

SUBSTITUENT AND SOLVENT EFFECT ON THE CHIROPTICAL PROPERTIES
OF THE OXAZIRANE CHROMOPHORE

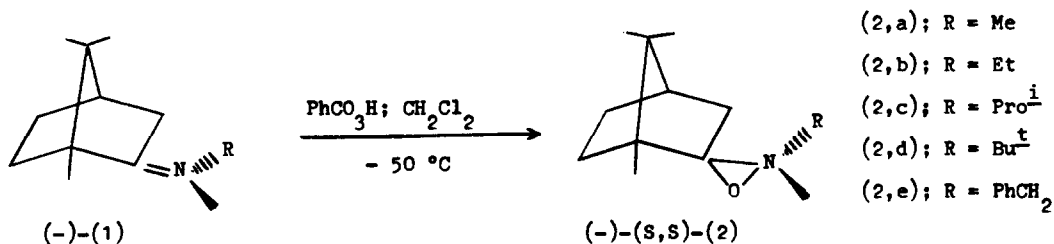
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It is well known that problems of configurational and conformational analysis can be adequately tackled by chiroptical techniques if there is knowledge of the type of electronic promotion which gives rise to the absorption band and to the circular dichroism band under consideration. In these cases, the symmetry properties of the orbitals involved can allow non-empirical determination of the effect of substituents and of variations in conformation in the optical activity.¹ Moreover, circular dichroism, like absorption data, are of value also in helping to solve the converse problem: i.e., to test the merit of theoretical treatments of optical activity for systems of uncertain electronic states.²

Until now, the chiroptical properties of the oxazirane chromophore have been very scarcely studied, both from theoretical and experimental point of view, having circular dichroism and absorption spectra been reported only for a limited series of steroidal oxaziridines of unknown absolute configuration at the asymmetric carbon and nitrogen atoms of the three membered ring.³ It was the purpose of present work to obtain a more clear experimental evidence of the substituent and solvent effect on the c.d. and u.v. behaviour of optically active oxaziridines of known absolute configuration and rigidly fixed conformation at the carbon site of the oxazirane ring.

SCHEME



Optically N-alkyl and N-benzyl oxaziridines of type (2), (Scheme), were synthesized by oxidation of the corresponding (-) camphorimines (1), as previously described.^{4,5} In every case we

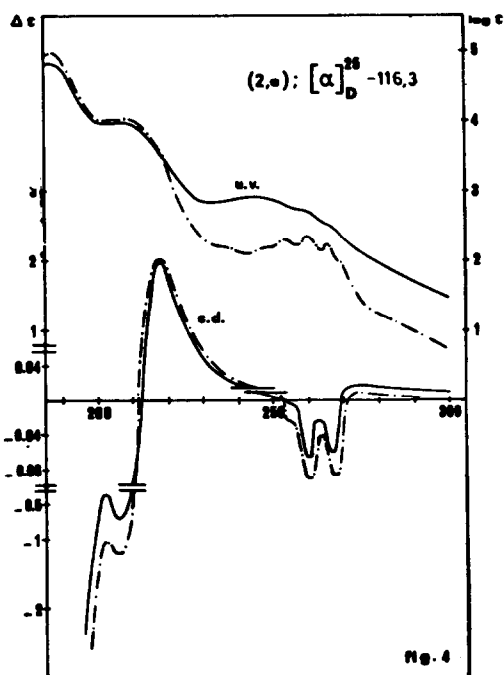
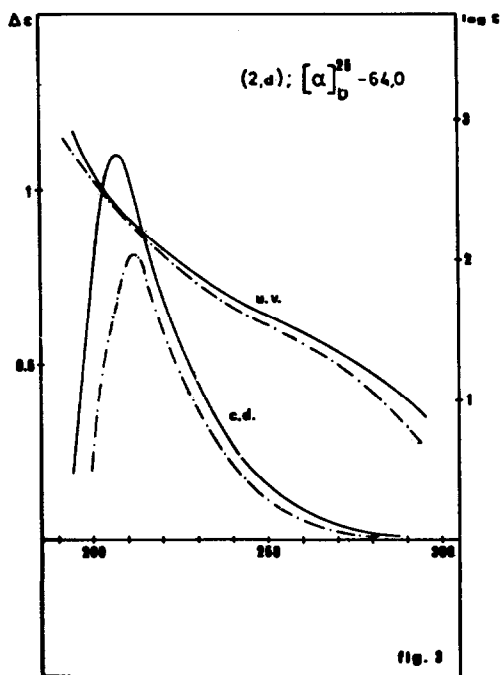
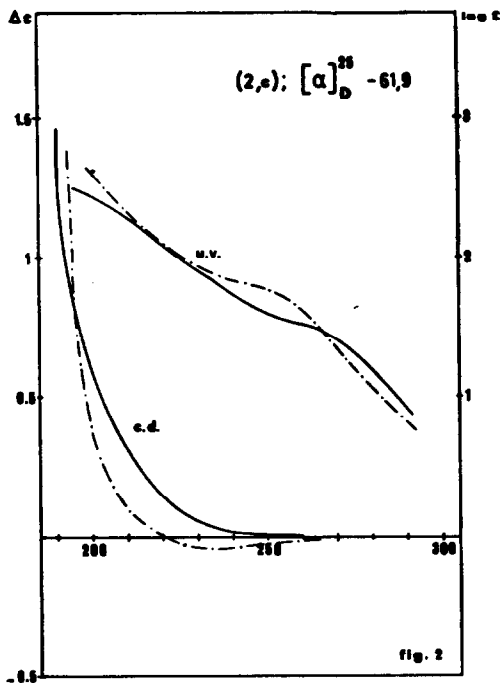
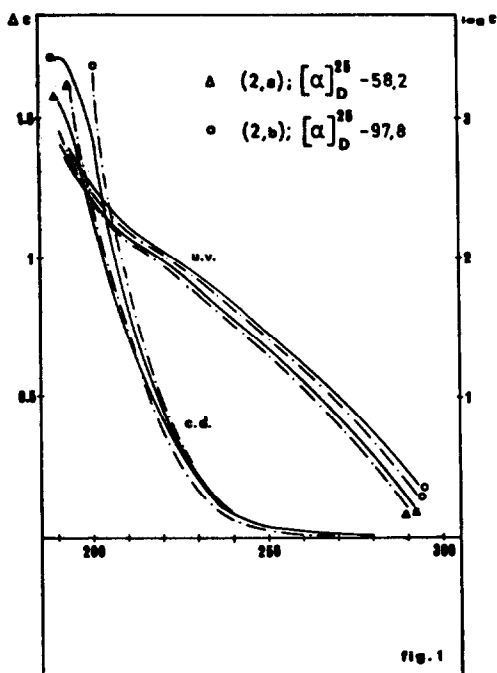
obtained a much higher proportion ($> 95\%$) of one oxaziridine isomer, which could be isolated in a pure form by column chromatography and fractional crystallization or high vacuum distillation of the crude products. N.m.r. spectra,⁸ space filling molecular models, and the stereochemistry which characterizes many reactions of compounds containing the 1,7,7-trimethylbicyclo[2,2,1]eptane structure⁹ suggest that, independently of whether N-methyl, ethyl, isopropyl, t-butyl, or benzyl substituent is used, the absolute configuration at asymmetric carbon and nitrogen atoms of the three membered ring of (2) is (S,S).

