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OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF ARYL OXIRANES.

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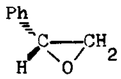
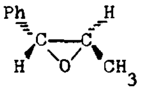
The contribution of three-membered rings to the optical properties of a molecule, especially for compounds containing the carbonyl chromophore, has been widely studied (1). The recent development of optical rotatory dispersion and circular dichroism equipments capable of measuring optical activity below 200 mμ has allowed the investigation of aromatic transitions in phenylcyclopropane derivatives (2) and of π—π^* Cotton effects in α-cyclopropyl and α-epoxy-ketones (3).

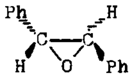
We wish to report the results of u.v., o.r.d., and c.d. studies of optically active aryl oxiranes 1-4 of established absolute configuration.



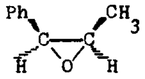
(+)-(R) 1



(+)-(1R,2R) 2



(+)-(R,R) 3



(+)-(1S,2R) 4

The spectra* reported in Figs. 1-4 clearly show that:

i) the electronic transitions in the aromatic region are optically active;

ii) the sign of the Cotton effect at 250-275 mμ reflects the configuration of the carbon linked to the phenyl ring; i.e., positive or negative Cotton effects are observed when the phenyl ring is bonded to an (R) carbon (oxiranes 1-3), or to an (S) carbon (oxirane 4), respectively;

iii) the values of optical activity for oxiranes 1 and 2, corresponding to aromatic transitions,

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* The u.v., o.r.d., and c.d. measurements were made at 25°C in 95%-ethanol. The o.r.d. spectra in cyclohexane did not show any significant difference with respect to those in 95%-ethanol. The optical values were corrected to optical purity.

are lower than that of the cis derivative 4 at 217 mμ and that those of the trans-diphenyloxirane 3 everywhere in the spectrum.

The conjugative properties arising from the unsaturated character of three-membered rings have been documented (4) and the optimum geometry for the interaction of the rings and a p orbital on an adjacent carbon has been shown to be that where the plane of the rings and the axis of the p orbital are parallel (5). Neverthless it has also been emphasized that the magnitude of the overlap between the rings and adjacent p orbitals should undergo proportionately less change over a rather wide range of dihedral angle than does the magnitude of the overlap between two adjacent p orbitals (5). In other words, the fact that conjugation does occur in both arylcyclopropanes and oxiranes does not necessarily mean that a highly specific orientation of the rings is required in these systems.

According to this hypothesis the relatively low optical values of 1 and 2 (Figs. 1,2) with respect to those of 3 (Fig. 3) and 4 (Fig. 4) should be due to the superimposition of the spectra of several rotational isomers.*

Steric or conjugative effects in 4 or 3 respectively should modify or reduce the conformational mobility postulated for the aromatic ring of oxiranes 1,2 and could therefore change the corresponding spectra.

More relevant changes with respect to phenyloxirane 1 (Fig. 1) are found in the spectra of trans-diphenyloxirane 3 (Fig. 3). The aromatic transitions, particularly the "primary" band $'L_a$ (7), are red-shifted, the absorptions are enhanced and the corresponding Cotton effects are much stronger. The c.d. spectra, both in 95%-ethanol and in cyclohexane solutions, exhibit two strong bands with opposite sign and nearly equal areas at shorter wave-lengths, corresponding to the split components of the unpolarized absorption which appears at 195 and 198 mμ in cyclohexane. These results strongly suggest for oxirane 3 the presence of an aromatic system with extended conjugated chromophores that is considerably more rigid than in the other oxiranes examined.

In particular the splitting phenomenon observed for oxirane 3 below 200 mμ, could be due to the respective positions in which the two aromatic chromophores are in the most favoured conformation (8). In fact it should be noted that in order to allow the maximum conjugation

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* It should be noted that the experimental line shapes reported in Figure 1 are very similar to those of the open chain compounds, $Ph\overset{*}{C}H(OH)R$, with the same chirality at the asymmetric carbon atom (6).

