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DISCOVERY AND CRYSTAL STRUCTURE OF A NOVEL CHLOROCARBON HOST: PERCHLOROFLUORENE-9-SPIROCYCLOHEXA-2',5'-DIENE

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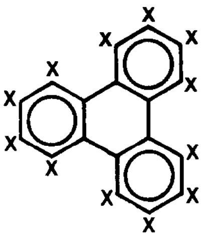
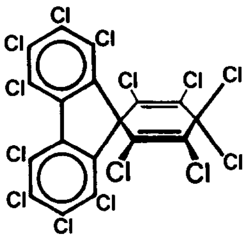
Summary. Chlorination of triphenylene (1a) employing a mixture of aluminium trichloride and sulphur monochloride in sulphuryl chloride leads to rearrangement with formation of the title chlorocarbon (2), a new host, as main product. X-ray crystal structure analyses of the unsolvated spirocycle (2) as well as of its inclusion compounds with guests benzene and cyclohexa-1,4-diene are described.

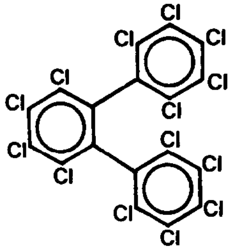
In the course of systematic studies[1] on the design of novel host molecules we recently wished to prepare the synthetic intermediate perchlorotriphenylene (1b). Chlorination of triphenylene (1a) itself appeared to offer a viable route to this highly hindered[2] chlorocarbon, provided that chlorinolysis or fragmentation of the carbon framework could be avoided. In view of this we selected mild and efficient BMC conditions,[3] employing mixtures of $AlCl_3$ and S_2Cl_2 in SO_2Cl_2. We now report that even under these conditions we could isolate none of the desired compound, the main product (ca. 60%) being a new chlorocarbon (2), m.p. 293-294.5°C (sublimed sample); m/e 706 (M^+), with microanalysis establishing a composition $C_{18}Cl_{14}$; and exhibiting ten singlets in its ^{13}C n.m.r. spectrum.[4] Perchloro-o-terphenyl (3), formed by chlorinolysis, was positively identified[5] as a second product of the reaction. The structure (2) for the principal product was unambiguously assigned on the basis of an X-ray crystal structure analysis[†§] (vide infra) of the unsolvated crystal. Most interestingly, compound (2) is itself a new host capable of forming beautifully crystalline inclusion compounds with for example, benzene, cyclohexane,



(1a), X = H
(1b), X = Cl



(2)



(3)

[†] The atomic co-ordinates for unsolvated (2) and its adducts are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[§] Supplementary data available for (2) and its adducts, structure factors. See Announcement to Authors, Tetrahedron Letters, 47, 5154 (1983).

cyclohexene, cyclohexa-1,3-diene, cyclohexa-1,4-diene, and 1,4-dioxan; the host-guest ratio[6] being 2:1 in each case.[7] Following a detailed X-ray analysis of the benzene adduct, described below, we went on to investigate the cyclohexa-1,4-diene inclusion compound of (2) at ambient temperature and also at -105°C, with a view to determining the conformation of this non-conjugated, carbocyclic guest. Crystal data[8] for (2) and its inclusion compounds are summarised in Table 1.

TABLE 1. Crystal data for unsolvated (2) and its benzene and cyclohexa-1,4-diene adducts

	(2)	2(2).C_6H_6	2(2).C_6H_8	2(2).C_6H_8
Temperature	20°C	20°C	20°C	-105°C
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	12.234(1)	7.377(3)	7.364(3)	7.325(1)
b	14.669(3)	12.151(2)	12.170(4)	12.107(3)
c (Å)	14.159(2)	16.437(3)	16.575(4)	16.377(6)
α		72.54(1)	72.35(3)	72.59(3)
β	107.65(1)	78.22(3)	78.45(3)	78.70(3)
γ (°)		73.27(3)	73.10(3)	73.26(2)
U (Å^3)	2421.3	1334.8	1344.2	1317.5
Z	4	1	1	1
D_c (gcm^{-3})	1.95	1.87	1.86	1.90
Number of independent reflections with $F_o^2 > 2\sigma(F_o^2)$	3242	3369	3983	5249
Final R	0.030	0.041	0.035	0.037

Figure 1 shows a general view of the host molecule (2) in its benzene adduct. Interestingly, the molecule, which occupies a general position in the unit cell, has approximately C_2 symmetry,[9] the two-fold axis passing through the atoms C(4') and C(9), and bisecting the C(4a)-C(4b) bond. As can be seen from the selected torsion angles in Table 2, only minor changes between corresponding parameters are found for the benzene and the cyclohexa-1,4-diene adducts of (2). The conformation of unsolvated (2), which retains approximate C_2 symmetry, is however signific-

