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STEREOISOMERISM IN MOLECULAR BEVEL-GEARS. OPTICAL RESOLUTION OF THE DL ISOMERS OF BIS(2- AND 3-CHLORO-9-TRIPTYCYL)METHANES AND ETHERS [1]

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Resolution of the dl isomers of bis(2- and 3-chloro-9-triptycyl)-methanes and ethers into the optical antipodes has been achieved by hplc using a column of the silanized silica gel coated with chiral poly(triphenylmethyl methacrylate).

The rotational motions around the two C-X bonds at the bridgehead of molecules (9-triptycyl)$_2$X (X = O and CH$_2$) are rapid and disrotatorily coupled. Labeling of one of the benzene rings on each triptycene unit in these di-triptycyl compounds gives birth to new stereoisomerism due to the different phase relationship between the labeled rings. A dl pair and a meso isomer thus generated by symmetrical single labeling are shown in Figure 1.[3] These isomers are expected to have only a minute difference in their macroscopic properties, since each isomer consists of three different rotamers which are interconverting rapidly. The corresponding property attributable to each rotamer would be averaged out. In spite of these pessimistic expectation, the separation of the dl and meso isomers was realized by hplc and described recently.[4] This paper reports further separation of the dl isomers into the optical antipodes, completing the separation of all the possible stereoisomers in the singly labeled molecular bevel-gear of bis(9-triptycyl)methanes and ethers.

The optical resolution was effected by hplc on a column developed by Okamoto et al:[5] the packing material was the micro silica gel coated with (+)-poly(triphenylmethyl methacrylate) (ca. 20 wt %).[6] Chromatogram of analytical separation on a 4.6 (i.d.) × 250 mm column using 0.6 ml/min flow of methanol is reproduced in Figure 2. While almost complete separation was achieved for 2-chloro derivatives **1** and **3**, the results on 3-chloro compounds **2** and **4** were les satisfactory. The chiral recognition of the chlorine labels in the conformationally fluxional gear-shaped molecules is firstly surprising.

