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 °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 $C_{24}Cl_{12}$.

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 naphthalenes[3] these have the **abababababab** conformation† (or its enantiomer)

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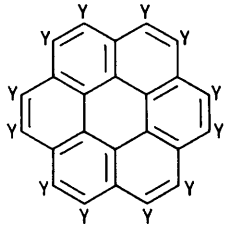
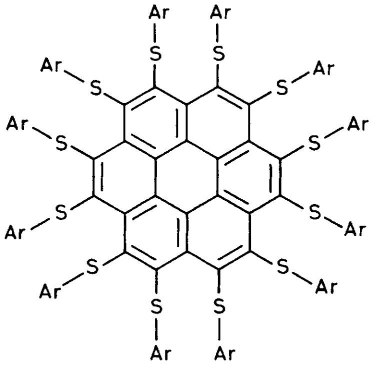
† Lettering is carried out clockwise from C(1) to C(12). In addition, there are another four chiral forms possible, one with D_2 symmetry and three with C_2 symmetry; along with two achiral forms having idealised symmetries of C_{2h} and C_s.

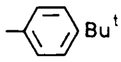


(**1a**), Y = H

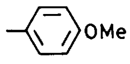
(**1b**), Y = Cl



(**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.

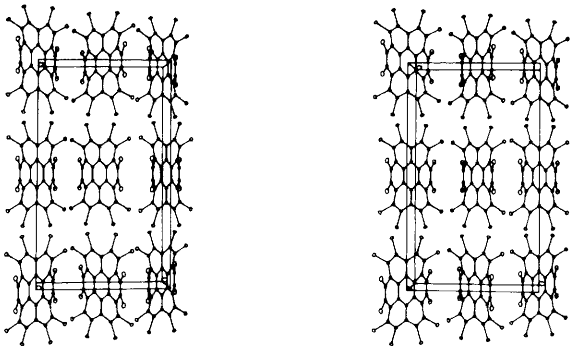


Figure 1. A stereoview, looking along the *b* axis, illustrating the molecular packing of perchlorocoronene (**1b**).

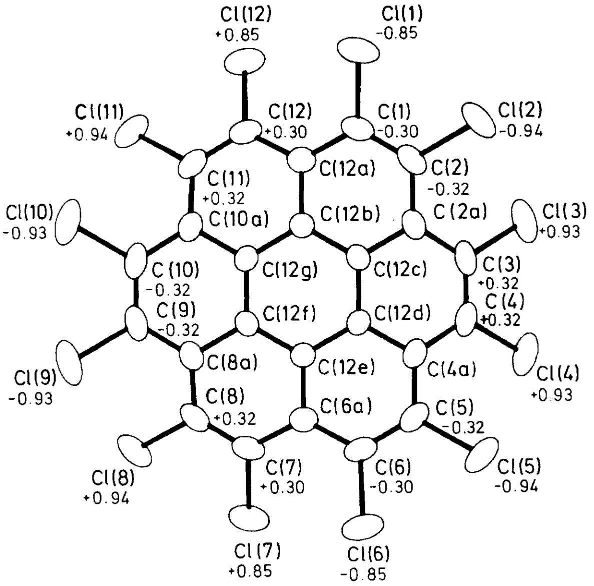


Figure 2. Atomic numbering scheme and displacements (Å) of atoms of (**1b**) from the mean plane of the carbon atoms. Atoms for which no displacements are given (the central ring and directly-attached carbon atoms) do not deviate significantly from coplanarity. The mean bond lengths of the central ring, 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 view[4] that complete chlorine substitution of polynuclear aromatic hydrocarbons[5] 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 calculated[6] bond order for coronene, is found to be the shortest. The two independent Cl· · ·Cl distances for *peri*-related atoms, Cl(1)· · ·Cl(12) and Cl(2)· · ·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 dodeca-substituted coronenes dodecakis(*p*-t-butylphenylthio)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-

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‡ *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, $U = 2358(1)$ Å^3, $Z = 4$, $D_c = 2.01$ 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 × 0.3 × 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.

pounds (**2a**) and (**2b**) have spectroscopic properties (^{1}H, ^{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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References

1 See, for example, 'Inclusion Compounds,' eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Vols. 1—3, Academic Press, 1984; 'Topics in Current Chemistry,' ed. E. Weber, Vol. 140, Springer-Verlag, Berlin, 1987.

2 M. Ballester, C. Molinet, and J. Castañer, *J. Am. Chem. Soc.*, 1960, **82**, 4254.

3 D. D. MacNicol, P. R. Mallinson, and C. D. Robertson, *J. Chem. Soc., Chem. Commun.*, 1985, 1649.

4 F. H. Herbstein, *Acta Crystallogr., Sect. B.*, 1979, **35**, 1661.

5 Literature examples may be found in ref. 4 (naphthalene and octachloronaphthalene) and F. H. Herbstein, M. Kapon, and R. Merksamer, *Acta Crystallogr., Sect. B*, 1976, **32**, 2205 (phenanthrene and decachlorophenanthrene); A. C. Hazell and S. Jagner; *ibid.*, 1976, **32**, 682 (pyrene and decachloropyrene).

6 J. K. Fawcett and J. Trotter, *Proc. R. Soc. London, A*, 1965, **289**, 366.

7 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, *ibid.*, 1985, **18**, 51.