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An efficient sonochemical synthesis of novel fulleropyrazolines through the reaction of [60] fullerene with phenylhydrazones and $PhI(OAc)_2$

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Abstract. To obtain a rapid, efficient and green synthesis of fulleropyrazoline derivatives, ultrasonic irradiation has been applied to the reaction mixtures containing substituted phenylhydrazones, C_{60} and $PhI(OAc)_2$. This procedure allowed products, at room temperature, to be achieved in good yield and in a short time without any side products. This convenient procedure will provide a further increase of diversity within the fullerene derivatives.

1. Introduction

Fullerenes, as the third allotrope of carbon, were discovered by Kroto et al. [1] in 1985. The chemistry of fullerenes began to develop greatly after W. Kratschmer and D. Huffman [2] who discovered a method for the preparation of fullerene soot by burning graphite rods in arc discharge in an inert atmosphere. Fullerene-based nanomaterials display an extensive range of interesting chemical, physical, biological [3-7] and other scientific properties [8-10]. Surface modification of fullerenes is an attractive approach in materials science and pharmaceutical applications [5,11,12]. The electron withdrawing nature of the closed cage alkene C_{60} makes it an excellent dienophile for cycloadditions [13-15], addition of organometallic reagents [16], and photo-induced electron transfer reactions [17]. Four main types of cycloaddition reaction on C_{60}, including [1+2], [2+2], [3+2] and [4+2] cycloadditions, have been largely investigated [18-21]. Functionalization of fullerenes gives, principally, products of monoaddition, basically, 1,2-addition to a [6-6] bond, which is energetically more favorable than addition to a [6-5] bond [11]. The addition of 1,3-dipoles to alkenes to give five-member rings is a usual organic reaction. In fact, 1,3-dipolar cycloaddition reactions are efficient for the construction of carbon-carbon bonds and the preparation of heterocyclic compounds [22-24]. So far, different 1,3-dipoles, including azomethine ylides, diazo compounds, azides, nitrile oxides, nitrile ylides, nitrile imines, pyrazolinium ylides, and carbonyl ylides, have been reported to react with fullerenes [25-32]. Among the various types of fullerene derivative, fullerene-fused pentagonal heterocyclic rings, such as fulleropyrolidines [33], fulleroindolines [34], fullerene-fused lactones [35], pyrazolo- and oxazolo-fullerenes [22], have been reported in the literature. Fulleropyrazolines and fulleroisoxazolines are a promising class of fullerene derivative that can be readily synthesized through several methods, such as the addition of nitrile oxides or nitrilimines to C_{60} in moderate yields. For the first time, the addition reaction of C_{60} with nitrile oxides

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was reported by Meier [36]. The most common approach used for the synthesis of fulleroisoxazolines and fulleropyrazolines has two steps, including synthesis of hydroximinoyl halides or hydrazonoyl halides resulted from the reaction of aldoxime or hydrazone with NCS or NBS, and then reacting with C_{60} in the presence of an organic base [37-39]. Also, isoxazoline-fused fullerenes can also be synthesized from the reaction of C_{60} with nitrile oxides [40] and N-silyloxynitrones [41]. Recently, one-step synthesis of several fulleroisoxazolines and fulleropyrazolines, at room temperature, and the synthesis of various fullerene derivatives under microwave irradiation have been reported [42-45].

Utilization of ultrasonic waves in organic synthesis has, interestingly, been used in recent years [46,47]. This technique is more easily controlled in comparison with conventional methods, which can increase temperature gradients within the sample, and which, then, results in decomposition of products, substrates and reagents. Ultrasound is known to accelerate diverse types of organic reaction and has been established as an effective and green approach to organic synthesis [47,48]. Sonication also increases the reaction rate and avoids the use of high reaction temperatures [47]. Furthermore, related literature on ultrasonically synthesized fullerene derivatives has been reported [49-52]. The unique effect of sonochemistry in organic synthesis is duo to the phenomenon of cavitation, which is a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid, thus, enhancing themes transfer and allowing chemical reactions to occur [53,54].

In this study we have aimed to investigate the synthesis and characterization of various new pyrazolino [60] fullerenes under ultrasound irradiation for the first time.

