

Isolation of axial conformers of chloro- and bromocyclohexane in a pure state as inclusion complexes with 9,9'-bianthryl, and the discovery of a novel 1,3 diaxial Cl \cdots H weak interaction

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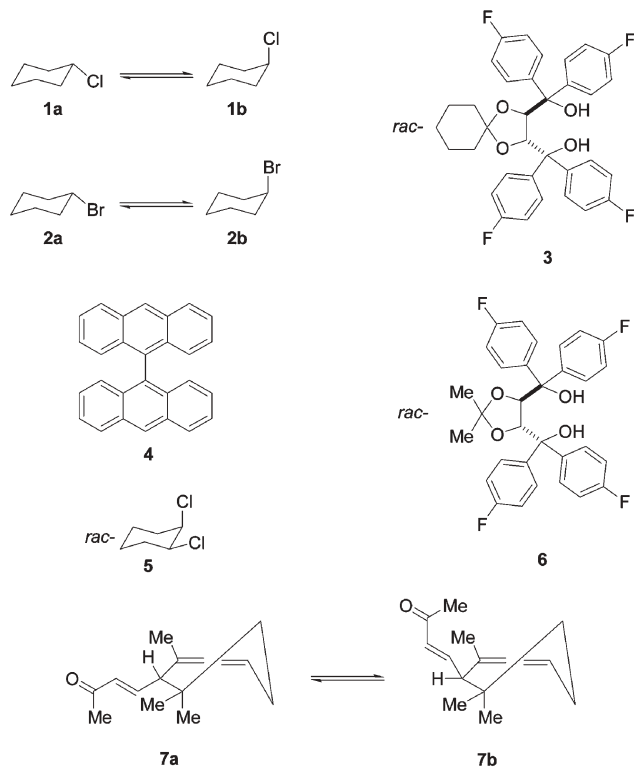
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The axial conformers of chloro- and bromocyclohexane were isolated in a pure state as inclusion complexes with 9,9'-bianthryl, and a 1,3 diaxial Cl \cdots H weak interaction was discovered by X-ray analysis of the axial conformer of chlorocyclohexane.

Conformational studies of cyclohexanes substituted with sterically less bulky groups, such as chloro- (**1**) and bromocyclohexane (**2**) are of considerable interest. Nevertheless, it is not easy to isolate conformational isomers of halocyclohexanes in a pure state at room temperature due to the dynamic equilibrium between the equatorial and axial conformers, although in the solid state at sufficiently low temperature or high pressure **1** and **2** exist only in the equatorial form (**1a**, **2a**).¹

Isolation of equatorial conformers of chloro- (**1a**) and bromocyclohexane (**2a**) in a pure state as inclusion complexes with racemic *trans*-2,3-bis[di(*p*-fluorophenyl)hydroxymethyl]-1,4-dioxaspiro[4.5]decane (**3**) and their structural study by IR and X-ray analysis has been reported.² Although this is the first example of the isolation of equatorial conformers of chloro- (**1**) and bromocyclohexane (**2**) in a pure state at room temperature, it is easier to isolate the relatively stable equatorial conformers rather than the unstable axial conformers. Isolation of the axial conformers of halocyclohexanes **1b** and **2b** is difficult and has not succeeded by any method so far. In this paper, we report isolation of the axial conformers **1b** and **2b** in a pure state as inclusion complexes with a 9,9'-bianthryl host (**4**).³ We also report the interesting finding of a 1,3 diaxial Cl \cdots H weak interaction in **1a** and *cis*-1,2-dichlorocyclohexane (**5**) as their inclusion compounds with **4** and racemic *trans*-5,5-dimethyl-2,3-bis[di(*p*-fluorophenyl)hydroxymethyl]-1,4-dioxacyclopentane (**6**), respectively.

Previously, we have reported that solid **4** contains a small cavity in which a molecule of compact and cubic shape may be accommodated.³ For example, of two α -ionone conformers, the equatorial (**7a**) and axial quasi-chair form (**7b**), the latter, of more compact and cubic shape, is exclusively included in the cavity of **4**.⁴ The former conformer, which has a longer and less compact structure, is not included by **4** since the cavity **4** is too small. On the basis of these data, the host **4** was employed to trap the axial conformers **1b** and **2b**. Recrystallization of **4** from **1** or **2** gave a 1:1



inclusion complex of **1b** (**8**) or **2b** (**9**) with **4** as orange block crystals in 66 and 41% yields, respectively.

