Preparation and 13C NMR Spectroscopic Characterisation of $C_{60}Cl_6$

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Reaction of an excess of iodine monochloride with C_{60}, in either benzene or toluene at room temperature, gives a quantitative yield of $C_{60}Cl_6$, the 13C NMR spectrum of which indicates that it is isostructural with $C_{60}Br_6$.

The specific derivatisation of C_{60} is a key target in the development of its chemistry. Because halogeno compounds are generally important synthons, preparation and characterisation of halogenofullerenes is of particular significance. Previously, we prepared and characterised $C_{60}Br_6$ and $C_{60}Br_8$ (*via* single crystal X-ray spectroscopy).[1] We[1] and Tebbe *et al.*[2] also prepared $C_{60}Br_{24}$; its structure was inferred from that of $C_{60}Br_8$[1] and was proved by single crystal X-ray spectroscopy.[2]

Interesting though the bromo compounds are from the structural viewpoint, they are very insoluble in most organic solvents, which limits their usefulness as synthons. By contrast, the fluorofullerenes are very soluble,[3] but at present there is no reliable way to prepare specific compounds because fluorination is carried out under heterogeneous conditions and, therefore, lacks control. Preliminary reports[4] indicated that approximately twenty-four chlorines can be added to C_{60}.

We have confirmed this result, and have sought to control the reaction so that fewer chlorines could be added. In this communication, we report the preparation and characterisation of $C_{60}Cl_6$.

A freshly prepared solution of iodine monochloride (150 mg, 0.924 mmol) in dry benzene (5 cm³) was added to a solution of C_{60} (46.6 mg, 0.0647 mmol) in dry benzene (60 cm³). The mixture was stirred and then left to stand at room temp. during 3 days. Solvent and evolved iodine were then removed under reduced pressure leaving an orange, microcrystalline solid (60.7 mg, 100.5%). Calc. for $C_{60}Cl_6$.2PhH: C, 79.4; H, 1.11. Found: C, 78.9; H, 1.08%. The product was washed with pentane and heated to 60 °C under reduced pressure (0.1 mmHg) during 5 h to give deep-orange crystals of $C_{60}Cl_6$. Calc. for $C_{60}Cl_6$: C; 77.2. Found, C; 77.4%; hydrogen was not detected. IR (KBr):

v/cm^{-1} 1468, 1448, 1421, 1289, 1267, 1199, 1148, 1094, 1088, 1064, 948, 934, 884, 855, 844, 818, 800, 781, 756, 728, 711, 664, 613, 583, 571, 561, 541, 516, 499 and 473. UV (cyclohexane), λ_{max}/nm: 211, 257, 280 and 386 (Fig. 1). The product is very soluble in benzene, carbon disulfide, and tetrachloromethane, moderately soluble in chloroform, dichloromethane, and toluene, and slightly soluble in pentane, hexane, diethyl ether and acetone.

The same product can be obtained by using toluene as a solvent, but in this case reaction is slower, suggesting that radicals are involved and are scavenged by the toluene; this possibility is under further investigation. It is important to allow all of the iodine monochloride to decompose (this occurs on standing) before work-up, otherwise further reaction takes place during this latter procedure.

