第 17 卷　第 3 期
2009 年 6 月
含　能　材　料
CHINESE JOURNAL OF ENERGETIC MATERIALS
Vol. 17, No. 3
June, 2009

文章编号： 1006-9941(2009)03-0287-06

Synthesis and Characterization of Nitro Fulleropyrrolidine Derivatives

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Abstract: Six nitro fulleropyrrolidine derivatives were synthesized by the 1,3-dipolar cycloaddition reactions of [60] fullerene and the nucleophilic substitution reaction of N-unsubstituted fulleropyrrolidine. The structures of the products were characterized by ultraviolet-visible spectroscopy (UV-Vis), Fourier transform infrared spectrometer (FT-IR), mass spectrometry (MS) and ^{1}H, ^{13}C nuclear magnetic resonance (NMR) techniques. The effects of the different products on the impact sensitivity and friction sensitivity of HMX were tested. The friction and impact sensitivities of HMX reduces from 100% to 48% and to 50%, respectively when 1% *N*-methyl-2-(3-nitrophenyl) fulleropyrrolidine 2 added in HMX.

Key words: organic chemistry; fullerene; nitro fulleropyrrolidine; HMX; sensitivity

CLC number: TJ55; O621.25; TQ225.26$^+$ **Document code**: A **DOI**: 10.3969/j.issn.1006-9941.2009.03.009

1 Introduction

[60] Fullerene, the most abundant representative of the fullerene family, was discovered in 1985[1] and produced for the first time on a preparative scale in 1990[2]. The unique molecular structure and physical properties of fullerene rendered it and its derivatives special potential applications[3-7]. [60] Fullerene become an excellent solid rocket fuel additive to bear a huge pressure in the propellants for its good anticompression property[8-9]. Some energetic groups such as nitryl were introduced into [60] fullerene to get new energetic derivatives[10-11].

The chemical derivatization of fullerene represents an important frontier of active research, and an impressive number of fullerene derivatives have been synthesized by various functionalization methods[12-14]. Among the numerous methods for functionalizing fullerenes, 1,3-dipolar cycloadditions have been extensively applied[15-16]. In this paper, we reported the synthesis of fulleropyrrolidines with nitryl groups via 1,3-dipolar cycloaddition reactions of azomethine producing [60] fullerene and the nucleophilic substitution reactions of nitro benzene halide to *N*-unsubstituted fulleropyrrolidine. Simultaneously, the effects of the four different nitro fulleropyrrolidines on HMX were studied experimentally.

2 Experimental

2.1 Materials and methods

All materials used in this study are of analytical grade (AR). Fullerene C_{60} (99%) was purchased from Henan Tian′an Company. Sarcosine and glycine were procured from Acros and Chengdu Kelong Chemical Reagents Company respectively. 3-Nitrobenzaldehyde and 2,4-dinitrobenzaldehyde was purchased from Beijing Chemical Reagents Company. 2,4-Dinitrofluorobenzene was purchased from Fluka. HMX and TNT were provided by Chinese Academy of Engineering Physics, and the particle size distribution of HMX was 1 to 100 μm. All solvents for the reactions were analytical grade and dried before using.

The infrared spectra were measured on Nicolet 380 FT-IR spectrometer (KBr pellet) with a resolution of 4 cm^{-1}, in the range 4000 - 400 cm^{-1}. The ^{1}H and ^{13}C nuclear magnetic resonance were recorded on Brucker AVANCE 600 and Brucker AVANCE 300 spectrometers. The UV-Vis spectra were recorded on UNICON UV-2102 PCS spectrometer . The mass spectra were measured on

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Received Date: 2008-07-09; **Revised Date**: 2008-11-28

Project Supported: National Science Fund of China (No. 10576026), Sichuan Bureau of Science and Technology (No. 05GG009-018-05), Institute of Chemical Materials, China Academy of Engineering Physics

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Brucker BIFLEXIII MALDI-TOF spectrometer. The friction sensitivity and impact sensitivity were tested according to the GJB772A-97 602.1 and GJB772A-97 601.1 and method respectively. The testing conditions of friction sensitivity were that the switch angle was 90°, and the pressure was 3.92 MPa and the quality of sample was 20 mg. Twenty-five samples were tested and calculated the firing percents. The testing conditions of impact sensitivity were that the weight of dropping hammer was 10 kg, and the height of dropping hammer was 25 cm and the quality of sample was 50 mg. Twenty-five samples were tested and calculated the firing percent.

