Notizen / Notes

Circulardichroism, XCII[1)]

Proof of the Sector Rule for α Band CD of the o-Dialkyl-Substituted Benzene Chromophore

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The sector rule for the correlation of the α band Cotton effect of o-disubstituted benzene derivatives with an achiral skeleton has been unequivocally proved by measurement of the CD of benzonorpinene **3**.

For the correlation of the sign of the α band CD with the absolute configuration of simple benzene derivatives three different rules have been proposed in the past. Kuriyama et al.[2)] introduced a quadrant rule for tetrahydroisoquinolines using the C_2 axis of the skeleton as z axis. DeAngelis and Wildman[3)] also published a quadrant rule, used, however, as z axis the direction of the bond from the benzene chromophore towards the nearest centre of chirality. The first of these rules had been suggested to be mainly applicable to the first CD band, the second preferably to the second one. Both groups of authors assumed sign inversion between the first and second Cotton effect.

In our rule[4)] we followed the general principle that one has to combine the symmetry-determined nodal planes with the MO-determined nodal spheres. In first approximation the latter can also considered to be planes. This leads to a rule with 16 sectors for the α-band and with 12 for the p band CD in case of a tetralin. Although rules with so many sectors seem to be of no great practical value one should take into account that usually the chiral part of the molecules lies within only four or eight sectors. Such a sector rule is, however, only applicable to the estimation of the contributions to the CD of groups which are farther away from the chromophore; those of substituents in benzylic position should be treated by the appropriate helicity rule[4)]. As a support for the presence of (at least) two more nodal planes as had been proposed by Kuriyama et al.[2)] we cited e.g. the CD spectra of the stereoisomeric alkaloids haemanthamine and crinamine[2)]: within the α band both epimers show identical Cotton effects, whereas differences are found for the p band[4)].

The signs for the contributions of groups in the individual sectors had been taken from empiry[2−4)]; in no case, however, compounds had been used whose molecules *firstly* are rigid, and *secondly* do not give contributions which have to be treated by the helicity rule.
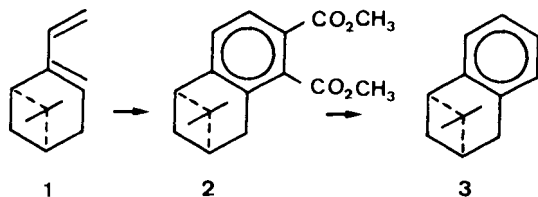
To this latter mentioned class belong e.g. all hitherto investigated tetralins (tetrahydroisoquinolines), for which the sense of helicity of the condensed cyclohexene (piperideine) ring determines in first approximation the sign of the Cotton effect.

We have, therefore, synthesized the model compound **3** in enantiomerically pure form, following the procedure described by Paquette et al.[5)], who published, however, no spectroscopic data for their product. The starting material (−)-(1R,5S)-nopadiene was provided to us by Kuhn[6)], and transformed into **3** via the dimethyl ester **2**, following the literature[5)]. Helicity contributions to the CD compensate each other, since the skeleton is achiral. Both methyl groups are positioned within the same sector, which according to all three mentioned rules[2−4)] is considered to be "positive" (Figure 1). For **3** in isooctane solution a relatively strong positive Cotton effect with pronounced fine structure within the α band was found (CD
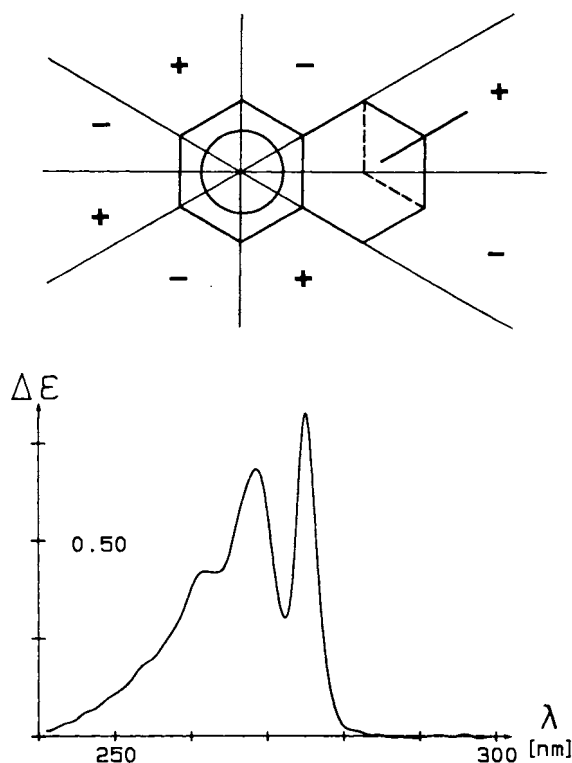

Figure. 1. Top: Sector rule for the α band of the o-dialkylated benzene chromophore; signs refer to the upper sectors. Bottom: CD of **3**

for the 0—0 line is +0.83 at 275 nm). This proves thus unequivocally that the signs for the CD contributions of groups in those sectors which are close to that nodal plane which is perpendicular to the benzene ring had indeed been assumed correctly before.

