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CHIROPTICAL PROPERTIES OF 2-BENZOYLBENZOIC ACID - CHIRAL AMINE SYSTEMS

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Ion-pairs of 2-benzoylbenzoic acid-chiral amine display a large induced circular dichroism (ICD) on the $n-\pi^*$ transition of the carbonyl group under lower concentration of the salt than 10^{-2} mole/l in non-polar solvents such as carbon tetrachloride and benzene[1]. The origin of the large ICD effect is assumed to be preferential formation of the optically active rotamer of 2-benzoylbenzoic acid, on a time average, due to asymmetric interaction between the chiral amine and the acid in the contact and/or solvent separated ion-pairs[2].

In this communication, we would now like to demonstrate the correlation of the absolute configuration of the chiral amines with the sign of the ICD effect, and utility of the ICD method for determining the absolute configuration of chiral amines.

Although the magnitude of the ICD of the system becomes rapidly small by increase of solvent-polarity, the sign does not change in all cases (Table I) in carbon tetrachloride, benzene, chloroform and acetonitrile. The ICD often shows the opposite sign in ethereal solvents because of complicating solvations for the ammonium ion[3]. The sign and magnitude of the ICD are dependent upon the R; i.e., the ratio

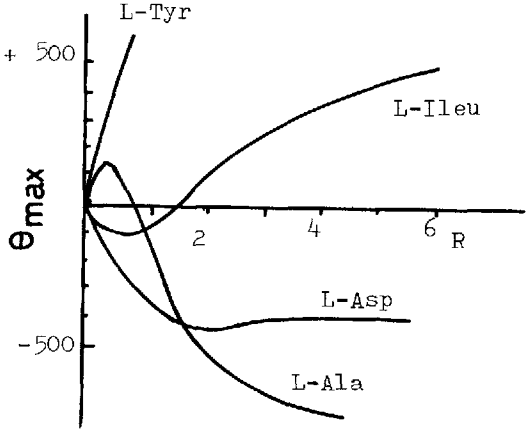
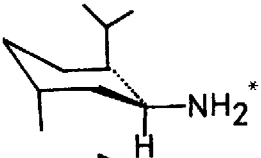
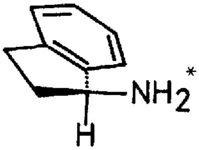
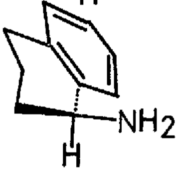


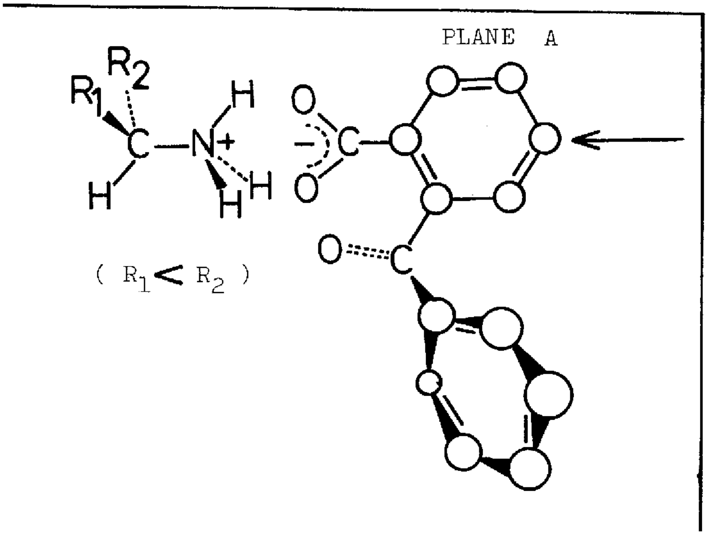
Fig. I Plots of R vs. Θ_{max} of methyl esters of respective amino acid-2-benzoylbenzoic acid system in benzene at 22°C

