Chemistry of Heterocyclic Compounds, Vol. 40, No. 2, 2004

HETEROCYCLIC DERIVATIVES OF FULLERENE C_{60}. 1. SYNTHESIS OF NEW FULLEROPYRAZOLINES BY THE 1,3-DIPOLAR CYCLOADDITION OF NITRILE IMINES

M. V. Reinov, M. A. Yurovskaya, D. V. Davydov, and A. V. Streletskii

New stable [6,6]-closed cycloadducts, fulleropyrazolines containing aryl, hetaryl, trifluoromethyl, and other substituents in the five-membered ring, have been obtained by the 1,3-dipolar cycloaddition of nitrile imines to C_{60}. Two methods of generating nitrile imines in situ have been used, the dehydrohalogenation of the corresponding hydrazonoyl halides by the action of triethylamine and the thermal decomposition of 2,5-diaryltetrazoles.

Keywords: hydrazonoyl halides, 2,5-diaryltetrazoles, [6,6]-closed cycloadducts, nitrile imines, fullerene C_{60}, fulleropyrazolines, 1,3-dipolar cycloaddition.

1,3-Dipolar cycloaddition of nitrile imines to C_{60} is the standard method for annelating the pyrazoline ring to the fullerene sphere (see review [1] and cited literature). Further development of investigations in this direction may be connected primarily with the synthesis of new representatives of this class of compounds or secondly with the application of new methods of generating nitrile imines. Both aspects have been studied in the present work.

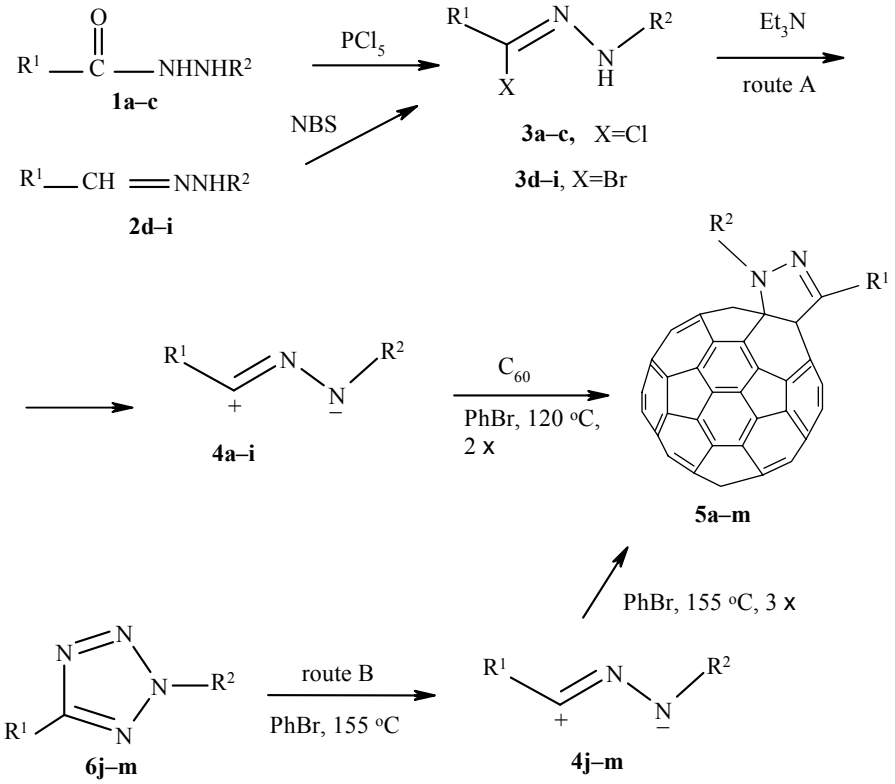
The known method of generating nitrile imines *in situ* (route A), the dehydrohalogenation of substituted hydrazonoyl halides by the action of triethylamine, has made possible a significant expansion of the variety of 1,3-disubstituted fulleropyrazolines.

The cycloadducts **5a-i** synthesized contain aryl and trifluoromethyl substituents in the five-membered heterocyclic fragment.

