Free Radicals as Clathrate Hosts: Crystal and Molecular Structure of 1 : 1 Perchlorotriphenylmethyl Radical–Benzene

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The perchlorotriphenylmethyl radical (2) acts as a clathrate host for benzene, halogenobenzenes, and 1,4-dioxane giving inclusion compounds with different stabilities; the structure of (2)·C_6H_6, established by *X*-ray diffraction, shows the guest molecules located in channels between the hosts.

The design of new host molecules is currently an object of increasing interest. Molecular bulkiness and limited conformational flexibility are general structural features of many clathrands.[1] Molecular symmetry (especially three- or two-fold symmetry) also plays an important role in determining the inclusion ability of a host compound, providing a new principle for the design of novel hosts.[2] The perchlorotriphenylmethyl radical (2) is an exceptionally stable carbon free radical with considerable bulkiness.[3] It has been suggested that (2) has a propeller-like conformation (D_3 symmetry) with a high enantiomerization barrier for the reversal of propeller helicity, due to the congestion of the three pairs of *ortho*-chlorine atoms.[4] These supposed clathratogenic features encouraged us to study the inclusion properties of (2) and its derivatives.

Radical (2) was prepared quantitatively from tris(pentachlorophenyl)methane (1) in a 'one pot' reaction by treatment with aqueous tetra-n-butylammonium hydroxide in tetrahydrofuran (THF), followed by oxidation of the resulting carbanion with *p*-chloranil (Scheme 1). (2) was obtained as an

$$\underset{(1)}{(C_6Cl_5)_3CH} \longrightarrow \underset{(2)}{(C_6Cl_5)_3C\cdot}$$

Scheme 1. *Reagents:* $Bu^n{}_4N^+OH^-$, THF, then *p*-chloranil (96% yield).

Table 1. Inclusion compounds of radical (2): stoicheiometries and stabilities.

Guest[a]	$T_d{}^b$/K	$\Delta H_d{}^c$/ kJ mol^{-1}	log $K_o{}^d$	$E_{act}{}^d$/ kJ mol^{-1}
C_6H_6	361	16.0	25.3	194
C_6H_5F	352	13.1	15.2	122
C_6H_5Cl	340	30.5	10.3	83
C_6H_5Br	344	30.2	13.4	95
$C_4H_8O_2$	318	27.0	13.7	106

[a] Host : guest ratio 1 : 1 in all cases, determined by thermogravimetry, elemental (C, H, and Cl) analyses, and i.r. spectral subtraction techniques. [b] Decomposition temperature observed on non-isothermal differential scanning calorimetry (DSC) measurements. [c] The enthalpy change on non-isothermal DSC measurements. [d] Frequency factor, K_o in s^{-1}, and activation energy, E_{act}, calculated with r^2 = 0.9940—0.9996.

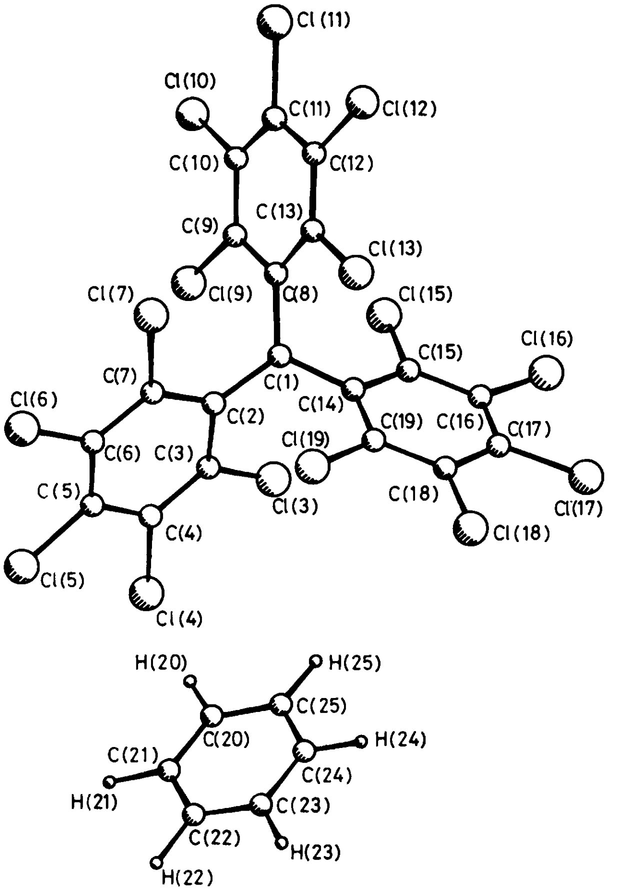

Figure 1. Perspective view of $(\mathbf{2})\cdot C_6H_6$ showing atom numbering scheme. Mean bond distances (with r.m.d.s.) are host: C(1)–C(Ar) 1.47(1), C(Ar)–C(Ar) 1.39(1), C(Ar)–Cl 1.72(2) Å; guest: C–C 1.34(3) Å.