X-Ray analysis of **8** showed that only the axial conformer (**1b**) is accommodated in the cavity, although half of the **1b** molecules are disordered (Fig. 1).[†] The reason why half of the **1b** molecules are normal and the other half are disordered is not clear. However, as shown in Fig. 1, the closest contacts between Cl atoms and the host molecules suggest that the spaces in the structure allow two disordered positions. The host molecules **4** form a multi-layer structure with cavities in each layer. The closest contacts of the axial Cl atoms shown in Fig. 1 are to the hosts in the adjacent layer. Fig. 2 shows the packing diagram of **8** in one layer viewed along the C–C single bond of **4**. Two independent **1b** molecules are located in the space surrounded by four propeller-like anthracene moieties. X-Ray structures of both the normal and disordered **1b** molecules are shown in Figs. 3 and 4, respectively.

However, X-ray analysis of **9** could not be carried out, since **9** did not form an appropriate crystal for analysis. Nevertheless, it is probable that the axial conformer (**2b**) is also accommodated in **9**.

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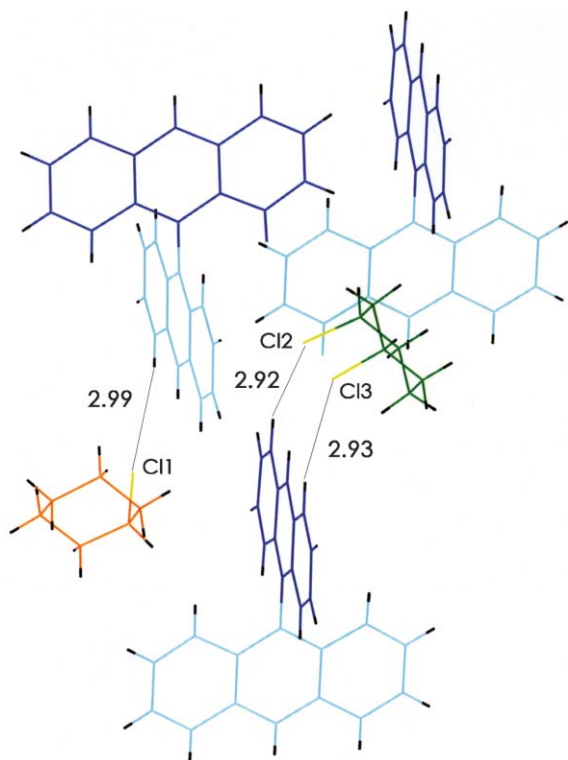


Fig. 1 X-Ray structure of **8** showing the closest contacts between Cl atoms of **1b** and **4**.†

This was confirmed by IR spectral analysis of **9** (Fig. 5) and by comparison of its X-ray powder diffraction pattern with that of **8** (Figs. 6 and 7). The IR spectra of **2** itself, **4** and **9** are shown in Fig. 5. Although **2** shows equatorial and axial C–Br stretching absorptions at 687 and 659 cm^{-1} , respectively, **9** showed only the axial C–Br absorption at 659 cm^{-1} but not any equatorial absorption at around 687 cm^{-1} . The X-ray powder diffraction pattern of **9** (Fig. 7) is quite similar to that of **8** (Fig. 6).

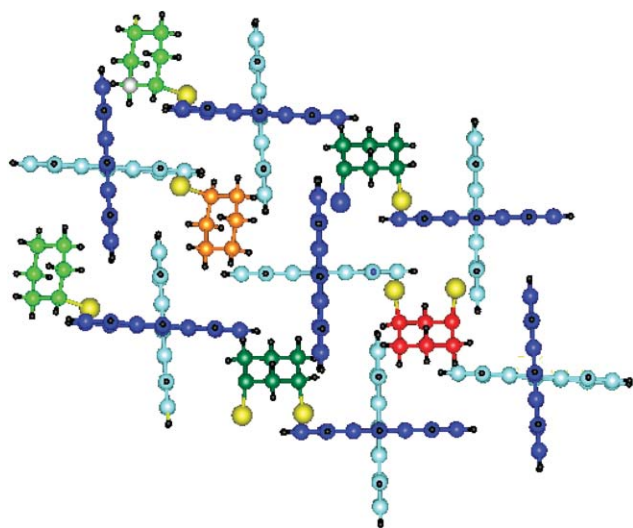


Fig. 2 Packing diagram of **8** in one layer viewed along the C–C single bond of **4**.

