

Induced Circular Dichroism in the 2-Benzoylbenzoate Anion Paired with Polymer-supported Optically Active Quaternary Ammonium Ions

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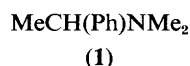
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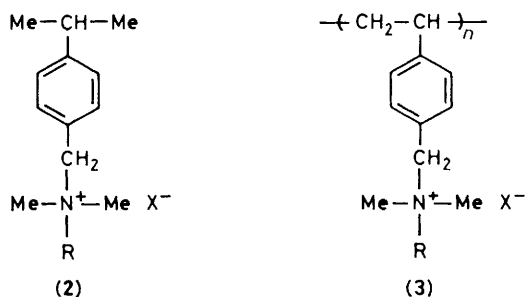
Induced circular dichroism in the 2-benzoylbenzoate anion paired with optically active ammonium ions provides a potentially useful and highly convenient probe for assessing chiral phase transfer catalysts.

A number of groups have been examining the possibility of achieving either asymmetric induction or kinetic racemate resolution in phase transfer catalysed reactions,¹ and one or two analogous polymer-supported systems have been reported.² During phase transfer catalysis using a chiral onium salt, an achiral anion becomes paired with the chiral cation, and then undergoes a reaction with either an achiral or a racemic reactant to produce chiral products. In the absence of specific interactions between the onium group and the substrate it seems most likely that the achiral anion itself should experience a significant chiral influence, and behave subsequently as an essentially chiral entity, if enantioselection is to be achieved. One potential method of quantifying the asymmetric influence of a chiral species on an achiral one is to monitor the *induced* circular dichroism in a convenient absorption band of the latter.³ Tokura and co-workers⁴ have applied this technique to the *in situ* formation of optically active primary and secondary ammonium ion pairs with ketonic carboxylate counter-ions. In our preliminary work we have used, for the first time, pre-formed optically active quaternary ammonium phenoxides and carboxylates and in particular we have compared the behaviour of low molecular weight ammonium salts with their corresponding high molecular weight polymer-supported analogues.

(*S*)-*N,N*-Dimethyl-1-phenylethylamine (**1**) was prepared by a literature method⁵ from the corresponding primary amine. Vacuum distillation gave a middle fraction with $[\alpha]_D^{25} = -67.8^\circ$ (neat), which was virtually optically pure.⁶ Salt (**2a**) was prepared by heating (**1**) with 4-isopropylbenzyl chloride (equimolar) in the absence of solvent for 3 h at



60 °C. It was purified by dissolution in dry acetone and precipitation with dry ether (twice) to yield an oily solid,

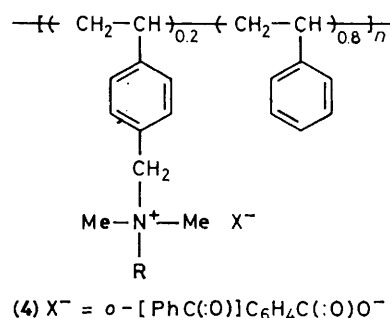


a; X⁻ = Cl⁻

b; X⁻ = PhO⁻

c; X⁻ = *p*-NO₂C₆H₄O⁻

d; X⁻ = *o*-[PhC(:O)]C₆H₄C(:O)O⁻



R = Me-CH(Ph)-

n ca. 1000

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Table 1. Molar optical rotations, $[\Phi]_D^{25}$, and molar extinction coefficients, ϵ , of quaternary ammonium salts in methanol.

Salt	$[\Phi]_D^{25}/^\circ$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	λ^a/nm
(2a)	-91.1	659	270 (m)
(3a)	-83.2	675	265 (m)
	-82.0 ^b		
(2b) ^c	-77.9	1060	300 (s)
		2190	275 (s)
		4170	230 (m)
(3b) ^c	-69.4	886	330 (s)
		1590	275 (s)
		3670	230 (m)
(2c) ^d	-90.5	16600	400 (m)
		18400	250 (m)
(3c) ^d	-57.4	11200	400 (m)
		14800	250 (m)
(2d)	-89.5	113	325 (s)
		3170	275 (s)
		12100	240 (m)
(3d)	-60.9	121	325 (s)
		6430	275 (s)
		13000	250 (m)
(4)	-71.5	151	325 (m)
		4270	275 (m)
		16900	250 (m)

^a m = absorption maximum, s = absorption shoulder. ^b Duplicate preparation. ^c 10^{-3} M NaOH in methanol. ^d 10^{-4} M NaOH in methanol.

$[\alpha]_D^{25} = -28.7$ (methanol). The corresponding salts (2b—d) were prepared from (2a) by anion exchange in methanol using equimolar amounts of the sodium salts of the corresponding phenoxides and carboxylate. Each was purified by dissolution in methanol and precipitation with n-hexane. Polymer (3a) was prepared by heating (1) with poly(4-chloromethylstyrene) in 1,2-dichloroethane for 13 h at 60 °C. The product precipitated during this period, and was washed repeatedly with diethyl ether, $[\alpha]_D^{25} = -27.2^\circ$ (methanol). Polymer derivatives (3b—d) were prepared from (3a) by anion exchange as before using methanol as the solvent. Each was washed repeatedly with toluene. Co-polymer (4) was prepared by a similar route from the corresponding co-polymer of styrene and chloromethylstyrene. ¹H N.m.r. studies established the functional styrene content at ca. 20%.

