

Perchlorocoronene: a Novel Host Precursor

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The title compound (**1b**), a new non-planar chlorocarbon possessing approximate D_{3d} symmetry, has been prepared by chlorination of coronene (**1a**); complete substitution of (**1b**) by arenethiolate nucleophiles in the dipolar aprotic solvent DMEU (1,3-dimethylimidazolidin-2-one) yields the dodecathioethers (**2a**) and (**2b**), members of a new prospective host series.

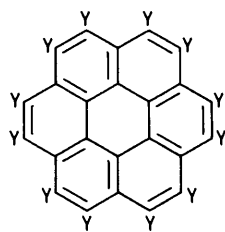
A fascinating aspect of the design of multimolecular inclusion compounds is the recognition of the importance of molecular symmetry in the discovery of entirely new host series.¹ In this respect we were attracted to the highly symmetrical molecule perchlorocoronene (**1b**) as potential host precursor. We now report the synthesis of this new chlorocarbon, its structure in the molecular crystal, and briefly, its one-step conversion into molecules of a new type, highly prospective for the formation of crystalline inclusion compounds. Chlorination of the hydrocarbon coronene (**1a**) under mild and efficient BMC conditions,² employing a mixture of AlCl_3 and S_2Cl_2 in SO_2Cl_2 (typical reflux time 28 h) is found, after workup, to give (**1b**), m.p. $>320^\circ\text{C}$ in high (*ca.* 90%) yield. The yellow crystalline product is hydrogen-free (by i.r. and microanalysis) and mass-spectral analysis established its composition as $\text{C}_{24}\text{Cl}_{12}$.

Interestingly, perchlorocoronene would appear to be a suitable candidate for direct molecular imaging by high-

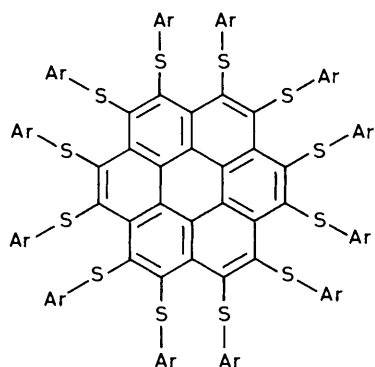
resolution electron microscopy, as indicated by initial studies (down to 3 Å resolution) on epitaxial thin films readily produced by evaporation of (**1b**) *in vacuo* onto KCl substrates.


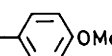
Chlorocarbon (**1b**), to our knowledge the first persubstituted coronene prepared (apart from isotopic substitution) presents a unique conformational situation owing to the six pairs of *peri*-related chlorine atoms. Owing to severe *peri*-interactions destabilising a planar D_{6h} form, the highest-symmetry chiral and achiral conformations possible have, respectively, symmetries of D_6 and D_{3d} . Employing an extension of our earlier nomenclature for naphthalenes³ these have the **abababababab** conformation† (or its enantiomer)

† Lettering is carried out clockwise from C(1) to C(12). In addition, there are another four chiral forms possible, one with D_2 symmetry and three with C_2 symmetry; along with two achiral forms having idealised symmetries of C_{2h} and C_s .



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



(2a), Ar = 
(2b), Ar = 

[Type I] and the **aabbaabbaabb** conformation [Type II], where **a** and **b** represent chlorine atoms above and below the mean plane of the carbon atoms.

To resolve this interesting conformational situation in the crystalline state we have carried out a single-crystal X-ray diffraction analysis.[‡]

The molecular structure of (1b) may be appreciated from the stereo packing diagram shown in Figure 1. The molecule has the Type II or **aabbaabbaabb** conformation with pairs of chlorine atoms situated alternately above and below the mean molecular plane; smaller corresponding displacements are found for pairs of chlorine-bearing carbon atoms. The molecule displays two concave faces, and its symmetry quite closely approximates to D_{3d} , as can be seen from the atom displacements given in Figure 2. Located on a point of $2/m$ symmetry the molecule is constrained to have exact C_{2h} symmetry.

[‡] Crystal data for $C_{24}Cl_{12}$, (1b): $M = 713.7$, orthorhombic, space group $Cmca$, $a = 22.217(4)$, $b = 8.214(2)$, $c = 12.921(2)$ Å, $U = 2358(1)$ Å³, $Z = 4$, $D_c = 2.01$ g cm⁻³. λ (Mo- K_{α}) = 0.7107 Å, $\mu = 14.4$ cm⁻¹. $T = 293$ K. Number of independent intensities: 1327 from orange plate, $0.3 \times 0.3 \times 0.1$ mm. $R = 0.033$, $R' = 0.042$ for 937 observed [$I/\sigma(I) > 2.0$] reflections. X-Ray intensity measurements for all possible reflections with $\sin\theta/\lambda < 0.64$ Å⁻¹ were made by θ - ω scan on a Nonius CAD4 diffractometer. The principal computer programs used in structure solution and refinement are listed in ref. 7. 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.

