrile oxide and $C_{60}$.[25] Also microwave-assisted 1,3-dipolar cycloadditions between $C_{60}$ and azomethine ylides generated from decarboxylation of imminium ions derived from the condensation of glycine with benzaldehydes, was reported.[26] Oviedo showed the synthesis of [60]fullerene-donor dyads by 1,3-dipolar cycloadditions of azomethineylides.[27] The same authors reported microwave-assisted synthesis of [60]fullerene adducts from nitrile imines, generated *in situ* from the corresponding hydrazones and NBS in the presence of $Et_3N$, and $C_{60}$.[28] Also the isoindazolylpyrazolino[60]fullerene dyads were isolated from 1,3-dipolar cycloadditions between isoindazolyl nitrile imines, generated *in situ* from the related isoindazolehydrazones and $C_{60}$ under microwave irradiation.[29]

In this contribution we report the efficient microwave-assisted synthesis of fulleropyrazolines/fulleroisoxazolines throughout 1,3-dipolar cycloaddition mediated by (diacetoxyiodo)benzene for the first time.

## 2. Results and discussion

### 2.1. Synthesis

(Diacetoxyiodo)benzene was prepared from benzene, AcOH, $I_2$ in the presence of $K_2S_2O_8$ as an oxidant.[30] Compounds (**1a–e**) and (**3a–d**) were synthesised in good yields according to the literature methods (Scheme 1).[31]

In this research, microwave irradiation is discussed as a green and complementary technique to promote 1,3-dipolar cycloaddition reactions. Cycloaddition reactions of $C_{60}$ with substituted phenylhydrazones/oximes in the presence of $PhI(OAc)_2$ under conventional (25 °C/60 °C) and microwave conditions occurred to prepare the corresponding fulleropyrazolines/fulleroisoxazolines in two steps as described in Scheme 2.

To our satisfaction, when a mixture of $C_{60}$ (36.0 mg), benzaldehyde phenylhydrazone **1a** (1 equiv.) and $PhI(OAc)_2$ (1 equiv.) was stirred in 20 mL toluene for 60 min at room temperature (Table 1, entry 1), the desired fulleropyrazoline **2a** was obtained. In order to extend the utility of this reaction, we carried out the reaction using different types of phenylhydrazone/oxime under the same conditions. Finally, for the examination of influence of green approach in this reaction, it was investigated using microwave procedure (200 W).

Then we carried out all syntheses at 60 °C. For example, for the synthesis of **2a**, when a mixture of reaction was heated, the related fulleropyrazoline was obtained after 25 minutes comparing to room temperature (60 min) and microwave irradiation (10 min). The same reactions under thermal conditions produced the same or lower yields because of producing by product comparing to room temperature.

According to Table 1, the results demonstrated that method B (microwave irradiation) is excellent in both yields and especially in the reaction times better than method A (conventional conditions). Under microwave irradiation, the high yields transformations were carried out without any significant amounts of undesirable side product.

Under conventional heating conditions, the reactions usually need long reaction times, high temperatures and resulting in partial or total decomposition of sensitive compounds. These problems have been properly overcome by the use of microwave irradiation. The short reaction time associated with microwave activation avoids decomposition of reagents and products, and prevents polymerization of the diene or dienophile. Some heterocyclic compounds such as pyrazoles and oxazoles systems that are very reluctant to participate in cycloaddition reactions can be induced to react under microwave irradiation conditions. The application of this method to the chemistry of [60]fullerene has permitted derivatization of this system while avoiding the problems of polycycloaddition and cycloreversion.[32]

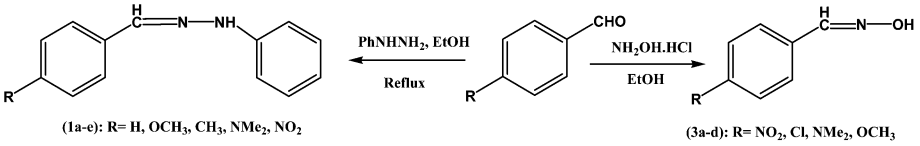
It was found that the process was an easy, mild and appropriate method for constructing pyrazoline/oxazoline cycle on fullerene through 1,3-dipolar reaction and greatly accelerated under microwave irradiation as compared to conventional conditions. In all cases, the experimental results showed that the reaction times are very short and the yields of the products are higher under microwave conditions.

