Conformational Studies on a 1,2,3,4,5-Pentachloro-8-phenyltetralin

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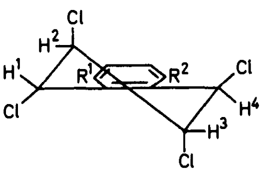
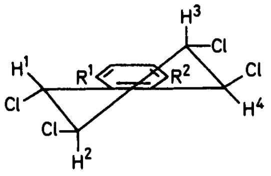
The structure of *r*-1,*t*-2,*c*-3,*t*-4,5-pentachloro-8-phenyltetralin has been determined from single-crystal *X*-ray analysis by direct methods. The crystal data for the title compound are a = 9.600(5), b = 13.647(7), c = 12.132(6) Å, β = 90.1(1)°, monoclinic, space group $P2_1/c$, Z = 4. Full-matrix least-squares refinement based on 1 075 reflections with intensities $I > 2\sigma(I)$ converged to R 0.044. Both aromatic rings are planar, within experimental error; the angle between the two best mean planes C(1)–C(10) (fused benzene and alicyclic ring) and C(11)–C(16) (phenyl ring) is 61.6°, resulting in a remarkable decrease of conjugation between the two aromatic systems. The alicyclic moiety of the molecule assumes a half-chair conformation, with the four chlorine atoms in axial and pseudoaxial positions. The above results, together with those inferred from ^{1}H n.m.r. and chemical methods, indicate the identical conformational preference of the title compound in both the solid state and in solution.

AMONG the products of heterolytic chlorination of 1-phenylnaphthalene, we have isolated in low yields a chlorophenyltetralin (1), an isomer of the previously described 1,2,3,4,5-pentachloro-8-phenyltetralins,[1] where the four alicylic chlorine atoms show β-, δ-, ε-, and ζ-like configurations.



(1) R¹=Ph, R²=Cl
(2) R¹=Me, R²=Cl
(3) R¹=CH₂Cl, R²=H



(4) R¹=R²=H
(5) R¹=Ph, R²=Cl

We assigned to (1) the structure of a γ-like adduct, *i.e.* *r*-1,*t*-2,*c*-3,*t*-4,5-pentachloro-8-phenyltetralin, on the basis of ^{1}H n.m.r. spectroscopy, alkaline dehydrochlorination, and isomerization with aluminium trichloride[2] (see Experimental section). Its conformation in solution shows the rather unfavourable stereochemistry of four axially bonded halogen atoms, even if in this conformer the 1-Cl-8-Ph and 4-Cl-5-Cl non-bonding interactions are relieved by the pseudoaxial conformation of the 1- and 4-halogen atoms. Similar conformations were found to be preferred by the γ-like isomers *r*-1,*t*-2,*c*-3,*t*-4,5-pentachloro-8-methyl- (2) and *r*-1,*t*-2,*c*-3,*t*-4-tetrachloro-5-chloromethyltetralin (3), detected as minor products of the homolytic chlorination of 1-methylnaphthalene.[3] On the other hand, in chloroform solution, *r*-1,*t*-2,*c*-3,*t*-4-tetrachlorotetralin (naphthalene γ-tetrachloride) (4), unsubstituted in the aromatic ring, was found to prefer[4] a conformation where the chlorine atoms are all equatorial and pseudoequatorial. Furthermore, another γ-like isomer, *i.e.* *r*-1,*t*-2,*c*-3,*t*-4,5-pentachlorotetralin, has been proposed[5] to exist in a distorted half-boat arrangement, as an alternative to the usual half-chair conformations, as in (1)—(3) and (4) and (5).

These apparent discrepancies prompted us to investigate the crystal structure of compound (1), in order to verify the occurrence of any distortion of the alicyclic ring from the generally accepted half-chair arrangement, which would release the double diaxial repulsive interaction of chlorine atoms. The occurrence of a definite conformation, *i.e.* (1), once verified in the solid state for the title compound, would support, with a high degree of probability, the same stereochemical preference in a less constrained situation, as in solution.

It was established that *r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralin (naphthalene α-tetrachloride) occurs predominantly in the same form, both in solution (tetrahydrofuran) and in the crystalline state.[4,6] *X*-Ray crystallographic data are also available for the isomer *r*-1,*t*-2,*t*-3,*c*-4-tetrachlorotetralin (naphthalene ε-tetrachloride).[7]

EXPERIMENTAL

Synthesis and Structure Assignment of r-1,t-2,c-3,t-4,5-*Pentachloro*-8-*phenyltetralin* (1).—Some addition products were isolated and characterized by chlorinating 1-phenylnaphthalene in AcOH.[1,8,9] Among them small amounts, *ca.* 3%, of (1) were isolated by preparative t.l.c. on Merck silica gel GF$_{254}$ (type 60) plates, with light petroleum containing increasing amounts of chloroform as eluant. The *pentachlorotetralin* (1) melts at 172—174 °C (uncorrected) (from light petroleum) (Found: C, 50.6; H, 2.7; Cl, 46.7. $C_{16}H_{11}Cl_5$ requires C, 50.5; H, 2.9; Cl, 46.6%).