The starting materials for generating nitrile imines **4a-c** *in situ*, the hydrazonoyl chlorides **3a-c**, were obtained by the action of PCl_5 [2] on the hydrazides of the appropriate acids **1a-c**. The preparation of nitrile imine precursors **4d-i** by this method was unsuccessful. Good results were obtained on generating nitrile imines, not from the corresponding hydrazonoyl chlorides but from the bromides **3d-i**, which, in turn, were synthesized by the bromination of hydrazones **2d-i** by the action of NBS [3]. An interesting fact may be noted that on bromination of *p*-ethoxybenzaldehyde phenylhydrazone (**2e**) under these conditions the *p*-bromophenylhydrazonoyl bromide of *p*-ethoxybenzaldehyde (**3f**) is formed in parallel. This was indicated by the isolation of cycloadduct **5f** together with fulleropyrazoline **5e** from the reaction mixture obtained on interacting the unexpected bromination product, fullerene, and triethylamine.

Moscow M. V. Lomonosov State University, Moscow 119234, Russia; e-mail: yumar@org.chem.msu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 223-228, February, 2004. Original article submitted November 1, 2003.

 0009-3122/04/4002-0188



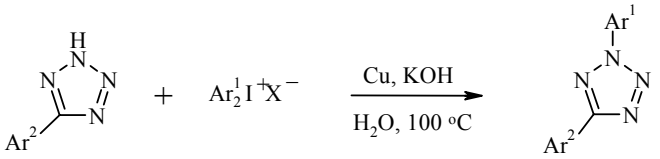
1–**4** **a** R^1= *p*-$O_2NC_6H_4$, R^2= Ph; **b** R^1=Ph, R^2= *p*-$O_2NC_6H_4$; **c** R^1= Ph, R^2=2,4-$Cl_2C_6H_3$;
d R^1= R^2= *p*-$O_2NC_6H_4$; **e** R^1= *p*-$EtOC_6H_4$, R^2=Ph; **f** R^1= *p*-$EtOC_6H_4$, R^2= *p*-BrC_6H_4;
g R^1= CF_3, R^2= Ph; **h** R^1= CF_3, R^2= *p*-MeC_6H_4; **i** R^1= CF_3, R^2= *o*-$MeOC_6H_4$;
3–**5** **j** R^1= 2-thienyl, R^2= *p*-MeC_6H_4; **k** R^1= R^2=Ph; **l** R^1= 4-Py, R^2= Ph;
m R^1= Ph, R^2= *p*-$MeOC_6H_4$

All the hydrazonoyl halides **3a-i** synthesized were used for generating *in situ* the corresponding nitrile imines **4a-i** by the action of triethylamine directly in the reaction mixture already containing C_{60}. Reaction was carried out in bromobenzene. The cycloaddition of nitrile imines **4a-i** leads smoothly to the formation of stable [6,6]-closed monofulleropyrazolines **5a-i**. Literature data indicate that mainly monoadducts are formed as a result of cycloaddition of nitrile imines [3]. However, there is a reference [4] that on interacting 1,3-diphenylnitrile imine with C_{60} under similar conditions the monoadduct is not formed but the main compound isolated is the bisadduct. In our case the addition of practically all the nitrile imines **4a-i** leads to the formation of monoadducts as the chief product, when using nitrile imine **4h** the bisadduct was recorded as a side product (according to data of MALDI mass spectrometry).

In addition to the described standard method we used for the first time a procedure (route B), preparatively simple, for generating nitrile imines by the thermal decomposition of 2,5-diaryltetrazoles. Cycloadducts **5j-m,** containing aryl and hetaryl substituents such as thienyl and pyridyl in the pyrazoline fragment, were synthesized by this method. The availability of 2,5-diaryltetrazoles of various structure generates a greater possibility for functionalization of the fullerene spheroid than route A, which is limited by the availability of the appropriate hydrazonoyl halides.

5-(2-Thienyl)-2-*p*-tolyltetrazole (**6j**) was obtained by the known procedure of [5]. For the synthesis of the remaining diaryltetrazoles **6k-m** we developed a new original procedure. Several methods of obtaining 2,5-diaryltetrazoles are known. It is possible to synthesize them by regioselective arylation of 5-aryltetrazoles under the action of diaryliodonium salts in the presence of palladium and copper catalysts in DMF [6], or on

oxidation of stannylated 5-aryltetrazoles with Cu(II) acetate in the presence of $Ar_2I^+X^-$ in CH_2Cl_2 [7]. Our method comprises the regioselective arylation of 5-aryltetrazoles by various diaryliodonium salts in water using metallic copper catalyst.