2.2 Synthesis of nitro fulleropyrrolidine derivatives

The nitro fulleropyrrolidines **1 – 4** were synthesized by the 1,3-dipolar cycloaddition reactions and **5 – 6** were synthesized by the nucleophilic substitution reactions.

2.2.1 Synthesis of 2-(3-nitrophenyl)fulleropyrrolidine (1)

A mixture of $\mathrm{C_{60}}$ (36.0 mg, 0.05 mmol), glycine (22.6 mg, 0.3 mmol) and 3-nitrobenzaldehyde (30.1 mg, 0.2 mmol) was heated to 100 ℃ for 24 hrs in toluene (80 ml). After the solvent had been removed in vacuo, flash chromatography of the residue on a silica gel column, with carbon disulfide and toluene as the eluents respectively, gave the unreacted $\mathrm{C_{60}}$ and product **1**. Yield = 82.1%. UV-Vis($\mathrm{CHCl_3}$) $\lambda_{\max}$: 257(s), 311(s), 431(w) nm; ^{1}H NMR($\mathrm{CS_2}$/DMSO, 300 MHz) δ: 4.25 (d, J = 10.4 Hz, 1H), 4.91(s, 1H), 4.96(d, J = 10.4 Hz, 1H), 7.52(t, J = 8.1 Hz, 1H), 8.11(d, J = 8.1 Hz, 2H), 8.70(s, 1H); ^{13}C NMR($\mathrm{CS_2}$/DMSO, 75 MHz) δ: 156.51, 154.45, 153.56, 152.36, 148.71, 147.34, 146.73, 146.61, 146.47, 146.44, 146.31, 146.28, 146.13, 146.07, 145.94, 145.75, 145.66, 145.59, 145.54, 145.49, 145.42, 144.95, 144.70, 144.61, 144.55, 143.42, 143.30, 142.95, 142.88, 142.83, 142.80, 142.59, 142.53, 142.51, 142.43, 142.35, 142.32, 142.17, 142.13, 141.98, 141.81, 141.12, 141.09, 141.06, 140.49, 140.47, 140.34, 139.79, 137.77, 136.61, 136.44, 136.09, 134.68, 129.98, 123.60, 123.20, 78.14(CH), 76.89, 62.67(CH2), 59.10; IR(KBr) ν: 2956, 2924, 2860, 1617, 1529, 1460, 1427, 1346, 1184, 1095, 854, 805, 768, 694, 574, 527 cm^{-1}; MS(MAIDI-TOF) m/z: 883.1([M-1]$^+$), 838.2([M-$\mathrm{NO_2}$]$^+$, $\mathrm{C_{68}NH_8^+}$), 720.5($\mathrm{C_{60}^+}$).