The above derivative has undergone substitution in the phenyl-substituted ring and addition in the other. Its ^{1}H n.m.r. spectrum ($CDCl_3$ solution, tetramethylsilane as internal standard, Varian model EM 360 A spectrometer) shows four alicyclic and seven aromatic protons. One chlorine substituent is assigned to the 5-position, since this compound was also obtained from 1-chloro-4-phenylnaphthalene. The alicyclic part of the spectrum (ABCD system), consisting of four multiplets, requires computer-simulation, which was carried out by using the LAOCN3 program,[10] including a sub-routine for plotting calculated spectra on a line-printer (IBM 370/115 computer). Spacing and intensities of signals in the calculated and experimental spectra are coincident, giving the following values: δ 5.66 (1-H), 4.95 (2-H), 5.10 (3-H), and 5.79 (4-H) ($J_{1,2} = J_{3,4}$ 1.89, $J_{1,3} = J_{2,4}$ 1.30, $J_{2,3}$ 2.37 Hz). These parameters are consistent with a γ-like structure for the new chlorophenyl-tetrachloride (1).

The signal at δ 5.79, rather than that at δ 5.66, was assigned to 4-H, adjacent to 5-Cl. The assignment of the higher field absorption (δ 4.95) to 2-H, shielded by 8-Ph, compares well with the ^{1}H n.m.r. data for the structurally analogous *r*-1,*t*-2,*c*-3,*t*-4,5-pentachloro-8-methyltetralin (2),[3] where 2- and 3-H both resonate at δ 5.10.

The small values of the above reported vicinal coupling constants show that, in $CDCl_3$ solution, compound (1) prefers a conformation where all alicyclic protons are equatorial and pseudoequatorial, their long-range spin–spin coupling being indicative of an M or W steric relationship between 1- and 3-H, and 2- and 4-H, respectively. The alternative conformation (5) appears to be not relevant in the equilibrium mixture, owing to the magnitude of $J_{2,3}$.

The results of alkaline dehydrohalogenation and $AlCl_3$ isomerization[2] support the above assignment. The fast benzylic isomerization of (1) in nitromethane gives, as the main product, the known δ-like adduct *r*-1,*c*-2,*t*-3,*c*-4,5-pentachloro-8-phenyltetralin.[1] Alkaline dehydrochlorination of (1) yields mainly 1,3,8-trichloro-5-phenylnaphthalene, together with the isomeric 1,3,5-trichloro-8-phenylnaphthalene.[1]

X-Ray Analysis.—Crystals of the title compound (1), suitable for *X*-ray diffraction, were obtained by slowly cooling a light petroleum solution.

Crystal data. $C_{16}H_{11}Cl_5$, $M = 380.5$, $a = 9.600(5)$, $b = 13.647(7)$, $c = 12.132(6)$ Å, $\beta = 90.1(1)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $U = 1\,589.4$ Å^3, $F(000) = 768$.

All diffraction measurements were performed on a Siemens–Stoe four-circle diffractometer by using graphite monochromatized Mo-K_α radiation. 20 Reflections between 10 and 15° in θ were located by a random search procedure and subsequently centred. These reflections were used as a basis for indexing.

The cell constants and the orientation matrix were refined by a least-squares fit.

Intensities were collected at room temperature in the range $3 \leqslant \theta \leqslant 23°$. A θ–ω scan was used with a 0.5 s count at each of 120 steps of 0.01° for each reflection and a 30 s background count at each end of the scan. No reflections were sufficiently intense to require the insertion of attenuators into the beam. Crystal and electronic stability were confirmed by the constancy of three reference reflections whose intensities were monitored every 100 reflections. Of the 1 812 thus considered, 1 075, having a net intensity $> 2\sigma(I)$ (σ is the standard error, based on count statistics) were used in the structure determination and refinement. The data were corrected for Lorentz and polarization effects.