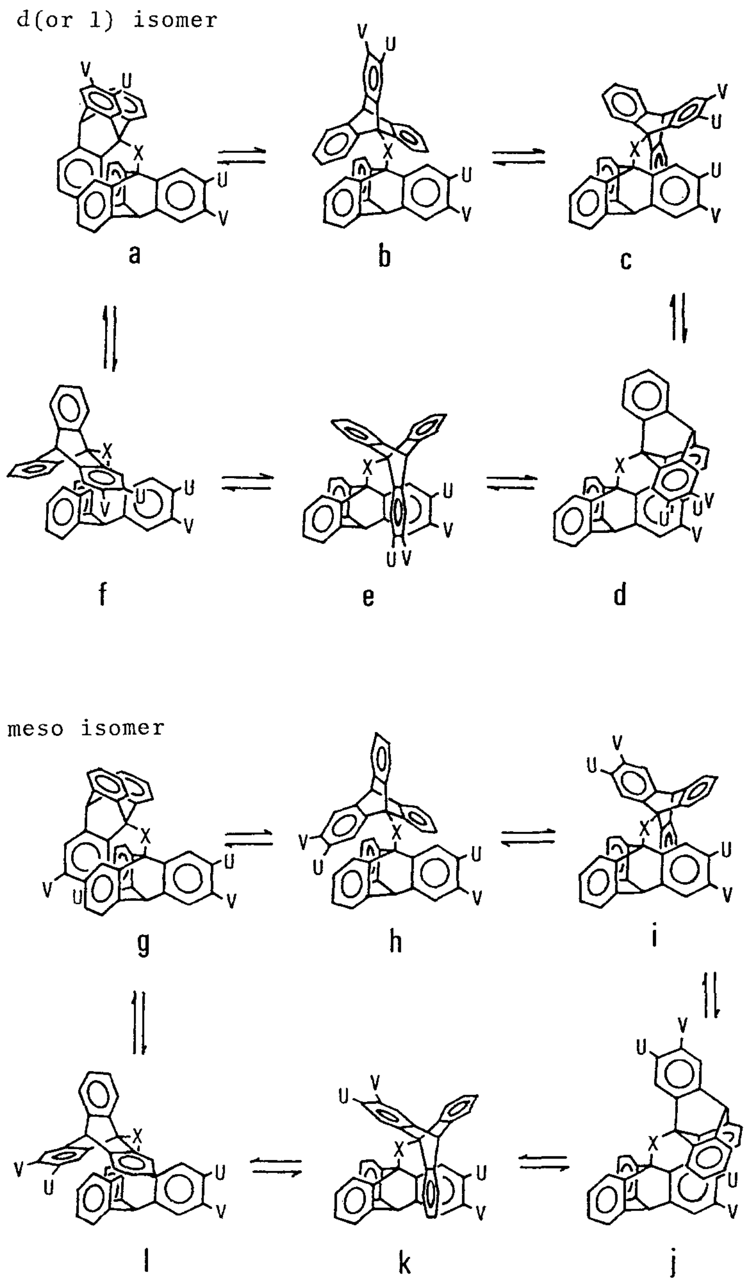

Figure 1. Perspective view of the d(or 1) and meso isomers. Note that rotamers a = b, c = f and d = e are all chiral, while g = j has a plane of symmetry and h = i is a mirror image of k = 1.

Secondly, the different degree of separation seems to be understandable, since the 2-chloro substituents are located closer to each other than the chlorine atoms at the position 3. We recall separation of even the racemic and meso isomers was not successful in the case of bis(4-methyl-9-triptycyl) ether in which the labels were farther apart.[1]

Preparative works were carried out on a 7.2 (i.d.) × 250 mm column with a flow rate of 3 ml/min. Two ml of saturated solutions of 1 or 3 (ca. 0.5 mg) in acetonitrile were injected at a time. The amount was less in the case of 2 and 4 because of poorer resolution of the enantiomers. The faster eluting enantiomers of 1 and 3 were obtained in high optical purity by a single chromatographic procedure. The other enantiomers eluting last were obtained in the pure form only after repeated chromatography. For the racemic compounds of 2 and 4, even the enantiomers corresponding to the first peak were difficult to obtain in reasonable optical purity.

Compound No.	X	U	V
1	CH_2	Cl	H
2	CH_2	H	Cl

Compound No.	X	U	V
3	O	Cl	H
4	O	H	Cl

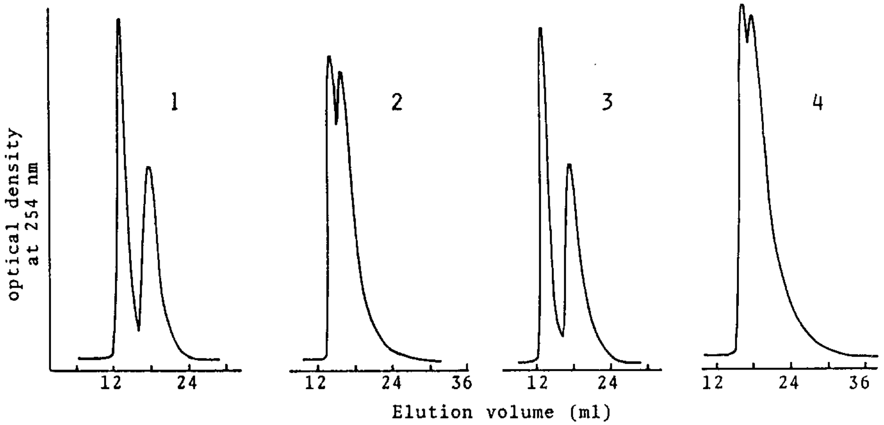

Figure 2. Hplc resolution of the dl isomers of 1 ~ 4 into the enantiomers.