Ar^1 = Ph, *p*-MeO-C_6H_4; Ar^2 = Ph, 4-Py

The simplicity of carrying out the experiment (reaction in water), the ease of isolating the desired compounds, and the fairly high yields (60-85%), depending on the structure of the iodonium salt, serve as an irrefutable advantage of the proposed method of synthesis of diaryltetrazoles **6**.

Thermal decomposition of tetrazoles **6** at a temperature of the order of 150°C in bromobenzene solution in the presence of fullerene-60 leads to the intermediate formation *in situ* of the corresponding nitrile imines **4j-m** and their subsequent cycloaddition. Bromobenzene is the optimum solvent for carrying out the reaction. The reaction also proceeds in chlorobenzene and toluene but the yields of the cycloadducts were far less.

Assignment of the synthesized fulleropyrazolines **5a-m** to the [6,6]-closed isomers was made on the basis of ^{13}C NMR data. Analysis of all the obtained adducts was unsuccessful, because of the difficulties linked with the long time for accumulation of ^{13}C NMR spectral signals due to the low solubility of adducts. Two signals were present in the spectra of adducts **5b** and **5h** in the 75-110 ppm region which correspond to the $C_{(3)}$ and $C_{(4)}$ nuclei of the pyrazoline ring. When forming [5,6]-open fulleroid structures the signals of the $C_{(3)}$ and $C_{(4)}$ atomic nuclei will not be present in the aliphatic portion of the spectrum. The ^1H NMR spectral data indicate the presence in adducts **5a-m** of an annelated five-membered heterocyclic fragment. The main characteristics are the signals in the 7.6-8.3 region assigned to the *ortho* protons of the N-aryl substituent, and in the 8.1-8.4 ppm region assigned to the *ortho* protons of the C-aryl substituent. Such a large displacement towards low field compared with the initial hydrazonoyl halides is caused by intramolecular charge-transfer between the fullerene fragment and the aryl substituents of the fulleropyrazoline ring [3,8]. The MALDI spectra confirm that monocycloaddition proceeds under the indicated conditions.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Varian XL 400 instrument (^1H at 400 and ^{13}C at 100 MHz), internal standard was TMS. The NMR spectra of the fullerene adducts **5** were obtained for solutions in CS_2–acetone-d_6, 5:1. Mass spectral analysis by the MALDI method was carried out on a Vision 2000 instrument with a N_2 laser, the wavelength of the radiation of which was 336 nm, and a time of flight mass analyzer. As matrices we successfully used orthorhombic sulfur, [3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB), and 9-nitroanthracene. Both negative and positive ions were recorded. Each mass spectrum was obtained by summing the signals of 20 to 50 laser impulses. The order of preparing samples of substances for analysis was as follows: several drops (less than 1 μl) of a saturated toluene solution of the matrix were applied to a metallic target with the aid of a fine capillary to form, after evaporation of the solvent, a thin film. A fraction of the substance being analyzed, obtained by TLC, was also dissolved in toluene, after which the surface of the matrix film was moistened with several drops of this solution with the aid of a fine capillary. The best conditions for analysis were achieved on using this procedure with a matrix of sulfur or DCTB when recording negative ions. In the mass range of the substance being analyzed the molecular radical-anion $[M]^{-\cdot}$ had the greatest intensity, while the intensity of the $C_{60}^{-\cdot}$ fragment ion was low.

A check on the progress of reactions and the purity of the compounds obtained was effected by TLC on Silufol UV 254 plates. Separation and purification of substances were carried out on columns of silica gel L 40/100, eluting with hexane–benzene, 3:1.

Hydrazides **1a-c** and hydrazonoyl halides **2a-c** were synthesized by the procedure of [2].

Phenylhydrazonoyl Chloride of *p*-Nitrobenzaldehyde (3a). Yield 55%; mp 184-188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.10 (1H, t, 4-H); 7.35 (2H, m, 3-, 5-H); 7.48 (2H, d, 2-, 6-H); 8.23 (2H, d, 2'-, 6'-H); 8.40 (2H, d, 3'-, 5'-H); 10.56 (1H, s, NH). Found, %: C 56.76; H 3.66; N 15.61. $C_{13}H_{10}ClN_3O_2$. Calculated, %: C 56.64; H 3.66; N 15.24.

