# Isolation of a nearly eclipsed chiral rotamer of 1,2-dichloroethane as an inclusion crystal with a chiral host compound

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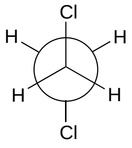
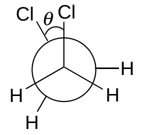
**A nearly eclipsed chiral rotamer of 1,2-dichloroethane has been isolated in a pure state as an inclusion complex crystal with the chiral host compound, (*S*)-(−)-2-bromo-3,3a,8-triphenyl-1,3a-dihydrocyclopenta[*a*]inden-1-one and an X-ray crystal structure of the complex has been studied.**

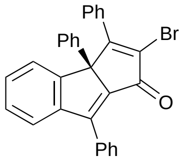
The conformation of simple acyclic molecules has long been studied, mostly spectroscopically and theoretically.[1] By these studies, it has been established that the energetically most stable rotamer (rotational isomer) around the C–C bond of 1,2-disubstituted ethane is the *trans* form. For example, 1,2-dichloroethane **1** exists in the *trans* form **1a**, the structure of which was elucidated by X-ray analysis of **1** crystallised at 212 K using a miniature zone melting procedure,[2] although the energy difference between the *trans* and *gauche* form of gaseous **1** has been estimated to be small (0.9–1.3 kcal $mol^{-1}$ by experiment and 0.91 kcal $mol^{-1}$ by calculation; 1 cal = 4.184 J).[1] The existence of **1** in the eclipsed form of the two chlorine atoms **1b** ($\theta$ = 0) is excluded, because of its instability due to strong repulsions between not only the chlorine atoms but also hydrogen atoms. The possibility of isolation of the *gauche* form **1b** ($\theta$ = 60°) would also be excluded, and isolation of the *gauche* form has never been reported.



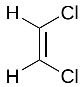
**1a**
*trans*-form



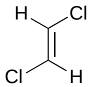
(*M*)-**1b**
eclipsed-form



(*S*)-(−)-**2**



**4**



**6**

We here report isolation of a nearly eclipsed form of **1** as a 1 : 1 inclusion complex crystal with a host compound. Recrystallisation from **1** of the optically active host compound, (*S*)-(−)-2-bromo-3,3a,8-triphenyl-1,3a-dihydrocyclopenta[*a*]-inden-1-one **2**,[3,4] gave their 1 : 1 inclusion complex **3**§ as yellow prisms in quantitative yield (mp 100–104 °C). In comparison, a 1 : 1 inclusion complex **5**§ of **2** and *cis*-1,2-dichloroethylene **4** was also prepared as pale yellow prisms by recrystallization of **2** from **4**. However, *trans*-1,2-dichloroethylene **6** did not form an inclusion complex with **2**. The 1 : 1 host–guest ratio in **3** and **5** was determined by $^1$H NMR spectroscopy, thermogravimetric measurement and elemental analyses.

In order to study the molecular conformation of **1** in **3**, an X-ray crystal structure of **3** was determined.¶ The X-ray analysis established that **1** exists as the nearly eclipsed form **1b** [$\theta$ = 36(2)°] as shown in Fig. 1. This is the first example of the isolation of the nearly eclipsed rotamer. The molecule **1b**, which adopts a conformation between the *gauche* and eclipsed form is chiral. Since **2** is an optically active (*S*)-(−)-host,‖ only one enantiomer of **1b**, the left-handed helical form (*M*)-**1b**,[6] is accommodated in **3**. This is also the first case of the isolation of an optically active rotamer of 1,2-dichloroethane. The reason for this surprising finding that sterically the very unfavourable rotamer can be trapped at room temperature in an inclusion complex was studied by comparison of the molecular and crystal structures of **3** with those of **5**.¶ The crystal structure of **5** is shown in Fig. 2. The two crystal lattice parameters are surprisingly similar, with only the 0.09–0.4% difference as shown in the footnote.¶ The two crystals adopt the same space group of $P2_12_12_1$. The location of the host and guest molecules, as well as their conformation, closely resemble to each other, as expected from the cell parameter comparison. The intramolecular Cl••Cl distance is retained, at 3.205(5) and 3.315(5) Å for **1a** in **3** and **4** in **5**, respectively. The closest contacts between the host and the guest are observed for the C=O oxygen of **2** and the Cl atom of **1b** [3.288(6) Å], and the C=O oxygen of **2** and the Cl atom of **4** [3.247(7) Å].

