Induced Optical Rotation and Circular Dichroism of Symmetric and Racemic Aliphatic Carbonyl Compounds

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Summary The intermolecular asymmetric perturbation of a symmetric chromophore, (induced optical rotatory power), was observed as circular dichroism of achiral carbonyl compounds in chiral media.

WE report optical activity induced in *symmetric* aliphatic carbonyl compounds by the presence of chiral molecules in the same solution. These experiments were conceived from the theory that the c.d. of symmetric chromophores originates from perturbation by intramolecular centres[1] and extend earlier work with aromatic ketones[2] and metal complexes.[3,4]

When the ground electronic states of certain chiral environment compounds[4] have higher energies than that of an achiral compound (A), in the same solution, optical activity is induced in (A) and is observed in the c.d. spectrum of the system as a positive or negative dichroic absorption band appearing near the same frequency as the lowest energy isotropic electronic transition of (A).

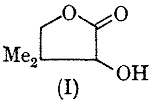
TABLE. *Induced c.d. bands of achiral or racemic carbonyl compounds in acetonitrile solutions at 29°*

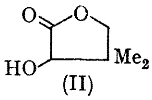
Carbonyl compound	*M*	Environment compound[a]	$[\alpha]_D$	*M*	Induced c.d. band λ_{max}(±2nm.)	$[\theta]_{max}$
Cyclohexanone (IX)	0·12	(V)	+45°	1·37	287	+20[b]
Cyclohexanone (IX)	0·06	(I)	+50°	1·53	292	−10
Cyclohexanone (IX)	0·07	(II)	−50°	1·53	290	+12
3-Methylcyclohexanone (XI)	0·08	(II)	−50°	1·61	285	+11
3-Methylcyclohexanone (XI)	0·11	(III)	− 5°	0·96	287	+13
3-Methylcyclohexanone (XI)	0·10	(IV)	+90°	0·68	288	+14
3-Methylcyclohexanone (XI)	0·08	(V)	+45°	1·37	287	+20
3-Methylcyclohexanone (XI)	0·10	(V)	+45°	0·63	287	+12
3-Methylcyclohexanone (XI)	0·09	(V)	+45°	1·37	285	+11[c]
3-Methylcyclohexanone (XI)	0·11	(VI)	+21°	0·68	290	+ 8
Propanol (VII)	0·24	(V)	+45°	1·37	289	+ 8
Acetone (VIII)	0·13	(V)	+45°	1·37	280	+14
2-Methylcyclohexanone (X)	0·12	(V)	+45°	1·37	290	*ca.* +11
2-Cyclohexylcyclohexanone (XII)	0·05	(V)	+45°	1·37	290	*ca.* +16

[a] (I) = L-(+)-pantolactone, (II) = D-(−)-pantolactone, (III) = 1,4-anhydro-L-threitol, (IV) = 1,4 : 3,6-dianhydro-D-mannitol, (V) = 1,4 : 3,6-dianhydro-D-glucitol, (VI) = 1,4 : 3,6-dianhydro-L-iditol.

[b] The isotropic absorption was λ_{max} 287 nm, ϵ_{max} 18.

[c] In dimethyl sulphoxide solution.


(I)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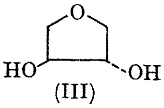
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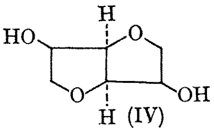
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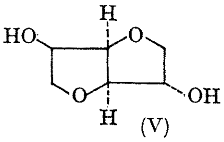
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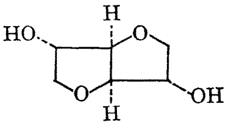
(VI)

Thus the chiral tetrahydrofuranols (I)–(VI) in acetonitrile solutions showed no c.d. bands above 225 nm. Addition of achiral (VII)–(IX) or racemic (X)–(XII) carbonyl compounds to these solutions generated c.d. bands at wavelengths characteristic of the isotropic absorption of their carbonyl chromophores (Table). The sign of the induced c.d. band was independent of the sign of the rotation of the chiral environment compound at the same wavelength. Replacement of environment compound (I) by its enantiomer (II) reversed the sign of the induced c.d. band from carbonyl compound (IX); with approximately equimolar quantities of (I) and (II) (racemic mixture) the induced c.d. signal was essentially zero.

The area of the c.d. band at *ca.* 290 nm. of the (+)-isomer of compound (XI) was increased by 10% on addition of environment compound (V). The positive induced c.d. band of the racemic form of (XI) was generated at approximately the same wavelength.

To rule out instrumental sources of the new c.d. bands, acetonitrile solutions of compounds (V) and (IX) in separate cells were placed in tandem, in that order, in the light beam of the dichrometer.† No detectable c.d. signal was produced by the arrangement; the effect of the birefringence of the environment compound was negligible as predicted by the equation of Velluz, Legrand, and Grosjean.[5]

Not all chiral compounds tested generated c.d. bands from the achiral carbonyl compounds in acetonitrile or dimethyl sulphoxide solutions. Thus no detectable induced c.d. signal was obtained with D-glucose, methyl-α-D-glucopyranoside, D-glucitol, 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose, 1,2-*O*-isopropylidene-α-D-glucofuranose, tri-*O*-methylene-D-mannitol, D-octan-2-ol, or the di-*O*-acetyl derivative of compound (V). No induced c.d. signal was obtained from a solution of compound (XI) in (−)-bornyl acetate. Other systems of environment and symmetric compounds are being examined.

† JASCO UV/ORD/CD-5.

An implication of our results together with those of Bosnich,[2] is that all solution o.r.d. spectra, being integral functions of c.d.,[6] probably contain positive and negative rotational components originating in induced c.d. of the solvent (and any impurities). These rotations may have significant magnitudes and can no longer be discounted on the basis of apparent molecular symmetry.

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