Structure determination and refinement. The structure was solved by the application of direct methods, refined by full-matrix least-squares techniques. Values of the atomic scattering factors were from usual sources.[11] Refinement of an isotropic model converged to R 0.08. A difference Fourier map calculated at this point revealed the positions of the majority of the hydrogen atoms; however their contribution to F_C was calculated (C–H 0.95 Å) and used for the final cycles of refinement which included anisotropic thermal parameters for the chlorine atoms and isotropic parameters for all other atoms. In the calculation of the fixed contribution of the hydrogen atoms an isotropic thermal parameter of 4 Å^2 was assigned to each hydrogen atom. The refinement was carried out by minimizing the quantity $\Sigma w(F_o - F_C)^2$, where $w = 1$. The final R value for the observed reflections was 0.044. A final difference Fourier map was essentially featureless. All computations were performed on the CYBER 76 computer of the Centro di Calcolo Interuniversitario, Italia Nord-Orientale, with SHELX 76 Programs package.

TABLE 1

Final atomic fractional ($\times 10^4$) parameters for non-hydrogen atoms of (1) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cl(1)	1 799(2)	−798(2)	−42(2)
Cl(2)	−556(2)	−80(2)	2 794(2)
Cl(3)	1 822(3)	−2 609(2)	1 819(2)
Cl(4)	1 830(2)	−703(2)	4 603(2)
Cl(5)	5 359(2)	−1 059(2)	4 157(2)
C(1)	1 441(7)	−226(5)	1 277(5)
C(2)	464(7)	−880(6)	1 937(6)
C(3)	1 174(8)	−1 632(6)	2 670(6)
C(4)	2 432(7)	−1 254(6)	3 326(6)
C(5)	4 654(8)	−353(6)	3 106(6)
C(6)	5 473(8)	367(6)	2 662(6)
C(7)	4 963(7)	934(6)	1 808(6)
C(8)	3 633(7)	779(5)	1 384(5)
C(9)	2 820(7)	23(5)	1 820(5)
C(10)	3 298(7)	−532(5)	2 719(6)
C(11)	3 129(7)	1 441(5)	493(6)
C(12)	3 875(9)	1 510(6)	−482(6)
C(13)	3 476(9)	2 178(7)	−1 286(8)
C(14)	2 367(8)	2 795(7)	−1 118(7)
C(15)	1 628(8)	2 735(6)	−155(6)
C(16)	2 016(8)	2 060(5)	635(6)

Final atomic co-ordinates are shown in Table 1. Thermal parameters, hydrogen atom co-ordinates, and observed and calculated structure factor data are contained in Supplementary Publication No. SUP 23346 (10 pp.).*

DISCUSSION

Figure 1 and Tables 2 and 3 summarize most of the structural data for adduct (1); the arrangement of the molecules in the unit cell is shown in Figure 2.

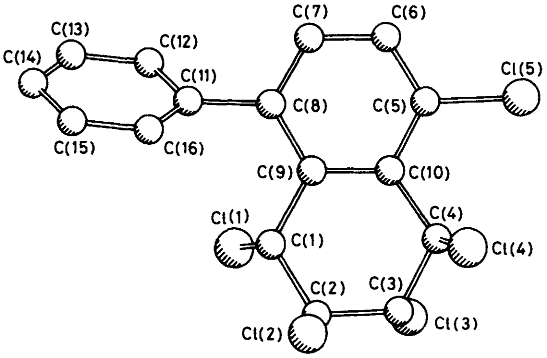


FIGURE 1 Projection of the molecule onto the plane of the fused benzene ring

The crystal structure described by the cell constants, symmetry operations of the space group, and atomic parameters consists of the packing of discrete molecules of *r*-1,*t*-2,*c*-3,*t*-4,5-pentachloro-8-phenyltetralin (1), separated by van der Waals contacts, in agreement with those inferred from radii-sum rules.

The two aromatic rings are planar within experimental error, and the angle between the best mean planes of the C(1)–C(10) system and the C(11)–C(16) phenyl ring is