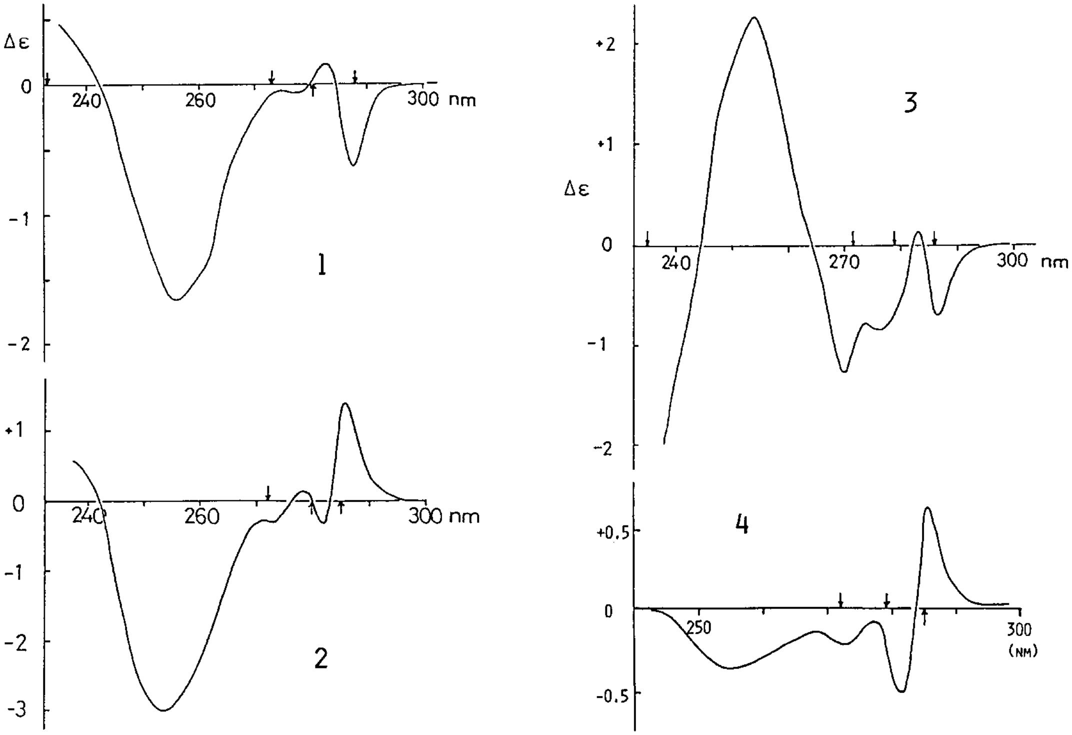

Figure 3. CD curves for the first eluted enantiomers of 1 ~ 4. The arrows indicate the λ_{max} in the absorption spectra.

In Figure 3 are shown CD spectra of the first eluted enantiomers of **1** ~ **4** obtained in dichloromethane solutions.[7] The smaller elipticity of **4** indicates the lower optical purity of the sample. The shape and appearance of the CD curves are not simple and seem to depend not only on the position of the chlorine atoms but also on the kind of the central atom X. Since these molecules are conformationally flexible (see Figure 1), there should be more than one sets of arrangements of the transition dipoles due to the triptycene unit, giving rise to several optically active transitions.

The first eluted enantiomers of **1** and **3** had the $[\alpha]_D^{25}$ values of +(8 ± 1.5)° (C 0.27, CH_2Cl_2) and -(13 ± 1)° (C 0.53, CH_2Cl_2), respectively.

In conclusion, the stereoisomers due to different phase relationship between the labeled cogs in a bevel gear-shaped molecule are the chemical entity amenable to modern separation and characterization.

References and Notes

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3) For tabulation of the number of possible isomers in labeled gear molecules, see: W. D. Hounshell, C. A. Johnson, A. Guenzi, F. Cozzi, and K. Mislow, Proc. Natl. Acad. Sci. U.S.A., **77**, 6961 (1980). Y. Kawada and H. Iwamura, Tetrahedron Lett., **22**, 1533 (1981).
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6) Hplc was accomplished on a Waters model ALC/GPC apparatus by using methanol as eluant. The column was jacketted with the circulating water kept at 15 °C. Tailing of the chromatographic peaks was unaviodable probably because of strong hydrophobic interaction between the triphenylmethyl parts of the stationary phase and the aromatic solutes. Solvents like hexane and acetonitrile gave no separation of the enantiomers.
7) To avoid possible contamination with chiral impurities due to the column packing material, the eluted samples were purified by preparative layer chromatography before the CD measurements.

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