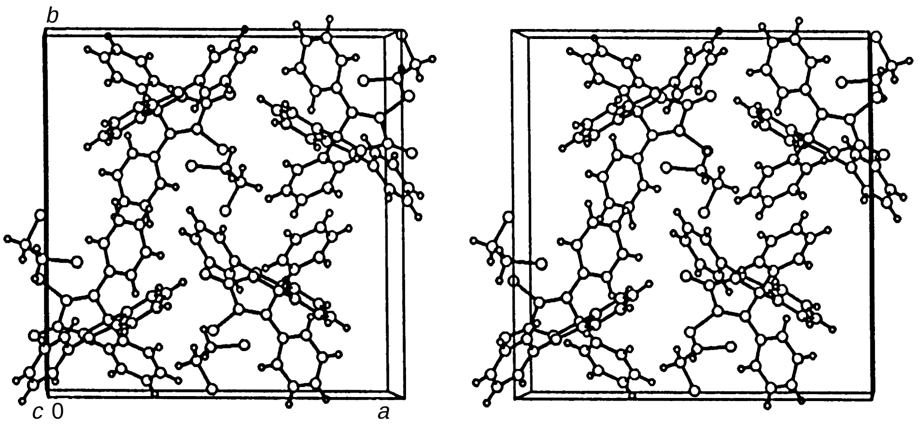


**Fig. 1** Stereoview of the 1 : 1 inclusion complex **3** of **2** and (*M*)-**1b**

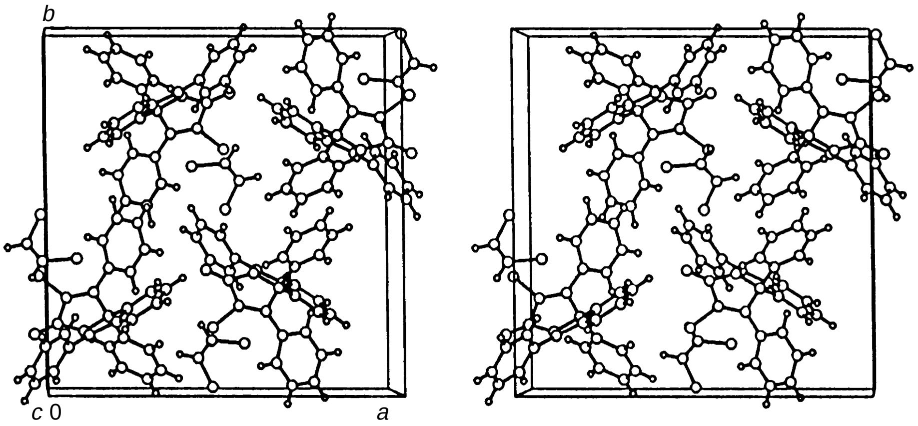


**Fig. 2** Stereoview of the 1 : 1 inclusion complex **5** of **2** and **4**

The dissociation energies of **3** (51 kJ mol$^{-1}$) and **5** (59 kJ mol$^{-1}$), which were estimated from their differential scanning calorimetry data, are also comparable, however, the slightly more stable **5** should be formed a little more readily. In fact, recrystallization of (+)-**2** (40 mg) from a 1 : 1 mixture of **1** (200 mg) and **4** (200 mg) gave **5** (32 mg, 67% yield) exclusively. This is a good example of extremely precise molecular recognition in molecular assembly.

The chlorine atoms of **1** and **4** seem to be the key to deciding whether the inclusion of the guest in the cavity occurs or not. Thus, in the two cases, the two chlorine atoms are located in similar positions. Since the *trans*-isomer of **4** (**6**) cannot be included with **2**, a guest molecule in which the two chlorine atoms are located in a *trans*-position such as **1a** would be unfavourable for accommodation in the cavity of the complex with **2**. Presence of **1b** in **2** also suggests that some electrostatic interaction between the two chlorine atoms is contributing to the stabilisation of the sterically unfavourable eclipsed-form.

