

Determination of Enantiomeric Excess of Some Anthroates *via* Differences in Their Luminescence Properties in the Crystal

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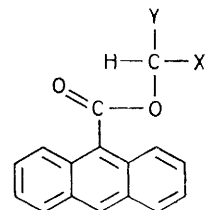
The differences in luminescence properties between the chiral resolved and the racemic compounds of some 9-anthroates have been exploited for the determination of the enantiomeric excess in these esters.

The sensitivity of the fluorescence of crystals of aromatic molecules to crystal structure has been described elsewhere.^{1,2} This sensitivity is exemplified by a change in the fluorescence spectrum, from a structured monomeric type to a structureless excimer type, accompanying a solid-solid phase transition,³ and by the existence of two different excimer emissions from the two crystal forms of a given compound, when the two structures are based on pairwise packing of molecules.^{2,4}

In a recent paper⁵ we discussed the various packing arrangements of chiral 9-anthroates. We noted that, owing to the bulkiness of the chiral 'handle,' there can be no appreciable overlap of molecules related by a translation axis. Moreover, pairing *via* a two-fold symmetry axis is very rarely observed, since it does not lead to a close-packed structure for molecules of arbitrary shape.⁶

By virtue of these symmetry and energy considerations, it can be inferred that in crystals of a resolved sample of such chiral molecules which have a chiral structure (containing only symmetry elements of translation or rotation, or both), there cannot be appreciable plane-to-plane overlap of the

aromatic chromophores. The structure would then probably be of the γ -type,² with adjacent molecules in a stack parallel, but appreciably laterally displaced, with respect to one another. The emission would then be of the monomer type [structured, short-lived (*ca.* 10 ns), and with small Stokes shift].



	X	Y
(1)	Ph	Et
(2)	Ph	Pr ⁱ
(3)	2-ClC ₆ H ₄	Me
(4)	4-ClC ₆ H ₄	Me
(5)	4-EtC ₆ H ₄	Me

On the other hand, a racemic mixture may crystallise in a centrosymmetric structure, where the two heterochiral molecules make close plane-to-plane contact across a centre of inversion (α -type packing) and with the aromatic moieties strongly overlapped. Consequently, molecules consisting of an aromatic chromophore attached to an enantiomerically enriched sample of, for example, an alcohol, amine, or acid, will in many cases yield a mixture of two types of crystals; one is the racemic compound, which will display excimer emission (structureless with decay time of the order of 100–200 ns, large Stokes shift), while the other is the resolved conglomerate, with its monomer emission. This difference in spectroscopic properties can be exploited, under suitable circumstances, for the determination of the enantiomeric excess (e.e.) of materials which crystallize in this way. We describe here an application of this method to the determination of the e.e. of some secondary alcohols in the form of their 9-anthraotes.

Partially enriched alcohols were treated with 9-anthroyl chloride, and the corresponding esters were purified by column

chromatography, and consequently crystallized.† Of the ten 9-substituted anthraotes investigated, five, (1)–(5), obey the principles just discussed (Table 1).

Figure 1 shows the fluorescence spectrum of racemic and enantiomeric 1-phenylpropyl anthroate. Owing to the large differences in the spectra of the two crystal emissions it is easily possible to distinguish between the two crystals even by visual examination‡ under u.v. light (254 nm). In Figure 2 we show the correlation, for this and other anthraotes, between the e.e. as estimated from the fluorescence spectra and, direct, from the optical rotation of the dissolved samples.§

From Figure 2 it is clear that, for these materials, when the racemate phase is present in excess the relative intensity of the monomer emission varies linearly with the optical purity. There is a similar linear relationship when the excimer emitting racemic phase is in excess, but here the accuracy of the measurements is lower.

The minimal detectable concentrations of enantiomeric and racemic phases were of the order of 2%. However, repeated recrystallizations of the same sample mixture led to results which were reproducible to within 1%, under uniform treatment and identical measuring conditions. The present limit depends on the sensitivity of our detector and on the mutual solubility of the two enantiomers in the two phases. Whereas the accuracy of detection can be improved by applying time-resolved spectroscopy, since the two emissions differ considerably in their decay times, the mutual solubility can be only little affected. In fact, once the sensitivity of detection

Table 1

Compound	Type of emission	λ_{\max}/nm of excimers	Space group	Ref.
(1) (RS) (R) or (S)	Excimer { Form A monomer Form B monomer	500	$P2_1/a$ $P2_12_12_1$ $P6_5$	8
(2) (RS) (R) or (S)	Excimer Monomer	490	$P2_1/a$ $P2_12_12_1$	5 5
(3) (RS) (R) or (S)	Excimer Monomer	500	$P2_1/a$ $P2_12_12_1$	5 5
(4) (RS) (R) or (S)	Excimer Monomer	508	$P\bar{1}$ $P2_1$	
(5) (RS) (R) or (S)	Excimer Monomer	485	$P\bar{1}$ $P2_1$	