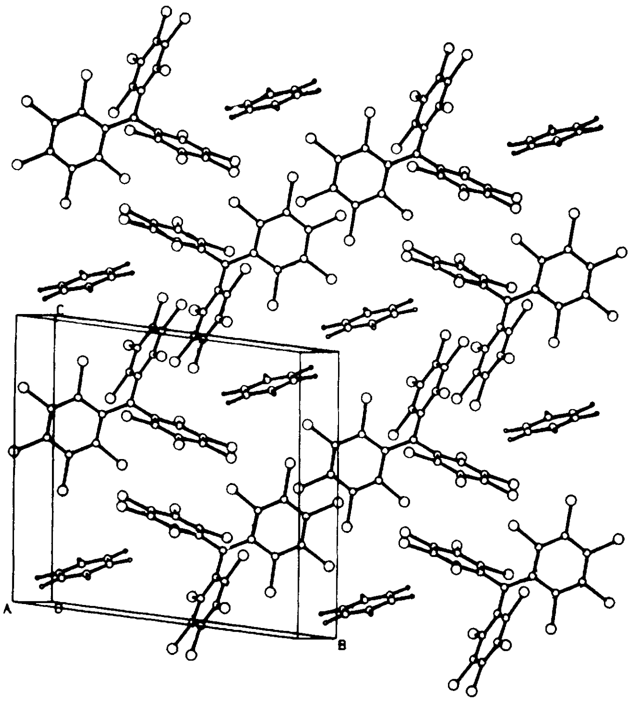

Figure 2. Packing in the $(\mathbf{2})\cdot C_6H_6$ clathrate.

amorphous powder which could be recrystallized from benzene, fluorobenzene, chlorobenzene, bromobenzene, or 1,4-dioxane to give transparent red crystals, identified as inclusion compounds of (**2**), *i.e.* (**2**) · guest (Table 1). These compounds were stable *in vacuo* (15 Torr) at room temperature. However, heating resulted not only in opacity and weight decrease with guest evolution but also in an endothermic change (Table 1) within a specific temperature range for each compound. The rate constants for such declathrations were evaluated for each compound at several temperatures, by fitting isothermal thermogravimmetric (TG) curves to different kinetic mechanisms of solid state reactions (diffusion, nucleation, growth, and nucleation–growth).[5] The kinetic parameters (Table 1) were calculated from an Arrhenius plot of the rate constants and finally the declathration mechanisms were assigned on the basis of agreement between these calculated parameters and those determined from non-isothermal TG curves by means of the Coats–Redfern method.[6] Two types of thermal behaviour can be differentiated on the basis of thermodynamic and kinetic parameters and also from the declathration mechanisms: one type is preferred by the smaller guests (C_6H_6 and C_6H_5F), where a growth mechanism is observed, and the other type by the larger ones (C_6H_5Cl, C_6H_5Br, and $C_4H_8O_2$), where a nucleation–growth mechanism is operative. It is noteworthy that neither decomposition temperatures (T_d) nor kinetic stabilities (E_{act}) correlate with the thermodynamic stabilities (ΔH_d) in contrast with the reported results for inclusion compounds where a cyclophane is the host.†

The clathrand properties of (**2**) and the thermal behaviour described above prompted us to undertake an *X*-ray diffraction study. Figure 1 shows the structure of $(\mathbf{2})\cdot C_6H_6$,‡ which represents the second example of a triphenylmethyl radical structure.[8] The C(1), C(2), C(8), and C(14) atoms lie in a plane (reference plane), confirming the expected sp^2 hybridation of C(1). The conformation of the three pentachlorophenyl rings can be described by the dihedral angles (46.3, 53.4, and 53.8°) between the reference plane and the mean planes of the phenyl rings showing a non-symmetrical propeller conformation. Such a situation relieves the strong steric repulsion between *ortho*-chlorine atoms favouring the steric shielding of the radical centre C(1).

The packing scheme (Figure 2) shows the C_6H_6 molecules located in continuous channels, which are formed by the packing of six neighbour host molecules through their coplanar phenyl groups. This structural arrangement is similar to that observed for the xylene clathrate of tris(naphthalene-1,8-dioxy)cyclotriphosphazene[11] but differs substantially from those observed for most of the families of hosts with trigonal symmetry.[2]

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† A correlation between the differences $T_d - T_b$ (b.p. of pure guest) and $\Delta H_d - \Delta H_{vap}$ (of pure guest at 1 atm) is observed in compounds with aromatic guests.[7]

‡ *Crystal data* for $(\mathbf{2})\cdot C_6H_6$: $C_{19}Cl_{15}\cdot C_6H_6$, $M = 838.1$, triclinic, space group $P\bar{1}$, $a = 8.771(3)$, $b = 13.416(3)$, $c = 13.537(3)$ Å, $\alpha = 96.91(2)$, $\beta = 90.14(2)$, $\gamma = 101.85(2)°$, $U = 1547.2$ Å^3, $Z = 2$, $D_c = 1.80\,g\,cm^{-3}$. Intensity data were collected on an Enraf-Nonius CAD4 diffractomer in the range $1 < \theta < 25°$, using Mo-K_α radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu = 13.6\,cm^{-1}$. Data were corrected for Lorentz and polarization effects. The structure was solved by a direct method using MULTAN 11/84[9] and refined by the full-matrix least-squares technique with SHELX-76[10] to $R = 0.074$ and $R_w = 0.054$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We anticipate that other polychlorinated triphenylmethyl radicals, even with functional groups, may form similar or higher inclusion compounds. Radical (**2**) may be considered the first representative of a series of host compounds having radical character and therefore providing a stable paramagnetic contour with possible useful applications.

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