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

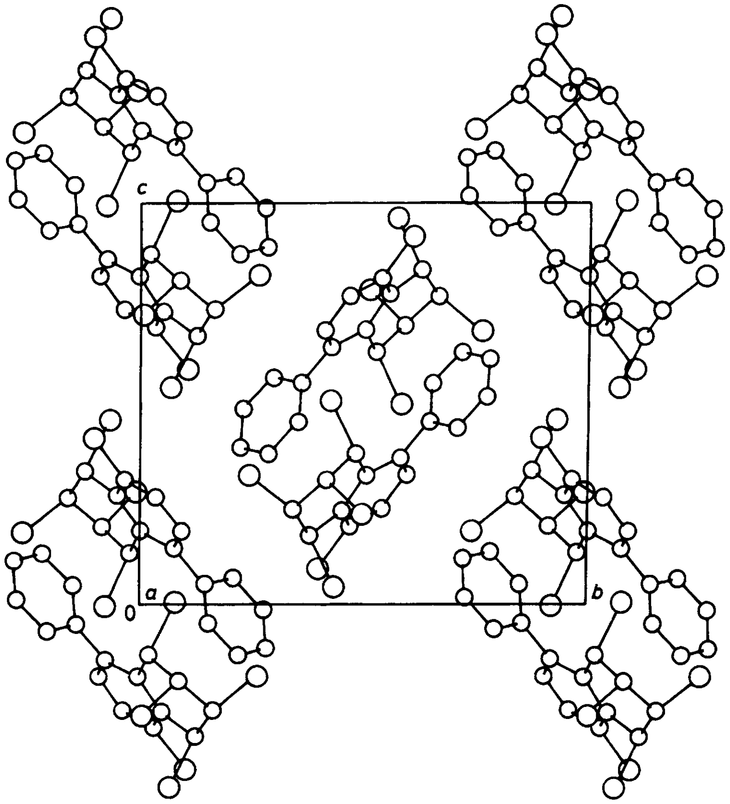

FIGURE 2 Unit cell content as viewed down the *a* axis

TABLE 2

Some relevant interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Cl(1)–C(1)	1.814(7)	C(6)–C(7)	1.38(1)
Cl(2)–C(2)	1.799(8)	C(7)–C(8)	1.39(1)
Cl(3)–C(3)	1.798(8)	C(8)–C(9)	1.40(1)
Cl(4)–C(4)	1.818(7)	C(8)–C(11)	1.49(1)
Cl(5)–C(5)	1.734(7)	C(9)–C(10)	1.40(1)
C(1)–C(2)	1.52(1)	C(11)–C(12)	1.39(1)
C(1)–C(9)	1.52(1)	C(12)–C(13)	1.39(1)
C(2)–C(3)	1.52(1)	C(13)–C(14)	1.37(1)
C(3)–C(4)	1.54(1)	C(14)–C(15)	1.37(1)
C(4)–C(10)	1.49(1)	C(15)–C(16)	1.38(1)
C(5)–C(6)	1.37(1)	C(16)–C(11)	1.37(1)
C(5)–C(10)	1.40(1)		
Cl(1)–C(1)–C(2)	109.2(5)	C(6)–C(7)–C(8)	121.0(7)
Cl(1)–C(1)–C(9)	108.3(4)	C(7)–C(8)–C(9)	119.0(6)
Cl(2)–C(2)–C(1)	106.6(5)	C(7)–C(8)–C(11)	118.2(6)
Cl(2)–C(2)–C(3)	108.4(5)	C(8)–C(9)–C(10)	120.7(6)
Cl(3)–C(3)–C(2)	108.7(5)	C(8)–C(11)–C(12)	119.5(7)
Cl(3)–C(3)–C(4)	105.9(5)	C(8)–C(11)–C(16)	122.2(6)
Cl(4)–C(4)–C(3)	109.3(5)	C(9)–C(8)–C(11)	122.8(6)
Cl(4)–C(4)–C(10)	109.1(5)	C(9)–C(10)–C(4)	124.1(6)
Cl(5)–C(5)–C(6)	117.7(6)	C(9)–C(10)–C(5)	117.8(6)
Cl(5)–C(5)–C(10)	120.6(6)	C(10)–C(4)–C(3)	114.0(6)
C(1)–C(2)–C(3)	115.3(6)	C(10)–C(5)–C(6)	121.7(7)
C(1)–C(9)–C(8)	119.3(6)	C(11)–C(12)–C(13)	120.1(8)
C(1)–C(9)–C(10)	120.0(6)	C(12)–C(13)–C(14)	120.8(9)
C(2)–C(1)–C(9)	116.2(6)	C(13)–C(14)–C(15)	119.6(9)
C(4)–C(3)–C(2)	115.3(7)	C(14)–C(15)–C(16)	119.5(8)
C(4)–C(10)–C(5)	117.9(6)	C(15)–C(16)–C(11)	122.1(7)
C(5)–C(6)–C(7)	119.6(7)	C(16)–C(11)–C(12)	118.0(7)

61.6° (see Table 3). In the fused benzene ring the aromatic carbon–carbon bonds range from 1.37(1) to 1.40(1) Å; the mean value, 1.39(1) Å, is comparable with the accepted value of 1.397 Å. On the other hand, in the C(11)—C(16) ring, the mean value is 1.38(1) Å, the shortening probably being due to libration effects. The C(8)–C(11) bond distance of 1.49(1) Å is close to the accepted value for a C(sp^2)–C(sp^2) single bond, 1.504 Å,[12] thus indicating greatly reduced conjugation between the two aromatic systems, as expected on the basis for two non-coplanar aromatic rings.

