Pergamon

Tetrahedron Letters 41 (2000) 3947–3950

TETRAHEDRON
LETTERS

Synthesis and optical properties of tetraethyl methano[60]fullerenediphosphonate

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Received 6 January 2000; accepted 21 March 2000

Abstract

A novel C_{60} organophosphonate derivative, tetraethyl methano[60]fullerenediphosphonate **2**, was synthesized by the reaction of C_{60} with tetraethyl methylenediphosphonate **1** in the presence of I_2 and NaH. It has high solubility in polar solvents and the nonlinear optical properties of the new compound were better than those of C_{60}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: C_{60}; tetraethyl methylenediphosphonate; optical limiting; third-order nonlinear.

The optical properties, including optical limiting and the third-order nonlinearity of the fullerenes, have aroused great attention for some years.[1] Recently, many researchers have aimed to study the functionalized fullerenes[2] because fullerene derivatives usually have greater solubility than fullerenes themselves. Another reason is that specific functionalization of fullerenes can efficiently change the symmetry and electronic properties of the fullerene ball, which might result in the improvement of their optical properties. Since the bulk preparation of C_{60} in 1990, many different kinds of functional groups have been covalently linked to the parent C_{60}.[3] However, there is no report on the synthesis of organophosphonate derivatives of C_{60}. In this paper, a novel C_{60} derivative, tetraethyl methano[60]fullerenediphosphonate **2**, was synthesized by the reaction of C_{60} with tetraethyl methylenediphosphonate **1** in the presence of I_2 and NaH (Scheme 1). Then the optical limiting and third-order nonlinear properties of the new C_{60} derivative were measured.

Compound **2** was prepared by the following procedure. To a stirred dry toluene solution (200 ml) containing C_{60} (250 mg, 0.35 mmol), I_2 (91 mg, 0.35 mmol) and NaH (1.0 g) was added tetraethyl methylenediphosphonate (87 µl, 0.35 mmol). After stirring at room temperature under Ar for 9 h, the mixture was filtered and the filtrate was submitted to column chromatography (SiO_2). Residual C_{60} was eluted with toluene and the product with $CHCl_3$. After evaporation, the solid product was washed with alcohol and dried under vacuum at 60°C for 20 h: 146 mg (38%).

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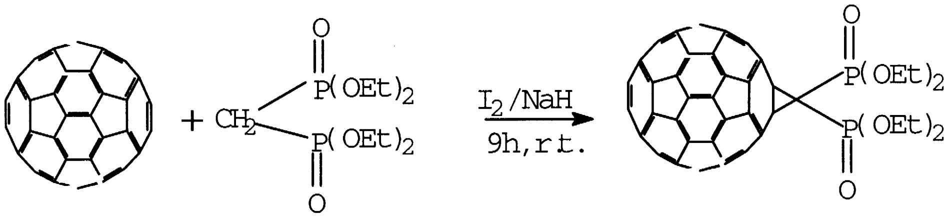
PII: S0040-4039(00)00491-3



Scheme 1. Synthesis of tetraethyl methano[60]fullerenediphosphonate **2**

The mechanism of the reaction of C_{60} with tetraethyl methylenediphosphonate was possibly similar to the mechanism of the Bingle reaction.[4] The reaction of I_2 with the phosphonate in situ produces iodomethylenediphosphonate which then generates α-iodocarbanions in the presence of NaH. Compound **2** was formed by the addition of the stabilized α-iodocarbanions to C_{60}, followed by an intramolecular displacement of iodide by the anionic center generated on the fullerene core.

Compound **2** was characterized by FT-IR, MALDI–TOF-MS, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR and UV–vis spectra.[5] In the FT-IR spectrum (KBr), two sharp and strong peaks at 1265 and 1250 cm^{-1} are observed, possibly corresponding to the absorption resulting from vibrational coupling of two P=O groups and at 1046 and 1028 cm^{-1} there are two much sharper and stronger peaks which may be due to the absorption resulting from anti-symmetrical vibrational coupling of two P–O groups. The characteristic absorptions of the C_{60} skeleton appear at 1430, 1183 and 530 cm^{-1}. The MALDI–TOF-MS (with α-cyano-4-hydroxylcinnamic acid as matrix) shows three molecular ion peaks with *m/z* 1007 $[M+1]^+$, 1029 $[M+Na]^+$, 1045 $[M+K]^+$ and two fragment peaks with *m/z* 733 $[M\text{-}2PO(OEt)_2+1]^+$, 720 $[M\text{-}C(PO(OEt)_2)_2]^+$. ^{1}H NMR ($CDCl_3$): δ 4.53–4.40 (q, 4H), 1.56–1.26 (t, 8H). ^{31}P NMR spectrum exhibits only a single peak at δ 15.57. Its ^{13}C NMR spectrum displays 18 signals for the fullerene C-atoms in the sp^2-region and two signals corresponding to the sp^3 C-atoms of $-OCH_2CH_3$. Unfortunately, the signal for the C-atom of the methylene bridge and the sp^3 C-atoms of the fullerene core is too weak to be unambiguously identified. In the UV–vis spectrum at 282 and 329 nm, there are two strong peaks which are due to the characteristic absorption of C_{60}; at 427 nm, a medium intensity peak appears which proves that **2** is a 6,6-closed product. All these data are in agreement with the structure of **2**.

Compound **2** is easily solubilized in most organic solvents such as toluene, $CHCl_3$ and DMF. In $CHCl_3$ the solubility of **2** is more than 60 mg/ml. Because of its novel organophosphonate functional group and good solubility we think **2** may find applications in the optical field. In this paper, the optical limiting and third-order nonlinear properties of the C_{60} derivative were measured.