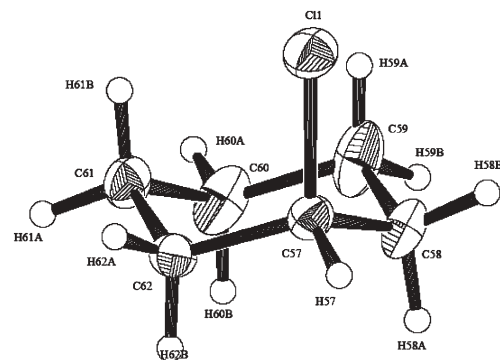


Fig. 3 X-Ray structure of normal **1b** in **8**.

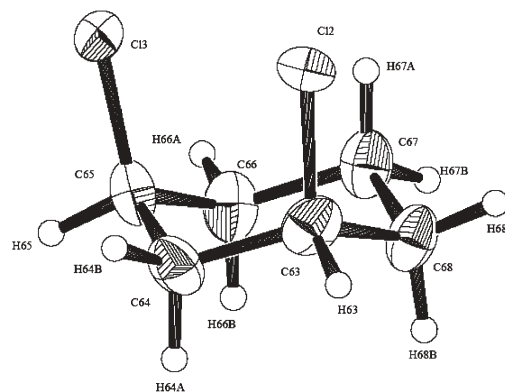


Fig. 4 X-Ray structure of disordered **1b** in **8**.

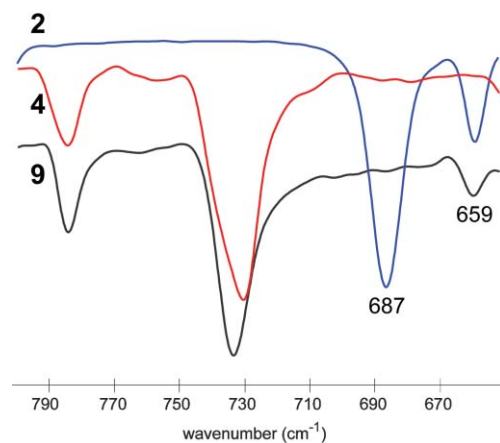


Fig. 5 IR spectra of **2** (neat), and **4** and **9** using the ATR (attenuated total reflection) method.

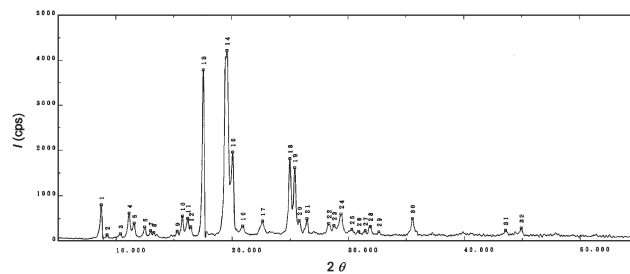


Fig. 6 X-Ray powder diffraction pattern of **8**.

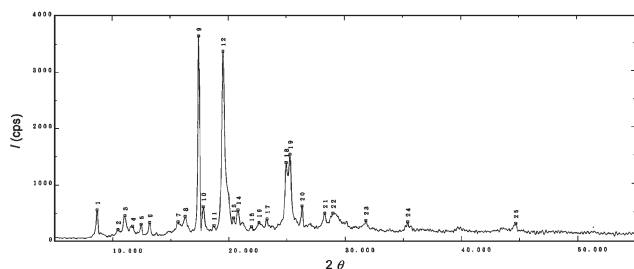


Fig. 7 X-Ray powder diffraction pattern of **9**.

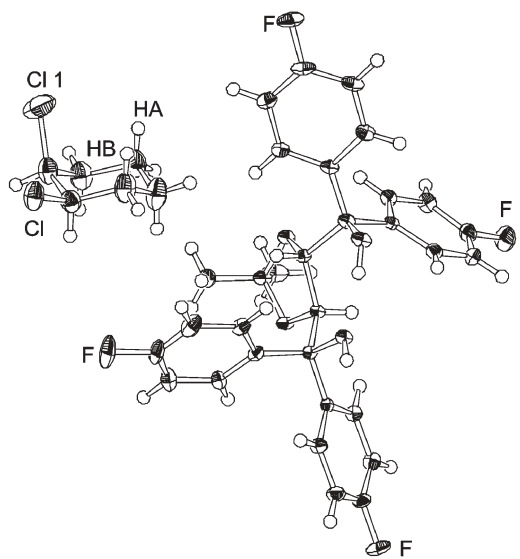


Fig. 8 X-Ray structure of **10**.[†]