2.2.2 Synthesis of *N*-methyl-2-(3-nitrophenyl) fulleropyrrolidine (2)

The compound **2** was prepared as described for **1**, from $\mathrm{C_{60}}$ (36.0 mg, 0.05 mmol), sarcosine (8.9 mg, 0.1 mmol) and 3-nitrobenzaldehyde (7.6 mg, 0.05 mmol). Yield is 84.3%. UV-Vis($\mathrm{CHCl_3}$) $\lambda_{\max}$: 255(s), 327(s), 405(w), 431(w) nm; ^{1}H NMR($\mathrm{CS_2}$/DMSO, 300 MHz) δ: 2.79(s, 3H), 4.30(d, J = 9.3 Hz, 1H), 4.98(d, J = 9.3 Hz, 1H), 5.06(s, 1H), 7.56–8.58(b, 4H); ^{13}C NMR($\mathrm{CS_2}$/DMSO, 75 MHz) δ: 154.12, 151.80, 150.84, 150.22, 146.86, 145.60, 144.62, 144.55, 144.53, 144.45, 144.28, 144.00, 143.96, 143.77, 143.74, 143.69, 143.62, 143.59, 143.52, 143.06, 142.85, 142.75, 142.65, 141.49, 141.40, 141.07, 140.98, 140.96, 140.90, 140.60, 140.56, 140.51, 140.47, 140.39, 140.35, 140.26, 140.14, 140.05, 139.95, 138.65, 138.64, 138.48, 137.90, 135.60, 134.71, 134.49, 134.02, 133.28, 128.63, 122.49, 122.12, 80.69(CH), 75.01, 68.37 ($\mathrm{CH_2}$), 67.23, 37.70(N-$\mathrm{CH_3}$); IR(KBr) ν: 2920, 2850, 2777, 1601, 1579, 1529, 1452, 1427, 1345, 1179, 798, 765, 701, 569, 526, cm^{-1}; MS(MAIDI-TOF) m/z: 897.7([M-1]$^+$), 720.5($\mathrm{C_{60}^+}$).

2.2.3 Synthesis of *N*-methyl-2-(2,4-dinitrophenyl) fulleropyrrolidine (3)

This compound was prepared as described for **1**, from $\mathrm{C_{60}}$ (36.0 mg, 0.05 mmol), sarcosine (26.7 mg, 0.3 mmol) and 2,4-dinitrobenzaldehyde (19.6 mg, 0.1 mmol). The reaction temperature and time were 95 ℃ and 40 h respectively. Yield is 65.8%. UV-vis($\mathrm{CHCl_3}$) $\lambda_{\max}$: 257(s), 328(s), 431(w) nm; ^{1}H NMR($\mathrm{CS_2}$/$\mathrm{CDCl_3}$, 300 MHz) δ: 2.80(s, 3H), 4.25(d, J = 9.4 Hz, 1H), 4.91(s, 1H), 4.96(d, J = 9.4 Hz, 1H), 7.23-7.77(m, 3H); IR(KBr) ν: 2946, 2838, 2781, 1603, 1577, 1525, 1452, 1428, 1347, 1178, 848, 574, 527 cm^{-1}; MS(MAIDI-TOF) m/z (%): 943.0([M]$^+$), 720.3($\mathrm{C_{60}^+}$).

2.2.4 Synthesis of *N*-methyl-2-(2,4,6-trinitrophenyl) fulleropyrrolidine (4)

2,4,6-trinitrotoluene(TNT) (91 mg, 0.4 mmol), potassium permanganate (63.2 mg, 0.4 mmol), sodium carbonate (21.2 mg, 0.2 mmol) and TBAC (0.1 ml) were added into 30 ml NaOH solution (0.1 mol/L) and heated to 54 ℃ for 5 h. After cooling to room temperature, the mixture was filtered and extracted with ether. After removal of the ether in vacuo, the residue was refluxed with C_{60} (36.0 mg, 0.05 mmol) and sarcosine (22.6 mg, 0.3 mmol) for 24 hrs in toluene (60 ml). After the solvent had been removed in vacuo, flash chromatography of the residue on a silica gel column, with carbon disulfide and toluene as the eluents respectively, gave the unreacted C_{60} and product **4**. Yield is 74.0%. UV-Vis($CHCl_3$) λ_{max}: 260(s), 309(m), 431(w) nm; ^1H NMR($CS_2/CDCl_3$, 600 MHz) δ: 2.84(s, 3H), 4.28(d, *J* = 9.2 Hz, 1H), 4.95(s, 1H), 5.00(d, *J* = 9.2 Hz, 1H), 7.79(s, 2H); ^{13}C NMR($CS_2/CDCl_3$, 150 MHz) δ: 156.22, 153.99, 153.42, 153.30, 147.35, 146.80, 146.50, 146.38, 146.33, 146.28, 146.22(2C), 146.20, 146.16, 146.00(2C), 145.83, 145.68, 145.61, 145.58, 145.46(2C), 145.36, 145.30(2C), 145.29, 145.22, 144.78, 144.71, 144.45, 143.23, 143.09, 142.76, 142.69, 142.66(2C), 142.35, 142.32, 142.23, 142.17, 142.15, 142.13, 142.08, 142.00, 141.90, 141.77, 141.62, 140.31, 140.26, 140.00, 139.59, 136.97, 136.92, 136.67, 135.92, 135.82, 129.41, 128.87, 128.63, 83.70(CH), 70.17, 69.03(CH_2), 63.00, 40.10(CH_3); IR(KBr) υ: 2944, 2831, 2779, 1602, 1539, 1463, 1453, 1428, 1333, 1179, 1107, 940, 905, 767, 574, 527, 479 cm^{-1}; MS(MAIDI-TOF) *m/z*: 987.4($[M\text{-}1]^+$).