Mechanistically, at first the generation of nitrilimine/nitriloxide dipole is due to contacting phenylhydrazone/oxime and (diacetoxyiodo)benzene. Then 1,3-dipolar cycloaddition reaction occurred by these dipoles with fullerene (Scheme 3).

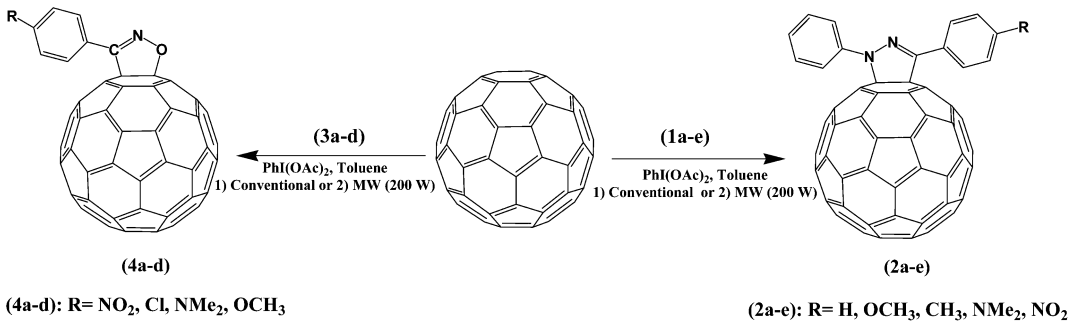
In most cases, under microwave irradiation spectacular accelerations and great improvements in yields and reaction conditions are observed.

Under microwave irradiation, nitrilimine/nitriloxide dipoles as very reactive chemical species are produced very fast, thus facilitating 1,3-dipolar cycloaddition that is a critical step in this type of cycloaddition reactions.

All known products were confirmed by comparison of their spectral data with those reported in the literature. The identification of new compounds **2d–e** was confirmed by their MS, $^1H$ NMR, $^{13}C$ NMR, FT-IR and CHN analyses. Consider **2e** (Table 1, entry 5) as an example. In the IR spectra, the stretching frequency of aromatic C=C is produced in the area between *m*




Scheme 1 Synthesis of phenylhydrazone/oxime derivatives.




Scheme 2 Synthesis of fulleropyrazolines/fulleroisoxazolines under (1) conventional and (2) microwave conditions.

= 1490–1600 $cm^{-1}$. The stretching vibration of C–H in the aromatic ring was appeared at $m$ = 3050 $cm^{-1}$. Also the stretching frequency of C=N of pyrazoline ring appears at 1630 $cm^{-1}$. In the mass spectrum (EI, 70 eV), the peak at $m/z$ 957 is related to the molecular ion of **2e**. In the $^1$H NMR spectra, an imine proton signal appears around $\delta$ = 9–10 ppm in phenylhydrazones while this peak disappears in the fulleropyrazoline spectrum because of connection of phenylhydrazone to $C_{60}$. The signals about $\delta$ = 6.6–7.6 are assigned by protons of CH–CH of aromatic rings in phenylhydrazone while these protons are deshilded in fulleropyrazolines and the related signals appear in $\delta$ = 6.8–8.5 (Fig. 1).

In the $^{13}$C NMR spectra, carbon of C=N has a chemical shift in $\delta$ = 88 and 98 ppm is assigned by two carbon-sp3 of pyrazole ring on $C_{60}$ while the signals related to the sp$^2$ carbons of the $C_{60}$ skeleton and aromatic rings appear in $\delta$ = 100–170 ppm (Fig. 2).

