46. Circular Dichroism of Planar, Exocyclic s-*cis*-Butadienes Remotely Perturbed[1])

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In memorian Professor Dr. *Pierre Crabbé*[4]), General Secretary of the International Organization for Chemical Sciences in Development (IOCD)

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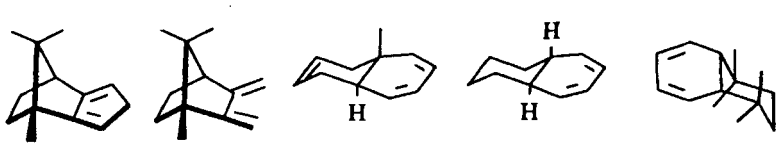
Optically pure 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl derivatives have been prepared. The sign of the *Cotton* effects associated with the lowest-energy transition of 2-(dicyanomethylidene)-((−)-(1*S*,4*S*)-**15**), (*E*)-2-(methoxyimino)-((+)-(1*S*,4*S*)-**16**), (*Z*)-2-(methoxyimino)-5,6-dimethylidenebicyclo[2.2.1]heptane ((−)-(1*S*,4*S*)-**17**), and 2,3,5-trimethylidenebicyclo[2.2.1]heptane ((−)-(1*R*,4*S*)-**18**) is opposite to the chirality constituted by the coupling of the electric transition moments of the two homoconjugated π-chromophores (*Kuhn-Kirkwood* dipole-coupling mechanism). When the substituents at C(2) are not π-functions, no general rule can be retained for the chiroptical properties of the 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl systems as shown for dimethyl acetal (−)-(1*S*,4*S*)-**19**, ethylene acetal (+)-(1*R*,4*R*)-**20**, *exo* and *endo* methyl ethers (+)-(1*R*,2*S*,4*R*)-**21** and (+)-(1*R*,2*R*,4*R*)-**22**, and for spiro[5,6-dimethylidenebicyclo[2.2.1]heptane-2,2'-oxiranes] (−)-(1*S*,2*S*,4*S*)-**23** and (−)-(1*S*,2*R*,4*S*)-**24**.

Introduction. – The chiroptical properties of non-planar, homoannular *'cisoid'* dienes have been studied in details [2] [3]. The circular dichroism (CD) of planar, or nearly planar s-*cis*-butadienes have been less studied. In 1976, *Burgstahler et al.* [4] reported the circular dichroism (CD) spectra of dienes **1** and **2**, two compounds whose asymmetry arises from allylic substitution. More recently, the same authors presented a multisector chirality rule for non-planar conjugated *'cisoid'* dienes which delimits the contribution of homoallylic and bis-homoallylic alkyl groups to the *Cotton* effects (CE) of the endocyclic dienes **3**–**5** [5]. *Paquette et al.* [6] described recently the CD spectra of the planar, less flexible conjugated dienes **6** and **7** (R = D, CH_3). In 1980, we reported on the CD spectra and the preparation of optically pure exocyclic dienes[5]) **8**–**12** whose chirality is due to



1 **2** **3** **4** **5**

[1]) Interaction between non-conjugated chromophores, Part 29. Part 28, see [1].

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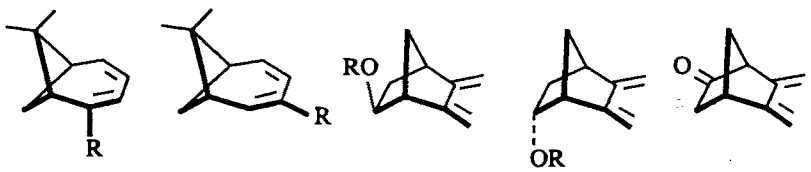
[5]) An exocyclic butadiene moiety means that each double bond is in an exocyclic position on the ring skeleton.



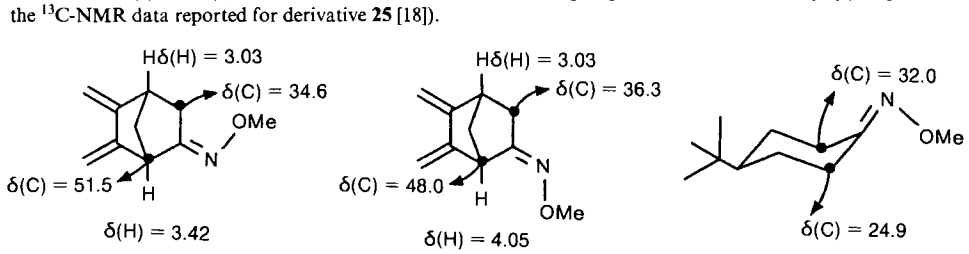
6 **7** **8** R = H, **10** R = Ac, **13** R = ArCO **9** R = H, **11** R = Ac, **14** R = ArCO **12**

homoallylic substituents [7]. We have also investigated the application of the chiral exciton coupling method on the CD spectra of the *para*-substituted benzoates **13** and **14** [8]. Typical exciton split CE's were observed for the *endo* derivatives **14** only. Their origin was attributed to the coupling of the benzoate and diene electric transition moments, consistent with the *Kuhn-Kirkwood* dipole-coupling mechanism [9] [10].

We report the synthesis of new, optically pure exocyclic s-*cis*-butadiene derivatives **15**–**24** displayed in the *Table*. Their chiroptical properties will be compared with those of dienes **8**, **9**, and **2**. The asymmetry in these molecules is due to the substitution at C(2). We shall see that the sign and rotational strength (as given by $\Delta\varepsilon$) of these dienes depend on the nature of the substituents at C(2). The possible origin of the CE's will be discussed in light of the *Kuhn-Kirkwood* dipole-coupling mechanism [9], the 'allylic axial chirality rule' [11], and the 's-*cis*-diene helicity rule' [2] [3] [12].