2.2.5 Synthesis of *N*-(2,4-dinitrophenyl)-2-(3-nitrophenyl)fulleropyrrolidine (5)

1(21.0 mg, 0.02 mmol) was treated with 2,4-dinitrofluorobenzene(37.2 mg, 0.2 mmol) in the presence of TBAB(32.6 mg, 0.1 mmol) as PTC agent and potassium carbonate(28.0 mg, 0.2 mmol) as base, at 150 ℃ for 12 hrs. After the mixture was cooled to room temperature and then dissolved in CS_2 (10 mL) followed by filtration. After removal of the solvent, the product was further purified by flash chromatography [SiO_2, hexane/toluene (1:2)] to give the product 5 and the starting material **1**. Yield is 22.1%. UV-Vis($CHCl_3$) λ_{max}: 257(s), 317(m), 431(w) nm; ^1H NMR($CDCl_3$, 600 MHz) δ: 4.88(d, *J* = 10.2 Hz, 1H), 5.47(d, *J* = 10.2 Hz, 1H), 6.43(s, 1H), 7.49(t, *J* = 8.1 Hz, 1H), 7.66(d, *J* = 9.1 Hz, 1H), 8.06(d, *J* = 7.9 Hz, 1H), 8.10(d, *J* = 7.4 Hz, 1H), 8.32(d, *J* = 8.5 Hz, 1.9 Hz, 1H), 8.56(s, 1H), 8.75(d, *J* = 1.5 Hz, 1H); IR(KBr) υ: 2969, 2925, 2873, 1601, 1559, 1531, 1458, 1398, 1385, 1347, 1187, 1097, 1049, 916, 832, 768, 735, 685, 669, 574, 527 cm^{-1}; MS(MAIDI-TOF) *m/z*: 1050.0($[M]^+$), 1034.1(M^+-O), 720.1(C_{60}^+).

2.2.6 Synthesis of *N*-(2,4,6-trinitrophenyl)-2-(3-nitrophenyl)fulleropyrrolidine (6)

This compound was prepared as described for **5**, from **1**(10.5 mg, 0.01 mmol), 2,4,6-trinitrochlorobenzene(12.6 mg, 0.05 mmol), TBAB(16.6 mg, 0.05 mmol) and potassium carbonate(14.2 mg, 0.1 mmol). The reaction time was 8 hrs. Yield = 60.5%. UV-Vis($CHCl_3$) λ_{max}: 263(s), 316(s), 430(w) nm; ^1H NMR($CS_2/CDCl_3$, 600 MHz) δ: 5.42(d, *J* = 10.8 Hz, 1H), 5.56(d, *J* = 10.4 Hz, 1H), 7.54(t, *J* = 8.0 Hz, 1H), 7.95(d, *J* = 8.0 Hz, 1H), 8.18(d, *J* = 8.4 Hz, 1H), 8.48(s, 1H), 8.75(s, 1H); IR(KBr) ν: 2961, 2923, 2852, 1603, 1576, 1530, 1508, 1448, 1436, 1346, 1175, 898, 843, 765, 704, 575, 527 cm^{-1}; MS(MAIDI-TOF) *m/z*: 1096.3($[M+1]^+$), 720.3(C_{60}^+).