***p*-Nitrophenylhydrazonoyl Chloride of Benzaldehyde (3b).** Yield 70%; mp 190-195°C. Found, %: C 56.70; H 3.64; N 15.35. $C_{13}H_{10}ClN_3O_2$. Calculated, %: C 56.64; H 3.66; N 15.24.

2,4-Dichlorophenylhydrazonoyl Chloride of Benzaldehyde (3c). Yield 47%; mp 90°C. IR spectrum (nujol), ν, cm^{-1}: 1600 (C=N), 3330 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.16 (1H, dd, ^oJ = 8.8, ^mJ = 2.3, 5-H); 7.26 (1H, d, ^mJ = 2.3, 3-H); 7.35 (3H, m, 3'-, 4'-, 5'-H); 7.45 (1H, d, °*J* = 8.8, 6-H); 7.86 (2H, m, 2'-, 6'-H); 8.63 (1H, s, NH).

Phenylhydrazone of *p*-Ethoxybenzaldehyde (2d). *p*-Ethoxybenzaldehyde (1.39 g, 9.3 mmol) was added to a solution of phenylhydrazine (1 g, 9.3 mmol) in methanol (10 ml) and the mixture was heated until the beginning of solid precipitation, after which the reaction mixture was cooled. The solid was filtered off and used directly in the next stage.

***p*-Nitrophenylhydrazone of *p*-Nitrobenzaldehyde (2e).** A solution of *p*-nitrobenzaldehyde (0.99 g, 6.5 mmol) was added with stirring to a hot solution of *p*-nitrophenylhydrazine (1 g, 6.5 mmol) in methanol (20 ml). The mixture was heated for several minutes and cooled. The precipitated solid was filtered off.

Phenylhydrazone of Trifluoroacetaldehyde (2g), *p*-Tolylhydrazone of Trifluoroacetaldehyde (2h), and *o*-Methoxyphenylhydrazone of Trifluoroacetaldehyde (2i). $CF_3CH(OH)_2$ (15 mmol), obtained by the procedure of [9], was added to a solution of freshly distilled arylhydrazine (10 mmol) in methanol (10 ml), and the mixture was stirred at ~20°C for 1 h in an inert atmosphere. After the end of the reaction the methanol was distilled off at ~20°C, benzene (20 ml) was added to the reaction mixture, and the solution dried over sodium sulfate. A large portion of the benzene was distilled off at ~20°C, hexane (10 ml) was added, and the mixture cooled. The resulting crystals were filtered off, and used in the next stage without further purification.

Hydrazonoyl Halides (3d-i). N-Bromosuccinimide (NBS) (36 mg, 0.2 mmol) was added to a solution of hydrazone **2** (0.21 mmol) in bromobenzene (10 ml), and the mixture was stirred for 20 min. The synthesis of compounds **3e** and **3f** was carried out at 0°C, of compound **3d** at 70-80°C, and of the remaining hydrazonoyl halides at room temperature. The precipitated succimide was filtered off and the solution obtained was used in the next stage.

5-(2-Thienyl)-2-(*p*-tolyl)tetrazole (6j) was obtained by the procedure of [5].

Diaryltetrazoles (6k-m) (General Method). Potassium hydroxide (1 mmol) was added as aliquots of a titrated aqueous solution with stirring to 5-aryltetrazole (1 mmol) in water (10 ml), then diaryliodonium salt (1.5 mmol) and freshly activated metallic copper (1.5 mmol) were added after homogenization of the solution. The reaction mixture was boiled for 16 h in a stream of argon. After the end of the reaction the solution was extracted three times with chloroform. The extract was dried over Na_2SO_4 and passed through a layer of Al_2O_3 (separation from the initial 5-aryltetrazole and salts). The solution obtained was evaporated, and the residue crystallized from CCl_4 or $CHCl_3$.

2,5-Diphenyltetrazole (6k). Yield 60%; mp 100°C. UV spectrum (EtOH), λ_{max} (log ε): 272 nm (4.24). Mass spectrum, *m/z* (*I*, %): 223 (2) $[M+H]^{+\cdot}$, 222 (<1) $[M]^{+\cdot}$, 194 (40) $[M-N_2]^{+\cdot}$, 103 (10) $[M-N_2-C_6H_5N]^{+\cdot}$, 91 (100) $M-N_2-C_7H_5N]^{+\cdot}$. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.54-7.62 (4H, m, *m*-H_{Ph}); 7.67-7.71 (2H, m, *p*-H_{Ph}); 8.20-8.24 (4H, m, *o*-H_{Ph}).