Results and Discussion. – *Knoevenagel* condensation [13] of (−)-(1*S*,4*S*)-5,6-dimethylidenebicyclo[2.2.1]heptan-2-one ((−)-(1*S*,4*S*)-**12**) with malonodinitrile gave triene (−)-(1*S*,4*S*)-**15**. With *O*-methylhydroxylamine hydrochloride, (−)-(1*S*,4*S*)-**12** gave (aq. EtOH, AcONa, 20° [14]) a 1:1 mixture of the (*E*)- and (*Z*)-*O*-methyloximes (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17**, respectively, which were separated and purified by HPLC (see *Exper. Part*).

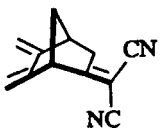
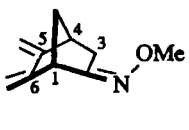
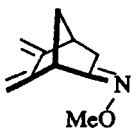
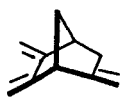
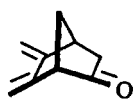
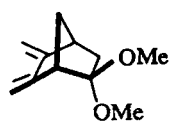
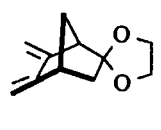
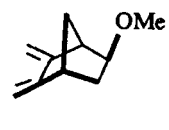
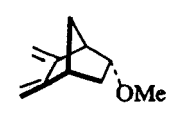
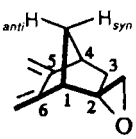
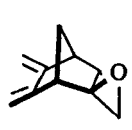
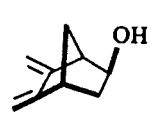
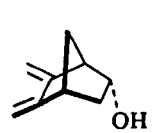
The relative configurations (*E vs. Z*) of the *O*-methyloximes (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17**, was established by 360-MHz ^{1}H-NMR and with the help of [Eu(dpm)$_3$]-induced chemical shifts [15]. Coordination of the lanthanide to the O-atom of the MeO group led to quite different induced chemical shifts for olefinic protons CH_2=C(6) (see *Exper. Part*) whether the *O*-methyloxime is (*E*) or (*Z*). Our attribution was also consistent with the comparison of the ^{1}H-(δ(H)) and ^{13}C-NMR (δ(C)) chemical shifts of (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17** as shown below [14] [16]. The deshielding effect of the MeO group on H–C(1) is larger in the case of (−)-(1*S*,4*S*)-**17** than for (−)-(1*S*,4*S*)-**16**, consistent with data reported for other derivatives [14] [16]. Typical shielding γ-effects are observed for C(1) and C(3) in the ^{13}C-NMR spectra when the MeO group is *cis* to these C-atoms [17] (compare with the ^{13}C-NMR data reported for derivative **25** [18]).



(+)-(1*S*,4*S*)-**16**[a] (-)-(1*S*,4*S*)-**17**[a] **25**[a]

[a] δ's in ppm.

Table. *CD Characteristics* (*Cotton* Effects, $\Delta\varepsilon_\lambda$[a])) *and Dihedral Angles* β *between the Methylidene Moieties of 5,6-Dimethylidenebicyclo[2.2.1]hept-2-yl Derivatives as obtained by the MNDO Technique* (completely minimized geometries)[b])

				
(−)-(1*S*,4*S*)-**15** $\Delta\varepsilon_{281} = +4.5$ $\Delta\varepsilon_{272} = 0$ $\Delta\varepsilon_{233} = -28.0$ $\beta = +0.9°$	(+)-(1*S*,4*S*)-**16** $\Delta\varepsilon_{248.5} = +8.86$[e]) $\Delta\varepsilon_{239} = 0$ $\beta = +1.5°$[c])	(−)-(1*S*,4*S*)-**17** $\Delta\varepsilon_{248} = +22.5$[e]) $\Delta\varepsilon_{235} = 0$ $\Delta\varepsilon_{219} = -65.3$ $\beta = +0.1°$[c])	(−)-(1*R*,4*S*)-**18** $\Delta\varepsilon_{250} = +0.9$ $\beta = +0.9°$	(−)-(1*S*,4*S*)-**12** $\Delta\varepsilon_{318} = -0.59$ $\Delta\varepsilon_{287} = +1.2$ $\Delta\varepsilon_{248} = -10.3$ $\beta = +0.9°$
				
(−)-(1*S*,4*S*)-**19** $\Delta\varepsilon_{243} = +1.25$ $\beta = -4°$	(+)-(1*R*,4*R*)-**20**[d]) $\Delta\varepsilon = +0.47$ $\beta = +2.8°$	(+)-(1*R*,2*S*,4*R*)-**21**[d]) $\Delta\varepsilon_{243} = -0.46$ $\beta = +0.8°$	(+)-(1*R*,2*R*,4*R*)-**22**[d]) $\Delta\varepsilon_{249} = +0.56$ $\beta = +0.8°$	
				
(−)-(1*S*,2*S*,4*S*)-**23** $\Delta\varepsilon_{242} = -2.0$[e]) $\beta = +0.6°$	(−)-(1*S*,2*R*,4*S*)-**24** $\Delta\varepsilon_{241} = +0.5$[e]) $\Delta\varepsilon_{233} = +0.66$ $\beta = +0.1°$	(+)-(1*R*,2*S*,4*R*)-**8**[d]) $\Delta\varepsilon_{245} = +0.33$ $\beta = +0.6°$	(+)-(1*R*,2*R*,4*R*)-**9**[d]) $\Delta\varepsilon_{244} = +1.8$ $\beta = +1.2°$	

[a]) Measured in isooctane. Similar spectra were obtained in 95% EtOH, except in the cases of (+)-(1*R*,4*R*)-**20** and (+)-(1*R*,2*R*,4*R*)-**22** for which sign inversion of the CE accompanied the change of solvent!