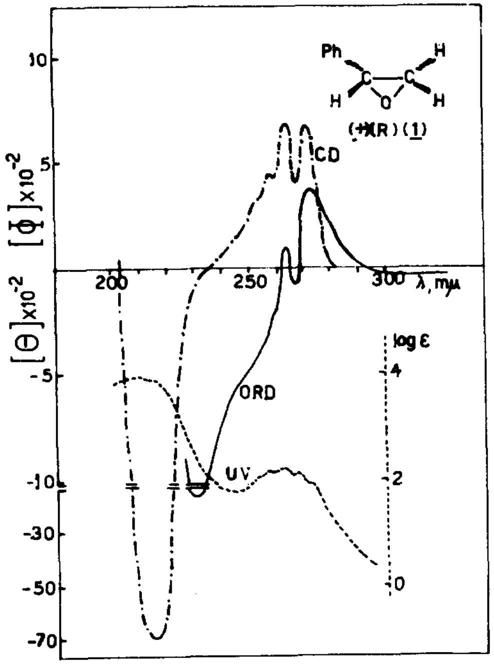

Fig. 1

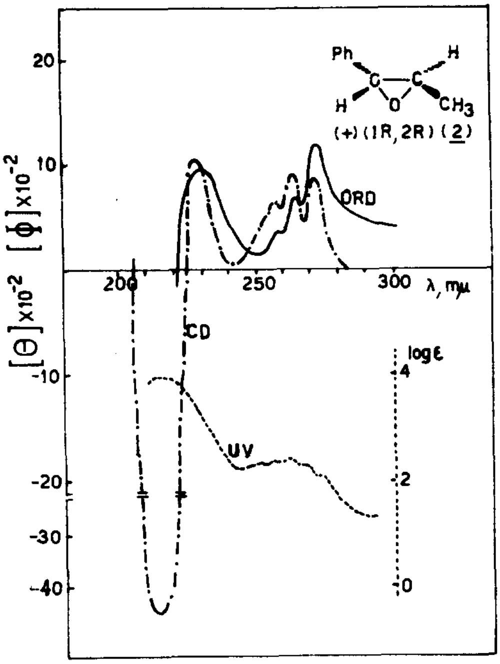

Fig. 2

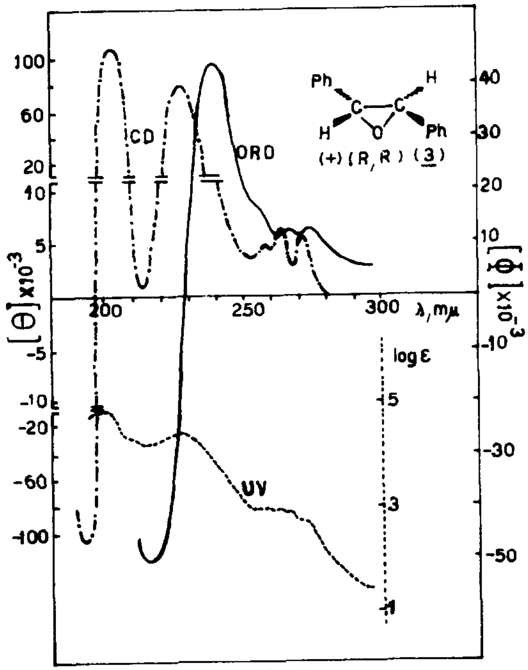

Fig. 3

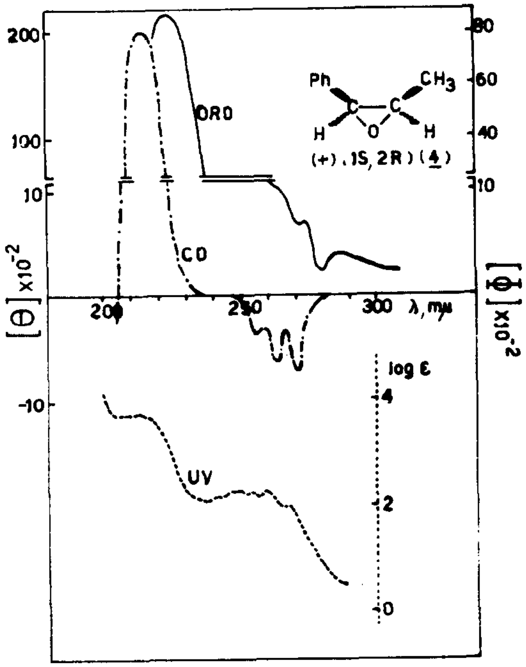

Fig. 4

in 3 the phenyl rings should be perpendicular to the oxirane ring and therefore distorted with respect to each other.

Acknowledgements.

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