2-(*p*-Methoxyphenyl)-5-phenyltetrazole (6l). Yield 85%; mp 101-102°C. UV spectrum (EtOH), λ_{max} (log ε): 300 nm (4.10). Mass spectrum, *m/z* (*I*, %): 253 (3) $M+H]^{+\cdot}$, 252 (<1) $[M]^{+\cdot}$, 224 (20) $[M-N_2]^{+\cdot}$, 121

(100) $[M-N_2-C_6H_5N]^{+\cdot}$, 106 (25) $[M-N_2-C_6H_5N-CH_3]^{+\cdot}$, 103 (10) $[M-N_2-C_7H_7NO]^{+\cdot}$. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.88 (3H, s, CH_3O); 7.45 (2H, d, 2-, 6-H_{Ar^1}); 7.55-8.10 (5H, m, Ph); 8.20 (2H, d, 3-, 5-H_{Ar^1}).

2-Phenyl-5-(4-pyridyl)tetrazole (6m). Yield 72%; mp 146°C. UV spectrum (EtOH), λ_{max} (log ε): 270 nm (4.41). Mass spectrum, *m/z* (*I*, %): 224 (1) $[M+H]^{+\cdot}$, 223 (<1) $[M]^{+\cdot}$, 195 (20) $[M-N_2]^{+\cdot}$, 104 (5) $[M-N_2-C_6H_5N]^{+\cdot}$, 91 (100) $[M-N_2-C_6H_4N_2]^{+\cdot}$, 64 (40) $[M-N_2-C_6H_4N_2-HCN]^{+\cdot}$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.30-7.90 (5H, m, Ph); 7.60 (2H, d, 4-Py); 8.10 (2H, d, 4-Py).

Fulleropyrazolines (5a-i) (General Method). A solution of hydrazonoyl halide **3** (0.21 mmol) in bromobenzene (10 ml) was added with stirring during 1.5 h to a solution of fullerene C_{60} (50 mg, 0.07 mmol) and triethylamine (50 μl) in bromobenzene (20 ml) at 120-130°C. The mixture was stirred at this temperature for a further 2 h, the solvent was distilled off, and the residue treated with methanol. The resulting solid was filtered off, and washed several times with methanol. The adduct was isolated from the mixture obtained by column chromatography. Eluents were benzene–hexane, 1:1 (for adducts **5a-c**), benzene–hexane, 1:3 (for compounds **5d-f**), and benzene–hexane 1:10 (for adducts **5g-i**).

Fulleropyrazolines (5j-m) (General Method). A solution of fullerene C_{60} (50 mg, 0.07 mmol) and tetrazole **6** (0.2 mmol) in bromobenzene was boiled for 3 h. The mixture was then treated analogously to the previous procedure. Eluents were benzene–hexane, 1:3 (for adducts **5j,k,m**), and benzene–ethyl acetate, 10:1 (for **5l**).

3-(*p*-Nitrophenyl)-1-phenylpyrazolo[4',5':1,2]fullerene[60] (5a). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.47 (3H, m, 3-, 4-, 5-H_{Ph}); 7.93 (2H, d, 2-, 6-H_{Ph}); 8.30 (2H, d, *J* = 9.1, 2-, 6-$H_{p\text{-}NO_2C_6H_4}$); 8.60 (2H, d, *J* = 9.1, 3-, 5-$H_{p\text{-}NO_2C_6H_4}$). MALDI mass spectrum: $[M]^{-\cdot}$ 959.7.

1-(*p*-Nitrophenyl)-3-phenylpyrazolo[4',5':1,2]fullerene[60] (5b). ^{1}H NMR spectrum, δ, ppm: 7.54 (3H, m, 3-, 4-, 5-H_{Ph}); 8.25 (6H, m, 2-, 3-, 5-, 6-$H_{p\text{-}NO_2C_6H_4}$; 2-, 6-H_{Ph}). ^{13}C NMR spectrum, δ, ppm: 75 (C*sp*^{3}); 106 (C*sp*^{3}); 129, 135, 138.5, 139, 140, 141, 145.5, 146.5, 149, 151.4, 152, 152.5, 152.6, 153, 153.8, 154, 154.5, 155, 155.2, 155.5, 155.7, 156, 156.8, 157.3, 159, (C*sp*^{2}). MALDI mass spectrum: $[M]^{-\cdot}$ 960.