[b]) A positive dihedral angle β means that CH_2=C(6) bends toward the *exo* face above CH_2=C(5) and thus confers a right-handed screwness (positive helicity) to the s-*cis*-butadiene unit. Similar β values were calculated with the force-field approach (MM2 [39]) on model 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl derivatives.

[c]) Values calculated for the corresponding oximes.

[d]) The enantiomers of these compounds must be compared with the other systems of the *Table*.

[e]) Similar CE's (no change in the sign) were observed in the gas phase.

Methylenation [19] of (−)-(1*S*,4*S*)-**12** gave triene (−)-(1*S*,4*S*)-**18**. The dimethyl acetal (−)-(1*S*,4*S*)-**19** was derived from (−)-(1*S*,4*S*)-**12** by reaction with methyl orthoformate in MeOH containing a trace of *Amberlyst 15* [20]. The ethylene acetal (+)-(1*R*,4*R*)-**20** was obtained similarly by heating (+)-(1*R*,4*R*)-**12** with ethylene glycol [21]. The methyl ethers (+)-(1*R*,2*S*,4*R*)-**21** and (+)-(1*R*,2*R*,4*R*)-**22** were derived (NaH/THF, MeI) from dienols (+)-(1*R*,2*S*,4*R*)-**8** and (+)-(1*R*,2*R*,4*R*)-**9**, respectively. Treatment of (−)-(1*S*,4*S*)-**12** with the sulfur-ylide derived from trimethylsulfoxonium iodide and NaH [22] gave a 1:1 mixture of epoxy-dienes (−)-(1*S*,2*S*,4*S*)-**23** and (−)-(1*S*,2*R*,4*S*)-**24** (68%) which were separated and purified by HPLC.

The *endo* (**23**) *vs. exo* (**24**) relative configuration of the epoxide moiety was established by 360-MHz ^{1}H-NMR with the help of nuclear *Overhauser* effect (NOE) measurements between the spiro-oxirane protons $CH_2(3')$ and H_{exo}–C(3) (2.14 ppm) in the case of (–)-(1*S*,2*S*,4*S*)-**23**, and H_{endo}–C(3) (1,70 ppm) in the case of (–)-(1*S*,2*R*,4*S*)-**24**. Distinction between H_{endo}–C(3) and H_{exo}–C(3) in these molecules was based on the vicinal coupling constants between these protons and the bridgehead proton H–C(4) [23]. Irradiation of H_{exo}–C(3) of (–)-(1*S*,2*S*,4*S*)-**23** (2.14 ppm) gave NOE's at 2.94 (H–C(4)), 1.46 (H_{endo}–C(3), and 2.79 ppm (H of $CH_2(3')$ of the oxirane *cis* to C(3)). Similarly, irradiation of H_{endo}–C(3) of (–)-(1*S*,2*R*,4*S*)-**24** (1.70 ppm) led to NOE's at 1.91 (H_{exo}–C(3)), 2.60 (H of $CH_2(3')$) of the oxirane *cis* to C(3), and 2.76 ppm (H–C(4)). A 2D-NMR spectrum of (–)-(1*S*,2*S*,4*S*)-**23** correlating δ(H) and δ(C) [24] demonstrated the existence of a ^3J(C,H) of 6 Hz between C(3') (δ(C) = 54.3 ppm) of the oxirane moiety (*exo*-$CH_2(3')$) and H_{exo}–C(3) (δ(H) = 2,14 ppm). Such coupling constant was not detected for the *exo* epoxide (–)-(1*S*,2*R*,4*S*)-**24**. [Eu(dpm)$_3$]-induced ^{1}H-NMR chemical shifts also confirmed the structures of the epoxy-dienes (see *Exper. Part*). The *endo vs. exo* configuration of the epoxides was further confirmed by the difference in reactivity of (–)-(1*S*,2*S*,4*S*)-**23** and (–)-(1*S*,2*R*,4*S*)-**24** toward acidic ionizing media. While (–)-(1*S*,2*S*,4*S*)-**23** (*endo* epoxide) was stable in $CF_3CH(OH)CF_3$ containing a trace of CF_3COOH, (–)-(1*S*,2*R*,4*S*)-**24** was decomposed in 10 min at 20°, consistent with the existence of a participation of the homoallylic diene moiety of the acid-promoted ring opening of the epoxide, possible only in (–)-(1*S*,2*R*,4*S*)-**24** [25].

The absolute configurations of compounds shown in the *Table* were given by their mode of formation. Those of (+)-(1*R*,2*S*,4*R*)-**8**, (+)-(1*R*,2*R*,4*R*)-**9**, and (–)-(1*S*,4*S*)-**12** were given unambiguously by X-ray crystallography of the *exo*-Fe(CO)$_3$ complex of (1*S*,2*R*,4*S*)-5,6-dimethylidenebicyclo[2.2.1]hept-2-*exo*-yl *p*-bromobenzoate [26].

The λ_{max} in the UV-absorption spectra (isooctane) of (dicyanomethylidene)-cyclohexane and 2,3-dimethylidenebicyclo[2.2.1]heptane are found at 236 (ε = 18 200) [27] and 248 nm (ε = 9000) [28], respectively. Comparison of these data with the UV data (isooctane) of 2-(dicyanomethylidene)-5,6-dimethylidenebicyclo[2.2.1]heptane ((–)-(1*S*,4*S*)-**15**), which displays two maxima at 236 (ε = 26 600) and 280 nm (ε = 3230), suggested, but did not prove (effects of the *Franck-Condon* contours associated with the two transitions?), the existence of a transannular interaction between the s-*cis*-butadiene and dicyanoethylene chromophores in (–)-(1*S*,4*S*)-**15**. Support for this hypothesis was given, however, by the observation of two CE's at the same wavelengths as the maxima recorded in the UV-absorption spectrum. The two CE's observed for (–)-(1*S*,4*S*)-**15** have opposite signs. If they would belong to a chiral exciton couplet, involving the s-*cis*-butadiene and 1,1-dicyanoethylene chromophores, opposite signs (negative CE for the lowest-energy transition (281 nm) and positive CE for the second transition (233 nm)) would be expected for the CE's of (–)-(1*S*,4*S*)-**15** since a negative chirality is obtained for the electric transition moments of the lowest energy transition of these chromophores, as shown in *Fig. 1*. One possible hypothesis for this discrepancy is to invoke the existence of charge-transfer transitions between the s-*cis*-butadiene and 1,1-dicyanoethylene chromophores. This type of interactions are obviously not interpreted by the *Kirkwood-Kuhn* mechanisms [9] [10].