It was found that the distances between the axial Cl and H of normal **1b** in **8** (Fig. 3), Cl1–H59A (2.90 Å) and Cl1–H61B (2.88 Å), are shorter than the sum (2.95 Å) of the van der Waals radii of Cl (1.75 Å) and H (1.20 Å). The distances between the Cl and H of disordered **1b** in **8** (Fig. 4), Cl2–H67A (2.90 Å) and Cl3–H67A (2.90 Å), are also shorter than the sum of the van der Waals radii of Cl and H. These data suggest the presence of a weak interaction between the axial Cl and H in **1b**. The common knowledge that 1,3 diaxial interactions in the chair form of a cyclohexane ring destabilize the molecule due to a steric repulsion seems not always to be correct.

In order to confirm that the 1,3 diaxial Cl···H interaction is not special for the axial chlorocyclohexane (**1b**), the structure of *cis*-1,2-dichlorocyclohexane (**5**), which is included in the complex (**10**) with

the host **6**, was studied. Recrystallization of **6** from **5** gave a 1:1 complex of **5** and **6** (**10**) as colorless block crystals. X-Ray analysis of **10**[†] showed that distances between Cl1–HA (2.93 Å) and Cl1–HB (2.94 Å) in **5** are again shorter than the sum (2.95 Å) of the van der Waals radii of Cl and H (Fig. 8). The data support the concept that the 1,3 diaxial Cl···H interaction is general in cyclohexane ring systems. The interaction is expected to be general for cyclohexane derivatives which have an electron rich and hence proton-attractive group in their axial position. This idea has been proposed by Nishio and his co-workers.⁵

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Notes and references

[†] Crystallographic data for **8** were collected at 173 K on a Rigaku Mercury with Mo-K α . Formula = C₂₈H₁₈·C₆H₁₁Cl, M_r = 473.06, crystal system = triclinic, space group = $P\bar{1}$ (#2), lattice parameters a = 12.043(4) Å, b = 19.012(6) Å, c = 10.994(3) Å, α = 96.075(12)°, β = 102.296(11)°, γ = 89.397(12)°, V = 2445.3(14) Å³, Z = 4, D_{calc} = 1.285 g cm⁻³, number of unique reflections = 10053, R_{int} = 0.0170 up to a 2θ = 55°, number of parameters = 641, R_1 = 0.0800, wR = 0.2610, gof = 1.130 for 4738 reflections. CCDC 263448. See <http://www.rsc.org/suppdata/cc/b5/b501633a/> for crystallographic data in CIF or other electronic format.

Crystallographic data for **10** were collected at 123 K on a Rigaku RAXIS-IV imaging plate diffractometer with Mo-K α . Data for **10**; formula = C₃₁H₂₆F₄O₄·C₆H₁₀Cl₂, M_r = 691.59, crystal system = triclinic, space group = $P\bar{1}$ (#2), lattice parameters a = 10.1223(4) Å, b = 12.6116(6) Å, c = 13.7458(3) Å, α = 86.930(1)°, β = 89.931(1)°, γ = 71.358(1)°, V = 1660.09(14) Å³, Z = 2, D_{calc} = 1.383 g cm⁻³, number of unique reflections = 6942, R_{int} = 0.0160 up to a 2θ = 55°, number of parameters = 424, R_1 = 0.0564, wR = 0.1750, gof = 1.403 for 5431 reflections. CCDC 263445.

Preparation of inclusion complexes. When a solution of **4** (30.0 mg) in **1** (0.5 ml) was kept at room temperature for 2 h, **8** [26.4 mg, 66% yield based on **4**, mp 302–315° (dec.)] was obtained as orange block crystals. By a similar method, **9** was prepared from **4** (30.0 mg) and **2** (0.5 ml) as orange block crystals [17.8 mg, 41% yield, mp 302–315° (dec.)]. When a solution of **6** (48.0 mg) in **5** (0.2 ml) was kept at room temperature for 1 h, **10** was obtained as colorless block crystals (32.7 mg, 53% yield based on **6**, mp 136.5–199.0°).

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