## Footnotes

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§ *Preparation of inclusion complexes*. Compound **3**: When a solution of **2** (50 mg) in 1,2-dichloroethane (0.5 ml) was kept at room temperature for 2 h, a 1 : 1 inclusion complex **3** was obtained as yellow prisms (39 mg, 69% yield, mp 100–104 °C); $\nu_{max}$ (Nujol)/cm$^{-1}$ 1688 (C=O); $^1$H NMR ($CDCl_3$): $\delta$ 3.7 (s, $CH_2$, 4 H) and 7.1–7.8 (m, Ar, 19 H); Calc. for $C_{32}H_{23}OBrCl_2$: C, 66.92, H, 4.04. Found: C, 67.00, H, 4.11%.

Compound **5**: When a solution of **2** (50 mg) in *cis*-dichloroethylene (0.5 ml) was kept at room temperature for 2 h, a 1 : 1 inclusion complex **5** was obtained as yellow prisms (48 mg, 73% yield, mp not clear); $\nu_{max}$ (Nujol)/cm$^{-1}$ 1693 (C=O); $^1$H NMR ($CDCl_3$): $\delta$ 6.4 (s, =CH, 2 H) and 7.1–7.8 (m, Ar, 19 H); Calc. for $C_{32}H_{21}OBrCl_2$: C, 67.16, H, 3.70. Found: C, 67.22, H, 3.63%. When a solution of **2** (50 mg) in a mixture of 1,2-dichroloethane (0.25 ml) and *cis*-1,2-dichloroethylene (0.25 ml) was kept at room temperature for 2 h, **5** (45 mg, 68% yield) was obtained in the pure state.

¶ *Crystal data* for **3**: $C_{32}H_{23}OBrCl_2$, $M$ = 574.34, orthorhombic, space group $P2_12_12_1$, $a$ = 16.748(2), $b$ = 17.113(3), $c$ = 9.351(3) Å, $U$ = 2680.1(9) Å$^3$, Mo-K$\alpha$ ($\lambda$ = 0.71069 Å), $D_c$ = 1.423 g cm$^{-3}$, $Z$ = 4, $F$(000) = 1168, pale yellow plates, crystal dimensions 0.22 × 0.20 × 0.40 mm, $\mu$(Mo-K$\alpha$) = 17.41 cm, 2$\theta$–$\omega$ scan, 3480 independent reflections (5 < 2$\theta$ < 55.0°). The final $R$ = 0.045 and GOF = 1.53 for the 1775 reflections with $I > 3\sigma(I)$. Reflection data were collected on a Rigaku AFC5S four-circle diffractometer and the structure was solved by TEXSAN software using a VAXstation 3200.

*Crystal data* for **5**: $C_{32}H_{21}OBrCl_2$, $M$ = 572.343, orthorhombic, space group $P2_12_12_1$, $a$ = 16.763(2), $b$ = 17.033(1), $c$ = 9.318(1) Å, $U$ = 2660.5(6) Å$^3$, Mo-K$\alpha$ ($\lambda$ = 0.71069 Å), $D_c$ = 1.429 g cm$^{-3}$, $Z$ = 4, $F$(000) = 1160, pale yellow plates, crystal dimensions 0.35 × 0.25 × 0.50 mm, $\mu$(Mo-K$\alpha$) = 17.53 cm, 2$\theta$–$\omega$ scan, 3456 independent reflections (5 < 2$\theta$ < 55.0°). The final $R$ = 0.045 and GOF = 1.46 for the 1579 reflections with $I > 3\sigma(I)$. Reflection data were collected on a Rigaku AFC5S four-circle diffractometer and the structure was solved by TEXSAN software using a VAXstation 3200.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/478.

‖ The absolute configuration of the host (−)-**2** has been determined to be ($S$) by comparison of the converged $R$-factors, *i.e.* 0.045 and 0.066 for the ($S$)- and ($R$)-enantiomers, respectively.

## References

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