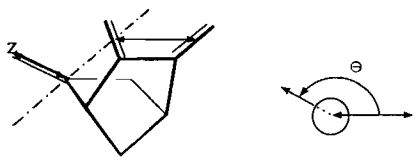


Fig. 1. *Projection of (–)-(1S,4S)-***15** (Z=C(CN)$_2$) *using MNDO optimized geometry*. The $V_1 \leftarrow N$ electric transition moments of the s-*cis*-butadiene moiety is taken parallel with C(5)–C(6), the extremities of the vector corresponding to the mid-points of CH_2=C(5) and CH_2=C(6) [29]. The lowest-energy transition electric moment of the Z=C(2) chromophore is taken aligned with Z=C(2) [29a].

The CD spectra of the *O*-methyloximes (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17** (see *Table, Fig. 2*) showed relatively strong positive CE's for their lowest-energy transitions. Assuming electric transition moments of the *O*-methyloximes to be more or less aligned with the C(2)=N direction, the electric dipole moment coupling with the homoconjugated s-*cis*-butadiene chromophore constitutes a negative exciton chirality as in the case of (−)-(1*S*,4*S*)-**15** (*Fig. 1*). One thus would expect negative CE's for the $V_1 \leftarrow N$ transition of dienes (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17** if the *Kirkwood-Kuhn* mechanism could be applied to these bichromophoric systems, which is contrary to our observations. For reason of instrumental limitation, the second CE was observed clearly only in the case of (−)-(1*S*,4*S*)-**17** ($\Delta\varepsilon_{219} = -65.3$). However, the 'exciton split' type of spectra were well defined for both (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17** in their gas-phase CD spectra (*Fig. 2*). Thus, as in the case of (−)-(1*S*,4*S*)-**15**, one cannot rule out yet the hypothesis of the existence of charge-transfer transitions or of another type of transannular interactions between the two homoconjugative functions which govern the dichroic properties of (+)-(1*S*,4*S*)-**16** and (−)-(1*S*,4*S*)-**17**.

The relatively weak, positive CE observed at 250 nm for the $V_1 \leftarrow N$ transition of (−)-(1*R*,4*S*)-2,3,5-trimethylidenebicyclo[2.2.1]heptane ((−)-(1*R*,4*S*)-**18**; *Table*) cannot be explained by the *Kirkwood-Kuhn* mechanism either since a negative chirality is realized by the interaction of the electric transition moments of the s-*cis*-butadiene and ethylene chromophores (*Fig. 1*). Optimized geometry of (−)-(1*R*,4*S*)-**18** obtained by the MNDO technique [30] suggested a twist of 0.9° about bond C(2)–C(3) for the s-*cis*-butadiene moiety, which confers a positive helicity to that π-function. If real, it could explain the positive CE observed for the lowest-energy transition of (−)-(1*R*,4*S*)-**18**.

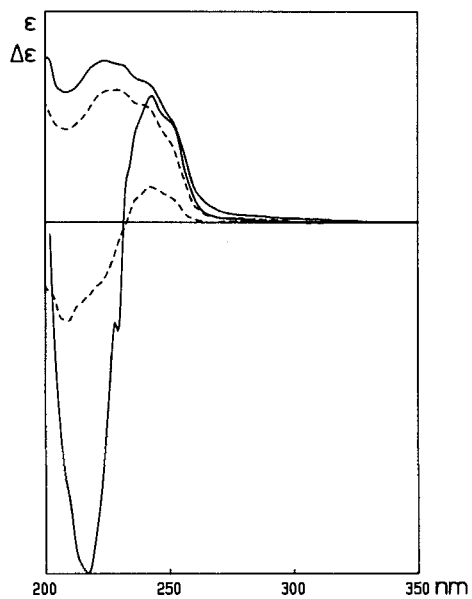
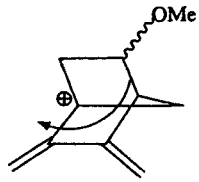


Fig. 2. *Gas-phase UV absorption and CD spectra of (+)-(1S,4S)-***16** [----] *and (−)-(1S,4S)-***17** [——]. Arbitrary vertical scale.

Figure 3



Between 200 and 350 nm, the gas-phase CD spectrum of dienone (−)-(1*S*,4*S*)-**12** displayed the following CE's: $\Delta\varepsilon_{205} \approx -15$, $\Delta\varepsilon_{216} \approx +4.5$, $\Delta\varepsilon_{245} \approx -10$, $\Delta\varepsilon_{280} \approx +0.9$, $\Delta\varepsilon_{318} \approx +1$ [7] [31]. CNDO/S calculations [32] suggested that the first three lowest-energy transitions of **12** are mainly associated with the carbonyl $n \rightarrow \pi^*_{CO}$ transition, a mixed transition with substantial charge-transfer components of the form $\pi(\text{diene}) \rightarrow \pi^*_{CO}$ and $n(CO), \sigma \rightarrow \pi^*(\text{diene})$ and the $V_1 \leftarrow N$ transition of the s-*cis*-butadiene chromophore. The complexity of the CD spectrum of (−)-(1*S*,4*S*)-**12** and the juxtaposition of at least two mechanisms (electric transition moment coupling and coupling of the magnetic moment of the C=O with the electric moment of the diene moiety) for the interactions between the two homoconjugated functions preclude any simple interpretation. It is interesting, however, to note that the sign of the longest-wavelength transition of (−)-(1*S*,4*S*)-**12** ($n \rightarrow \pi^*_{CO}$) followed the 'generalized octant rule' [32–34].