Table I The ICD Effects of 2-Benzoylbenzoic acid
Chiral Amine Systems

Chiral Amines*1		θ_{max}(λ_{max}, nm)	
R^{R_1}	R_2	R = 0.4*2	R = 3.0*2
CH_3	$COOCH_3$	59 (327)	-597 (324)
$CH(CH_3)_2$	$COOCH_3$	-109 (336)	135 (324)
$CH_2CH(CH_3)_2$	$COOCH_3$	-63 (336)	251 (326)
$CH(CH_3)CH_2CH_3$	$COOCH_3$	-102 (336)	221 (326)
$CH_2CH_2SCH_3$	$COOCH_3$	-7 (334)	139 (331)
$CH_2CH_2SCH_3$	$COOCH_2CH_3$	-32 (333)	55 (333)
$CH_2C_6H_5$	$COOCH_3$	76 (326)	122 (326)
$CH_2C_6H_4$-p-OH	$COOCH_3$	640 (326)	2000 (327)*3
CH_3	CH_2CH_3*4		-493 (325)
$CH(CH_3)_2$	CH_3*5		346 (324)
$CH_2CH_2CH_3$	CH_3*5		288 (324)
$CH_2C_6H_5$	CH_3*6		1161 (322)
 *7			237 (325)
 *8			-1780 (320)
 *9			-2035 (317)

The CD spectra were recorded under appointed salt concentration in benzene at 22. *1; see Fig. II, *2; R is the ratio of concentration of amines to the acid (1.0 x 10^{-2}mole/l), *3; R = 1.0, *4; A. Kjaer and S. H. Hansen, Acta Chem. Scand., 11, 898, 1957, *5; S. R. Landor, O. O. Sonola and A. R. Tachell, J.C.S. Perkin I, 1902, 1974, *6; J. C. Craig, R. P. K. Chan and S. K. Roy, Tetrahedron, 23, 2573, 1957, *7; A. K. Bose, J. F. Kristner and L. Farber, J. Org. Chem., 27, 2925, 1962 *8; J. H. Brewster and J. G. Buta, J. Am. Chem. Soc., 88, 2233, 1966, *9; The absolute configuration has not been assigned. The S-(+)-configuration is now assigned by the reason of the similarity of the ICD spectrum to that of S-(-)-indanamine, b.p. 102-104°/4mmHg, $[\alpha]_D$ = + 35.5 (neat, at 22°)

of concentration of amines to the acid, as shown in Fig. I where four typical curves are indicated. The Θ_{max} values at the ratio of 0.4 and 3.0 are summarized in Table I. At the ratio of 0.4 where homoconjucate ions of 1:2 and/or 1:3 seems to be formed[4], the ICD spectra display a complicating feature and the sign is difficult to correlate with physical and chemical properties of chiral amines. On the other hand, at the ratio of 3.0 where ion-pairs of 1 : 1 are formed mainly[1], the sign of the ICD has a good correlation with difference in the bulkiness of R_1 and R_2 around the ammonium group (Fig. II). That is, the sign of the ICD is always positive when R_1 is larger than R_2 with regard to the bulkiness around the ammonium group. Hence very simple sectors where the space is simply devided into two sectors by plane A as shown in Fig. II, are set up for the Cotton effect of the $n - \pi^*$ transition of the carbonyl group. The sector rule[5] may be interpreted by the following crude ion-pair model.



Bulkiness of R_1, R_2	Sign of ICD for $n - \pi^*$
$R_1 > R_2$	+
$R_1 < R_2$	-

Fig. II Ion-pair model for chiral amine - 2-benzoylbenzoic acid

In Fig. II, 2-benzoylbenzoate anion approaches along the arrow to chiral ammonium cation in the plane A to minimize the steric effect, and the phenyl moiety of the benzoyl group orientates either upper or lower sites of the plane owing to sterical repulsion between the benzoyl group and substituents, R_1 and R_2, giving preferentially either of the optically active rotamers(P- or M-helices) on a time average. As is evident from the model, the rule is effective only in primary amines, and it is inapplicable to secondary amine such as L-proline methyl ester(θ = +275(326 nm), at R = 2.0), and primary amines such as L-threonine methyl ester(-216(330)), L-aspartic acid dimethyl ester(-287(328)), S-alaninol(+243(330)) and S-leucinol(+534(326)) which make a cyclic structure by strong intramolecular hydrogen bond and behave like secondary amine. The sign of the ICD in these cases coinsides with the sign predicted from the sector rule for secondary amines.[6] Although tertiary amines also display the similar ICD effects, it is not easy to find out the rule for tertiary amines because of difficulty of construction of the ion-pair model. Considering the mechanism of the ICD appearance, this method must be useful for determining the absolute configuration of chiral amines similar to conventional methods.[7,8]

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5. The word 'sector rule' in this case may be different from the word defined conventionally with regard to the essential meaning.
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