# 3. Experimental

## 3.1. Chemicals and apparatus

Crystalline $C_{60}$ powder used in this work was over 99.90% purity from TCI (Tokyo Chemical Industry Co.). All solvents and chemical reagents were purchased from Aldrich and Fluka and used without further purification. Melting points were determined on Electro thermal 9200, and are not corrected. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. EIMS (70 eV) was performed by Finnigan-MAT-8430 mass spectrometer in $m/z$. Microwave irradiation was carried out using a Litres Solo Microwave Oven ME3410W apparatus (200 W). The elemental analyses (C, H, N) of the samples were performed using a LECO CHNS 923 analyser.

## 3.2. General procedure for synthesis of (diacetoxyiodo)arene

A mixture of benzene, AcOH, $C_2H_4Cl_2$, concd $H_2SO_4$ and $I_2$ was heated with stirring to 40 °C for 15 min. Next, $K_2S_2O_8$ was added portionwise for 10 min and the stirring was continued for 12–30 h until TLC analysis indicated completion of the reaction. After the reaction was completed, water was added. Then the precipitated solid was washed with $CH_2Cl_2$ three times and finally washed with $H_2O$ followed by drying (anhydrous $Na_2SO_4$), filtration, and removal of the solvent by evaporation under reduced pressure. The crude product was purified by washing with hexane or recrystallized from AcOH.

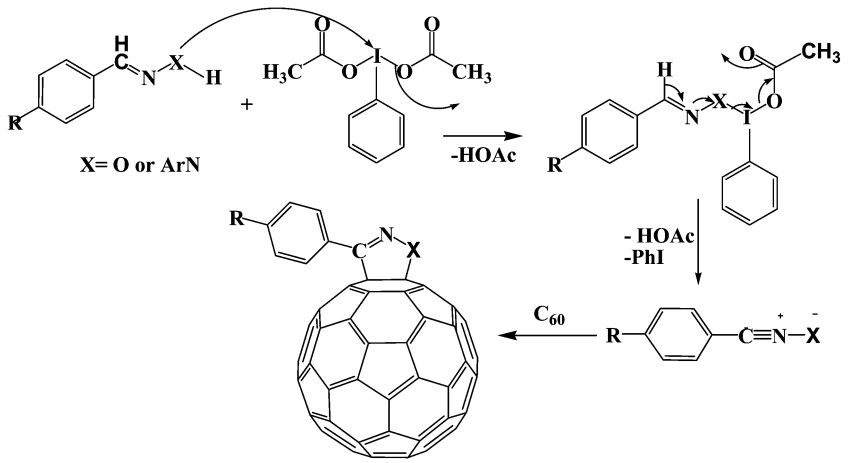
**(Diacetoxyiodo)benzene.** White solid; mp = 161–163, yield 65%, $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 1.84 (s, 6H, $CH_3$), 7.2–8.2 (m, 5H, ArH).

Table 1 Synthesis of fulleropyrazoline/fulleroisoxazoline derivatives under conventional and microwave conditions

| | | | Method A[a] 25 °C/60 °C | | | Method B[b] | | |
|---|---|---|---|---|---|---|---|---|
| Entry | Ar in reactant | Product | Time (min) | Yield[c] (%) | Recovered $C_{60}$ (%) | Time (min) | Yield[c] (%) | Recovered $C_{60}$ (%) |
| **1a** | H | **2a**[22] | 60/25 | 30/28 | 49/48 | 10 | 40 | 45 |
| **1b** | 4-$NO_2$ | **2b**[22] | 30/17 | 31/30 | 45/40 | 5 | 43 | 39 |
| **1c** | 4-$OCH_3$ | **2c**[22] | 45/22 | 25/22 | 46/51 | 8 | 38 | 41 |
| **1d** | 4-$CH_3$ | **2d** | 100/30 | 31/27 | 53/49 | 15 | 42 | 43 |
| **1e** | 4-$NMe_2$ | **2e** | 40/20 | 22/17 | 51/53 | 10 | 39 | 45 |
| **3a** | 4-$NO_2$ | **4a**[22] | 90/30 | 36/34 | 41/40 | 15 | 41 | 47 |
| **3b** | 4-Cl | **4b**[22] | 90/35 | 41/35 | 42/45 | 15 | 45 | 39 |
| **3c** | 4-$NMe_2$ | **4c**[19b] | 60/20 | 32/30 | 40/42 | 10 | 41 | 42 |
| **3d** | 4-$OCH_3$ | **4d**[22] | 90/30 | 34/29 | 45/47 | 15 | 42 | 38 |