The signs of the CE's of dienes **8**–**13** [7] were found to follow the 'allylic axial chirality rule' as illustrated in *Fig. 3* for alcohols (+)-(1*R*,2*S*,4*R*)-**8** and (+)-(1*R*,2*R*,4*R*)-**9**. This was fortuitous because, as we observe now, this rule is not obeyed by the dimethyl acetal (−)-(1*S*,4*S*)-**19**, the methyl ether (+)-(1*R*,2*S*,4*R*)-**21** and the *exo*-epoxide (−)-(1*S*,2*R*,4*S*)-**24** (see *Table*). Crystallographic X-ray data of (−)-camphorquinone and derivatives [35] suggested that the bicyclo[2.2.1]heptane skeleton can adapt for out-of-plane deformations of the exocyclic dienes grafted onto it. The MNDO-optimized geometries of **8**, **9**, and **19**–**24** (*Table*) confirmed this hypothesis, although the dihedral angle between the two methylidene groups were calculated to be very small, except in the case of the diene-acetals (−)-(1*S*,4*S*)-**19** and (+)-(1*R*,4*R*)-**20**. Surprisingly, the inherent diene helicity calculated by this approach did not correlate in all cases with the sign of the CE's. The most striking examples are the pairs of compounds (−)-(1*S*,4*S*)-**19**/(+)-(1*R*,4*R*)-**20** and (+)-(1*R*,2*S*,4*R*)-**21**/(+)-(1*R*,2*R*,4*R*)-**22**. Since the rotational strengths of the CE's of dienes **8**–**13** and **19**–**24** are relatively small and given the approximate nature of the MNDO calculations, it is not possible, at this moment, to evaluate the relative importance of the contributions due to the homoallylic oxy-substitution at C(2) and of the diene intrinsic helicity to the rotational strength of 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl derivatives.

Conclusion. – No general rule can be proposed yet to interprete the chiroptical properties of 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl derivatives with substituents at C(2) that are not *endo*-benzoates [8a]. If a π-system different from a carbonyl group substitutes C(2) (*e.g.* 1,1-dicyanoethylene, *O*-methyloximes), the CE associated with the $V_1 \leftarrow N$ transition of the s-*cis*-butadiene chromophore can have a relatively large rotational strength, and its sign is opposite to that of the exciton chirality of the two homoconjugated π-chromophores. In the case of (−)-(1*R*,4*S*)-2,3,5-trimethylidenebicyclo[2.2.1]heptane ((−)-(1*R*,4*S*)-**18**), the relatively weak positive CE observed of the s-*cis*-

butadiene chromophore might be associated with the small twist of the diene moiety about the C(2)–C(3) bond as suggested by MNDO calculations. Nevertheless, the calculated diene helicity obtained by that technique did not correlate with the sign of the CE's of all the 5,6-dimethylidenebicyclo[2.2.1]hept-2-yl derivatives presented in this study.

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Experimental Part

General. See [8a] [36].

(–)-(1S,4S)-2-(Dicyanomethylidene)-5,6-dimethylidenebicyclo[2.2.1]heptane ((–)-(1*S*,4*S*)-**15**). A mixture of (–)-(1*S*,4*S*)-**12** [7] (345 mg, 2.6 mmol), malonodinitrile (730 mg, 5.5 mmol), and a few drops of piperidine in anh. MeOH (20 ml) was heated to 55–60° for 80 min. After cooling to 20°, the solvent was evaporated and the residue purified by filtration through a short column of silica gel (AcOEt/petroleum ether 15:85). After recrystallization from pentane (*ca.* 20 ml), 244 mg (52%) of colourless needles were obtained. M.p. 78–80°. $[\alpha]^{22}_{589} = -262$, $[\alpha]^{22}_{578} = -275$, $[\alpha]^{22}_{546} = -315$, $[\alpha]^{22}_{436} = -586$, $[\alpha]^{22}_{365} = -931$ (*c* = 1.25, $CHCl_3$). CD (*c* = 0.0144, isooctane, 25°): 281 (+4.5), 272 (0), 233 (–28.0). CD (*c* = 0.0133, 95% EtOH): 288 (+3.6), 266 (0), 237 (–26.4). CD (*c* = 0.0084, CH_3CN): 286 (+3.4), 267 (0), 235 (–27.8). CD (*c* = 0.0124, $CHCl_3$): 290 (+3.9), 267 (0). CD (*c* = 0.009, AcOH): 285 (+3.3), 267 (0). Other spectral data, see [19]. Anal. calc. for $C_{12}H_{10}N_2$ (182.225): C 79.10, H 5.53, N 15.37; found: C 79.07, H 5.35, N 15.36.

(+)-(1S,4S)-5,6-Dimethylidenebicyclo[2.2.1]heptan-2-one (E)-O-Methyloxime ((+)-(1*S*,4*S*)-**16**) *and (–)-(1S,4S)-5,6-Dimethylidenebicyclo[2.2.1]heptan-2-one (Z)-O-Methyloxime* ((–)-1*S*,4*S*)-**17**). A soln. of $MeONH_2 \cdot HCl$ (166 mg, 1.99 mmol) in EtOH (1 ml) and a soln. of AcONa (170 mg, 2.07 mmol) in H_2O (1 ml) were added to a stirred soln. of (–)-(1*S*,4*S*)-**12** (242 mg, 1.81 mmol) in EtOH (1 ml). After stirring at 20° for 4 h, H_2O (10 ml) was added and the mixture extracted with CH_2Cl_2 (10 ml, 4 times). After drying ($MgSO_4$), the solvent was evaporated and the residue purified by HPLC (*Du Pont Instruments 830* liquid chromatograph, silica gel, 25 cm × 1 cm, AcOEt/hexane 6:94), yielding 100 mg (31%) of (–)-(1*S*,4*S*)-**17** and 90 mg (28%) of (+)-(1*S*,4*S*)-**16**.

