

# Glow discharge synthesis and molecular structures of perchlorofluoranthene and other perchlorinated fragments of buckminsterfullerene

Su-Yuan Xie, Rong-Bin Huang,\*† Li-Hua Chen, Wei-Jie Huang and Lan-Sun Zheng

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China

A series of perchlorinated fragments of buckminsterfullerene were prepared by glow discharge using chloroform vapor; their structural features are of significance in understanding the formation mechanism of fullerenes.

Although there have been a great many achievements in the experimental and theoretical investigation of fullerenes, their formation mechanism is still a puzzle to chemists and physicists.<sup>1</sup> Various schemes have been put forward to explain the formation of fullerenes.<sup>2-7</sup> Each of these schemes rationalise the available experimental evidence. None of them, however, can explain the formation process of the mid-sized intermediates (about 20–30 carbon atoms) and none show the formation of five-membered carbon rings that is known to be critical for fullerene formation. In order to understand the process, there has also been tremendous interest in the trapping of intermediates.<sup>8,9</sup> In our laboratory, a series of perchlorinated polycyclic compounds with a five-membered ring and various six-membered rings, such as perchloroacenaphthylene ( $C_{12}Cl_8$ ), perchlorofluoranthene ( $C_{16}Cl_{10}$ ) and perchlorocorannulene ( $C_{20}Cl_{10}$ ), have been synthesized *via* discharge in liquid  $CHCl_3$  rather than *via* conventional organic synthesis. These compounds were characterized as perchlorinated fragments of fullerene, so the work is helpful in understanding the formation mechanism of fullerenes.<sup>10</sup> Recently, we extended the discharge reaction to the vapor phase, and detected fullerenes and other larger perchlorinated fragments among the products. We were able to obtain single crystals of perchloroacenaphthylene and perchlorofluoranthene, and their structures, determined by X-ray diffraction, may provide more information about the formation mechanism.

The synthesis† described here was carried out using a typical procedure developed by this group in recent years. After separation procedures, the pure products were collected, and single crystals of high enough quality for X-ray diffraction analysis were obtained after four months growing in solution. The crystals were characterized as perchloroacenaphthylene ( $C_{12}Cl_8$ ) and perchlorofluoranthene ( $C_{16}Cl_{10}$ ) by X-ray diffraction.‡ As shown in Fig. 1, octachloroacenaphthylene is a flat molecule, with all its carbon and chlorine atoms effectively located in the same plane. In contrast, perchlorofluoranthene is a very crowded molecule. If it were planar, some of the intramolecular Cl...Cl distances between neighboring chlorine atoms would be about 2.5 Å, whereas the sum of their van der Waals radii is 3.6 Å; the shortest Cl...Cl distances found in similar compounds are about 3.0 Å, as in perchloronaphthalene (3.032 Å),<sup>11</sup> perchloropyrene (3.003 Å),<sup>12</sup> perchlorophenanthrene (3.037 Å)<sup>13</sup> and 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (3.082 Å).<sup>14</sup> Thus, 3 Å is likely to be the shortest possible distance between chlorine atoms in this kind of overcrowded perchlorinated polycyclic compound. The structural data§ shows that the mean planes of the benzene and naphthalene rings are not in a same plane, and the dihedral angle between the planes is 26.09(5)°. Distortion of the molecule is due to the steric effects of its component chlorine atoms and mainly involves its five-membered ring, so the molecule bends with the axis through its five-membered ring. Compared with

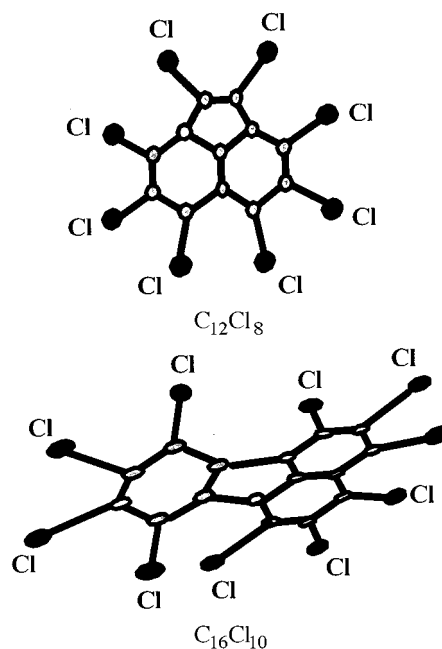
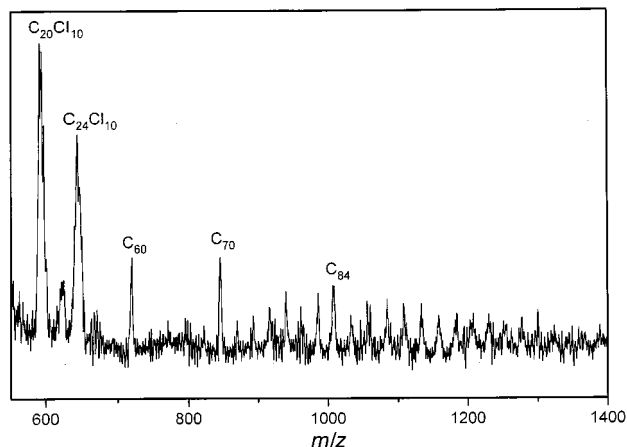