The extinction coefficient of each species in methanol was measured at room temperature using a Varian DMS 80 spectrophotometer. In each case only a single convenient concentration was monitored in a 1 cm cell. Optical rotations in methanol solution were measured at 25 °C with a Perkin Elmer 241 spectropolarimeter. The results are summarized in Table 1. In each case the molar optical rotation of the polymeric analogue of each low molecular weight salt is somewhat lower than that of the salt itself. With (2b) and (3b) the absorption bands of the PhO⁻ anion are substantially overlapped by the strong absorption of the aryl ammonium cation. With (2c) and (3c) the anion absorption band at λ_{max} ca. 400 nm, stands resolved from the aryl ammonium cation bands. With (2d) and (3d) there is some overlap but a clear shoulder is manifest at ca. 325 nm. Of great importance are the relative extinction coefficients of the bands of each anion type, that for the 2-benzoylbenzoate anion in (2d), (3d), and (4) is ca. 5—8 times smaller than that of PhO⁻, and ca. 100 times smaller than that of *p*-NO₂PhO⁻.

Circular dichroism spectra for all the species were recorded on a Jobin Yvon Dichrograph III instrument and molar ellipticities, $[\theta]$ ($^\circ \text{ cm}^{-1} \text{ dm}^3 \text{ mol}^{-1}$), were calculated from the equation $[\theta] = 3300 \Delta\epsilon$.⁷ In each case solutions were prepared with an optical density in a 1 cm cell of ca. 0.9 at the

Table 2. Molar ellipticities, $[\theta]$, of the induced circular dichroism band at ca. 325 nm.

Solvent	$[\theta]/^\circ \text{ cm}^{-1} \text{ dm}^3 \text{ mol}^{-1}$		
	(2d)	(3d)	(4)
10% methanol in water	0	27	^a
methanol	0	14	37
dimethylformamide	7	37	26
dimethyl sulphoxide	9	33	44
n-butanol	80	14	58
dichloromethane	124	insoluble	104
tetrahydrofuran	203	insoluble	103
carbon tetrachloride	440	insoluble	insoluble

^a Not determined.

absorption maximum (or shoulder) corresponding to the anion absorption. With (2a—c) and (3a—c) only the intrinsic dichroism of the optically active ammonium ion was observed as a structured band at *e.g.* 265 nm for (2b) in chloroform with $[\theta]$ ca. 1200, and 265 nm for (3a) in methanol with $[\theta]$ ca. 700. For (2d), (3d), and (4), however, there is an additional induced band at ca. 325 nm confirming that the 2-benzoylbenzoate anion experiences a significant asymmetric influence from optically active quaternary ammonium ions, as it does from primary and secondary ions.⁴ Furthermore the intensity of this band is very solvent dependent and the relevant molar ellipticities are shown in Table 2. For (2d) the solvent dependence is as might be expected and corresponds to the results with primary ammonium ions.^{4a} It confirms the hypothesis that as the solvation power of the medium increases, ion pair interaction grows weaker and the induced circular dichroism falls to zero. Whether this reflects the strength of a given ion pair interaction or simply reflects a shift in equilibrium from 'tight' to 'loose' ion pairs (or indeed free ions) is not clear, but most probably both factors contribute. The behaviour of the homopolymer analogue (3d) is quite different. This displays measurable induced circular dichroism even in very polar solvents and quite obviously the microenvironment in this instance is different from that in the low molecular weight salt. It might be that the high local concentration of chiral ammonium ions on the hydrophobic polymer backbone creates charged aggregates,⁸ and that even a solvent like methanol does not completely break these down. On the other hand the source of the induced dichroism is almost certainly the existence of chiral rotamers of the 2-benzoylbenzoate anion and the preferential formation of one of these when paired with an optically active cation.^{4c} The difference in solvent behaviour of (2d) and (3d) may therefore also be associated with differences in the ability of the anion to adopt or reject particular conformations.

Co-polymers of styrene and chloromethylstyrene are essentially random and hence the quaternary ammonium groups in co-polymer (4) are probably well separated along the polymer chains. Such a distribution would discourage aggregation of ionic species and yet significant induced circular dichroism arises with (4) even in methanol. This tends to favour the idea, therefore, that macromolecular species (3d) and (4) profoundly influence the conformational behaviour of the 2-benzoylbenzoate anion.

The phenoxide anion in (2b), (3b), (2c), and (3c) cannot adopt chiral conformations and this may explain the absence of any observed induced circular dichroism. However, the extinction coefficients of these anions are ca. 10—100 times larger than that of the 2-benzoylbenzoate species and the lack of any dichroic absorption might be due to the unfavourable anisotropy factor ($\Delta\epsilon/\epsilon$). As a result the possi-

bility remains that these anions also experience an asymmetric influence that cannot be experimentally shown.

We believe we have now established a technique for probing those chiral onium structures which should provide good asymmetric induction in phase transfer catalysed reactions. We have also shown that the behaviour of polymer-supported species can be quite different from that of low molecular weight analogues. Although polymer-supported catalysts have so far apparently shown poorer results in enantioselection than their non-supported counterparts, both systems remain vitally important, since they can each provide asymmetric environments in complementary solvents.

This research was performed within the framework of 'CNR Programma Finalizzato Chimica Fine e Secondaria.' We thank the Ciba-Geigy Trust for a Senior Fellowship to D.C.S.

Received, 24th May 1982; Com. 587

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