[a] Reaction of phenylhydrazone/oxime, $C_{60}$ and $PhI(OAc)_2$ in toluene under conventional conditions (25 °C/60 °C) and nitrogen atmosphere. [b] Reaction of phenylhydrazone/oxime, $C_{60}$ and $PhI(OAc)_2$ in toluene under microwave irradiation (200 W). [c] Isolated yields based on the reacted $C_{60}$.




Scheme 3 Possible mechanism for the formation of fulleropyrazoline/fulleroisoxazoline mediated by $PhI(OAc)_2$.

### 3.3. General procedure for synthesis of substituted phenylhydrazone/oxime derivatives

Substituted phenylhydrazones were obtained by mixing equimolar quantities of phenylhydrazine and the aldehydes in ethanol under reflux condition. The precipitated hydrazones were filtered, washed, recrystallized from ethanol. Oxime derivatives were synthesized from aldehyde and hydroxylamine hydrochloride in the alkali conditions.

**Spectral data for phenylhydrazone/oxime derivatives**

*Benzaldehyde phenylhydrazone (**1a**).* $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 6.82 (t, 1H), 7.13 (d, 2H), 7.27 (d, 2H), 7.40–7.67 (m, 5H), 8.17 (s, 1H). FT-IR (KBr): 3310, 3056, 2916, 1633, 1594, 1521, 1489, 1258, 1135, 812, 758, 753, 692, 507 cm$^{-1}$. Cream solid, mp 158 °C.

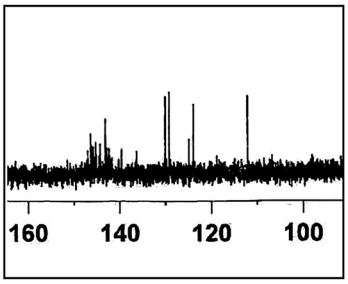



Fig. 2 $^{13}$C NMR spectrum of 1′-phenyl-3′-(4-*N*,*N*-dimethylamino-phenyl) pyrazolino-[4′,5′:1,2][60]fullerene.

*4-Nitrobenzaldehyde phenylhydrazone (**1b**).* $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 6.86 (t, 1H, ArH), 7.22 (d, 2H, ArH), 7.27 (t, 2H, ArH), 7.91 (s, 1H, NH), 7.96 (m, 3H, ArH), 7.46 (m, 1H, ArH),

