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# CHARGE-TRANSFER BANDS OF BICYCLIC β,γ-UNSATURATED KETONES. CIRCULAR DICHROISM OF (+)-(1R)-5,6-DIMETHYLIDENE-2-BICYCLO[2.2.2]OCTANONE AND (+)-(1R)-2-BICYCLO[2.2.2]OCT-5-ENONE

Pierre-Alain Carrupt and Pierre Vogel*

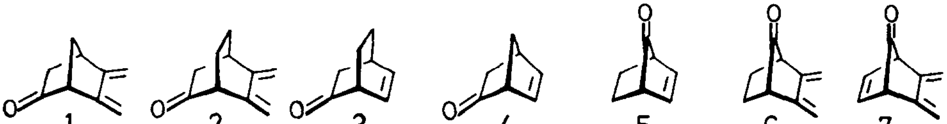
*Institut de chimie organique de l'Université, 2 rue de la Barre,*
*CH-1005 Lausanne, Switzerland*

Summary: *An "extra" band between those attributed to the carbonyl and olefinic chromophores has been found in the CD spectra of bicyclic ketones homoconjugated to endocyclic olefins or exocyclic dienes.*

The CD spectrum of (+)-(1R)-5,6-dimethylidene-2-norbornanone (1) in isooctane[1] or in the gas phase[2] displays unexpected features between 265 and 340 nm. Instead of showing a strong Cotton effect for the β,γ-unsaturated carbonyl[3], it presents the superposition of two Cotton effects of opposite sign. The low energy signal has a fine Franck-Condon contour typical of a "localized" n(CO) → $\pi^*$(CO) transition. The second is a broad band suggesting a "delocalized" charge-transfer diene-skeleton-carbonyl transition. CNDO/S calculations[4] including singly and doubly excited configuration interactions on 1 reproduced the observed CD spectrum. We have calculated also the electronic spectra of the rigid bicyclic ketones 2 - 7 (using MNDO[5] minimized geometries) and predicted that an "extra" band between those attributed to the carbonyl and olefinic chromophores must be present in the UV and CD spectra of all these systems (see Table). A recent publication by *Lightner et al.*[6] on the chiroptical properties of derivatives of 5 urges us to disclose our results on 2 - 7.

The keto-diene (+)-(1R)-2 was prepared by Collins oxidation of the 5,6-dimethylidene-*exo*-2-bicyclo[2.2.2]octanol obtained by asymmetric hydroboration of endo-5,6-bis(tosyloxymethyl)-2-

Table: Calculated (CNDO/S) and experimental (in parenthesis, by CD) transitions (nm) in:



| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| n → $\pi^*$ (CO) : | 276 (318) | 293 (320) | 267 (295) | 265 (306)[10] | 253 (275)[6] | 271 | 285 |
| "extra" band : | 238 (288) | 237 (280) | 189 (213) | 198 (<200) | 209 (233) | 242 | 235 |
| π → $\pi^*$ (olefin) : | 196 (248) | 203 (253) | 179 (203) | 180 (214) | 178 | 197 | 211 |

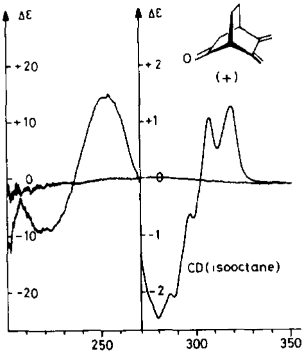


Figure 1: CD of 2

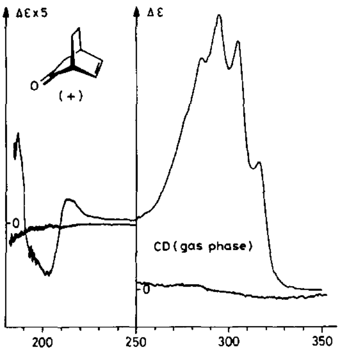


Figure 2: CD of 3

-bicyclo[2.2.2]octene[7] with monoisopinocampheylborane[11] followed by elimination. Its CD spectrum in isooctane is reproduced in Fig. 1. A similar spectrum was measured in the gas phase. As expected by comparison with 1 and from our calculations, two Cotton effects of opposite sign are observed between 270 and 330 nm. The CD spectrum of the simpler ketone 3[8] (gas phase) is reported in Fig. 2. It shows also the "extra" band between those expected for the CO and C=C chromophores, in agreement with our calculations (see Table). *Lightner et al.* have obtained similar results for two chiral derivatives of 5.

According to the CNDO/S calculations, the "extra" band in 1 - 7 is a mixed transition with substantial charge-transfer components of the form $\pi$(olefin) → $\pi^*$(CO) and n(CO), $\sigma \rightarrow \pi^*$(olefin).

In the case of $\beta,\gamma$-unsaturated ketones such as 1 and 2, it might be hazardous to apply the rules[9] that correlate the absolute configuration with the sign of the Cotton effect associated with the $n \rightarrow \pi^*$(CO) transition.

## References and notes.

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7. Details will be given in a full paper. The preparation of 2-substituted 5,6-dimethylidene-bicyclo[2.2.2]octanes will be reported elsewhere (M. Avenati, dissertation, University of Lausanne, 1981). The (+)-(1R) configuration of 2 is deduced from its CD spectrum and by comparison with that of 1. It will be confirmed by chemical correlation. UV(isooctane): 251.5 nm (ε, 6700), 289(280), 299(310), 307(220); IR(film): 3080, 1735 $cm^{-1}$, $[\alpha]_D^{25}$= +8.4, c = 2, $CHCl_3$.
8. We thank Prof. M. Nakazaki, Osaka University, for a sample of (+)-3 (e.e. 26%).
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