Enantiomeric 1-Phenylpropyl and 1-Phenylbutyl 9-Anthroates as Novel Chiral Inclusion Complexing Agents. Preparation and *X*-Ray Analysis of the 6:1 Inclusion Complexes with n-Hexane

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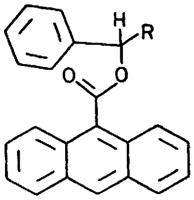
Summary Resolved 1-phenylpropyl and 1-phenylbutyl 9-anthroates, when crystallised from n-hexane, form 6 : 1 inclusion molecular complexes which are isostructural; *X*-ray analysis of the propyl derivative demonstrates the formation of a channel structure by the anthracenes, in which the n-hexane is included.

In the course of our systematic studies on the utilisation of differences in the packing modes of racemic compounds and enantiomeric crystals for the purpose of enantiomeric purification *via* topochemical photodimerisation methods,[1] and for determination of enantiomeric excess *via* differences in emission properties,[2] we observed that the optically active compounds (**1**) and (**2**), when recrystallised from n-hexane form inclusion molecular complexes of stoicheiometry 6 : 1. A combined differential scanning and thermal gravimetric analysis clearly demonstrates that the n-hexane leaves the crystal only on melting.



(1); R = Et
(2); R = Pr^n

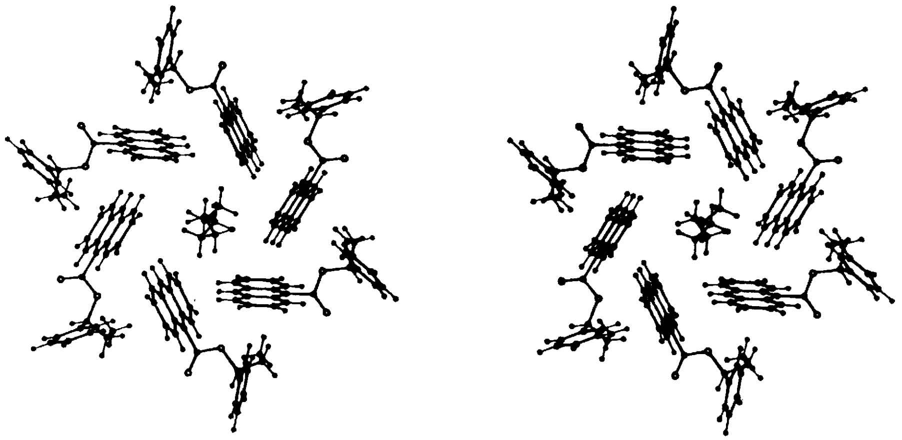


FIGURE 1. Stereoscopic view along *c*-axis of the channel structure of the (*R*)-(+)-(**1**)–n-hexane.

The propyl complex (*R*)-(+)-$C_{24}H_{20}O_2 \cdot \frac{1}{6}C_6H_{14}$, m.p. 106 °C, crystallises in the hexagonal space group $P6_5$, with $a = b = 18 \cdot 110(3)$, $c = 10 \cdot 715(1)$ Å, $Z = 6$ units of (**1**) and 1 of n-hexane; $D_c = 1 \cdot 16$, $D_m = 1 \cdot 15$ g cm^{-3}. The butyl derivative $C_{25}H_{22}O_2 \cdot \frac{1}{6}C_6H_{14}$ is isomorphous with $a = b = 18 \cdot 54$, $c = 10 \cdot 82$ Å, $Z = 6$ units of (**2**) and 1 of n-hexane.

A full *X*-ray analysis of (*R*)-(+)-(**1**) has been performed. *X*-Ray data were collected on a Siemens diffractometer with Cu-K_α radiation. The host molecule was located by direct methods,[3] and the guest molecule was located by difference Fourier techniques. The final *R* factor is 0·065 for 1833 reflections (266 treated as unobserved reflections).†

The host molecules, which adopt a helical arrangement along the 6_5 axis, are connected primarily by anthracene· · · and phenyl C–H· · · anthracene rings contacts (Figure 1). The contacts between the anthracene rings are similar to the herring-bone contacts in the structure of anthracene itself.[4] The n-hexane guest molecule (Figure 2) has an extended zig-zag planar chain but for the terminal C atom torsional angle C–C–C–C(H$_3$) = 100°. The long axis of the planar segment of n-hexane makes an angle of 18° with the *c*-axis.

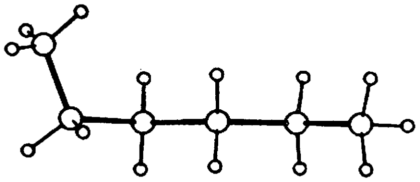


FIGURE 2. n-Hexane molecule in the channel of (**1**).

It is not clear why the guest molecule does not adopt a completely planar zig-zag structure with its long molecular axis parallel to the *c*-axis. The packing energies for the guest molecule of this suggested conformation, and lying along the channel axis with different orientations about the *c*-axis were calculated,‡ and yielded a most stable arrangement of energy −10·5 kcal mol^{-1}. The packing energy, when the guest molecule is as observed, is −10·2 kcal mol^{-1}, which is almost equal to, but not lower than, that of the above alternative structure.

The diameter of the channel is *ca.* 5 Å, comparable to the dimensions of the channel of urea, suggesting that this compound also may be used as a convenient reagent for the resolution of enantiomers of chiral paraffins,[5] or for the performance of stereospecific polymerisations[6] and asymmetric synthesis in the chiral channels.

(*Received, 8th August* 1977; *Com.* **834**.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The calculations were carried out by using the method of atom–atom potentials. We thank Dr. K. Mirsky for her help with this method.

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