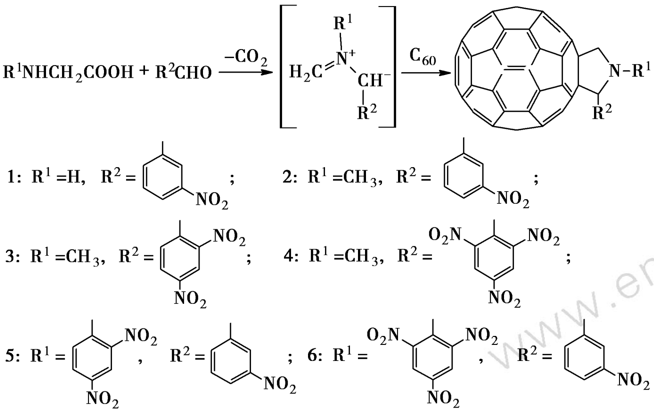
2.3 Preparation of nitro fulleropyrrolidine/HMX mixtures

20 mg **1** and 1.980 g HMX were added in an agate mortar and milled till the well-proportioned mixing(about 30 min) to prepare the **1**/HMX mixture. The mixtures of **2**/HMX, **3**/HMX and **4**/HMX were obtained with the same method.

3 Results and discussion

3.1 Synthesis and structure

A mixture of C_{60}, 6 equiv. of glycine and 4 equiv. of 3-nitrobenzaldehyde in toluene was heated to100 ℃ for 24 hours, then the solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with CS_2 and toluene as the eluents to give unreacted C_{60} and product **1**. The products **2** – **4** were prepared under the analogous conditions with C_{60}, corresponding nitryl benzaldehydes and amino acids as raw materials. The relative reaction conditions and yields are showed in Table 1. However, products **5** and **6** can't be produced via 1,3-dipolar cycloaddition pathway, as shown in Scheme 1.



(not obtained) (not obtained)

Scheme 1

Table 1 Reaction conditions and yields of final products

final product	solvent	temperature/℃	time/h	yield[1)]/%
1	toluene	100	24	82.1
2	toluene	90	24	84.3
3	toluene	95	40	65.8
4	toluene	110	24	74.0
5	toluene	110	48	–[2)]
6	toluene	110	48	–[2)]

Note: 1) Based on consumed C_{60}; 2) No. product **5** and **6**.

In order to explain the reactivity of C_{60} with the 1,3-dipoles **7 – 10** (see table 1) in this reaction, the HOMO and LUMO energy levels for the reactants employed were calculated by the program VAMP using the semiempirical method PM3. Frontier molecular orbital theory indicates that the reactive model of 1,3-dipolar cycloaddition is based upon the interaction between the HOMO of 1,3-dipole and the LUMO of fullerene. The reactivity of the cycloaddition is related to the LUMO(fullerene)-HOMO(dipole) energy gap, ΔE_1, as shown in Fig 1. The smaller the energy gap between LUMO(fullerene)-HOMO(dipole) is associated with the higher the reactivity.

The calculation results are summarized in Table 2. The energy gap ΔE_1 of 1,3-dipole **7** is the smallest. Consequently, the reaction temperature is lowest. The 1,3-dipoles **8**, **9** and **10** show a higher energy gap than **7**, so the higher reaction temperature is required. The reaction temperatures of the 1,3-dipoles **7**, **8** with [60]fullerene are 90 ℃ and 100 ℃ respectively, and 1,3-dipoles **9**, **10** don't react with [60]fullerene under refluent temperature(110 ℃) of toluene, as shown in Table 1. These results indicate that the LUMO(fullerene)-HOMO(dipole) energy gap of deficient electron dipole and fullerene is larger than the rich electron dipole, and a higher temperature are required in the reactions. Because of *N*-substituted deficient electron group 2,4-dinitrophenyl and 2,4,6-trinitrophenyl respectively, the 1,3-dipoles **9** and **10** have the higher ΔE_1, and the aim compound **5** and **6** can not be obtained under the ref-luent condition of toluene.