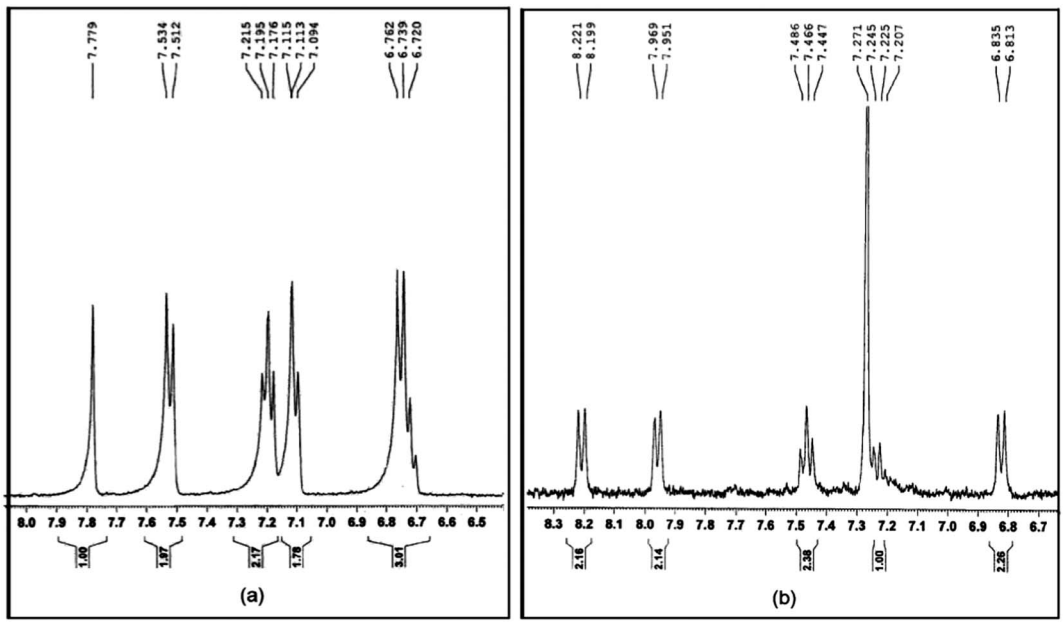



Fig. 1 $^1$H NMR spectrum of (a): 4-(*N*,*N*-dimethylamino)benzaldehyde phenylhydrazone; (b): 1′-phenyl-3′-(4-*N*,*N*-dimethylamino-phenyl) pyrazolino-[4′,5′:1,2][60]fullerene.

7.56 (m, 2H, ArH), 7.71 (m, 5H, ArH), 8.14 (m, 1H, ArH), 8.26 (s, 1H, CH), 8.23 (d, 2H, ArH). FT-IR (KBr): 3298, 3050, 2900, 1596, 1539, 1493, 1325, 848, 750, 691 $cm^{-1}$. Red solid, mp 159 °C.

*4-Methoxybenzaldehyde phenylhydrazone (**1c**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 3.82 (s, 3H, $CH_3$), 6.75 (t, 1H, ArH), 6.95 (d, 2H, ArH), 7.12 (d, 2H, ArH), 7.20 (t, 2H, ArH), 7.62 (d, 2H, ArH), 7.83 (s, 1H, CH), 9.27 (s, 1H, NH). FT-IR (KBr): 3313, 3024, 2951, 1597, 1501, 1245, 1128, 823, 748, 693 $cm^{-1}$. Yellowish solid, mp 121 °C.

*4-Methylbenzaldehyde phenylhydrazone (**1d**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 2.33 (s, 3H, $CH_3$), 6.77 (t, 1H, ArH), 7.13 (d, 2H, ArH), 7.20 (d, 2H, ArH), 7.22 (t, 2H, ArH), 7.56 (d, 2H, ArH), 7.84 (s, 1H, CH), 9.38 (s, 1H, NH). FT-IR (KBr): 3308, 3024, 2918, 1596, 1503, 1256, 1131, 816, 748, 692 $cm^{-1}$. Light yellow solid, mp 115 °C.

*4-(N,N-Dimethylamino)benzaldehyde phenylhydrazone (**1e**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 6.72 (t, 1H, ArH), 6.75 (d, 2H, ArH), 7.11 (d, 2H, ArH), 7.19 (t, 2H, ArH), 7.52 (d, 2H, ArH), 7.77 (s, 1H, CH), 9.10 (s, 1H, NH). FT-IR (KBr): 3312, 3030, 2890, 1599, 1509, 1259, 1129, 811, 748, 692 $cm^{-1}$. Yellow solid, mp 149 °C.

*4-Nitro benzaldehyde oxime (**3a**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 7.89 (d, 2H, ArH), 8.26 (d, 2H, ArH), 8.30 (s, 1H, CH), 8.79 (s, 1H, OH). FT-IR (KBr): 3306, 1603, 1536, 1347, 1214, 1107, 969, 847, 748, 686 $cm^{-1}$. Cream solid, mp 132 °C.

*4-Chloro benzaldehyde oxime (**3b**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 7.43 (d, 2H, ArH), 7.65 (d, 2H, ArH), 8.12 (s, 1H, CH), 10.45 (s, 1H, OH). FT-IR (KBr): 3299, 3996, 1594, 1398, 1594, 1492, 1313, 1212, 1087, 969, 873, 824, 691, 505 $cm^{-1}$. White solid, mp = 110 °C.