The IR spectrum [Fig. 2(a)] shows similarities to that of $C_{60}Br_6$ [Fig. 2(b)][1] indicating a similar structure. This is further confirmed by the ^{13}C NMR spectrum (Fig. 3), run in tetrachloromethane with deuteriated chloroform as lock signal (Table 1). The sample contained a trace of C_{60}, which provided a reference for the other resonances, and appeared at δ 142.21 (cf. δ 142.68 in benzene with $CDCl_3$ as lock signal,[5] and δ 143.2 in carbon disulfide using deuteriated acetone as lock signal[6]). The proposed structure for $C_{60}Cl_6$ is shown as a Schlegel diagram in Fig. 4. Because of the symmetry of $C_{60}Cl_6$, the diagram is shown in pentagonal rather than hexagonal format, but to avoid confusion, the recommended[7] numbering system of the latter is retained. The structure is thus 1,2,4,11,15,30-hexachlorofullerene-60 and this requires a 32 line spectrum consisting of 54 sp^2-hybridised carbons (26×2) + (2×1) and 6 sp^3-hybridised carbons (2×2) + (2×1), exactly as we find. The resonances at δ 66.47 and 69.41 are attributable to the two adjacent sp^3 carbons (C-1 and C-2), the more downfield signal being assigned to C-2, which is nearer to the other chlorines and, therefore, experiences a greater $-I$ effect. The signals at δ 54.93 and 55.42 are due to the four other chlorine-bearing carbon atoms, the more downfield peak being assigned to carbons C-4 and C-11, which are nearest to the other chlorine-bearing carbons. The plane of symmetry in the molecule passes through the C-55–C-60 interpentagonal bond, and this accounts for the half intensity resonances at δ 146.38 and 147.64. The resonances at δ 152.79 are probably due to

carbons C-3 and C-12 since they are alpha to two carbons that bear chlorines. There are six other pairs of carbons that are alpha to a carbon bearing chlorine and beta to another, and any one of these pairs (though not probably $C_6=C_9$) may account for the resonance at δ 150.96.
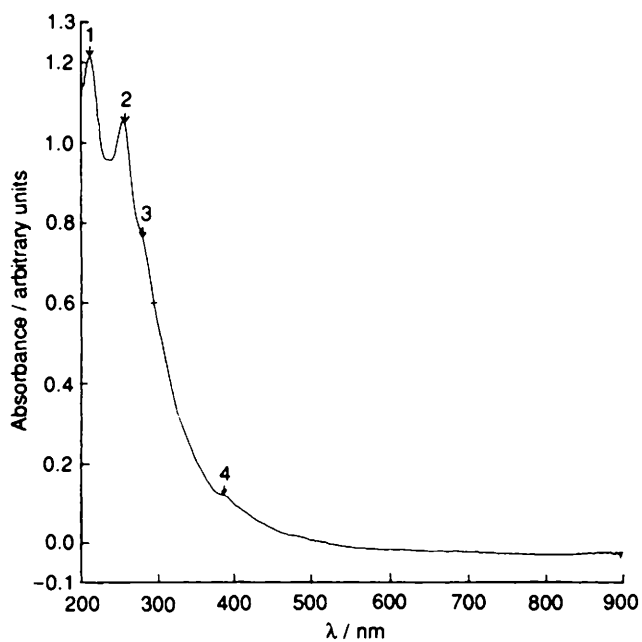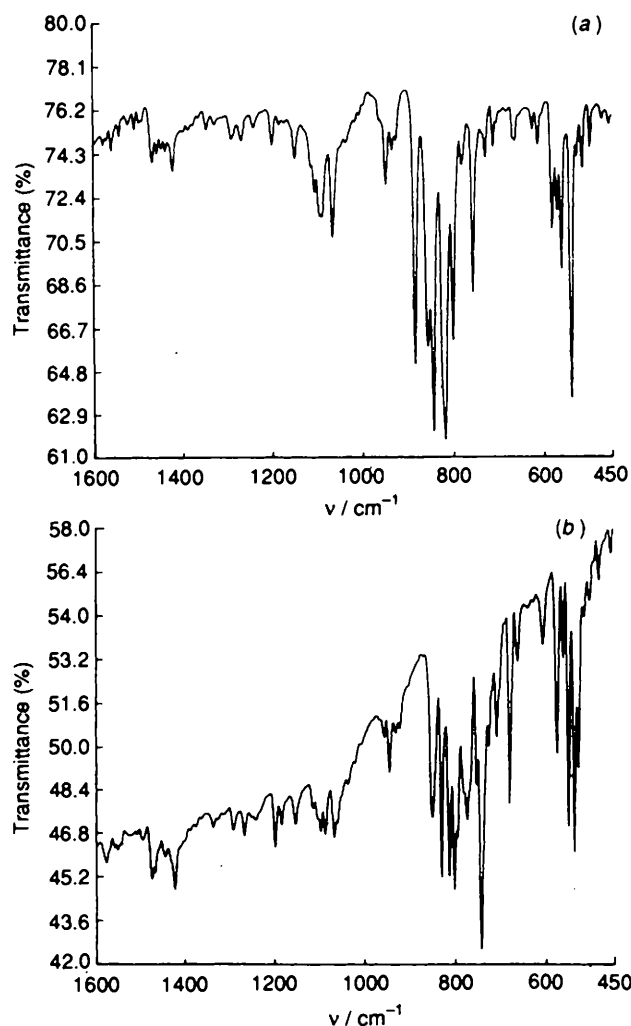

