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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS—XXII*

PERFLUOROTRIPHENYLENE

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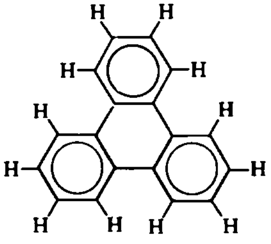
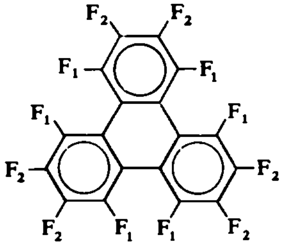
Perfluorotriphenylene has been prepared by the reaction of 1,2-diiodotetrafluorobenzene with dry copper powder at 200–230°. UV and ^{19}F NMR spectra suggest a distortion of the molecule from planarity due to steric interaction of the fluorine atoms in the 'ortho' positions.

THE crystal structure of triphenylene,[1] (Ia) shows that the molecule is somewhat distorted in the solid state, presumably due to steric interaction of the H atoms in the '*ortho*' positions. Since the van der Waals radius of hydrogen (1·2 Å) is less than that of fluorine (1·35 Å) it has been suggested either directly[2] or indirectly[3] that the fully fluorinated analogue of triphenylene (Ib) would be incapable of existence because of the increased steric interaction between the F_1 fluorine atoms.

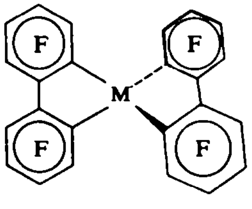


Ia



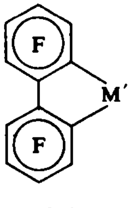
Ib

However the isolation in this laboratory of a wide variety of very stable perfluoroheterocyclic derivatives of the types II and III, in which similar adverse steric interactions might well be expected to occur, led us to attempt the preparation of perfluorotriphenylene. A preliminary account of the synthesis has already been given[4] and involved the simple heating under vacuum of 1,2-diiodotetrafluorobenzene with



M = Si, Ge, Sn

II



M' = S, Se, Te

III

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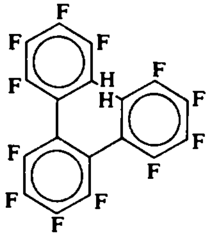
* For Part XXI, see D. M. Roe and A. G. Massey, *J. Organometal Chem*. in the press.

very dry copper powder; a mixture of perfluorophenylenes is obtained, perfluorotriphenylene being the principal isolable product. No perfluorotriphenylene was obtained when 1,2-dibromotetrafluorobenzene was treated with copper under similar conditions. We now wish to report our further studies on this molecule.

A possible product of this Ullman synthesis is the terphenyl derivative IV:



IV

the hydrogen arising from water occluded in either the reaction vessel walls or the copper powder; however, both the vessel and copper powder were extensively dried by heating under high vacuum (ca. 10^{-6} mm) before the reaction was carried out. The complete absence of IV in our perfluorotriphenylene was proved both by elemental analysis and by checking the intensities of the peaks at *m/e* 445 and *m/e* 446 (due to ^{13}C satelites of $C_{18}F_{12}^{+}$) compared to that of the parent ion at *m/e* 444 in the mass spectrum; as a cross-check the accurate mass of the peak at 446 (which would be the parent peak of IV) showed it to be due to $^{12}C_{16}{}^{13}C_{2}{}^{19}F_{12}$: observed mass 445·9876, calculated for $^{12}C_{16}{}^{13}C_{2}{}^{19}F_{12}$, 445·98757. An accurate mass of the ion giving rise to the peak at *m/e* 444 was also measured and it proved identical to that calculated for perfluorotriphenylene: observed mass, 443·9793; calculated for $^{12}C_{18}{}^{19}F_{12}$, 443·9809. The analytical sample 1 was used for these mass spectral measurements.