*4-(N,N-Dimethylamino)benzaldehyde oxime (**3c**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 2.97 (s, 6H, CH3), 7.72 (d, 2H, ArH), 7.44 (d, 2H, ArH), 7.99 (s, 1H, CH), 9.74 (s, 1H, OH). FT-IR (KBr): 3239, 2911, 2803, 1605, 1524, 1359, 1303, 1224, 1176, 954, 865, 811, 730, 569 $cm^{-1}$. White solid, mp 185 °C.

*4-Methoxybenzaldehyde oxime (**3d**).* $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ (ppm) 3.82 (s, 3H, $CH_3$), 6.94 (d, 2H, ArH), 7.55 (d, 2H, ArH), 8.07 (s, 1H, CH), 10.07 (s, 1H, OH). FT-IR (KBr): 3320, 3006, 2968, 1607, 1512, 1307, 1249, 1169, 1028, 960, 871, 825, 591 $cm^{-1}$. White solid, mp 45 °C.

### 3.4. General procedure for the synthesis of fulleropyrazolines/fulleroisoxazolines

**Typical stirring method (method A).** A mixture of $C_{60}$ (36.0 mg, 0.05 mmol), hydrazones (**1a–e**)/oximes (**3a–d**) (0.05 mmol), and $PhI(OAc)_2$ (0.05 mmol) was dissolved in 20 mL of toluene and stirred under nitrogen atmosphere at room temperature and 60 °C for a desired time. The course of the reaction was monitored by TLC with toluene as an eluent. At the end of reaction, the solvent was evaporated *in vacuo*, and the residue was separated on a silica gel column using toluene to afford adducts (**2a–e**)/(**4a–d**).

**Microwave irradiation method (method B).** In a similar process, the mixture was irradiated by microwave irradiation (200 W) for the desired times at 25 °C.

**Representative spectral data for different cycloadducts reported in Table 1**

*1′-Phenyl-3′-phenyl pyrazolino-[4′,5′:1,2][60]fullerene (**2a**, Table 1, entry 1).* Brown solid; $^1H$ NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 7.30 (d, 1H, ArH), 7.34 (d, 1H, ArH), 7.53 (m, 3H, ArH), 7.69 (m, 3H, ArH), 8.02 (d, 1H, ArH), 8.26 (d, 1H, ArH). FT-IR (KBr): 3005, 2924, 1726, 1633, 1457, 1262, 1098, 802, 730, 524, 464 $cm^{-1}$; $^{13}C$ NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 82, 92, 124.2, 125.5, 129.3, 129.4, 129.7, 129.8, 131.09, 132.9, 136.7, 136.8, 140.1, 140.7, 142.3, 142.6, 142.7, 142.8, 142.90, 143.2, 143.3, 144.6, 144.5, 144.7, 145.1, 145.3, 145.6, 145.8, 146.2, 146.3, 146.4, 146.5, 146.6, 146.8, 146.9, 147.61, 148.01.

*1′-Phenyl-3′-(4-nitrophenyl) pyrazolino-[4′,5′:1,2][60]fullerene (**2b**, Table 1, entry 2).* Brown solid; $^1H$ NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 7.19 (d, 1H, ArH), 7.37 (d, 2H, ArH), 7.53 (t, 2H, ArH), 7.97 (d, 2H, ArH), 8.67 (d, 2H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 89, 97, 109, 114, 117, 120, 122 (2C), 124 (2C), 126 (2C), 128 (2C), 129 (2C), 131, 138, 140 (2C), 142 (2C), 143 (2C), 146, 147 (2C), 148.5, 149, 150, 152, 154 (2C), 156, 161 (2C), 162, 165 (2C), 168. FT-IR (KBr): 3001, 2920, 1731, 1595, 1519, 1456, 1336, 1259, 850, 752, 692, 527 $cm^{-1}$.