At shorther wavelengths around 230 to 215 nm another CD could be recorded for **3**, whose sign is negative, i.e. opposite to that within the α band. In the past many CD spectra had been published in which the same sign pattern had been found; we have, however, also several cases, where both respective signs are the same. The situation is even more complicated by the fact that calculations by Allen and Schnepp[7] place an additional absorption band of E_{1u} symmetry (benzene notation) in between, which is electrically dipole-forbidden, but magnetically allowed. Since the signal-to-noise ratio is already quite low for this band, and because of the uncertainty of its parentage we merely cite the fact and refrain from more detailed interpretation.

Compound **2** is a derivative of phthalic acid, for which it is known that the COOR groups are not coplanar with the benzene ring[8]. If the chirality is localized in the alcohol part then the preferred torsional angle is determined by the absolute configuration of the alcohol, which in case of secondary ones could be correlated with the sign of the Cotton effect between 255 to 240 nm[9]. In a compound like **2** the chirality is on the contrary located in the acid part, and then a correlation with absolute configuration seems possible only when the torsional angles are in a simple way determined by the helicity of the attached ring. This is not the case with **2**, since its skeleton is achiral. For both Cotton effects, that between 255 to 240 nm as well as one with fine structure between 290 to 275 nm negative signs have been recorded, but from a single example it is impossible to draw conclusions about the type of such a sector rule.

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Experimental

Rotation: Perkin-Elmer Polarimeter 141. — IR spectra: Perkin-Elmer Model 1310. — UV: Varian CARY 17. — CD: Jobin Yvon Dichrographe III connected on-line to a PC. — ¹H-NMR spectra: Bruker WP 80, Bruker AM 400. — ¹³C NMR (DEPT), NOE difference spectra, 2D NMR: Bruker AM 400. — MS: Varian MAT CH-5, Varian MAT 711. — Preparative gas chromatography (GC): Varian Aerograph 920, 4-m × 0.35-cm column with 5% OV 17 on chromosorb W AW (100—120 mesh), 50 ml Helium/min. — Elemental analysis: Microanalytical Laboratory, Kossuth Lajós Tudományegytem, Box 20, Debrecen, Hungary.

(—)-Dimethyl (1R,9R)-10,10-Dimethyltricyclo[7.1.1.0²·⁷]undeca-2,4,6-triene-5,6-dicarboxylate (**2**): In analogy to the literature[5] 7.25 g (0.050 mol) of freshly distilled (2 Torr) (—)-(1R,5S)-nopadiene (**1**) was treated with 6.10 ml (0.060 mol) of dimethyl acetylenedicarboxylate (DMAD) and subsequently with 10.0 g (44 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). After column chromatography (CC) on alumina (ether) and on silica gel [hexane/dichloromethane (10:1)], diester **2** (9 g, 64%) was obtained as a colourless oil. For CD measurements a sample was sublimed and once more chromatographed [silica gel, hexane/dichloromethane (10:1)]. — $[\alpha]_D^{22}$ = −64 (c = 1.8, in hexane). — IR (CCl₄): ṽ = 1725 cm⁻¹ (C=O), 1590 (C=C_ar). — UV (hexane): λ_max (lg ε) = 290 nm (3.17), 280 (3.18), 247 (4.08), 210 (4.52). — CD (isooctane): λ (Δε) = 290 nm (−0.50), 281 (−0.45), 247 (−2.30). — ¹H NMR (400 MHz, CDCl₃): δ = 7.69 (d, J = 8 Hz, 1H), 6.99 (d, J = 8 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.93 (m, 2H), 2.80 (t, J = 5.7 Hz, 1H), 2.60 (m, 1H), 2.27 (m, 1H), 1.34 (s, 3H), 1.20 (d, J = 9.7 Hz, 1H), 0.60 (s, 3H). — ¹³C NMR (100 MHz, CDCl₃): δ = 169.7 (s),

166.4 (s), 152.7 (s), 134.6 (s), 132.6 (s), 127.4 (d), 126.8 (d), 125.3 (s), 52.4 (q), 52.2 (q), 48.1 (d), 39.8 (d), 38.9 (s), 31.1 (t), 30.5 (t), 25.9 (q), 21.2 (q). — ¹H-NMR NOE difference: Irradiation at δ = 0.60, response at δ = 1.34, 2.80, 2.93; irradiation at δ = 1.34, response at δ = 0.60, 2.27, 2.60, 2.80. — HH COSY: Signal at δ = 1.20 correlates with signal at δ = 2.60; δ = 2.27 corr. w. δ = 2.60, 2.80, and 2.93; δ = 2.60 corr. w. δ = 1.20, 2.27, and 2.80; δ = 2.80 corr. w. δ = 2.27, and 2.60; δ = 2.93 corr. w. δ = 2.27. — CH COSY: ¹³C signal at δ = 21.2 correlates with ¹H signal at δ = 0.60; δ = 25.9 corr. w. δ = 1.34; δ = 30.5 corr. w. δ = 2.93; δ = 31.1 corr. w. δ = 1.20 and δ = 2.60; δ = 39.8 corr. w. δ = 2.27; δ = 48.1 corr. w. δ = 2.80. — MS (70 eV): m/z (%) = 288 (2), 256 (40), 213 (100), 196 (28).