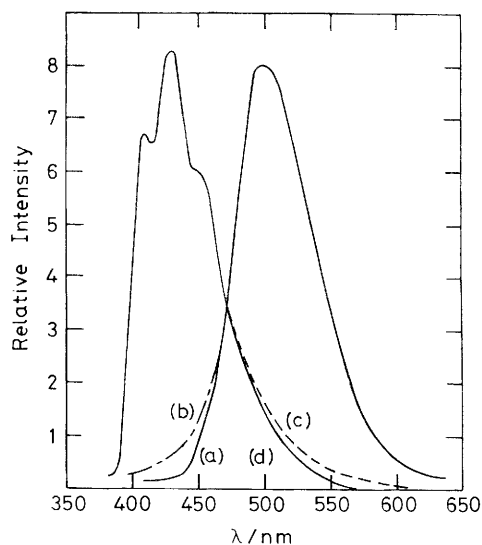


Figure 1. Fluorescence spectra of (a) racemic and (b) enantiomeric 1-phenylpropyl 9-anthroate (1) crystals at 77 K, and of (c) racemic crystals with 4.5% e.e., and (d) enantiomeric crystals with 91.5% e.e.

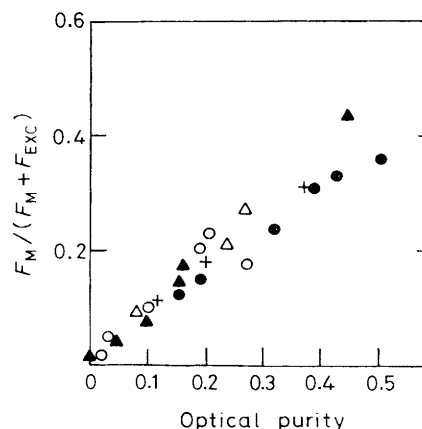


Figure 2. Correlation between e.e. determined by optical rotations and by means of the fluorescence method. F_M : monomeric structured yield and F_{EXC} : excimeric structureless fluorescence emission yield: +, (1); O, (2); Δ, (3); ●, (4); ▲, (5).

† The esters were prepared by esterification of the alcohol with 9-anthric acid in the presence of small amounts of thionyl chloride. Final purification of the esters was carried out by column chromatography on silica gel with n-hexane–benzene (1:1). The mixtures of crystals were crystallized from methylene dichloride–n-hexane (1:1).

‡ We noticed that generally the racemic compounds packing in the form of excimer-emitting crystals are yellow, whereas the resolved monomer-emitting enantiomers are white. Similar differences in colour between racemic and enantiomeric crystals have been observed in other materials: see V. Schurig, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 110, footnote 8.

§ The blanks were prepared by mixing accurately weighed amounts of powdered crystals of the resolved enantiomers and the corresponding racemates. The enantiomeric excess of the samples thus prepared was determined by optical rotation in solution.

of the two emissions is improved, it may prove possible to apply this method to the study of mutual miscibility in solids and to the detection of intergrowth of crystalline phases in chiral and racemic crystals.⁹

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References

- 1 B. Stevens, *Spectrochim. Acta*, 1972, **18**, 439.
 - 2 M. D. Cohen, Z. Ludmer, and V. Yakhot, *Phys. Status Solidi*, 1975, **B67**, 57.
 - 3 J. Tanaka and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 34; J. Tanaka, *ibid.*, 1963, **36**, 1237.
 - 4 Z. Ludmer, *Phys. Status Solidi*, 1977, **A43**, 695; R. Cohen, Z. Ludmer, and V. Yakhot, *Chem. Phys. Lett.*, 1975, **34**, 271.
 - 5 M. Lahav, F. Laub, E. Gati, L. Leiserowitz, and Z. Ludmer, *J. Am. Chem. Soc.*, 1976, **98**, 1620.
 - 6 A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973, pp. 33—37.
 - 7 For a review on methods for the determination of enantiomeric excess, see: R. Mislow and M. Raban, *Top. Stereochem.*, 1967, **2**, 199.
 - 8 M. Lahav, L. Leiserowitz, L. Roitman, and C. P. Tang, *J. Chem. Soc., Chem. Commun.*, 1977, 929.
 - 9 G. E. Berkovic and Z. Ludmer, *J. Chem. Soc., Chem. Commun.*, 1981, 768.
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