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A HELICAL CONDUCTOR MODEL OF OPTICAL ACTIVITY[1]: CALCULATION OF THE OPTICAL ROTATION OF TRICYCLO(4.4.0.0^{3,8})DECANE (TWISTANE)

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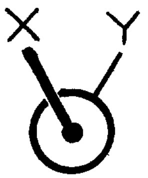
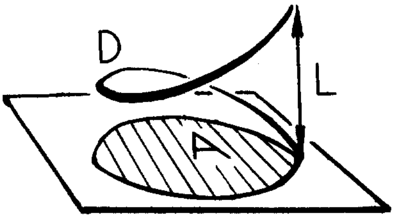
The large optical rotation reported[2,3] for tricyclo(4.4.0.0^{3,8})decane (twistane[4]) ($[M]_D$ 570[2], 590[3], in ethanol) makes it clear that the rotatory contributions of the "non-chromophoric framework" of a rigid chiral molecule may also be substantial. Twistane has a simplicity, rigidity and symmetry (three two-fold rotation axes) that make it an ideal case on which to test models of optical activity intended to take such rotatory effects into account.

We have presented two such models, conveniently identified here as, (a) the Conformational Dissymmetry Model[5] and, (b) the Helical Conductor Model[6]. The first attributes characteristic rotatory effects to twisted four-atom chains (I). It can be used with fair success with simple substances having flexible or relatively flat molecules, where longer chains would have little additional rotatory effect because they are conformationally free to adopt shapes that are essentially enantiomers of one another or are held rigidly in arrangements that are largely coplanar and so of low rotatory power. There are, however, cases[5,7], notably those of substances having rigid molecules with angular substituents or folded nuclei, where sizeable additional effects ("permolecular dissymmetry") would have to be invoked to account for the magnitude - or even the sign - of rotation. Thus, a calculation of the rotation of twistane by this method[2] gave a value ($[M]_D$ 140) which was too low and which has turned out[8], additionally, to be of the wrong sign. The Helical Conductor Model[6] subsumes the first model and is, in principle, applicable to twisted chains of any length, these being regarded now as irregular helices (II) with rotatory contributions in accord with the expression shown below.



$$[M]_D = +k \cdot XY$$

I



$$[M]_D = +652.4 \cdot \frac{LA}{D^2} \cdot \Sigma(\Delta R_D) \cdot f(n)$$

II

Here L is the straight-line distance between the ends of the chain, D is the distance along the chain and A is the area of a projection of the helix on a plane perpendicular to L (all in Ångstrom units). $\Sigma(\Delta R_D)$ is the sum of bond refractions for the chain, using octet refractions for terminal atoms, while f(n) is a function of the refractive index of the solution:

$$f(n) = \frac{1}{n}\left(\frac{n^2 + 2}{3}\right)^2$$

We wish now to report that this model allows a calculation of the rotation of twistane that is correct in sign and, roughly, magnitude as well.

Table I contains coordinates for the carbon atoms of 1R,3R,6R,8R-twistane for the case where all C-C bond distances are 1.540 Å and the bond angles of the central ring (1-2-3-8-7-6) and the two bridges (3-4-5-6 ; 8-9-10-1) are tetrahedral. Such strain as is present is concentrated in the bond angles 2-3-4 (2-1-10; 7-6-5; 7-8-9) (101°50') and 8-3-4 (1-6-5; 3-8-9; 6-1-10) (103°10'). It seems unlikely that the small adjustments required to distribute these strains more equitably would have much effect on the calculations presented here. Figures III-V present projections along the x,y and z axes, respectively; these are also the principal axes of polarizability for twistane and it can be considered that all displacements of charge occur along them. Each projection contains one pair of right-handed and one of left-handed helices. Table II presents a summary of the calculation of the rotatory contribution of each kind of helical unit, using the equation of figure II. The helices in figures III and V do not have terminal atoms; in such cases the only refraction values required are those for the bonds (R_{C-C}1.296)[6]. The helices of figure IV do have terminal atoms (2 and 7); each atom has two bonds in helices so we have split the octet refraction (5.944)[6] between those bonds. The value for f(n) is that for pure ethanol. The net rotation so calculated is: $[M]_D$ + 484 for this enantiomer. This result is in accord with that obtained by direct chemical correlation[8]. It is contrary to assignments[2,3] based on application of the Octant Rule to 2- and 4-twistanone, or of the simple Conformational Dissymmetry Model. This, of course, does not necessarily mean that that model is wrong - only that this is a case for which it is inappropriate and to which the more general model should be applied.

Table I

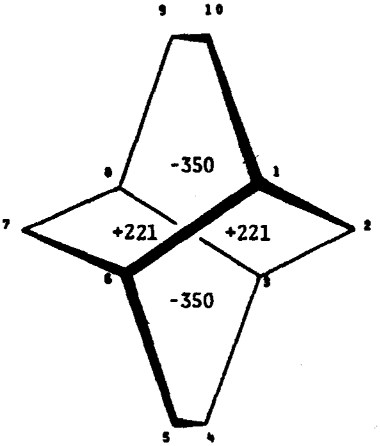
Coordinates for the Carbon Atoms of 1R,3R,6R,8R-Twistane

Atom	x	y	z
1	1.1846	0.6442	0.4218
2	0	1.5335	0
3	-1.1846	0.6442	-0.4218
4	-0.7512	0.1686	-1.8135
5	0.7512	-0.1686	-1.8135
6	1.1846	-0.6442	-0.4218
7	0	-1.5335	0
8	-1.1846	-0.6442	0.4218
9	-0.7512	-0.1686	1.8135
10	0.7512	0.1686	1.8135

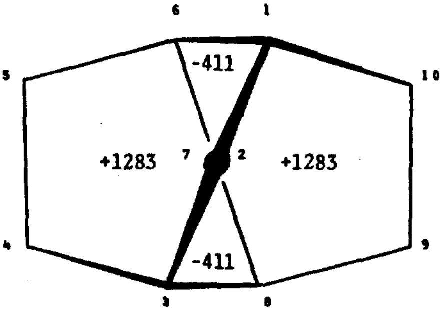
Table II

Rotatory Contributions of Individual Helices

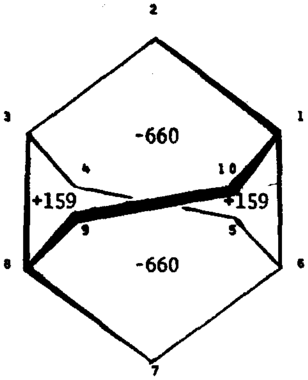
Projection Axis	x		y		z	
Helicity	+	-	+	-	+	-
L $(\mathring{A})$	2.369	2.369	3.067	3.067	3.627	3.627
D $(\mathring{A})$	4.620	6.160	7.700	4.620	6.160	7.700
A $(\mathring{A})^2$	0.6464	1.366	3.186	0.4981	0.4054	2.102
$\Sigma(\Delta R_D)$	3.888	5.184	9.832	7.240	5.184	6.480
f(n)	1.215	1.215	1.215	1.215	1.215	1.215
$\Delta[M]_D$	221.	-350.	1283.	-411.	159.	-660.



III



IV



V

FOOTNOTES AND REFERENCES

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