*1′-Phenyl-3′-(4-methoxyphenyl) pyrazolino-[4′,5′:1,2][60]fullerene (**2c**, Table 1, entry 3).* Brown solid; $^1H$ NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 3.88 (s, 3H, $OCH_3$), 7.05 (d, 2H, ArH), 7.25 (t, 1H, ArH), 7.48 (t, 2H, ArH), 7.96 (d, 2H, ArH), 8.24 (d, 2H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 55, 96, 99, 100, 104, 105, 107, 108, 109.5, 110, 112, 114 (2C), 115, 123 (2C), 124, 125, 126, 127.5, 128, 129 (2C), 130 (2C), 132, 133, 135, 136, 140, 141, 142, 143, 144, 145 (2C), 146, 159, 160, 161, 163, 165. FT-IR (KBr): 3000, 2980, 1650, 1603, 1497, 1332, 1251, 820, 752, 692, 526 $cm^{-1}$.

*1′-Phenyl-3′-(4-methylphenyl) pyrazolino [4′,5′:1,2][60]fullerene (**2d**, Table 1, entry 4).* Brown solid; $^1H$ NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 1.11 (s, 3H, $CH_3$), 7.18 (d, 1H, ArH), 7.26 (d, 1H, ArH), 7.21 (t, 1H, ArH), 7.33 (m, 3H, ArH), 7.46 (t, 2H, ArH), 7.95 (d, 1H, ArH), 8.16 (d, 1H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 29, 86, 90, 104, 110, 111, 114, 115 (2C), 116, 117, 118, 120, 124 (2C), 125, 128 (2C), 129 (2C), 131, 132 (2C), 134, 135, 137 (2C), 138, 139, 140 (2C), 142, 143, 147 (2C), 150, 154 (2C), 165, 166, 179 (2C). FT-IR (KBr): 3000, 2917, 1636, 1455, 1367, 1256, 801, 751, 573, 525 $cm^{-1}$. MS (EI, 70 eV): $m/z$ (%) = 928 ($M^+$, 2), 207 (71), 130 (37), 129 (52), 191 (49), 117 (34), 105 (75), 91 (100), 77 (69), 57 (69); anal. calcd for $C_{74}H_9N_2$: C, 95.69; H, 1.30; N, 3.02%. Found: C, 95.47; H, 1.25; N, 3.19%.

*1′-Phenyl-3′-(4-N,N-dimethylaminophenyl) pyrazolino-[4′,5′:1,2]-[60]fullerene (**2e**, Table 1, entry 5).* Brown solid; $^1H$ NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 3.05 (s, 6H, $NMe_2$), 6.82 (d, 2H, ArH), 7.21 (dd, 1H, ArH), 7.46 (t, 2H, ArH), 7.95 (d, 2H, ArH), 8.21 (d, 2H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 40, 58, 82, 91, 101, 104, 106, 108, 109.5, 110.8, 112 (2C), 114, 118, 119, 120, 123 (2C), 124, 129.2 (2C), 129.7 (2C), 130 (2C), 132, 133, 136.3 (2C), 137, 139, 142, 143 (2C), 143.5 (2C), 144, 145, 146.9 (2C), 151, 162, 163, 165, 168. FT-IR (KBr): 3000, 2919, 1603, 1522, 1488, 1431, 1357, 1097, 753, 692, 526 $cm^{-1}$. MS (EI, 70 eV): $m/z$ (%) = 957 ($M^+$, 5), 238 (6), 207 (82), 105 (89), 77 (66), 91 (100), 57 (66); anal. calcd for $C_{75}H_{15}N_3$: C, 94.04; H, 1.57; N, 4.39. Found: C, 94.25; H, 1.46; N, 4.17%.