2. Experimental

2.1. Materials and apparatus

Chemicals were purchased from Sigma-Aldrich and Merck in high purity. Crystalline C_{60} powder, used in this work from TCI (Tokyo Chemical Industry Co.), was over 99.90% purity. The FT-IR spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets, in the range of $400 - 4000$ cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as the internal standard. The EIMS (70 eV) was performed by a Finnigan-MAT-8430 mass spectrometer in m/z. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany) equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz, with a maximum power output of 30, 40 and 50 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. HPLC analysis was performed with ATI UNICAM Crystal HPLC apparatus (column type: Partisil P10ODS 25 cm $\times$ 1.4 $\times$ 4.6 mm, UV-Vis detector, toluene, flow rate 1000 μL/min, detection at λ=340 nm).

2.2. General procedure for synthesis of (diacetoxyiodo)arene

Diacetoxyiodo benzene was synthesized according to the previously reported method [55]. 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, over 10 min, and the stirring was continued for 12-30 h until TLC analysis indicated completion of reaction. After the reaction was completed, water was added. Then, the precipitated solid was washed with CH_2Cl_2 three times. Finally, it was 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; m.p = 161-163, Yield 65%, ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.84 (s, 6H, CH_3), 7.2-8.2 (m, 5H, ArH).

2.3. Synthesis of substituted phenylhydrazone derivatives

2.3.1. General procedure

The phenylhydrazone derivatives **(1a-g)** were synthesized by mixing equimolar quantities of phenylhydrazine and aldehyde derivatives in ethanol under reflux conditions. The precipitated phenylhydrazones were filtered, washed, and recrystallized from ethanol, according to methods in the literature [56].

Spectral data for phenylhydrazone derivatives

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

4-Methylbenzaldehyde phenylhydrazone **(1b)**. Light yellow solid; FT-IR (KBr): 3308, 3024, 2918, 1596, 1503, 1256, 1131, 816, 748, 692 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ (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).

4-(*N*,*N*-dimethylamino)benzaldehyde phenylhydrazone **(1c)**. Yellow solid; FT-IR (KBr): 3312, 3030, 2890, 1599, 1509, 1259, 1129, 811, 748, 692 cm^{-1}; ^{1}H NMR (400 MHz, acetone -d_6): δ (ppm) 2.9 (s. 6H, CH_3), 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).

4-chlorobenzaldehyde phenylhydrazone **(1d)**. Cream solid; FT-IR (KBr): 3310, 3052, 1596, 1517, 1484, 1256, 1132, 1008, 912, 825, 748, 693, 508 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): δ (ppm) 6.80 (t, 1H, ArH), 7.15 (d, 2H, ArH), 7.24 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.69 (d, 2H, ArH), 7.86 (s, 1H, CH), 9.57 (s, 1H, NH).

2-pyridinecarboxaldehyde phenylhydrazone **(1e).** Yellow solid; FT-IR (KBr): $\overline{v}$=3443, 2947 1603, 1566, 1494, 1271, 1149, 826, 739, 693 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): δ (ppm) 6.83 (t, 1H, ArH), 7.21 (m, 5H, ArH), , 7.76 (t, 1H, ArH), 7.92 (s, 1H, CH), 8.02 (d, 1H, ArH), 8.5 (d, 1H, ArH), 9.83 (s, 1H, NH).

2-thiophencarbaldehyde phenylhydrazone **(1f).** Cream solid; FT-IR (KBr): $\overline{v}$ = 3441, 3097, 1601, 1500, 1503, 1261, 1136, 909, 749, 654 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): δ (ppm) 6.77 (t, 1H, ArH), 7.03 (t, 1H, ArH), 7.07 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.14 (d, 1H, ArH), 7.19 (t, 1H, ArH), 7.23 (d, 1H, ArH), 7.37(d, 1H, ArH), 8.07 (s, 1H, CH), 9.44 (s, 1H, NH).

2-furancarbaldehyde phenylhydrazone **(1g).** Brown solid; FT-IR (KBr): $\overline{v}$ = 3308, 3053, 1598, 1496, 1341, 1257, 1131, 1014, 748, 692, 505 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): δ (ppm) 6.52 (dd, 1H, ArH), 6.60 (d, 1H, ArH), 6.77 (t, 1H, ArH), 7.09 (d, 1H, ArH), 7.11 (d, 1H, ArH), 7.20 (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.58 (d, 1H, ArH), 7.78 (s, 1H, CH), 9.45 (s, 1H, NH).