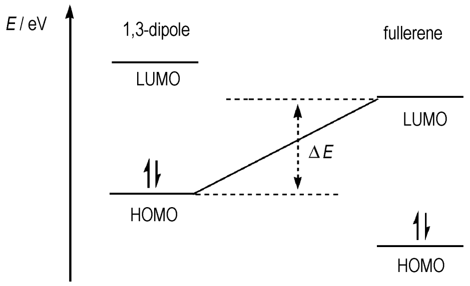
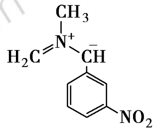
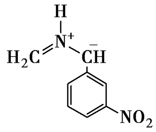
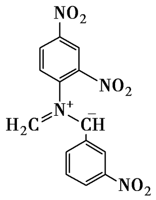
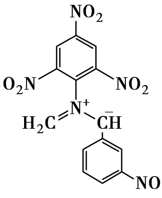


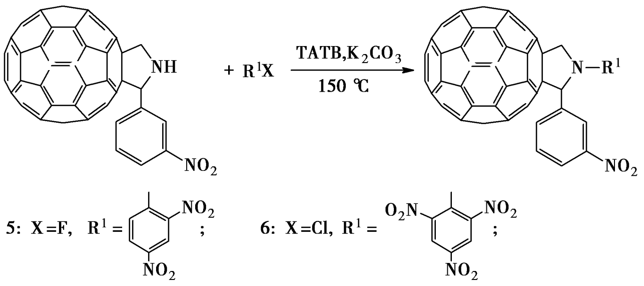
Fig. 1 The interactions of HOMO of 1,3-dipoles and LUMO of fullerene

Table 2 LUMO and HOMO levels of [60]fullerene and 1,3-dipoles calculated with PM3

	compound	E/eV	ΔE_1/eV	ΔE_2/eV
	C_{60}	LUMO: –2.887 HOMO: –9.482	——	——
7		LUMO: **–0.843** HOMO: **–8.021**	5.134	7.237
8		LUMO: **–0.843** HOMO: **–8.163**	5.276	7.316
9		LUMO: **–0.843** HOMO: **–8.163**	5.276	7.316
10		LUMO: **–3.211** HOMO: **–8.650**	5.763	5.439

Note: ΔE_1 = LUMO(C_{60}) – HOMO(dipole); ΔE_2 = LUMO(dipole) - HOMO(dipole).

N-unsubstituted fulleropyrrolidines can further react to produce new useful materials[17, 18]. In spite of the great interest in the chemistry of these compounds, only a few examples of arylation of *N*-unsubstituted pyrrolidino [60] fullerenes have been reported[19]. For the sake of the synthesis of product **5** and **6**, the arylation of 2-(3-nitrophenyl) fulleropyrrolidine was employed, as shown in Scheme 2. Product **5** was synthesized by the nucleophilic substitution reaction of **1** and 2, 4-dinitrofluorobenzene under the oil-bath heating and solvent-free phase-transfer-catalysis (PTC) conditions. Product **6** was also synthesized by the nucleophilic substitution reaction of **1** and 2,4,6-trinitrochlorobenzene under the same conditions.