*(+)-(1S,4S)-***16**: Colourless oil. B.p. 65°/0.4 Torr. $[\alpha]^{25}_{589} = +2.1$, $[\alpha]^{25}_{578} = +2.3$, $[\alpha]^{25}_{546} = +2.9$, $[\alpha]^{25}_{436} = +10.8$, $[\alpha]^{25}_{365} = 47.0$ (*c* = 13.33, $CHCl_3$). UV (isooctane): 199 (8640), 237 (8970), 246 (sh, 8300), 254 (sh, 6250). CD (*c* = 0.035, isooctane): 248.5 (+8.86), 239 (0). CD (*c* = 0.032, 95% EtOH): 249 (+8.74), 237 (0). IR ($CHCl_3$): 3000, 1470, 1045. ^{1}H-NMR (360 MHz, $CDCl_3$; relative [Eu(dpm)$_3$]-induced shifts in brackets): 5.24 (br. *s*, H of CH_2=C(5) *cis* to C(6) [*ca.* 0]); 5.19 (br. *s*, H of CH_2=C(6) *cis* to C(5) [*ca.* 0]); 5.03 (br. *s*, H of CH_2=C(5) and CH_2=C(6) *trans* to C(6) and C(5), resp. [*ca.* 0]); 3.79 (*s*, CH_3ON [100]); 3.42 (*m*, H–C(1) [92]); 3.03 (*m*, H–C(4) [26]); 2.42 (*dd*, ^2J = 17, ^3J = 3.6, H_{exo}–C(3) [88]); 2.16 (*dm*, ^2J = 17, H_{endo}–C(3) [88]); 1.66 (*m*, CH_2(7) [28]). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 162.8 (*s*, C(2)); 149.3 (*s*, C(5)); 146.0 (*s*, C(6)); 103.7 (*t*, ^1J(C,H) = 143, CH_2=C(6)); 102.0 (*t*, ^1J(C,H) = 156, CH_2=C(5)); 61.2 (*q*, ^1J(C,H) = 143, MeO); 51.5 (*d*, ^1J(C,H) = 150, C(1)); 43.7 (*d*, ^1J(C,H) = 148, C(4)); 39.9 (*tm*, ^1J(C,H) = 136, ^3J(C,H) = 8, C(7)); 34.6 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 163 (31, M^+), 130 (23), 105 (21), 91 (100). Anal. calc. for $C_{10}H_{13}NO$ (163.220): C 73.59, H 8.03; found: C 73.67, H 8.03.

*(–)-(1S,4S)-***17**: Colourless oil. B.p. 65°/0.4 Torr (Kugelrohr). $[\alpha]^{25}_{589} = -294$, $[\alpha]^{25}_{578} = -307$, $[\alpha]^{25}_{546} = -350$, $[\alpha]^{25}_{436} = -600$, $[\alpha]^{25}_{365} = -911$ (*c* = 12.67, $CHCl_3$). UV (isooctane): 203 (8320), 236 (8590), 247 (sh, 7780), 257 (sh, 5700). UV (95% EtOH): 207 (7340), 221 (7900), 229 (sh, 7860), 247 (sh, 7100). CD (*c* = 0.044, isooctane): 248 (+22.50), 235 (0), 218.5 (–65.3). CD (*c* = 0.032, 95% EtOH): 249 (+19.7), 236 (0), 219 (–63.3). IR ($CHCl_3$): 3000,1465, 1045. ^{1}H-NMR (360 MHz, $CDCl_3$; relative [Eu(dpm)$_3$]-induced shifts in brackets): 5.22 (br. *s*, H of CH_2=C(5) *cis* to C(6) [9], H of CH_2=C(6) *cis* to C(5) [23]); 5.04 (br. *s*, H of CH_2=C(6) *trans* to C(5) [41]); 4.96 (br. *s*, H of CH_2=C(5) *trans* to C(6) [7]); 4.05 (*m*, H–C(1) [90]); 3.83 (*s*, CH_3ON [100]); 3.03 (*m*, H–C(4) [19]); 2.48 (*dd*, ^2J = 15, ^3J = 4, H_{exo}–C(3) [96]); 2.13 (*dm*, ^2J = 15, H_{endo}–C(3) [96]); 1.62 (*m*, CH_2(7) [40]). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 161.0 (*s*, C(2)); 149.2 (*s*, C(5)); 144.7 (*s*, C(6)); 103.5 (*t*, ^1J(C,H) = 160, CH_2=C(6)); 102.2 (*t*, ^1J(C,H) = 158, CH_2=C(5)); 61.4 (*q*, ^1J(C,H) = 143, MeON); 48.0 (*d*, ^1J(C,H) = 154, C(1)); 43.6 (*d*, ^1J(C,H) = 147, C(4)); 39.1 (*t*, ^1J(C,H) = 138, ^3J(C,H) = 8, C(7)); 36.3 (*t*, ^1J(C,H) = 136, C(3)). MS (70 eV): 163 (29, M^+), 130 (23), 111 (24), 91 (100). Anal. calc. for $C_{10}H_{13}NO$ (163.220): C 73.59, H 8.03; found: C 73.67, H 8.11.

