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MICELLE-INDUCED CIRCULAR DICHROISM OF ALIPHATIC KETONES

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Recent studies in the induced circular dichroism /ICD/ allowed for generalizations referring to the mechanism of induction of optical activity in achiral species. With respect to the $n-\pi^*$ transition in ketones it has been shown both experimentally[1] and by theoretical considerations of electronic and vibrational states[2-4] that in non-associative systems: achiral ketones /A/ - chiral solvents or solutes /C/, coupling A and C exclusively by dispersion forces produces ketone ICD which sign does not depend on relative orientations of A and C. On the other hand, different mechanism for ICD seems to operate when achiral or racemic ketones are included in α- or β-cyclodextrin cavities[5].

In connection with these studies it appeared to us that micellar systems would represent intermediate degree of A-C association in solution and hence ICD would differ from the above cases. Of numerous micellar systems sodium desoxycholate /DCNa/ aqueous solutions have the advantage of being transparent down to 220 nm and their critical micellar concentrations /CMC/ have been determined by various methods[6]. It has been demonstrated that DCNa solutions induce pH-dependent Cotton effects within bilirubin electronic transitions[7]. However no comparison with other systems can be made as the electronic structure of bilirubin is also pH-dependent[8].

Here we present the results of our ICD measurements for 24 aliphatic ketones dissolved in DCNa solution at concentration well above CMC /Table 1/. We note that ICD for $n-\pi^*$ transition is strongly ketone nature dependent, i.e. no Cotton effects could be detected for relatively small ketones, up to 6-7 carbon atoms /entries 1,7,11/, while negative Cotton effects were found for unsymmetrically substituted ketones /entries 3-6,12/ and positive Cotton effects - for essentially symmetrical ketones /entries 2,8-10,13,14/. In the case of 4-t-butylcyclohexanone /entry 15/ bisignate induced Cotton effect was observed[9]. ICD remained basically unchanged when measured in 0.2 M DCNa and 0.1 M Na_2SO_4 solution which formed transparent gel at pH<7.8. In contrast, essentially no ICD was observed for ketones dissolved in 0.2 M desoxycholic acid /DCA/ in methanol. The interference of intrinsic optical activity of DCA could safely be neglected as DCNa shows only weak CD shoulder at 200 nm /$\Delta\varepsilon$ -0.05 in aqueous solution and -0.06 in the gel/ while DCA in methanol gives negative Cotton effect at 212 nm /$\Delta\varepsilon$ -0.123/.

The results presented here are at variance with those reported for non-associative A-C systems[1]. In the methyl alkyl ketone series the amplitude of negative induced Cotton effect increases distinctly with the alkyl size, indicating strong dependence on associative van

Table 1. ICD of aliphatic ketones in aqueous DCNa solution[a]

	Ketones	$\Delta\varepsilon x10^3$	λ/nm/
	Methyl alkyl ketones MeCOR		
1	R = Et, n-Pr, cyclopropyl, i-Bu, n-Bu	no ICD detected	
2	t-Bu	+0.4	287
3	n-pentyl	-2.0	283
4	n-hexyl	-5.2	280
5	n-nonyl	-9.7	280
6	n-hexadecyl	ca.-10[b]	283
	Dialkyl ketones RCOR′		
7	R = R′ = Me, Et, n-Pr, cyclopropyl	no ICD detected	
8	i-Bu	+0.8	290
9	n-Bu	+1.2	290
10	n-hexyl	ca.+3.0[b]	284
11	R = Et, R′ = n-Pr	no ICD detected	
12	R = Et, R′ = n-Bu	-0.7	282
	Cyclic ketones		
13	cyclopentanone, cyclohexanone, cycloheptanone	≽0	
14	2-methylcyclohexanone	+0.5	284
15	4-t-butylcyclohexanone	-2.0 +1.4	307 276

[a] relative to the baseline of the DCNa solution. The concentration of DCA in 0.1 M phosphate buffer at pH 8.0 was 0.05 M. The ketone concentration was 2-7 times lower, according to its molecular weight. All measurements were made with Jobin-Yvon Dichrographe III in 1 cm cell at temp. 21°C; [b] ketones not sufficiently soluble in the DCNa system.

der Waals type forces within A-C system. The positive induced Cotton effects of symmetrically substituted ketones are much lower, yet also increased with the increase of alkyl chain length.

It is known that under conditions employed here DCNa in water solution forms medium-sized micelles /aggregation number >15/ while there is no micellar structure in methanol solutions of DCA[6]. The dynamic micellar systems accomodate the ketone molecules here reported, therefore the differences in the magnitude of ICD reflect the strength of dispersive interactions between nonpolar β-side of DCNa and achiral ketone molecules or the extent of ketone molecule rotational freedom within the dynamically formed micellar structures. Furthermore, the opposite sign ICD of symmetrically and unsymmetrically substituted ketones implies that there is preferred mode of association of chiral DCNa molecules. Thus we conclude that ICD in DCNa micellar solutions is the function of symmetry of dynamically formed aggregates rather than the function of ketone molecular symmetry alone.

References and Footnotes

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9. ICD maxima are shifted batochromically by 5-12 nm relatively to the isotropic absorption maxima measured in the same system.