Scheme 2

The structures of compounds **1 - 6** were confirmed by the data from spectroscopic methods and mass spectrometry. The UV-Vis spectra of compounds **1 - 6** have typical absorption bands at 255 - 263 nm, 309 - 328 nm, and 430 - 431 nm of fulleropyrrolidines. The IR spectra of compounds **1 - 6** have absorption bands at 526 - 527 cm^{-1}, 569 - 575 cm^{-1}, 1178 - 1184 cm^{-1}, and 1427 - 1428 cm^{-1} belonging to stretching vibrations of the fullerene core and a series of other absorption bands corresponding to stretching vibrations of the attached fragments. The ^1H NMR spectra of compounds **1 - 6** have signals of the 2-arylfulleropyrrolidine system. Compound **2 - 4** have a singlet at $\delta = 2.79 - 2.84$ for *N*-methyl group, a singlet at $\delta = 4.91 - 5.06$ for H-2, an AB system at $\delta = 4.25 - 5.00$ for CH_2-5 with a $J_{AB} = 9.2 - 9.3$ Hz, and signals at $\delta = 7.2 - 8.6$ for the protons of the aromatic nucleus. Compounds **5** have a doublet at $\delta = 8.75$ ($J = 1.5$ Hz), a double doublet at $\delta = 8.32$ ($J = 8.5$ Hz, 1.9 Hz) and a doublet at $\delta = 7.66$ ($J = 19.1$ Hz) for *N*-(2,4-dinitrophenyl) group, a singlet at $\delta = 8.56$, a doublet at $\delta = 8.10$ ($J = 7.4$ Hz), a doublet at $\delta = 8.06$ ($J = 7.9$ Hz) and a triplet at $\delta = 7.49$ ($J = 8.1$ Hz) for 2-(3-nitrophenyl) group, a singlet at $\delta = 4.91 - 5.06$ and a AB system at $\delta = 4.25 - 5.00$ for CH-2 and CH_2-5 respectively. The compositions of **1 - 6** are also established by mass spectrometry. The molecule ion peaks of **1** ($[M-1]^+$, *m/z*: 883.1), **2** ($[M]^+$, *m/z*: 897.7), **3** ($[M]^+$, *m/z*: 943.0), **4** ($[M-1]^+$, *m/z*: 987.4), **5** ($[M]^+$, *m/z*: 1050.0) and **6** ($[M+1]^+$, *m/z*: 1096.3) are observed in their mass spectra respectively.

3.2 Sensitivity Properties

The products **1 - 4** have been used to desensitize HMX. The results are listed in Table 3. Compared with the pure HMX, when one percent of product **2** is added in HMX, the friction sensitivity and impact sensitivity can be decreased from 100% to 48 % and to 50 % respectively. The friction sensitivity and impact sensitivity of HMX also can be decreased to 90 % and 70 % respectively, when one percent of product **1** is added in HMX. However, there are no obvious desensitizing effects when one percent of products **3** and **4** are added in HMX.

Table 3 The mechanical sensitivity of products 1 - 4 /HMX

sample	mass ratio	friction sensitivity/%	impact sensitivity/%
HMX	100	100	100
1/HMX	1/99	90	70
2/HMX	1/99	48	50
3/HMX	1/99	90	100
4/HMX	1/99	100	100

4 Conclusions

In this work, we have successfully synthesized six nitro fulleropyrrolidine derivatives *via* the 1, 3-dipolar cycloadditions of azomethine ylides to [60] fullerene and the nucleophilic substitution reaction of nitro benzene halide to 2-(3-nitrophenyl) fulleropyrrolidine **1**. Simultaneously, the desensitizing effects of products **1 - 4** to HMX were tested, when 1% product **2** was added in HMX, the friction sensitivity could be decreased from 100% to 48% and impact sensitivity could be decreased from 100% to 50%.

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硝基富勒烯吡咯烷衍生物的合成与结构表征

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摘要：以氨基酸、硝基苯甲醛、C_{60}和硝基卤苯等为原料，通过1,3-偶极环加成反应和亲核取代反应合成得到了六种硝基富勒烯吡咯烷衍生物，经紫外可见光谱、红外光谱、质谱和核磁共振谱等结构表征手段对这六种产物的结构进行了表征；探讨了其中四种产物对HMX的钝感作用，结果表明添加1%的*N*-甲基-2-(3-硝基苯基)吡咯烷[3′,4′:1,2][60]富勒烯可以使HMX的摩擦感度由100%降低到48%，撞击感度降低到50%。

关键词：有机化学；[60]富勒烯；硝基富勒烯吡咯烷；奥克托今(HMX)；感度

中图分类号：TJ55；O621.25；TQ225.26^{+} **文献标识码：**A