The c.d. and u.v. spectra of oxaziridines (2) registered in ethanol and isooctane solution, and the relative optical rotatory powers in ethanol, are reported in Figures 1-4. These Figures show that the chiroptical properties of the oxazirane chromophore, having the absolute configuration drawn in Scheme, are generally characterized by a positive pattern in the spectral range 190-350 nm. Positive dichroism is, in fact, observed both in ethanol and isooctane solutions, in the c.d. spectra of the N-methyl (2,a) and N-ethyl (2,b) derivatives (Figure 1), and more clearly defined positive Cotton effects, centered at 212 nm. in isooctane and 206 nm. in ethanol ($\Delta \epsilon + 0.8$ and $+1.1$, respectively) are shown by the c.d. spectra of the N-t.butyl derivative (2,d), (Figure 3). The corresponding absorption curves of these compounds are much less characterized, showing in every case a faible inflection point at about 210 nm.

The spectra of the N-benzyl derivative (2,e), reported in Figure 4, show a more complex behaviour, owing to the presence of optically active 1L_b and 1L_a aromatic transitions which, quite probably, control the negative Cotton effects and the corresponding u.v. maxima centered, in both solvents used, at 240-270 and 205 nm., respectively. Nevertheless, outside these spectral regions, and more particularly between 280-300 and 212-252 nm., one can see positive curves which seem like to be considered as tails of extended and still positive c.d. bands of the oxazirane group.

Quite surprisingly, the chiroptical properties of the N-isopropyl derivative (2,c) do not completely follow this general pattern. In fact, while in ethanol the dichroism of (2,c) looks like the spectra of the (2,a) and (2,b) omologs depicted in Figure 1, the c.d. spectrum of the same (2,c) oxaziridine, when registered in isooctane solution, shows a clear negative Cotton effect at about 235 nm., followed by a positive curve at lower wavelengths. Moreover, in addition to the inflection point which is common to the other N-alkyl oxaziridines, the isotropic absorption spectra of (2,c) reveal a shoulder at 260-240 nm., both in ethanol and isooctane solution, (Figure 2).

The spectroscopic behaviour of oxaziridine (2,c) can be considered the most important result of present work. In our opinion, this behaviour can be interpreted in terms of solvation equilibria and conformational rotamers about the N-isopropyl bond, thus showing that the chiroptical properties of the oxazirane chromophore may be strongly influenced by the nature of solvents and of N-substituents. Nevertheless, a general explanation of the substituent and solvent ef-



Figures 1-4. U.v. and c.d. spectra in ethanol (—) and in isooctane (---), and optical rotatory powers in ethanol, of oxaziridines (2,a)-(2,e).

fect observed in the c.d. and u.v. spectra of oxaziridines (2,a)-(2,e) needs further work. In fact, the geometry and the nature of the optically active electronic transition of the oxazirane ring of (2), which seems to control the chiroptical properties of Figures 1-4, is far from being known¹⁰ and, on the other hand, the empirical c.d. data with oxaziridines of known absolute chirality are, until now, too limited, and this makes quite difficult to give a more defined structural rationalization of the results obtained in present work.

Acknowledgements.

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References.

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- 5) During the completion of present work, syntheses of the N-t.butyl (2,d)⁶ and N-benzyl (2,e)⁷ oxaziridines have been reported by other Authors. The stereochemical results obtained by these researchers are in very good agreement with those reported in present and previous work.⁴
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