## **Brief Communications**

# Concerning the existence of linear carbon molecules in soot obtained in an electric arc

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The presence of soluble linear carbon molecules in fullerene-containing soot obtained by arc spraying of graphite was confirmed by Fourier IR spectroscopy, electron diffraction, mass spectrometry, and NMR spectrometry data. Carbon chains are oriented in the layer perpendicular to the support surface and are packed in a hexagonal crystal lattice with  $d_{110} = 4.35$  Å.

Key words: linear carbon molecules; soot; fullerenes; electric arc.

With electric arc heating or laser vaporization of graphite in a helium atmosphere under reduced pressure, fullerenes are formed.<sup>1</sup> Under experimental conditions in an electric arc at temperatures higher than 3000 K, carbon chains  $C_n$  were observed along with fullerenes.<sup>2</sup> On the basis of quantum-chemical calculations the linear carbon chains and the  $C_n$  monocycles having sp-type chemical bonds are the most stable clusters at n < 40.3 Studies on IR spectra of carbon clusters vaporized from graphite and trapped in a solid Ar or Ne matrix demonstrated that the clusters are linear molecules  $C_n$  (n < 9).<sup>4</sup> These clusters are rather reactive:

they increase in length, when the temperature rises from 4 to 30 K.

Under condensation of carbon vapors from arc discharge or at ion spraying of graphite, the growth of oriented insoluble carbine films was observed,<sup>5</sup> these films consist of carbon chains having sp-hybridized atomic orbitals, while the axis of these chains are oriented perpendicular to the surface of the film.

In the present work, the soluble carbon chain molecules are observed in fullerene-containing soot obtained by electric arc spraying of graphite.

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#### Experimental

Soot was obtained by vaporization of graphite in an electric arc in a He atmosphere using the procedure from Ref. 6. A soluble fraction of soot was extracted with toluene in a Soxhlet apparatus. The isolated dark reddish brown solution was evaporated on a rotor evaporator. All of the operations were carried out under Ar. According to HPLC, the toluene-soluble fraction of soot contains 99 % of fullerenes  $C_{60}$  and  $C_{70}$  in a ratio of 85 : 14. Since the solubility of fullerenes in CCl<sub>4</sub> is very low, *e.g.*,  $\leq 0.3$  mg/mL for  $C_{60}$ , washing the powder obtained by evaporation of the toluene extract of soot with CCl<sub>4</sub> causes the extraction of low-molecular linear and cyclic carbon clusters and cumulene structures. The UV spectrum of the solution in CCl<sub>4</sub> does not contain the characteristic absorption bands of fullerenes and exhibits a continuously falling curve without a maximum.

### **Results and Discussion**

According to X-ray fluorescent microanalysis data, the toluene extract of soot consists predominantly of carbon and contains only traces of oxygen. In the mass spectrum of this product, along with peaks of fullerenes  $C_{60}$  and  $C_{70}$ , a set of peaks of low intensity in the mass range from 700 to 800 are observed, which can be interpreted as linear carbon clusters. The presence of cumulene structures in soot was confirmed by <sup>1</sup>H NMR spectra. The measurements were carried out with a Tesla BS-587A instrument (80 MHz) in C<sub>6</sub>D<sub>6</sub>. The solutions of powder obtained from the toluene extract of soot before and after treatment with CCl<sub>4</sub> and the CCl<sub>4</sub>-soluble fraction were studied. It was established that the treatment with CCl<sub>4</sub> of the powder of the toluene extract of soot causes complete extraction of carbon clusters with five- and six-membered rings along with linear cumulene structures C<sub>n</sub>, where n = 17-70. After treatment of the toluene extract of soot with CCl<sub>4</sub>, only signals of the solvent (C<sub>6</sub>D<sub>6</sub>(H)) were observed in the <sup>1</sup>H NMR spectra.

In the FT-IR spectrum of the toluene-soluble fraction of soot, a series of absorption bands is observed at 1600–3100 cm<sup>-1</sup> (Fig. 1). The bands at 1493, 1432, 1135, 796, 675, 643, 578, 536 and 462 cm<sup>-1</sup> are assigned to fullerenes  $C_{60}$  and  $C_{70}$ . The bands at 1600–2360 cm<sup>-1</sup> can be explained only by the presence of linear carbon chains. The absorption bands at 2880–3100 cm<sup>-1</sup> are assigned to the valent vibrations of CH and CH<sub>2</sub> groups.

The vibration frequencies of linear carbon chains  $(C_n, n < 9)$  were measured and calculated previously on the basis of simple theoretical model.<sup>4,7</sup> It was demonstrated that these calculations are in good agreement



Fig. 1. Fourier-transform IR spectrum of a powder of a toluene-soluble fraction prepared from soot obtained by arc spraying of graphite and data on calculation of vibrational frequencies of the  $C_{70}$  linear cumulene chain (bar graphs).

with the experimental data. In the present work, we interpreted the IR spectroscopy data on the basis of the similar model. The calculations of the active IR frequencies  $(v_k)$  of linear carbon chains  $(=C=C=)_n$  give a simple equation:

$$v_k = v_0^* \sin(\pi k/n), \tag{1}$$

where k is an integer number.

Using the mass spectral data, the calculations were performed for model cumulene chains  $C_n$  varying the *n* value from 60 to 80. The calculations correlate the most closely with the experimental data for n = 70. The active IR frequencies of longitudinal vibrations of linear carbon chains  $C_{70}$  calculated according to Equation (1) are shown in Fig. 1 (bar graphs). The force constant was chosen in such a way so that the calculated value of the characteristic frequency in  $C_3$  would coincide with the experimental value of 2040 cm<sup>-1</sup> (Ref. 7). This gives the value  $v_0 = 2356$  cm<sup>-1</sup>.

The comparison of the experimental IR spectrum (Fig. 1) with the calculated data allows one to assume the excellent correlation of the maximum IR absorption frequency  $v_0 = 2360 \text{ cm}^{-1}$  with the calculated value (2356 cm<sup>-1</sup>). In addition, in both cases, the density of vibration modes increases significantly near  $v_0$  that is the characteristic feature of one-dimensional systems.

A test with  $Br_2$  for cumulated double or conjugated triple bonds gives an immediate positive response with the  $CCl_4$ -soluble fraction of carbon black after addition of  $Br_2$  to the solution. After bromination, all of the absorption bands in the IR spectrum, which are assigned to cumulene chains, disappear completely and a new band at 670 cm<sup>-1</sup> assigned to C—Br stretchings appears. The high reaction rate with  $Br_2$  probably occurs due to increase in their reactivity towards  $Br_2$  in parallel to the number of conjugated bonds in cumulene molecules.<sup>8</sup>

The electron diffraction pattern of a thin film (Fig. 2), obtained from the solution of a powder of the toluene extract of carbon black in CCl<sub>4</sub>, is related to hexagonal crystal lattice with  $d_{110} = 4.35$  Å that coincides with  $d_{110}$  in oriented carbine films.<sup>5</sup> The carbon chains are oriented perpendicular to the support surface.

Recently, it has been found that fullerene  $C_{60}$  becomes superconducive when doped with alkaline metals.<sup>9</sup> The specific electron properties of one-dimensional



Fig. 2. Electron diffraction pattern of a separate part of a thin film obtained from the solution of the powder of the toluene extract of soot in  $CCl_4$ .

carbon chains<sup>3</sup> allow one to expect interesting physical properties of their intercalation compounds with metals.

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