Whilst this work was in progress, preliminary results from the crystal structure analysis of II (M = Ge) by M. B. Hursthouse and C. Heath of this department became available; these show that the F atoms in the 6,6′ positions approach to within 2·45 Å of each other without bestowing any significant instability to the molecule ($C_{24}F_{16}Ge$ is stable *in vacuo* to at least 500°[4]). Hence F atoms can be much closer to each other than might be expected from their accepted van der Waals radii and the isolation of perfluorotriphenylene does not therefore create a precedent. Indeed the preparation of perchlorotriphenylene has been claimed in a patent.[5] In the mass spectra[6] of $Ge(C_6F_5)_4$ and $B(C_6F_5)_3$ metastable transitions involving the migration of F atoms to Ge and B give rise to strong peaks due to the ion $C_{18}F_{12}^{+}$ which is probably ionized perfluorotriphenylene:

e.g. $$B(C_6F_5)_3^{+} \rightarrow C_{18}F_{12}^{+} + BF_3$$

Such a reaction is highly likely considering both the very high stability of boron trifluoride and the fact that perfluorotriphenylene appears to remain essentially intact in a mass spectrometer, $C_{18}F_{12}^{+}$ being the base peak in the spectrum with $C_{18}F_{12}^{++}$ one of the next most intense peaks.

The m.ps of normal aromatic derivatives and their perfluoro analogues seldom differ by more than 10–20°[6]; this is true of biphenylene (m.p. 109–110°) and perfluoro-biphenylene (m.p. 100–101·5°^{4}) and of tetraphenylene (m.p. 233°) and perfluorotetraphenylene (m.p. 249–251°).^{4} However the m.ps of triphenylene (198·5°) and perfluorotriphenylene (102–104°) suggest a considerable difference in the structures (molecular and/or crystal) of the two triphenylenes, no doubt due to the steric interactions discussed above. The UV spectrum of perfluorotriphenylene is considerably broader (Fig. 1) than its hydrogen analogue and, furthermore, the extinction coefficients for the various absorption peaks are very much smaller than those of triphenylene, again signifying a considerable distortion of the $C_{18}F_{12}$ molecule from planarity.

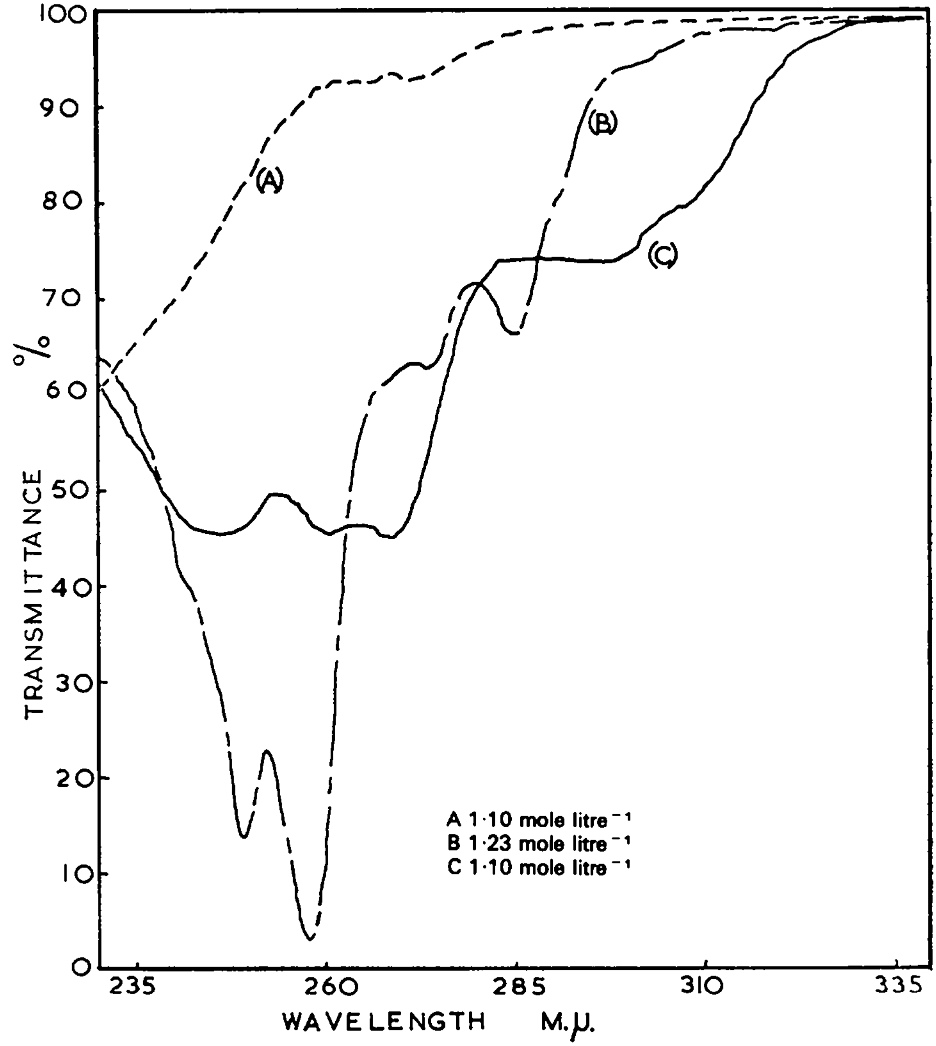
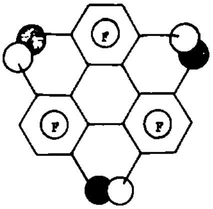