(−)-(1R,4S)-2,3,5-Trimethylidenebicyclo[2.2.1]heptane ((−)-(1*R*,4*S*)-**18**). Same procedure as for the racemic triene, starting with (−)-(1*S*,4*S*)-**12** [19]. This compound has been prepared first by *Barras* [37].

(−)-(1S,4S)-2,2-Dimethoxy-5,6-dimethylidenebicyclo[2.2.1]heptane ((−)-(1*S*,4*S*)-**19**). A mixture of (−)-(1*S*,4*S*)-**12** (100 mg, 0.746 mmol), $HC(OMe)_3$ (2 ml), *Amberlyst 15* (10 mg) in anh. MeOH (2 ml) was heated under reflux for 1 h. After cooling to 20°, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (30 ml). The soln. was washed with H_2O (30 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue distilled (bulb-to-bulb, 0.001 Torr), yielding 107 mg (80%), colourless oil. $[\alpha]_{589}^{25} = -36.5$, $[\alpha]_{578}^{25} = -38.6$, $[\alpha]_{546}^{25} = -43.4$, $[\alpha]_{436}^{25} = -69.3$, $[\alpha]_{365}^{25} = -95.5$ (*c* = 1.9, $CHCl_3$). UV (isooctane): 240 (8180), 246 (8950), 253 (6090). UV (95% EtOH): 240 (7200), 245 (9060), 253 (6220). CD (*c* = 0.037, isooctane): 243 (+1.25). CD (*c* = 0.032, 95% EtOH): 241 (+1.87). IR ($CHCl_3$): 2845, 1605, 1105. ^{1}H-NMR (80 MHz, C_6D_6): 5.23, 5.19, 4.94, 4.81 (4 br. *s*, olef. H); 3.10, 3.03 (2*s*, 2 MeO); 3.02 (*m*, H–C(1)); 2.64 (*m*, H–C(4)); 2.0–1.3 (*m*, CH_2(3), CH_2(7)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 150.6 (*s*, C(5)); 146.3 (*s*, C(6)); 109.3 (*s*, C(2)); 103.2 (*t*, ^1J(C,H) = 158, CH_2=C(6)); 100.0 (*t*, ^1J(C,H) = 159, CH_2=C(5)); 52.8 (*d*, ^1J(C,H) = 142, C(1)); 49.4, 47.9 (2*q*, ^1J(C,H) = 143, 2 MeO); 44.5 (*d*, ^1J(C,H) = 142, C(4)); 41.1 (*t*, ^1J(C,H) = 132, C(3)); 38.1 (*t*, ^1J(C,H) = 8, C(7)). MS (70 eV): 180 (21, $M^{+\cdot}$), 149 (41), 117 (47), 96 (50), 91 (100). Anal. calc. for $C_{11}H_{16}O_2$ (180.248): C 73.30, H 8.95; found: C 73.32, H 9.04.

(+)-(1R,4R)-2,2-(Ethylenedioxy)-5,6-dimethylidenebicyclo[2.2.1]heptane ((+)-(1*R*,4*R*)-**20**). To a stirred soln. of trimethylsilyl methanesulfonate (8 mg, 0.042 mmol) in anh. CH_2Cl_2 (1 ml), 1,2-bis(trimethylsilyloxy)ethane (1.92 g, 9.3 mmol) and (+)-(1*R*,4*R*)-**12** [7] (557 mg, 4.16 mmol) were added successively at −15° under Ar. The mixture was stirred at −15° for 4 h, then pyridine (0.1 ml) was added. The mixture was poured at once into ice-cold sat. aq. $NaHCO_3$ soln. (15 ml) and extracted with Et_2O (15 ml, 4 times). The combined extracts were dried (Na_2CO_3/Na_2SO_4 1:1), and the solvent was evaporated. The residue was purified by column chromatography on Al_2O_3 (AcOEt/hexane 5:95), yielding 509 mg (69%), colourless oil. B.p. 90°/1 Torr. $[\alpha]_{589}^{25} = +58.9$, $[\alpha]_{578}^{25} = +61.4$, $[\alpha]_{546}^{25} = +69.2$, $[\alpha]_{436}^{25} = +111.3$, $[\alpha]_{365}^{25} = +157$ (*c* = 20, $CHCl_3$). UV (isooctane): 238 (7720), 245 (8500), 254 (5200). UV (95% EtOH): 245 (7200). CD (*c* = 0.05, isooctane): 250 (+0.41), 240 (+0.47), 223 (−0.26). CD (*c* = 0.06, 95% EtOH): 230 (−0.57). IR ($CHCl_3$): 2990, 1645, 1080. ^{1}H-NMR (80 MHz, C_6D_6): 5.35, 5.18, 4.93, 4.78 (4 br. *s*, olef. H); 3.50 (*m*, OCH_2CH_2O); 2.64 (*m*, H–C(1), H–C(4)); 2.15–1.38 (*m*, CH_2(3), CH_2(7)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 150.3 (*s*, C(5)); 145.9 (*s*, C(6)); 114.6 (*s*, C(2)); 103.9 (*t*, ^1J(C,H) = 158, CH_2=C(6)); 100.9 (*t*, ^1J(C,H) = 158, CH_2=C(5)); 64.4, 63.8 (2*t*, ^1J(C,H) = 149, OCH_2CH_2O); 53.6 (*d*, ^1J(C,H) = 146, C(1)); 44.0 (*d*, ^1J(C,H) = 146, C(4)); 43.4 (*t*, ^1J(C,H) = 133, C(3)); 38.3 (*t*, ^1J(C,H) = 137, ^3J(C,H) = 8, C(7)). MS (70 eV): 178 (88, $M^{+\cdot}$), 105 (43), 91 (100). Anal. calc. for $C_{11}H_{14}O_2$ (178.232): C 74.13, H 7.92; found: C 73.98, H 7.84.

