Crystal Structure of Carbocamphenilone and the Visible Region Cotton Effects of Cyclic α-Diketones

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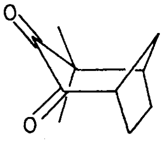
Summary *X*-Ray crystallography of carbocamphenilone shows that the cyclohexanedione ring has a chair conformation (Ib), which, according to crystal-film, KBr-disc, and temperature-dependent optical rotatory evidence, is almost completely retained in solution at 25° C.

From molecular orbital calculations of a skewed glyoxal model, Hug and Wagnière[1] have proposed that the positive 400 nm region Cotton effect of (+)-carbocamphenilone[2] is associated with a right-handed α-diketone chirality, implying predominance in solution of the boat-like cyclohexanedione conformation (Ia).

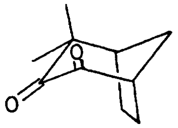
This interpretation was challenged[3] on the grounds that the methyl-methylene eclipsing in (Ia) favours the chair-like, left-handed dione conformation (Ib). Axial bond chirality contributions[4] were also considered[3] to be consistent with (Ib) but not with (Ia). In an independent molecular orbital treatment, Charney and Tsai[5] reached just the opposite Cotton-effect *vs.* dione-chirality correlation deduced by Hug and Wagnière.

To resolve these conflicting views, we have determined the solid-state conformation of carbocamphenilone by *X*-ray crystallography. We also report new c.d. data which indicate that the predominant conformation in solution is the same as that in the crystal and also help to clarify the relationship between the Cotton effect and chirality in cyclic α-diketones.

For the *X*-ray determination, (±)-carbocamphenilone, prepared by the method of Hückel[6] from (±)-camphene, was used. The moisture-sensitive[2] dione, m.p. 59—60°, crystallizes from ligroin in the monoclinic space group $P2_1/n$ with the cell dimensions: $a = 11{\cdot}730$, $b = 10{\cdot}250$, $c = 7{\cdot}785$ Å; $\beta = 95{\cdot}09°$. There is one molecule per asymmetric unit. The data were collected on a Syntex P1 autodiffractometer using Mo radiation and a graphite monochromator. The structure was determined by direct methods[7] using 834 reflections and was refined to an R index of 0·050. All bond lengths and angles are within expected values for the structure. The molecule has a chair cyclohexanedione conformation with a dione torsional angle of 33·9° [structure (Ib) for the (+)-enantiomer].



(Ia)



(Ib)

To study the c.d. behaviour, (−)-carbocamphenilone, m.p. 55—56°, $[\alpha]_D$(ether) −370°, was prepared from (−)-camphene of high optical purity derived from (−)-nopol.[8] In ether-isopentane (1:3), the dione exhibited a negative c.d. band at 393 nm ($\Delta\epsilon$ −1·59) and a positive one at 287 nm ($\Delta\epsilon$ +1·25). Essentially the same spectra were obtained in the solid state; in thin crystal films the negative longer wavelength band appeared at 415 nm, and in KBr discs it occurred at 390 nm. The rotational strength in ether–isopentane was also measured in the temperature range of 170—300 K. When analysed by the method of Moscowitz,[9] the data indicated that the free energy difference between the two conformers is at least 7·3 kJ mol^{-1}, corresponding to more than 95% of the more stable solid-state conformation [mirror image of (Ib)] in solution at 25 °C.

In addition, we noted that the 400 nm region c.d. band in solution is preceded by a much weaker band of opposite sign at 475 nm ($\Delta\epsilon$ +0·02, in ether–isopentane), which is almost undetectable in the o.r.d. curve.[2] Evidently this weak band is not observed in camphorquinone.[1,5] However, (−)-α-oxodaucone,[10] a rigid, right-handed chair-form cyclohexanedione,[3] exhibits a similar weak positive band at 464 nm ($\Delta\epsilon$ +0·04, in dioxan) accompanied by a much stronger negative one at 406 nm ($\Delta\epsilon$ −1·60).[10] This behaviour is also reminiscent of the u.v. region c.d. spectra of certain cisoid conjugated dienes and enones.[4]

We conclude that right-handed cyclic 1,2-diones having left-handed α-axial bond chirality[3] give rise to a substantial negative 350—500 nm Cotton effect associated with a comparatively weak positive band (when detectable) in the longer wavelength portion of this region.

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