FIG. 1 UV spectra of 2,3-bis(pentafluorophenyl)-4,5,6-trifluorobenzene (A), triphenylene (B), and perfluorotriphenylene (C) dissolved in cyclohexane.

The ^{19}F NMR spectrum of perfluorotriphenylene is shown in Fig. 2 and consists at room temperature of a broad, low-field singlet and a high-field triplet, both peaks being of equal intensity. On cooling the sample, the low-field peak begins to show a triplet structure but never becomes as sharply resolved as the peak to higher field. We suggest that the broad, low-field peak is due to the '*ortho*' F atoms, F_1, and that since only two peaks are observable even at low temperature, a 'propeller-like' distortion of the molecule must occur in solution—unlike the distortion which occurs in the solid state for $C_{18}H_{12}$ where one ring is tilted slightly at an angle to the other two which stay essentially co-planar:



A direct comparison of the NMR spectra of the two triphenylenes is not possible because even at 220 Mc/s the proton spectrum of triphenylene (Fig. 3) is still highly second order. We are now carrying out an X-ray structure determination on single

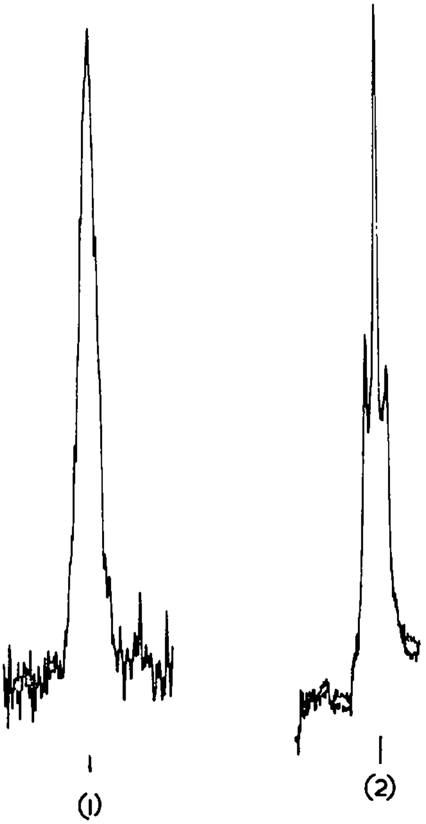


FIG. 2a ^{19}F NMR spectrum of perfluorotriphenylene recorded at room temperature and 94·1 Mc/s. Peak (1) occurred 12,065 c/s upfield from $CFCl_3$, peak (2) at 14,310 c/s.