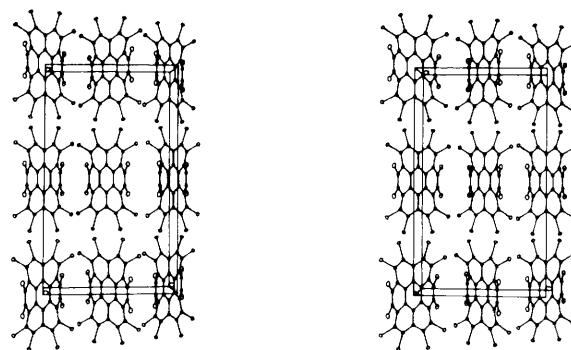


Figure 1. A stereoview, looking along the *b* axis, illustrating the molecular packing of perchlorocoronene (1b).

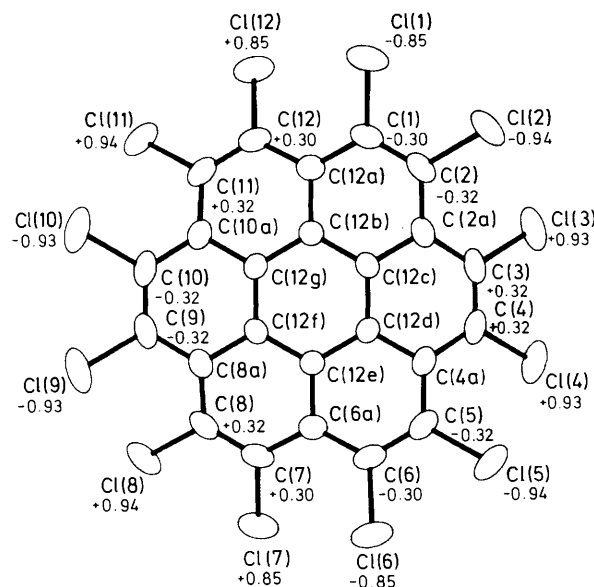


Figure 2. Atomic numbering scheme and displacements (Å) of atoms of (1b) from the mean plane of the carbon atoms. Atoms for which no displacements are given (the central ring and directly-attached carbon atoms) do not deviate significantly from coplanarity. The mean bond lengths of the central ring, radial, and second-outermost carbon-carbon bonds are 1.425(3), 1.420(3), and 1.425(2) Å, respectively. The independent angles C(1)-C(12a)-C(12) and C(2)-C(2a)-C(3), both 125.9(3)°, compare with a mean exterior angle for coronene (ref. 6) of 124.5(2)°, while all the valence angles involving a central ring carbon atom are 120° in each case.

Consistent with the view⁴ that complete chlorine substitution of polynuclear aromatic hydrocarbons⁵ has, at most, a minor effect on π -bond orders, the outermost carbon-carbon bond, mean length 1.360(4) Å, which has the highest calculated⁶ bond order for coronene, is found to be the shortest. The two independent Cl \cdots Cl distances for *peri*-related atoms, Cl(1) \cdots Cl(12) and Cl(2) \cdots Cl(3), 3.021(2) and 3.045(1) Å, are slightly greater than the (mean) contact distance of 3.004(2) Å found for the *peri*-chlorines in octachloronaphthalene.⁴

The dodecakis-substituted coronenes dodecakis(*p*-t-butylthio)coronene (2a) and dodecakis(*p*-methoxyphenylthio)coronene (2b), members of a new class of molecule, have been readily prepared in excellent yields by treatment (100 h) of perchlorocoronene (1b) with the appropriate sodium arenethiolate (24 mol. equiv.) in the solvent 1,3-dimethylimidazolidin-2-one (DMEU), employed to promote complete displacement of the chlorine atoms. The bright red com-

pounds (**2a**) and (**2b**) have spectroscopic properties (^1H , ^{13}C n.m.r., i.r., and mass) fully in accord with their formulated structure. Preliminary studies show inclusion behaviour for (**2b**) which includes, for example, ethyl acetate; whilst (**2a**) (from diethyl succinate) is currently under *X*-ray study.

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