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SUBSTITUENT EFFECT ON CIRCULAR DICHROISM OF CYCLIC IMIDES

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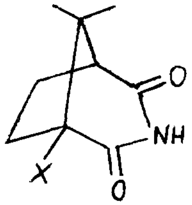
Abstract: CD spectra of α-substituted apocamphorimides show that Cotton effect is strongly effected by the nature of substituent.

Cyclic imides present an interesting model for the chiroptical studies due to their C_{2v} symmetry and rigid structure. However, this type of studies not been given too much attention.[1]

Imides have a strong absorption band of $\pi \rightarrow \pi^*$ character near 200 nm[2], and two less intense bands near 225 and 250 nm, both of $n \rightarrow \pi^*$ character.[3]. They probably correspond to transitions from orbitals which are a symmetrical and antisymmetrical combination of carbonyl n orbitals.

Using of imide model we attempted to find out in what way the Cotton effect is affected by the nature of the substituent responsible for perturbing chromophore symmetry. That problem had been widely studied on the example of ketones,[4,5] where certain substituents in suitable orientation toward the carbonyl group had shown "anti-octant" /"octant-dissignate"/[6] character.

Since a similar problem seems likely to arise in the case of other chromophores, the effect of the kind of substituent cannot be overlooked.



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To test that problem, we synthesized a series of α-substituted apocamphorimides 1-15. In this model, imide chromophore symmetry is perturbed by the substituent at C_α whose orientation toward the chromophore always remains the same.

We compared the perturbation effect caused by the methyl group in the camphorimide 1 with the effects caused by other perturbers which are either electrically charged or polar, or have anizotropic polarizability.

The data listed in the Table indicate that the signs and magnitudes of the Cotton effects for both $n \rightarrow \pi^*$ transitions are strongly affected by the nature of the substituent at C_α . All groups containing heteroatoms or unsaturated systems, apart from the amino-, hydroxy- and acetoxymethyl groups in 12, 14 and 15, contribute to both Cotton effects with a sign opposite to that for the methyl group in 1.

A clue to the elucidation of the effect of substituent on the CD of imides seems to be offered by the Höhn and Weigang's theory,[7] according to which anizotropic and polar perturbers can give contributions to the Cotton effect with signs reversed from those expected. A source of the anomaly may also be the quasi-equatorial orientation of the perturbing groups toward the nodal plane of the chromophore. Therefore, it seems indicated to analyse that questions more thoroughly by investigating the CD spectra of imides with perturbers in a different orientation to the chromophore.

Table. Circular dichroism spectra of imides in methanolic solution / λ in nm, $[\theta]$ in deg. mole^{-1} cm^2/.

Compound	X	λ	$[\theta]$	λ	$[\theta]$
1	Me	253	+ 1040	227	- 2090
2	F	261	- 1410	229	+ 2400
3	Cl	263	- 1440	229	+ 6500
4	Br	265	- 1050	230	+ 9000
5	OH	260	- 2730	227	+ 3150
6	OAc	262	- 2260	227	+ 3850
7	Ph	259	-10500		
8	CO_2H	258	- 3600	224	+ 1570
8 a/	CO_2^-	257	- 3600		
9	CO_2Me	258	- 3470	225	+ 1520
10	$CONH_2$	259	- 5370	224 sh	+ 800
11	CN	258	- 5870	227 c/	+ 3630
12	NH_2	260 c/	- 170	233 c/	- 1630
12 b/	NH_3^+	258	- 2140	231 c/	+ 2470
13	NHAc	254	- 5470	221	+11700
14	CH_2OH	258 c/	- 1090	233 c/	- 3000
15	CH_2OAc	258	- 1860	234 c/	- 1750

a/ in 1N $NaHCO_3$ b/ in MeOH pH 1 c/ the most intense vibronic band

References and Notes

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