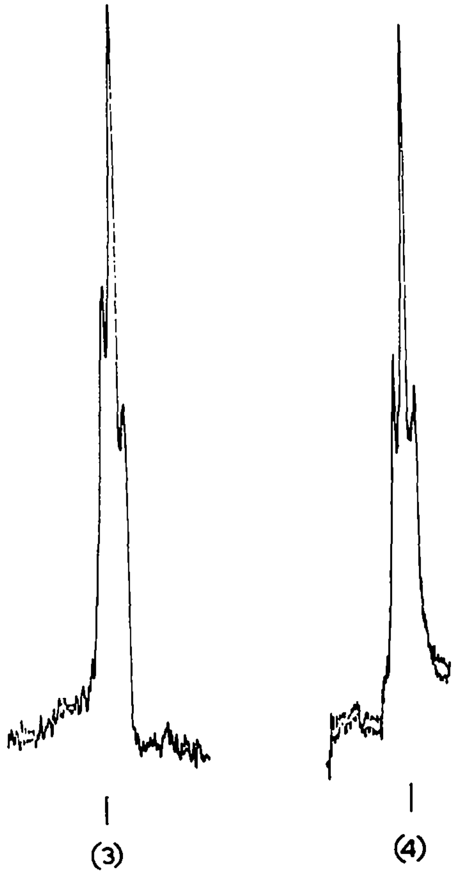


FIG. 2b ^{19}F NMR spectrum of perfluorotriphenylene recorded at −40°; triplet splitting was 5·2 c/s in both peaks.

crystals of perfluorotriphenylene to check the configuration of the molecule in the solid state.

Normal aromatic hydrocarbons and their highly fluorinated analogues form colourless, weak complexes with each other in the solid state; a typical example is the 1:1 complex formed by C_6H_6 and C_6F_6 which melts at 23·7°.[7] Although it appears general to assume that such complexes are held by bonding of the charge-transfer type, no extra bands appear in their UV spectra which can be assigned to the charge-transfer process. Perfluorotriphenylene forms similar complexes with several aromatic hydrocarbons and, in particular, a 1:1 highly crystalline adduct with triphenylene which melts with dissociation at 250–252° in a sealed tube. The mass spectrum of the 1:1 complex taken at 242° shows a peak due only to ions arising from the fragmentations of $C_{18}F_{12}$ and $C_{18}H_{12}$ separately and hence it must be dissociated in the vapour state at this temperature; at 80° a peak due to the 1:1 complex can be detected. The UV spectrum of the complex taken in cyclohexane is essentially identical to a superposition of the spectra of triphenylene and perfluorotriphenylene at the same molar concentrations, presumably indicating that complete dissociation occurs in solution. In agreement with this a solution of the complex in either light petroleum