2.3.2. General procedure for the synthesis of fulleropyrazolines

Typical stirring method (method A)

A mixture of C_{60} (36.0 mg, 0.05 mmol), phenylhydrazones (**1a-g**) (0.05 mmol), and $PhI(OAc)_2$ (0.05 mmol) were dissolved in 20 mL of toluene and stirred under nitrogen atmosphere at room temperature for a desired time. The course of the reaction was monitored by TLC, with toluene as an eluent. At the end of the reaction, the solvent was evaporated in vacuo, and the residue was separated on a silica gel column using toluene to afford adducts (**2a-g**).

Ultrasound irradiation method (method B)

In a similar process, the mixture was irradiated by ultrasound at various ultrasonic powers (30, 40 and 50 W) for the desired times at 25°C.

Representative spectral data

1′- phenyl- 3′- phenyl pyrazolino [4′, 5′: 1, 2] [60] fullerene **(2a)**. Brown solid; R_f= 0.90 (toluene); FT-IR (KBr): 3005, 2924, 1726, 1633, 1457, 1262, 1098,802, 730, 524, 464 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$- CS_2): δ (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); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (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- Methylphenyl) pyrazolino [4′, 5′: 1, 2] [60] fullerene **(2b)**. Brown solid; R_f= 0.80 (toluene); FT-IR (KBr): 3000, 2917,1636, 1455, 1367, 1256, 801, 751, 573, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 1.11 (s, 3H, CH_3), 7.18 (d, 1H, ArH), 7.26 (d, 1H, ArH), 7.33 (m, 3H, ArH), 7.46 (t, 2H, ArH), 7.95 (d, 1H, ArH), 8.16 (d, 1 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (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); MS (EI, 70 eV): m/z (%) = 928 (M^+, 2).

1′- phenyl- 3′- (4- *N*, *N*-dimethylaminophenyl) pyrazolino [4′, 5′: 1, 2] [60] fullerene **(2c)**. Brown solid; R_f= 0.65 (toluene); FT-IR (KBr): 3000, 2919,1603, 1522, 1488, 1431, 1357, 1097, 753, 692, 526 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$- CS_2): δ (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): δ (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; MS (EI, 70 eV): m/z (%) = 957 (M^+, 5).

1′- phenyl- 3′- (4- Chlorophenyl) pyrazolino [4′, 5′: 1, 2] [60] fullerene **(2d)**. Brown solid; R_f= 0.80 (toluene); FT-IR (KBr): 3010, 2922,2853, 1626, 1453, 1257, 1094, 872, 828, 527, 465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.10 (dd, 1H, ArH), 7.21 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.41 (d, 2H, ArH), 7.44 (t, 1H, ArH), 7.52 (d, 1H, ArH), 7.72 (d, 1 H, ArH), 8.12 (dd, 1 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 86, 90, 110, 112, 112, 113, 115, 116 (2C), 117, 118, 119, 122, 124, 125 (2C), 127 (2C), 128 (2C), 131, 133 (2C), 134, 136, 137 (2C), 137, 138, 141 (2C), 142, 145, 146 (2C), 152, 155 (2C), 163, 165, 169 (2C); MS (EI, 70 eV): m/z (%)= 948.5 (M^+, 4).

1′- phenyl- 3′- (2-pyrimidyl)pyrazolino[4′ 5′: 1, 2] [60] fullerene **(2e)**. Brown solid; R_f= 0.85 (toluene); FT-IR (KBr): $\overline{v}$ = 3050, 1650, 1629, 1566, 881,753, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.17 (t, 1H, ArH), 7.27 (d, 2H, ArH), 7.36 (t, 1H, ArH), 7.47

(d, 1H, ArH), 7.76 (m, 2H, ArH), 8.38 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 85, 92, 103, 105, 107, 109, 110, 111 (2C), 113, 114, 117, 119, 121, 122 (2C), 125, 126, 128, 129 (2C), 131 (2C), 132, 134, 135 (2C), 136, 138, 140, 141 (2C), 143 (2C), 144, 145, 148 (2C), 150, 155, 157, 159; MS (EI, 70 eV): m/z (%) = 915 (M^+, 6).