Fig. 2. (a) IR spectrum (KBr) for $C_{60}Cl_6$, (b) IR spectrum (KBr) for $C_{60}Br_6$

Table 1 ^{13}C NMR shifts[a] for $C_{60}Cl_6$

δ	Intensity	δ	Intensity
152.79	12.12	143.97	11.70
150.96	11.39	143.52	11.90
148.34	10.93	143.16	11.42
148.17	12.01	142.78	11.58
147.64	7.47	142.34	11.36
147.63	11.78	142.03	11.67
147.565	12.87	141.82	11.25
147.555	11.72	141.58	11.40
147.22	11.49	140.76	10.71
147.05	11.30	140.51	11.00
146.93	10.65	140.18	11.34
146.46	12.15	135.39	11.19
146.38	6.07	69.42	3.52
146.365	11.97	66.47	4.16
146.23	11.62	55.46	9.20
144.18	12.33	54.93	8.60

[a] Relative to C_{60} at δ 142.21.

Fig. 1 UV spectrum for $C_{60}Cl_6$ in cyclohexane

148.4 148.2 148.0 147.8 147.6|147.4 147.2 147.0 146.8 146.6 146.4 146.2

δ

150   140   130   80   70   60

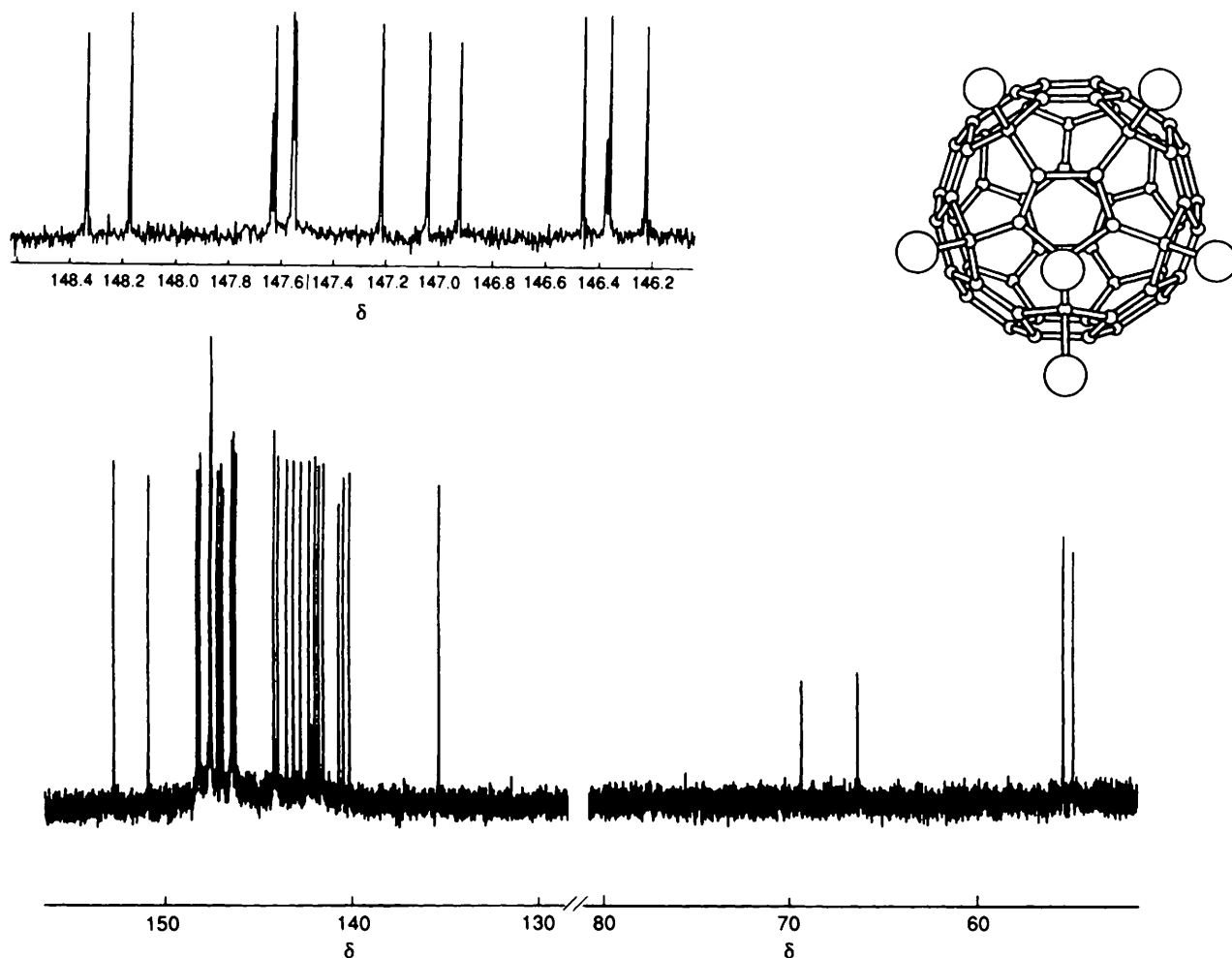δ   δ

Fig. 3 ^{13}C NMR spectrum for $C_{60}Cl_6$; the insets show the expanded spectrum between δ 146.2 and 148.6 and the proposed structure