*3′-(4-Nitrophenyl) isoxazoline-[4′,5′:1,2][60]fullerene (**4a**, Table 1, entry 6).* Brown solid; $^1$H NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm); 8.41 (d, 2H, ArH), 8.48 (d, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 85, 95, 110, 124.2 (2C), 126.0, 128.0, 129.08, 129.7 (2C), 135, 136.7, 138, 139, 140.4, 140.5, 141.8, 142.04, 142.3, 142.5, 142.9 (2C), 143.1 (2C), 143.6, 143.7 (2C), 144, 144.4, 144.6, 145.2, 145.3 (2C), 145.8, 146.0 (2C), 146.1, 146.4, 146.5. FT-IR (KBr): 3432, 2921, 2852, 1630, 1518, 1340, 848, 526 cm$^{-1}$.

*3′-(4-Chlorophenyl) isoxazoline-[4′,5′:1,2][60]fullerene (**4b**, Table 1, entry 7).* Brown solid; $^1$H NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 7.53 (d, 2H, ArH), 8.16 (d, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 79, 92, 104.16, 128.87, 129.03, 129.09, 130.61, 136.65, 137.02, 140.30, 140.33, 141.70, 142.09, 142.27, 142.32, 142.46 (2C), 142.84 (2C), 142.98 (2C), 144.07, 144.39, 144.47, 144.72 (2C), 144.76, 145.13, 145.21, 145.39, 145.61, 145.83, 145.92, 145.97, 146.23, 146.25, 146.38, 147.24, 147.74, 153.28; FT-IR (KBr): 2922, 2853, 1630, 1459, 1095, 810, 526 cm$^{-1}$.

*3′-(4-N,N-Dimethylaminophenyl) isoxazoline-[4′,5′:1,2][60]-fullerene (**4c**, Table 1, entry 8).* Brown solid; $^1$H NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 3.66 (s, 6H, $NMe_2$), 6.78 (d, 2H, ArH), 8.09 (d, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 49, 60, 85, 96, 102, 104, 105.2, 109, 112 (2C), 116 (2C), 130, 137 (2C), 137.2, 139 (2C), 140.5 (2C), 142.6, 142.7 (2C), 143.1 (2C), 144.0 (2C), 145.2, 145.4 (2C), 145.8, 146.2 (2C), 146.5 (2C), 148.0, 150.2, 151.8. FT-IR (KBr): 3020, 1728, 1603, 1459, 1274, 1122, 1076, 814, 525 cm$^{-1}$. MS (EI, 70 eV): $m/z$ (%) = 882 ($M^+$, 6), 163 (30), 147 (20), 121 (11), 91 (100), 77 (52), 57 (62).

*3′-(4-Methoxyphenyl) isoxazoline-[4′,5′:1,2][60]fullerene (**4d**, Table 1, entry 9).* Brown solid; $^1$H NMR (400 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 3.89 (s, 3H, $OCH_3$), 7.04 (d, 2H, ArH), 8.15 (d, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$–$CS_2$): $\delta$ (ppm) 54.9, 78.8, 103.6, 114.2 (2C), 121.1, 130.08, 136.3 (2C), 136.7, 140.0, 141.40 (2C), 141.8, 142.0, 142.06, 142.19 (2C), 142.56, 142.7 (2C), 143.8, 144.14, 144.52, 144.70 (2C), 144.84 (2C), 144.92, 145.12, 145.30, 145.62 (2C), 145.68, 145.9, 146.09, 146.9, 147.31, 152.01, 161.07. FT-IR (KBr): 3050, 1727, 1603, 1459, 1263, 1117, 800 cm$^{-1}$.

## 4. Conclusions

In this research we provide alternative methods to make fulleropyrazoline/fulleroisoxazoline from hydrazone/oxime and $C_{60}$ mediated by $PhI(OAc)_2$ under microwave irradiation. This procedure enables the design of milder reaction conditions that reduce the extent of decomposition of both the starting materials and the reaction products. Microwave-assisted technology as a very useful and green method for the functionalization of $C_{60}$ is quite often cleaner, faster, and higher-yielding than conventional ones. Mostly importantly, the major advantage of this methodology is efficient and environmentally friendly, particularly when discussing the basic green chemistry concepts.

## Acknowledgements

The authors are grateful to the University of Kashan for supporting this work by Grant no.: 159196/XXI.

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