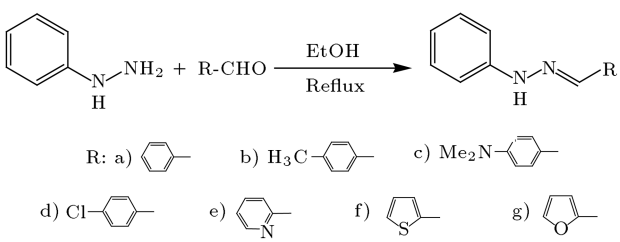
1′- phenyl- 3′- (2-thienyl) pyrazolino[4′, 5′: 1, 2][60] fullerene **(2f).** Brown solid; R_f= 0.90 (toluene); FT-IR (KBr): $\overline{v}$ = 3001, 1631, 1595, 1489, 1336, 1259, 751, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.13 (m, 2H, ArH), 7.24 (t, 1H, ArH),7.46 (m, 3H, ArH), 7.94 (d, 1H, ArH), 7.98 (d, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 52.2, 78.2, 123.9 (2C), 124.1, 124.5, 125.4 (2C), 125.9, 126.0, 126.2, 126.8, 127.6, 128.3 (2C), 128.7, 129.1 (2C), 129.3 (2C), 130.0, 130.5, 131.2, 132.5, 133.4, 135.6, 136.8, 137.0, 138.2, 139.7, 140.2, 141.5, 142.0, 143.1 (2C), 144.0, 145.2; MS (EI, 70 eV): m/z (%) = 920 (M^+,4).

1′- phenyl- 3′- (2-furanoyl)pyrazolino[4′, 5′: 1, 2][60] fullerene **(2g)**. Brown solid; R_f= 0.75 (toluene); FT-IR (KBr): $\overline{v}$ = 3005, 1728, 1628, 1080, 751, 693, 526 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$- CS_2): δ (ppm) 7.30 (m, 6H, ArH), 8.90 (d, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$- CS_2): δ (ppm) 70, 81, 121, 122 (2C), 123, 124, 125 (2C), 126.0, 126.5, 126.9, 127, 128.5 (2C), 129.1 (2C), 129.5 (2C), 130.0, 130.9, 131.2, 132 (2C), 133, 135 (2C), 136.8, 137(2C), 138, 139.5, 140 (2C), 141 (2C), 142.0, 143 (2C), 144.0, 145, 147, 148; MS (EI, 70 eV): m/z (%) = 904 (M^+, 10).

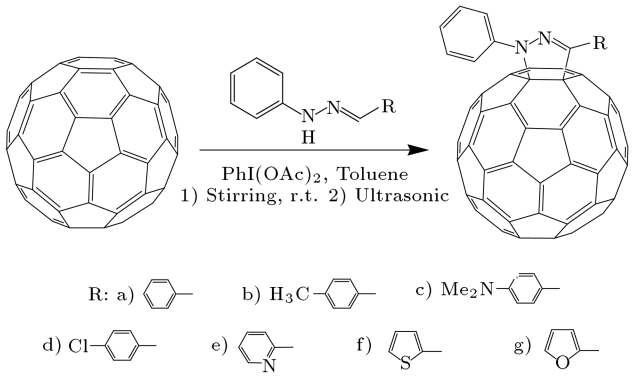
3. Results and discussion

In this research, mild synthesis of fullerene derivatives through 1,3-dipolar cycloaddition reactions under stirring and ultrasound irradiation is discussed. Various phenylhydrazone derivatives **(1a-g)** were readily prepared by the reaction of aldehydes and phenylhydrazine in EtOH under reflux conditions. After recrystallization from ethanol, they were purified enough to be used (Scheme 1).

Cycloaddition reactions of C_{60} with substituted phenylhydrazones, in the presence of $PhI(OAc)_2$, under stirring at room temperature and ultrasound irradiation, were occurred to prepare the corresponding fulleropyrazolines, as described in Scheme 2.



Scheme 1. Synthesis of phenylhydrazone derivatives.



Scheme 2. Synthesis of fulleropyrazolines under stirring, and ultrasound conditions.

Table 1. Synthesis of **2a** under ultrasound irradiation in various powers.

Entry	Power (W)	Time (min)	Yield (%)
1	30	8	35
2	40	8	41
3	50	8	41.28

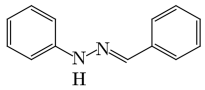
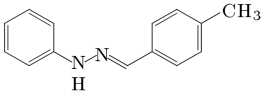
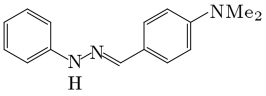
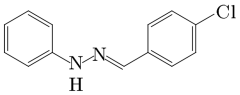
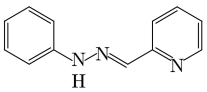
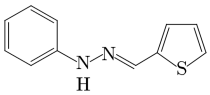
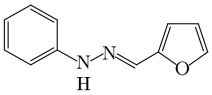
To our satisfaction, when a mixture of C_{60} (36.0 mg), benzaldehyde phenlhydrazone **1a** (1 equiv) and $PhI(OAc)_2$ (1 equiv) was stirred in 20 mL toluene for 60 min at room temperature (Table 1), the desired fulleropyrazoline **2a** was prepared.