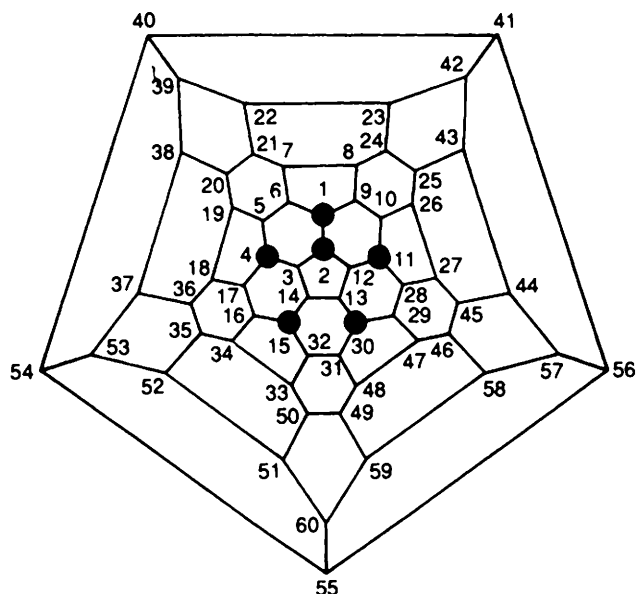

Fig. 4 Schlegel diagram showing locations of the chlorines, and numbering system

The chlorines at carbons 4, 11, 15 and 30 could be disposed symmetrically about the symmetry axis at other non-adjacent sites and nevertheless yield an NMR spectrum with the same number of lines and intensities. However, all other possibilities require more double bonds placed in pentagonal rings than is the case for the structure shown in Fig. 4. Since this is a

generally unfavourable feature for fullerenes,[8] we consider it to be improbable, especially in view of the similarities in the IR spectra. Moreover, the structure proposed is both analogous to that of $C_{60}Br_6$, and closely related to that indicated by ESR for the radical $C_{60}R_5$.[9]

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