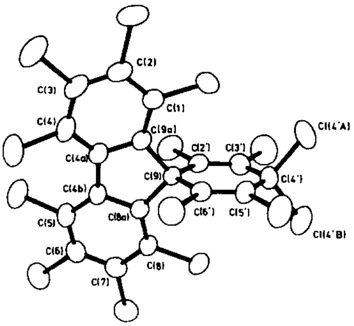


Figure 1

A general view of perchloro-9-spirocyclohexa-2',5'-diene (2) in its inclusion compound with benzene. There are two host molecules and one benzene guest in the triclinic unit cell.

TABLE 2. Selected torsion angles (°) for (a) unsolvated (**2**), (b) the benzene adduct of (**2**), and (c) the cyclohexa-1,4-diene adduct of (**2**) at -105°C. Torsion angles related by the approximate 2-fold axis are shown in pairs. Chlorine atoms are numbered according to the carbon atom to which they are attached.

	(a)	(b)	(c)
C(4) - C(4a) - C(4b) - C(5)	22.7(4)	27.1(5)	27.5(3)
C(4b)- C(4a) - C(4) - Cl(4)	12.7(3)	14.0(4)	14.5(3)
C(4a)- C(4b) - C(5) - Cl(5)	11.4(3)	6.4(4)	5.5(2)
Cl(4)- C(4) - C(3) - Cl(3)	-9.4(2)	-11.3(3)	-11.9(2)
Cl(5)- C(5) - C(6) - Cl(6)	-11.4(2)	-7.8(3)	-7.6(2)
Cl(3)- C(3) - C(2) - Cl(2)	-5.9(2)	-3.5(3)	-3.1(2)
Cl(6)- C(6) - C(7) - Cl(7)	1.1(2)	-2.0(3)	-1.0(2)
Cl(2)- C(2) - C(1) - Cl(1)	6.6(2)	4.8(3)	4.5(2)
Cl(7)- C(7) - C(8) - Cl(8)	1.8(2)	0.3(3)	0.2(2)
Cl(1)- C(1) - C(9a)- C(9)	5.6(3)	7.0(3)	7.4(2)
Cl(8)- C(8) - C(8a)- C(9)	1.9(3)	10.6(3)	10.5(2)
C(1) - C(9a) - C(9) - C(2')	65.5(3)	62.5(4)	62.6(3)
C(8) - C(8a) - C(9) - C(6')	58.6(3)	56.2(4)	55.9(3)

antly different. The room-temperature mean $C(sp^2)$-Cl distance of 1.719(5)Å for 36 independent observations agrees well with the corresponding mean 1.717(8)Å, found independently[10] for a number of perchlorinated aromatic hydrocarbons.

The host-guest packing in the cyclohexa-1,4-diene adduct (at -105°C) is illustrated in the stereoview in Figure 2. The guest molecules are accommodated in continuous channels which run parallel to the *a*-axis. Each diene guest is located on a point of $\bar{1}$ symmetry and this arrangement is directly analogous to that found for the benzene adduct, where the centrosymmetric benzene guest molecule is located in a unit cell of almost identical dimensions (Table 1). The stereoview in Figure 3 shows a van der Waals plot,[11] looking along the *a*-axis, for the cyclohexa-1,4-diene adduct of (**2**). Notwithstanding the apparent efficiency of host-guest interactions the diene guest molecule does not appear to be "clamped" in a unique orientation, and examination of the guest's ring bond lengths was consistent with rotational disorder. None of the hydrogen atoms of the guest could be unambiguously located. Careful inspection of the thermal ellipsoids, however, gave no evidence for marked non-planarity of the cyclohexa-1,4-diene guest molecule, though a limited degree of non-planarity cannot be excluded on this basis.[12] It is interesting to note that a planar conformation has been found by theoretical calculations[13] and electron diffraction measurements[14] for this non-conjugated diene in the vapour phase.

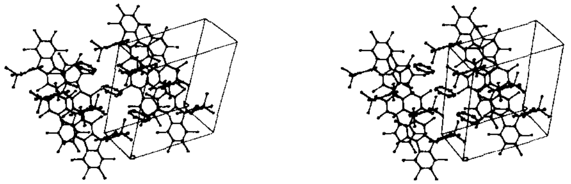


Figure 2

A view of the host-guest packing in the cyclohexa-1,4-diene inclusion compound of host (**2**). The guest molecules are located in continuous channels running along the *a*-direction.