As an example of further functionalization, we used 2-thiophencarboxaldehyde phenylhydrazone, **1f**, and the newly synthesized fulleropyrazoline derivative, **2f**, was prepared. We increased the scope of the present study by the reaction of different kinds of phenylhydrazones (**1a-g**) with C_{60} in the presence of $PhI(OAc)_2$ under the same conditions.

These fulleropyrazolines were prepared in 15-30% yield by a reaction with the corresponding phenylhydrazones and C_{60}, in the presence of $PhI(OAc)_2$ at room temperature. The yield of the reaction is higher when R_1 is phenyl, pyridine and thiophene, than when R_1 is in the furyl group. The substituent group, R, on the phenyl ring had little effect on the yields. This makes it obvious that $PhI(OAc)_2$ is a good oxidant to mediate the 1,3-dipolar reaction of C_{60} with phenylhydrazones.

Finally, for examination of the influence of a mild and green approach to this reaction, it was investigated using an ultrasound procedure. In order to verify the effect of irradiation power, the reaction was also performed in 30, 40, and 50 W. With a power of 40 W irradiation, the yield of **2a** was better than that with 30 W, within 5 min (41%, Table 1, entry 1). Increasing the irradiation power from 40 to 50 W (Table 1, entries 2, 3), did not change the reaction yield a considerable

Table 2. Synthesis of fulleropyrazoline derivatives under stirring conditions and sonication.

No.	Substrate	Method A[a]				Method B[b]		
		Product	Time (min)	Yield[c] (%)	Recovered C_{60} (%)	Time (min)	Yield[c] (%)	Recovered C_{60} (%)
1a		**2a**[40]	60	30	35	8	42	35
1b		**2b**	100	31	53	10	43	36
1c		**2c**	40	22	51	6	42	48
1d		**2d**	100	25	50	10	35	40
1e		**2e**	180	20	50	20	37	44
1f		**2f**	60	30	45	10	45	41
1g		**2g**	45	15	51	10	20	48

[a]: Reaction of phenylhydrazone, C_{60} and $PhI(OAc)_2$ in toluene at room temperature under nitrogen atmosphere.

[b]: Reaction of phenylhydrazone, C_{60} and $PhI(OAc)_2$ in toluene under ultrasound irradiation (40 W).

[c]: Isolated yields based on the reacted C_{60}.

amount (41.28% in the similar time). The results indicated that there is an optimum power for effective synthesis of **2a**, with the power of 40 W.

The results summarized in Table 2 demonstrated that method B (ultrasound irradiation) is better in both yields, and, especially, in the reaction time, than in method A (stirring conditions). Under sonication, the high yield transformations were carried out without any significant amount of undesirable side products.

It was demonstrated that the procedure was a simple, mild and suitable method of constructing a pyrazoline ring on fullerene through a 1,3-dipolar reaction, and greatly accelerated under ultrasound irradiation compared to stirring conditions at room temperature. In all reactions, the experimental results showed (Figure 1) that the yields of the products are higher under sonication.

According to the factors behind green chemistry, including safety, less waste and energy usage, ease of separation, and recovery in our approach, it is demonstrated that the ultrasound procedure is an efficient, mild and eco-friendly alternative to conventional methods for introducing energy. Recent research shows that under ultrasound irradiation with special operation, not only are the reaction times surprisingly