Fig. 1 Molecular structures of perchloroacenaphthylene and perchlorofluoranthene

the sandal structure of perchloropyrene,<sup>12</sup> one isomer of perchlorofluoranthene which has four six-membered rings but no five-membered ring, the twisted structure of perchlorofluoranthene is distorted more severely. The difference can also be found from comparison of another pair of isomers, fluoranthene and pyrene. The structure of the former is non-planar,<sup>15</sup> but the latter is nearly planar.<sup>16</sup> Obviously, formation of the five-membered ring makes the molecule more flexible, so that it can relieve the strain caused by the steric effect of the chlorine atoms. In fact, the five-membered ring is also found in the structures of other perchlorinated polycyclic compounds synthesized in the experiment.

Formation of the cage structure of the fullerenes also involves the five-membered rings. In fact,  $C_{60}$  and other fullerenes were also produced in the glow discharge experiment and were detected by laser-desorption mass spectrometry (Fig. 2). In the mass spectrum, in addition of various fullerene products, some larger perchlorinated fragments, such as  $C_{22}Cl_{10}$  and  $C_{24}Cl_{10}$ , are also observed. Although the fullerene products were not separated, they can be characterized by their particular size distribution.

Products from discharge reactions were expected to be very complicated. However, the products from the discharge reaction of  $CHCl_3$  are quite selective: The products were either fullerenes or their perchlorinated fragments. The distorted structure of perchlorofluoranthene suggests that it is the steric effects of the chlorine atoms that limits the possible number of the products and favors the formation of the five-membered ring. Although  $CHCl_3$  only contains a single carbon atom, in the



**Fig. 2** Laser desorption mass spectrum of fullerenes and other products synthesized from the glow-discharge reaction of  $\text{CHCl}_3$

discharging reaction it serves as a C1 building block for aggregation into fullerenes or their perchlorinated fragments.

This work was supported by the National Natural Science Foundation of China and by the State Educational Commission of China.

## Notes and References

† E-mail: rbhuang@xmu.edu.cn

‡ *Typical procedure:*  $\text{CHCl}_3$  was evaporated from a flask containing 100 ml liquid  $\text{CHCl}_3$  into a quartz tube with a diameter of ca. 40 mm and a length of ca. 250 mm; a pair of copper pipes, which acted as both electrodes and a gas passageway, were mounted at the two ends of the tube. When the vacuum pressure of the tube was reduced to less than 300 Pa and an ac voltage of > 10 kV with 25 kHz frequency was applied to the electrodes, a stable glow discharge emerged in the gap between the two electrodes which could be maintained by adjusting the gap. After reacting for several hours, ca. 5 g of black deposit was collected, followed by sublimating at 160 °C to separate hexachlorobenzene and the other volatile matter. The residue was extracted with toluene and separated *via* chromatography ( $\text{Al}_2\text{O}_3$ , light petroleum); the third (yellow) component part was perchlorofluoranthene, the fourth (red) component part was perchloroacenaphthylene, and the remainder were other larger perchlorinated fragments,  $\text{C}_{60}$  and other fullerenes products.