Optical limiting measurements were carried out using a frequency-doubled Nd:YAG laser with 10 ns pulses at 532 nm. For **2**, optical limiting measurements were performed in a DMF solution with a linear transmittance of 76 and 71%. As shown in Fig. 1, the output fluency value is nonlinear with the input fluency. Apparently, the optical limiting responses of **2** are stronger than those of C_{60} at the same linear transmittance (76%); In addition, the optical limiting response of **2** gets slightly stronger with the increase of the transmittance. The third-order optical nonlinearity of **2** was measured using the Z-scan technique. Fig. 2 is the normalized transmittance curve of the Z-scan with closed aperture case and Fig. 3 is the result of the Z-scan with open aperture case. The results show that the nonlinear absorption of the sample is very strong but the nonlinear refraction is relatively weak. The third-order optical susceptibility $\chi^{(3)}$ is 6.2×10^{-12} esu.

In conclusion, the newly synthesized organophosphonate derivative of C_{60} exhibits NLO properties better than C_{60} as well as greater solubility in polar solvents. We believe that the novel compound will stimulate the subsequent production of many other organophosphorous compounds of fullerenes. In fact,

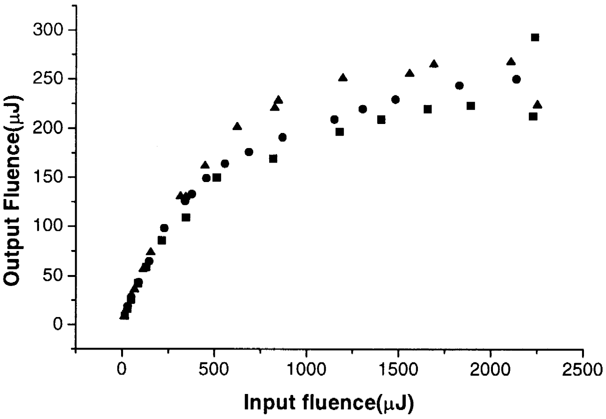


Fig. 1. Optical limiting results of **2** with a linear transmittance of 76% (■) or 71% (▲) and compared with those of C_{60} with a linear transmittance of 76% (●) at 532 nm

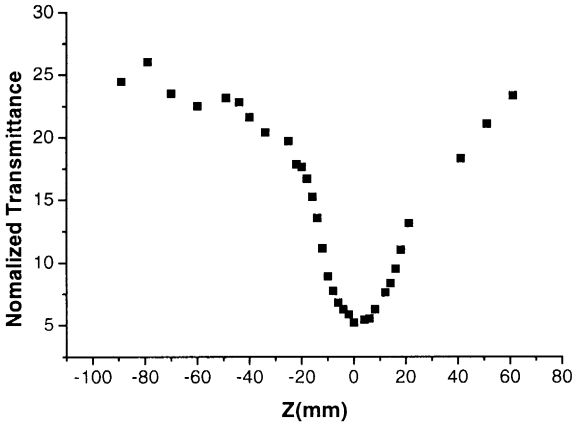


Fig. 2. The third-order optical nonlinearity of **2** measured by Z-scan with closed aperture case

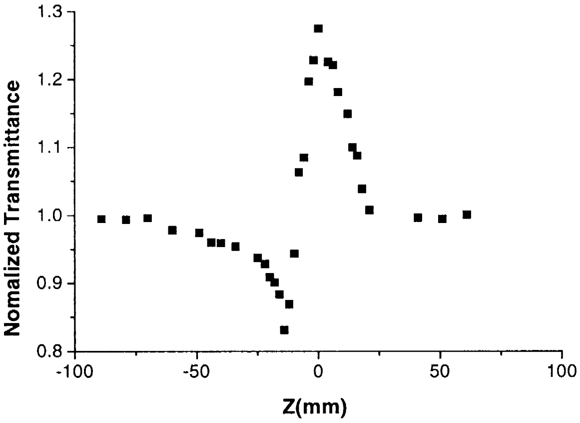


Fig. 3. The third-order optical nonlinearity of **2** measured by Z-scan with open aperture case

a highly water-soluble phosphonic acid derivative of C_{60} has been prepared from the hydrolysis of **2** in our lab and we are currently investigating its biological applications.[6]

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 59702009).

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4. Bingel, C. *Chem. Ber*. **1993**, *126*, 1957.
5. Selected data for **2**: FT-IR ν/cm^{-1} (KBr): 3452, 2977, 1430, 1389, 1366, 1265, 1252, 1192, 1183, 1160, 1105, 1046, 1028, 977, 965, 833, 801, 668, 608, 569, 540, 530. MALDI–TOF-MS (α-cyano-4-hydroxylcinnamic acid as matrix) *m/z* 1045 $[M+K]^+$, 1029 $[M+Na]^+$, 1007 $[M+1]^+$, 733 $[M\text{-}2PO(OEt)_2+1]^+$, 720 $[M\text{-}C(PO(OEt)_2)_2]^{+1}$. ^1H NMR (300 MHz, $CDCl_3$): δ 4.53–4.40 (q, J=7.0 Hz, 4H), 1.56–1.26 (t, J=7.0 Hz, 8H). ^{31}P NMR (300 MHz, $CDCl_3$): δ 15.57. ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.9, 145.9, 145.8, 145.1, 145.0, 144.9, 144.8, 144.7, 144.5, 143.9, 142.9, 142.8, 142.7, 142.1, 142.1, 140.8, 140.1, 63.8, 16.4. UV–vis (max/nm, toluene): 282, 329, 427.
6. To be submitted: the water-soluble phosphonic acid derivative of C_{60} was obtained by the dealkylation of **2** with bromotrimethylsilane and it showed a strong photo-induced cytotoxicity to HeLa cells.