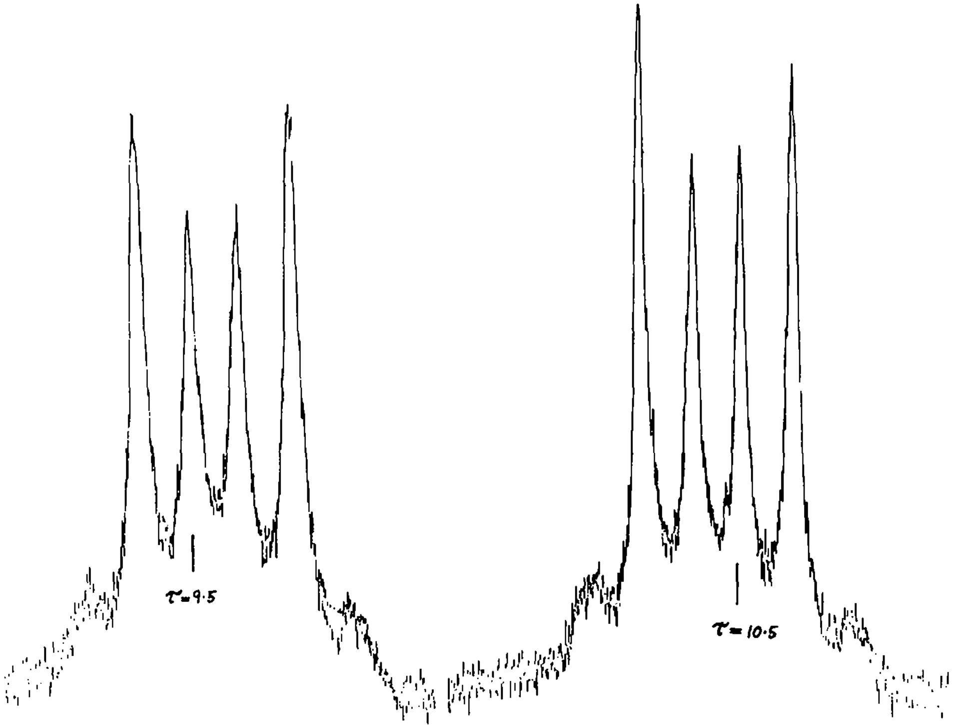


FIG. 3 ^{1}H NMR spectrum of triphenylene recorded at 220 Mc/s.

or cyclohexane can be separated into its pure components by TLC on Kieselguhr, no band due to the complex being detectable.

An alternative to bonding of the donor-acceptor type is that of hydrogen bonding between the C—H hydrogens and the C—F fluorine atoms; such an interaction would be expected to be very weak but, of course, in the 1 : 1 complex of the triphenylenes twelve CF—FC interactions are possible for each "molecule" of the complex. The band due to the C—H stretching vibration in the IR spectrum of the 1 : 1 complex appears to be either very weak or, more likely, to have broadened very considerably so making its detection rather difficult—which is compatible with the presence of H-bonding within the complex. It is perhaps also significant that attempts to recrystallize perfluorotriphenylene from alcohol yield large, colourless crystals of an alcoholate which, on standing at room temperature, slowly lose the alcohol.

EXPERIMENTAL

The analyses were carried out by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany and by the microanalytical department at Queen Mary College. We thank the Imperial Smelting Corporation for a generous gift of 1,2-diiodotetrafluorobenzene. Triphenylene was purchased from Koch-Light Laboratories Ltd.

Preparation of perfluorotriphenylene. 1,2-Diiodotetrafluorobenzene and activated copper bronze powder (previously dried by heating under high vacuum) were heated in an evacuated sealed tube at 200–230° for about 18 hr. The soluble contents of the tube were extracted with ether, subjected to fractional vacuum sublimation and the perfluorotriphenylene, m.p. 102–104°, collected at 50–80° (ca. 10^{-4} mm); yield was ca. 5%. (Found: Sample 1: C, 48·8; H, 0·15; F, 51·1; sample used later for mass spectral work; Sample 2: C, 48·55; H, 0·0: F, 51·4. Calc. for $C_{18}F_{12}$: C, 48·7; F, 51·3%).

Formation of 1:1 *complex between* $C_{18}F_{12}$ *and* $C_{18}H_{12}$. Solns containing equimolar amounts of perfluorotriphenylene and triphenylene gave an immediate ppt of colourless needles, m.p. 250–252°. (Found: C, 63·9; H, 1·7; calc. for $C_{36}H_{12}F_{12}$: C, 64·3; H, 1·8%). A m.p. composition diagram also indicated the formation of the 1:1 complex.

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