§ *Crystal data* for perchloroacenaphthylene:  $\text{C}_{12}\text{Cl}_8$ ,  $M = 428$ , monoclinic,  $P2_1/a$ ,  $a = 7.079(5)$ ,  $b = 22.396(5)$ ,  $c = 10.661(5)$  Å,  $\beta = 93.046(5)^\circ$ ,  $U = 1687.8(15)$  Å<sup>3</sup>,  $T = 298$  K,  $Z = 4$ ,  $\lambda = 105418$  Å,  $\mu(\text{Cu-K}\alpha) = 24.687$

$\text{cm}^{-1}$ ,  $F(000) = 532$ , red crystals with dimensions  $0.16 \times 0.17 \times 0.79$  mm. Data were collected on a Enraf-Nonius CAD-4 diffractometer in the  $\omega$ - $2\theta$  scan mode, and corrected for absorption by  $\psi$ . A total of 3768 independent reflections were collected in the range  $4 < 2\theta < 75^\circ$ , of which 1628 reflections with  $I > 2\sigma(I)$  are considered observed. The SIR92 and SHELXL93 program packages were used to solve and refine the structure, respectively. The final deviation factor  $R_w = 0.0749$ ,  $wR = 0.1955$ .

*Crystal data* for perchlorofluoranthene:  $\text{C}_{16}\text{H}_{10}$ ,  $M = 546.66$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.4590(7)$ ,  $b = 11.4920(7)$ ,  $c = 11.8800(8)$  Å,  $\alpha = 112.346(5)$ ,  $\beta = 90.858(6)$ ,  $\gamma = 106.277(6)^\circ$ ,  $U = 895.60(12)$  Å<sup>3</sup>,  $T = 298$  K,  $Z = 2$ ,  $D_c = 2.02$  Mg  $\text{cm}^{-3}$ ,  $\lambda = 1.5418$  Å,  $\mu(\text{Cu-K}\alpha) = 24.68$   $\text{cm}^{-1}$ ,  $F(000) = 532$ , orange crystals with dimensions  $0.04 \times 0.07 \times 0.075$  mm. Data were collected on an Enraf-Nonius CAD-4 diffractometer in the  $\omega$ - $2\theta$  scan mode, and corrected for absorption by  $\psi$ . A total of 3889 independent reflections were collected in the range  $4 < 2\theta < 75^\circ$ , of which 2111 reflections with  $I = 2\sigma$  were considered observed. The SIR92 and SHELXL93 programme packages were used to solve and refine the structure, respectively. The final deviation factor  $R_w = 0.064$ ,  $wR = 0.1362$ . CCDC 182/981.

- 1 S. G. Nancy, *Acc. Chem. Res.*, 1996, **29**, 77.
- 2 R. F. Curl and R. E. Smalley, *Sci. Am.*, 1991, **265**, 54.
- 3 R. E. Haufler, Y. Chai, L. P. E. Chibante, J. Conceicao, C. Jin, L. S. Wang, S. Maruyama and R. E. Smalley, *Mater. Res. Soc. Symp. Proc.*, 1991, **206**, 627.
- 4 R. E. Smalley, *Acc. Chem. Res.*, 1992, **25**, 98.
- 5 J. R. Heath, *ACS Symp. Ser.*, 1991, **481**, 1.
- 6 J. M. Hunter, J. L. Fye, E. J. Roskamp and M. F. Jarrold, *J. Phys. Chem.*, 1994, **98**, 1810.
- 7 K. B. Shelimov, J. M. Hunter and M. F. Jarrold, *Int. J. Mass Spectrom. Ion. Processes*, 1994, **138**, 17.
- 8 T. Grösser and A. Hirsch, *Angew. Chem.*, 1993, **105**, 1390; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1340.
- 9 T.-M. Chang, A. Naim, S. N. Ahmed, G. Goodloe and P. B. Shevlin, *J. Am. Chem. Soc.*, 1992, **114**, 7603.
- 10 Rongbin Huang, Weijie Huang, Yuhuang Wang, Zichao Tang and Lansun Zheng, *J. Am. Chem. Soc.*, 1997, **119**, 5954.
- 11 G. Gafner and F. H. Herbstein, *Nature (London)*, 1963, **200**, 130.
- 12 A. C. Hazell and S. Jagner, *Acta. Crystallogr., Sect. B*, 1976, **32**, 682.
- 13 F. H. Herbstein, M. Kapon and R. Merksamer, *Acta. Crystallogr., Sect. B*, 1976, **32**, 2205.
- 14 F. H. Herbstein, M. Kapon and D. Rabinovich, *Isr. J. Chem.*, 1972, **10**, 537.
- 15 A. C. Hazell, D. W. Jones and J. M. Sowden, *Acta. Crystallogr., Sect. B*, 1977, **33**, 1516.
- 16 A. Camerman and J. Trotter, *Acta. Crystallogr.*, 1965, **18**, 636.

Received in Columbia, MO, USA, 12th January 1998; revised manuscript received, 29th July 1998; 8/06160B