1-(2,4-Dichlorophenyl)-3-phenylpyrazolo[4',5':1,2]fullerene[60] (5c). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.42 (1H, dd, ^oJ = 8.47, ^mJ = 2.36, 5-H); 7.47 (3H, 3-, 4-, 5-H_{Ph}); 7.60 (1H, d, ^mJ = 2.36, 3-$H_{C_6H_3Cl_2}$); 7.88 (1H, d, ^oJ = 8.47, 6-$H_{C_6H_3Cl_2}$); 8.23 (2H, d, 2-, 6-H_{Ph}). MALDI mass spectrum: $[M]^{-\cdot}$ 983.7.

1-(*p*-Nitrophenyl)-3-(*p*-nitrophenyl)pyrazolo[4',5':1,2]fullerene[60] (5d). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.31 (2H, d, *J* = 6.8, 2-, 6-$H_{p\text{-}NO_2C_6H_4}$); 8.33 (2H, d, *J* = 6.8, 3-, 5-$H_{p\text{-}NO_2C_6H_4}$); 8.39 (2H, d, *J* = 9, 2'-, 6'-$H_{p\text{-}NO_2C_6H_4}$); 8.62 (2H, d, *J* = 9, 3'-, 5'-$H_{p\text{-}NO_2C_6H_4}$).

3-(*p*-Ethoxyphenyl)-1-phenylpyrazolo[4',5':1,2]fullerene[60] (5e). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 (3H, t, *J* = 6.9, $CH_2\underline{CH_3}$); 4.10 (2H, q, *J* = 6.9, $\underline{CH_2}CH_3$); 6.95 (2H, d, *J* = 8.6, 3-, 5-$H_{p\text{-}EtOC_6H_4}$); 7.17, (1H, t, 4-H_{Ph}); 7.40 (2H, t, 3-, 5-H_{Ph}); 7.88 (2H, d, 2-, 6-H_{Ph}); 8.14 (2H, d, *J* = 8.6, 2-, 6-$H_{p\text{-}EtOC_6H_4}$). MALDI mass spectrum: $[M]^{-\cdot}$ 958.2.

1-(*p*-Bromophenyl)-3-(*p*-ethoxyphenyl)pyrazolo[4',5':1,2]fullerene[60] (5f). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 (3H, t, *J* = 6.9, $CH_2\underline{CH_3}$); 4.10 (2H, q, *J* = 6.9, $\underline{CH_2}CH_3$); 6.96 (2H, d, *J* = 8.9, 3-, 5-$H_{p\text{-}EtOC_6H_4}$); 7.52 (2H, d, *J* = 9, 3-, 5-H_{Ph}); 7.84 (2H, d, *J* = 9, 2-, 6-H_{Ph}); 8.14 (2H, d, *J* = 8.9, 2-, 6-$H_{p\text{-}EtOC_6H_4}$). MALDI mass spectrum: $[M]^{-\cdot}$ 1038.

1-Phenyl-3-trifluoromethylpyrazolo[4',5':1,2]fullerene[60] (5g). ^{1}H NMR spectrum, δ, ppm: 7.29 (1H, m, 4-H_{Ph}); 7.38 (2H, m, 3-, 5-H_{Ph}); 7.56 (1H, d, 2-, 6-H_{Ph}). MALDI mass spectrum: $[M]^{-\cdot}$ 907.

1-(*p*-Tolyl)-3-trifluoromethylpyrazolo[4',5':1,2]fullerene[60] (5h). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 7.26 (2H, d, *J* = 8.6, 3-, 5-$H_{p\text{-}CH_3C_6H_4}$); 7.69 (2H, d, *J* = 8.6, 2-, 6-$H_{p\text{-}CH_3C_6H_4}$). ^{13}C NMR spectrum, δ, ppm: 31.7 (CH_3); 83.8 (C*sp*^{3}); 96.3 (C*sp*^{3}); 129.5 (CF_3); group of signals 135-161 (C_{arom} and C_{ful}); 179 (C=N). MALDI mass spectrum: $[M]^{-\cdot}$ 920.7.