TABLE 3

Least-squares planes with deviations (Å) of the relevant atoms from the planes in square brackets

Plane 1 C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)

$$-3.7829X + 9.0451Y + 7.7248Z = 0.3552$$

[C(1) 0.118, C(2) 0.170, C(3) −0.213, C(4) 0.160, C(5) −0.036, C(6) −0.037, C(7) 0.009, C(8) 0.044, C(9) 0.005, C(10) 0.016, Cl(1) −1.790, Cl(2) 1.941, Cl(3) −1.999, Cl(4) 1.872, Cl(5) −0.129]

Plane 2 C(11), C(12), C(13), C(14), C(15), C(16)

$$5.8130X + 9.2798Y + 5.0162Z = 3.4049$$

[C(11) −0.002, C(12) 0.007, C(13) −0.008, C(14) 0.004, C(15) 0.002, C(16) −0.003]

Angle between the planes 61.6°

The alicyclic moiety of the adduct shows a half-chair conformation with the four chlorine atoms in axial and pseudoaxial positions. Therefore, their configuration can be defined as 1ε,2x,3x,4ε.* The average length of the carbon–carbon single bonds in the cyclohexene

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* The relevant torsion angles (°) are Cl(1)–C(1)–C(2)–Cl(2) −149.7, Cl(3)–C(3)–C(2)–Cl(2) 165.5, and Cl(3)–C(3)–C(4)–Cl(4) −154.1.

ring, which has the C(9)–C(10) distance in common with the benzene ring, is 1.52(1) Å, shorter than the usual value:[12] nevertheless this slight difference has negligible significance on the energy. The average length of the C(sp^3)–Cl bond is 1.807(7) Å, in good agreement with previously reported values for similar chlorotetralins.[6]

The Cl(5)–C(5) distance of 1.734(7) Å is very close to the sum of single bond covalent radii, 1.74 Å, *i.e.* 0.75 Å for C(sp^2) and 0.99 Å for Cl,[12] but it is significantly longer than the reported values for chlorobenzenes (1.69 Å),[12] indicating that the amount of double bond character in this carbon–chlorine bond is very reduced.

The relative displacements of C(2) (+0.170 Å) and C(3) (−0.213 Å) with respect to the plane through C(1)–C(10) ring system establish the half-chair geometry of the puckered ring (see Table 3). A scale model shows that C(2) and C(3) are prevented from attaining their conformationally 'normal' positions, to reduce the mutual repulsions between Cl(2) and Cl(4) and Cl(1) and Cl(3) [contact distance 3.282(6) and 3.347(6) Å respectively].

The stereochemistry of (1) in the solid state, as deduced from *X*-ray data, parallels the situation of this adduct in solution, as found by ^{1}H n.m.r. studies (see Experimental section). The observed slight puckering of the half-chair ring releases the double 1,3-diaxial halogen repulsions: moreover, such an effect does not produce a remarkable enhancement in the relative *peri*-like adverse interactions between 1-Cl and 8-Ph and 4-Cl and 5-Cl (see Table 2).

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REFERENCES

[1] M. C. Aversa, G. Cum, P. Giannetto, and G. Romeo, *J. Chem. Res.*, 1977, (*S*) 176, (*M*) 1915.

[2] K. R. Bedford, G. W. Burton, and P. B. D. de la Mare, *Tetrahedron Lett.*, 1973, 3205.

[3] M. C. Aversa, G. Cum, P. Giannetto, and G. Romeo, *J. Chem. Res.*, 1979, (*S*) 338, (*M*) 3979.

[4] P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc. B*, 1966, 827.

[5] J. W. Barnett, K. R. Bedford, G. W. Burton, P. B. D. de la Mare, S. Nicolson, and H. Suzuki, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1908.

[6] M. A. Lasheen, *Acta Crystallogr.*, 1952, **5**, 593.

[7] J. E. Godfrey and J. M. Waters, *Cryst. Struct. Commun.*, 1973, **2**, 677.

[8] G. Cum, Ph.D. Thesis, University of London, 1967.

[9] K. R. Bedford, G. W. Burton, P. B. D. de la Mare, and H. Suzuki, *J. Chem. Soc., Perkin Trans. 2*, 1974, 459.

[10] D. F. DeTar, 'Computer Programs for Chemistry,' Benjamin, New York, 1968, vol. 1, pp. 1*ff*.

[11] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974.

[12] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1959.