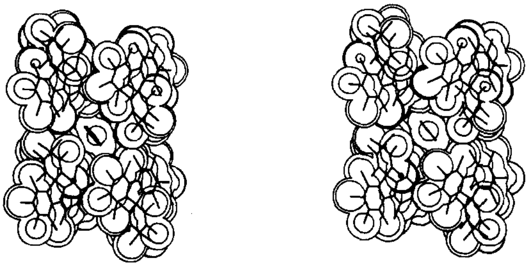


Figure 3

A van der Waals stereoview looking along the a-axis illustrating the efficiency of host-guest packing in the cyclohexa-1,4-diene adduct of (2) at -105°C. Sections normal to the a-axis are shown at 1 Å intervals.

References and Notes

1. See, for example, D.D. MacNicol in Inclusion Compounds, ed. by J.L. Atwood, J.E.D. Davies, and D.D. MacNicol, Academic Press, London, 1984, Vol. 2, Chs. 1 and 5.
2. A marked degree of distortion from planarity has been found for the less crowded molecule, perfluorotriphenylene: M.B. Hursthouse, V.B. Smith, and A.G. Massey, J. Fluorine Chem., 1977, 10, 145.
3. M. Ballester, C. Molinet, and J. Castañer, J. Am. Chem. Soc., 1960, 82, 4254. In a typical run, a solution of 1 g of (1a) dissolved in 25 ml of freshly distilled SO_2Cl_2 containing 1 ml of S_2Cl_2 was added dropwise over ½ h to a boiling solution of 0.3 g $AlCl_3$ in 75 ml SO_2Cl_2. After reflux for 7 h, work-up yielded (2) and (3) in a ratio of ca. 2:1. Runs employing varying times (7-30 h) and reagent concentrations (up to twenty times those above) gave essentially the same outcome.
4. For (2), found: C, 30.2%; Cl, 69.8%. $C_{18}Cl_{14}$ requires C, 30.3%; Cl, 69.7%. The ^{13}C n.m.r. spectrum, δ_C ($CDCl_3$), comprises singlets at 140.2, 138.2, 137.5, 135.2, 134.0, 128.8, 127.8, 126.4, 84.0, and 66.7 p.p.m. The i.r. spectrum (KBr disc) of (2) has bands at 1613(m), 1402(m), 1335(s), 1320(s), 1186(s), 1113(m), 1071(s), 851(m), 800(s), 763(s), 745(s), 697(s), 639(s), 562(m), and 544(m).
5. The structure of perchloro-o-terphenyl (3) was determined by X-ray analysis; a = 8.669(1), b = 16.199(3), c = 17.345(3) Å, β = 96.47(1)°, U = 2420.4 Å^3, space group $P2_1/c$, Z = 4; current R factor 8.5%.
6. Host-guest ratios were determined by weight loss and also by ^1H n.m.r., employing mesitylene as molarity standard.
7. By contrast, unsolvated (2) was obtained on recrystallisation from toluene or DMF. Host (2) exhibits significant selective clathration properties: for example, recrystallisation of unsolvated (2) from an equimolar mixture of benzene and cyclohexane gives a 2:1 adduct, the ratio of aromatic to non-aromatic guest included being ca. 4.5:1.
8. X-ray intensity measurements were made by θ-ω scan on a Nonius CAD4 diffractometer using graphite-monochromated MoK_α radiation. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 reflections. The principal computer programs used in structure solution and refinement are: MITHRIL, A Computer Program for the Automatic Solution of Crystal Structures from X-Ray Data, C.J. Gilmore, J. Appl. Crystallogr., 1984, 17, 42; The GX Crystallographic Program System, P.R. Mallinson and K.W. Muir, J. Appl. Crystallogr., 1985, 18, 51.
9. For the role of two-fold molecular symmetry in host design see, for example, N.Z. Huang and T.C.W. Mak, J. Chem. Soc., Chem. Commun., 1982, 543; E. Weber, I. Csöregh, B. Stensland, and M. Czugler, J. Am. Chem. Soc., 1984, 106, 3297; and references therein.
10. F.H. Herbstein, Acta Crystallogr., 1979, B35, 1661.
11. J.C. Hanson, computer program VDW, personal communication.
12. Also, a moderate degree of torsional oscillation about a minimum-energy, planar conformation cannot be ruled out: cf. J. Laane and R.C. Lord, J. Mol. Spectrosc., 1971, 39, 340; M.C. Grossel and M.J. Perkins, Nouv. J. Chim., 1979, 3, 285.
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