1-(*o*-Methoxyphenyl)-3-trifluoromethylpyrazolo[4',5']fullerene[60] (5i). ^{1}H NMR spectrum, δ, ppm: 3.90 (3H, s, CH_3O); 7.06 (2H, m, 3-, 5-$H_{o\text{-}CH_3OC_6H_4}$); 7.41 (1H, m, 4-$H_{o\text{-}CH_3OC_6H_4}$); 7.65 (1H, m, 6-$H_{o\text{-}CH_3OC_6H_4}$). MALDI mass spectrum: $[M-H]^-$ 935.

3-(2-Thienyl)-1-*p*-tolyl)pyrazolo[4',5':1,2]fullerene[60] (5j). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.10 (1H, m, 4-$H_{Thienyl}$); 7.22 (2H, d, *J* = 8, 3-, 5-H_{Ph}); 7.48 (1H, d, 3-$H_{Thienyl}$); 7.72 (2H, d, *J* = 8, 2-, 6-H_{Ph}); 7.91 (1H, d, 5-$H_{Thienyl}$). MALDI mass spectrum: $[M]^{-\cdot}$ 935.

1,3-Diphenylpyrazolo[4',5':1,2]fullerene[60] (5k). ^{1}H NMR spectrum, δ, ppm: 7.43 (6H, m, 3-, 4-, 5-H_{Ph}; 3'-, 4'-, 5'-H_{Ph}); 7.89 (2H, d, 2-, 6-H_{Ph}); 8.23 (2H, d, 2', 6'-H_{Ph}). MALDI mass spectrum: $[M]^{-\cdot}$ 915.

1-Phenyl-3-(4-pyridyl)pyrazolo[4',5':1,2]fullerene[60] (5l). MALDI mass spectrum: $[M]^{-\cdot}$ 916.

1-(*p*-Methoxyphenyl)-3-phenylpyrazolo[4',5':1,2]fullerene[60] (5m). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.81 (3H, s, CH_3O); 6.94 (2H, d, *J* = 9.5, 3-, 5-$H_{p\text{-}CH_3OC_6H_4}$); 7.45 (3H, m, 3-, 4-, 5-H_{Ph}); 7.73 (2H, d, *J* = 9.5, 2-, 6-$H_{p\text{-}CH_3OC_6H_4}$); 8.23 (2H, d, 2-, 6-H_{Ph}). MALDI mass spectrum: $[M\text{-}H]^-$ 944.3.

The authors are grateful to O. V. Boltalina for helpful comments. A. V. Streletskii is grateful to the Volkswagen Fund (Project No. I-77/855) and the RFFI fund (Project No. 03-03-32855) for material support.

REFERENCES

1. M. A. Yurovskaya and I. V. Trushkov, *Izv. Ross. Akad. Nauk, Ser. Khim.*, 343 (2002).
2. H. V. Pechmann and L. Seeberger, *Chem. Ber.*, **27**, 2122 (1894).
3. P. Cruz, A. Diaz-Ortiz, J. J. Garcia, M. J. Gomez-Escalonilla, A. Hoz, and F. Langa, *Tetrahedron Lett.*, **40**, 1587 (1999).
4. S. Muthu, P. Maruthamuthu, R. Ragunathan, P. R. Vasudeva Rao, and C. K. Mathews, *Tetrahedron Lett.*, **35**, 1763 (1994).
5. A. S. Shawali and A. A. Fahmi, *J. Heterocyclic Chem.*, **16**, 123 (1979).
6. D. V. Davydov, I. P. Beletskaya, and M. S. Gorovoy, *Tetrahedron Lett.*, **43**, 6221 (2002).
7. D. V. Davydov, I. P. Beletskaya, B. B. Semenov, and Y. A. Smushkevich, *Tetrahedron Lett.*, **43**, 6217 (2002).
8. Y. Matsubara, H. Tada, S. Nagase, and Z. Yoshida, *J. Org. Chem.*, **60**, 5372 (1995).
9. K. Tanaka, H. Masuda, and K. Mitsuhashi, *Bull. Chem. Soc. Jpn.*, **57**, 2184 (1984).