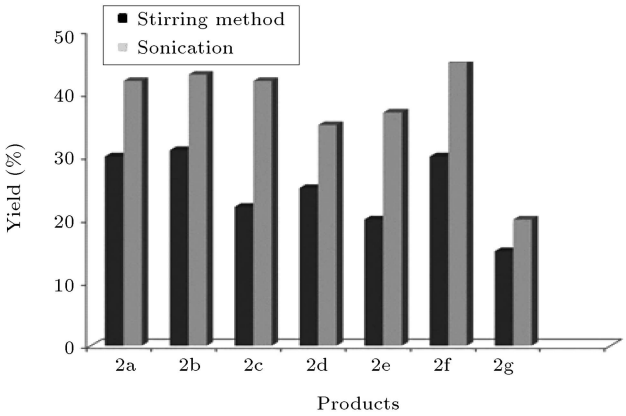
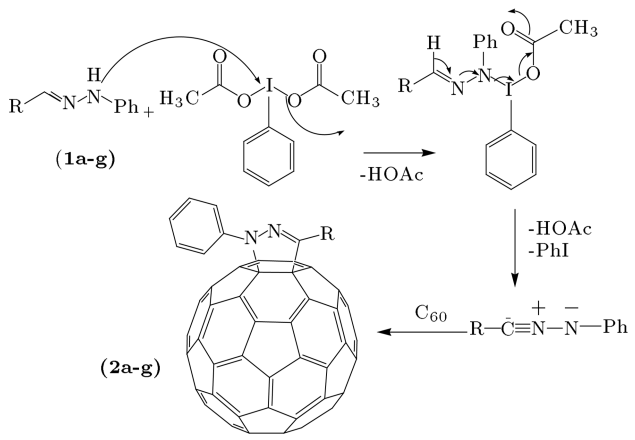


Figure 1. Comparison of the reaction yields of the products under stirring method and sonication.

reduced, but also, the yields are increased. This non-conventional energy source demonstrates its superiority, in terms of selectivity, reaction time and operational simplicity [57].

This result is due to the phenomenon of cavitation, which is grown by reducing the ambient pressure by static or dynamic means under ultrasound irradiation. It is well established that sonication introduces great physical and chemical effects, derived from acous-



Scheme 3. Possible mechanism for the synthesis of fulleropyrazolines mediated by $PhI(OAc)_2$.

tic cavitation. Such cavitation behaviour leads to many unique properties in the irradiated solution [58,59]. Under sonication, the reaction mixture is activated by inducing high local temperatures and pressure generation inside the cavitation bubble and its interfaces when it collapses, which speeds up reaction rate and shortens reaction time. The effects of ultrasound irradiation observed during organic reactions are due to cavitations [60-62].

Mechanistically, at first, generation of nitrilimine dipoles is due to contacting phenylhydrazone and (diacetoxy) iodobenzene. Then, a 1,3-dipolar cycloaddition reaction occurred by these dipoles with fullerene (Scheme 3).

Sonication of cycloaddition catalyzes the reaction through adequate contact between the substrates. Under this condition, nitrilimine dipoles, as very reactive chemical species, are produced very fast, thus, facilitating 1, 3-dipolar cycloaddition, which is a critical step in this type of cycloaddition reaction. The scope of the present study was increased by the reaction of several phenylhydrazones with C_{60} in the presence of $PhI(OAc)_2$ under ultrasound irradiation. As shown in Table 2, the reaction of various phenylhydrazones with C_{60} was accelerated by sonication. The corresponding products were obtained in good yields and excellent reaction times under ultrasound irradiation (Figure 2). It seems that this method for preparation of fulleropyrazolines has some advantages, including a one-pot reaction, very short time, high efficiency, and appropriate and mild conditions, in comparison to previously reported methods [38,39].

The new compounds (**2b-g**) were fully characterized by their MS, ^{1}H NMR, ^{13}C NMR and FT-IR. Further purification with HPLC analysis, at least for a couple of products (**2f** and **2g**), gave the desired cycloadducts at 5.1 and 4.0 min, respectively. Take **2f** (Table 2) as an example: After evaporation of the solvent, the product was separated roughly with a silica

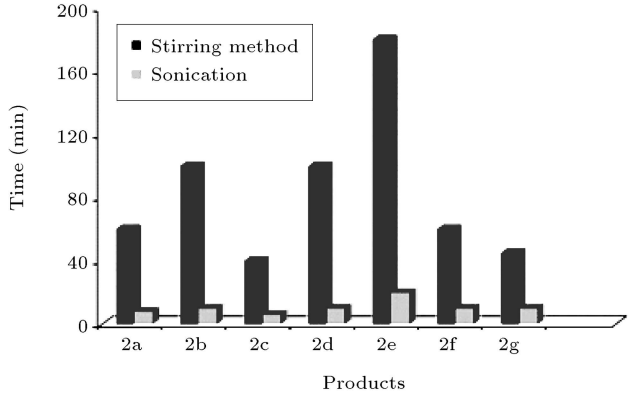


Figure 2. Comparison of the reaction times of the products under stirring method and sonication.