C₁₇H₂₀O₄ (288.3)   Calcd. C 70.81 H 6.99
                   Found C 70.83 H 7.10

(1R,9R)-10,10-Dimethyltricyclo[7.1.1.0²·⁷]undeca-2,4,6-triene (**3**): We used a procedure similar to Paquette's prescription[5]. The dimethyl ester **2** (5.6 g, 0.019 mol) was treated with aqueous potassium hydroxide instead of sodium hydroxide (15 h, 80°C). Workup afforded 5.0 g (99%) of the crude dicarboxylic acid, m.p. 134—136°C. A mixture of this acid (3.0 g, 0.012 mol), quinoline (20 ml), copper powder (1 g), and copper(I) oxide (50 mg) was stirred and heated to 230°C under argon. Already 10 min later the mixture was allowed to cool down in order to obtain the monocarboxylic acid, too. The mixture was diluted with ether (50 ml), washed 3 times with 1 N hydrochloric acid and with NaCl solutions, and concentrated by distillation under argon. Column chromatography (silica gel) permitted a rapid separation of the hydrocarbon **3** (pentane solution) from the monocarboxylic acid (dichloromethane solution with an increasing content of acetic acid); yield 1.1 g (44%). Preparative GC (110°C, retention time: 40 min) of **3** was carried out twice to obtain a sample (100 mg, 5%) of maximum purity. — IR (CCl₄): ṽ = 3070 cm⁻¹, 1600, 1580, 1515, 1265, 725. — UV (hexane): λ (lg ε) = 275 nm (2.95), 268 (2.83), 260 (2.64), 229 (3.34), 223 (3.73), 219 (3.84), 213 (4.00). — CD (hexane): λ (Δε) = 275 nm (+0.83), 268 (+0.68), 262 (+0.42), 229 (−1.0), 223 (−1.3), 219 (−1.3). — ¹H NMR (80 MHz, CDCl₃): δ = 6.9—7.2 (m, 4H), 3.03 (m, 2H), 2.7 (m, 2H), 2.33 (m, 1H), 1.42 (s, 3H), 1.31 (d, J = 8.5 Hz, 1H), 0.69 (s, 3H). — ¹³C NMR (100 MHz, CDCl₃): δ = 146.8 (s), 134.8 (s), 127.7 (d), 125.9 (d), 125.8 (d), 124.9 (d), 47.8 (d), 40.6 (d), 39.2 (s), 33.0 (t), 32.0 (t), 26.2 (q), 21.3 (q). — MS (70 eV): m/z (%) = 172 (10), 157 (7), 129 (100), 115 (14).

C₁₃H₁₆   Calcd. 172.1252   Found 172.1251 (MS)

CAS Registry Numbers

1: 30293-06-2 / **2**: 119945-27-6 / **2** (free acid): 119909-16-9 / **3**: 62291-58-1 / (MeO₂CC≢)₂: 762-42-5

[1] Part XCI: K. Netzke, G. Snatzke, *Chem. Ber.* **122** (1989) 1365.
[2] [2a] K. Kuriyama, T. Iwata, K. Moriyama, K. Kotera, Y. Hamada, R. Mitsui, K. Takeda, *J. Chem. Soc. B*, **1967**, 46. — [2b] S. Hagishita, K. Kuriyama, *Bull. Chem. Soc. Jpn.* **55** (1982) 3216.
[3] G. G. DeAngelis, W. C. Wildman, *Tetrahedron* **25** (1969) 5099.
[4] G. Snatzke, P. C. Ho, *Tetrahedron* **27** (1971) 3645.
[5] L. A. Paquette, W. P. Melega, J. D. Kramer, *Tetrahedron Lett.* **1976**, 4033.
[6] H. Kuhn, *Dissertation*, Ruhr-Universität Bochum, 1983. Kuhn prepared (−)-(1R,5S)-nopadiene from (−)-(1S,5S)-β-pinene. Several other authors found positive optical rotations for nopadiene synthesized from the same precursor. This discrepancy might be caused by isomeric impurities like (+)-homoverbenene.
[7] S. D. Allen, O. Schnepp, *J. Chem. Phys.* **59** (1973) 4547.
[8] O. Ermer, *Helv. Chim. Acta* **64** (1981) 1902.
[9] J. Frelek, A. Konowal, G. Piotrowski, G. Snatzke, U. Wagner, in *New Trends in Natural Product Chemistry* (Atta-ur-Rahman, P. W. Le Quesne Eds.), p. 477, Elsevier, Amsterdam 1986.

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