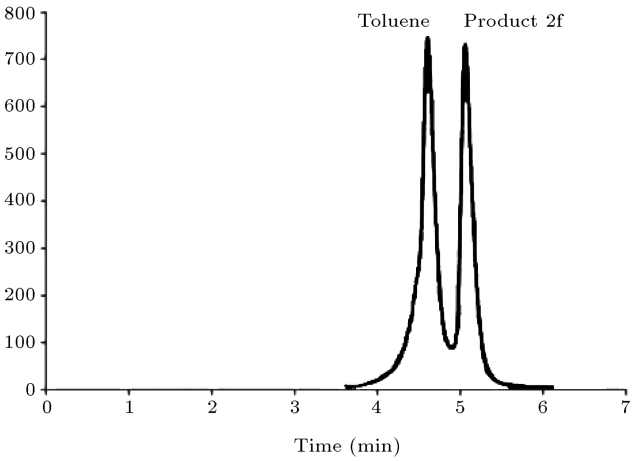
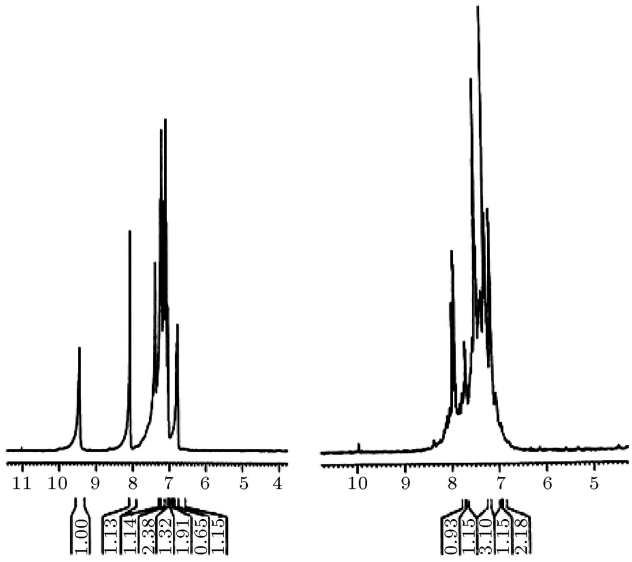


Figure 3. HPLC chromatogram of cycloadduct **2f** (eluted with toluene).

gel column (toluene) and then completely with HPLC (toluene) to give product **2f** (Figure 3). Finally, the structure was elucidated, as expected, **2f**, by spectral data.

In the mass spectrum (EI, 70 eV), the peak at m/z 920 is related to the molecular ion of M^+. In the IR spectra, the stretching frequency of aromatic C=C is produced in the area between = 1490-1600 cm^{-1}. Also, the stretching frequency of C=N of the pyrazoline ring appears at 1631 cm^{-1}. In the ^{1}H NMR spectra, the proton signal of imine appears around the δ= 9-10 ppm in phenylhydrazone (**1f**), while this peak disappears in the fulleropyrazoline (**2f**) spectrum because of the connection of phenylhydrazone to C_{60}. The signals about δ= 6.7-7.3 ppm are assigned by protons of the CH-CH of the aromatic rings in phenylhydrazone, while these protons are at really low field in fulleropyrazoline, and the related signals appear in δ = 7.1-8.0 (Figure 4). These shifts have been attributed in other fullerene derivatives to the formation of a charge transfer complex between the organic addend and the C_{60} cage, and to the electron-withdrawing property of the attached fullerene cage [63].



(a) (b)

Figure 4. ^{1}H NMR spectrum of (a) 2-thiophencarboxaldehyde phenylhydrazone, and (b) 1′-phenyl- 3′- (2-thienyl)pyrazolino[4′, 5′: 1, 2][60] fullerene.

4. Conclusion

In this research, an appropriate and green method for the functionalization of C_{60}, enabling the design of mild reaction conditions under ultrasonic irradiation, be developed here. It seems that the sonochemical method for preparation of fulleropyrazolines provides several advantages, including a one-pot reaction, environmental friendliness, short reaction time, good yields, no requirement base, and a simple workup procedure. We expect this technique to find extensive applications in the field of fullerene chemistry, green synthesis and sonochemistry.

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