*(+)-(1R,2S,4R)-5,6-Dimethylidenebicyclo[2.2.1]hept-2-*exo*-yl Methyl Ether* ((+)-(1*R*,2*S*,4*R*)-**21**). A suspension of NaH (520 mg, 21.6 mmol) in anh. THF (3.2 ml) was prepared from 80% NaH in oil (650 mg), washed with anh. THF (5 ml, 3 times). (+)-(1*R*,2*S*,4*R*)-**8** [7] (220 mg, 1.6 mmol) in anh. THF (1.2 ml) was added followed by the addition of CH_3I (2.4 ml, 38.5 mmol). After stirring at 20° for 1 h, the mixture was cooled to 0°, and H_2O (10 ml) was added dropwise under vigourous stirring. The mixture was extracted with CH_2Cl_2 (25 ml, 4 times). The org. phases were combined and washed with H_2O (30 ml, 4 times) and dried ($MgSO_4$). The solvent was evaporated and the residue distilled *in vacuo*, yielding 123 mg (52%), colourless oil. B.p. 70°/14 Torr. $[\alpha]_{589}^{25} = +40.6$, $[\alpha]_{578}^{25} = +42.4$, $[\alpha]_{546}^{25} = +48.5$, $[\alpha]_{436}^{25} = +81.2$, $[\alpha]_{365}^{25} = +136.7$ (*c* = 29.3, $CHCl_3$). UV (95% EtOH): 260 (8400). CD (*c*, 0.052, isooctane): 243 (−0.46), 234 (−0.68), 222 (−0.77), 211 (0). CD (*c* = 0.05, 95% EtOH): 235 (−0.75), 224 (−0.84), 212 (0). UV (isooctane): 259 (9300). IR (film): 3090, 2985, 2945, 2890, 2830, 1638, 1360, 1105, 1025, 885. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.24, 5.09, 4.94, 4.81 (4*s*, 4 H); 3.53–3.33 (*m*, H–C(1)); 3.32 (*s*, CH_3O); 3.01–2.73 (*m*, 2 H); 1.98–1.25 (*m*, 4 H). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 151.7 (*s*, C(5)); 148.0 (*s*, C(6)); 102.2 (*t*, ^1J(C,H) = 162, CH_2=C(6)); 99.8 (*t*, ^1J(C,H) = 161, CH_2=C(5)); 82.9 (*d*, ^1J(C,H) = 153, C(2)); 56.2 (*qd*, ^1J(C,H) = 144, ^3J(C,H) = 4, CH_3O); 49.8 (*d*, ^1J(C,H) = 148, C(1)); 44.6 (*d*, ^1J(C,H) = 148, C(4)); 38.7 (*t*, ^1J(C,H) = 134, C(3)); 35.5 (*t*, ^1J(C,H) = 138, C(7)). MS (70 eV): 150 (15, $M^{+\cdot}$), 135 (5), 118 (33), 117 (61), 105 (16), 92 (32), 91 (100). Anal. calc. for $C_{10}H_{14}O$ (150.221): C 79.96, H 9.39; found: C 79.98, H 9.12.

*(+)-(1R,2R,4R)-5,6-Dimethylidenebicyclo[2.2.1]hept-2-*endo*-yl Methyl Ether* ((+)-(1*R*,2*R*,4*R*)-**22**). Same procedure as above, using 780 mg of NaH in anh. THF (4.8 ml), 330 mg (2.43 mmol) of (+)-(1*R*,2*R*,4*R*)-**9** [7] in anh. THF (1.8 ml) and 3.6 ml of CH_3I (57.8 mmol). Yield: 332 mg (90%), colourless oil. B.p. 50°/0.1 Torr. $[\alpha]_{589}^{25} = +110.5$, $[\alpha]_{578}^{25} = +115.4$, $[\alpha]_{546}^{25} = +131.7$, $[\alpha]_{436}^{25} = +228$, $[\alpha]_{365}^{25} = +368.5$ (*c* = 10, $CHCl_3$). UV (isooctane): 260.5 (6500). UV (95% EtOH): 261 (6870). CD (*c* = 0.085, isooctane): 242 (+0.54), 245 (+0.47), 249 (+0.56). CD (*c* = 0.097, 95% EtOH): 230 (−0.58). IR (film): 3085, 2970, 2872, 2825, 1440, 1355, 1256, 1126, 1088, 1015, 955, 874. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.41, 5.19, 4.94, 4.84 (4*s*, 4 H); 3.88 (*m*, 1 H); 3.30 (*s*, CH_3O); 3.07 (br. *s*, 1 H); 2.80 (br. *s*, 1 H), 2.12 (*m*, 1 H), 1.70–1.16 (*m*, 3 H). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 151.4 (*s*, C(5)); 146.3 (*s*, C(6)); 103.7, 99.8 (2*t*, ^1J(C,H) = 158, CH_2=C(5), CH_2=C(6)); 8.08 (*d*, ^1J(C,H) = 150, C(2)); 56.5 (*q*, ^1J(C,H) = 140, CH_3O); 48.8 (*d*, ^1J(C,H) = 146, C(1)); 44.9 (*d*, ^1J(C,H) = 146, C(4)); 37.7 (*tm*, ^1J(C,H) = 136, ^3J(C,H) = 8, C(7));

36.8 (*t*, ^1J(C,H) = 134, C(3)). MS (70 eV): 150 (28, M^+), 135 (7), 120 (7), 119 (9), 118 (49), 117 (60), 115 (7), 105 (24), 92 (42), 91 (100). Anal. calc. for $C_{10}H_{14}O$ (150.221): C 79.96, H 9.39; found: C 79.73, H 9.44.

(–)-(1S,2S,4S)-Spiro[5,6-dimethylidenebicyclo[2.2.1]heptane-2,2'-oxirane] ((–)-(1*S*,2*S*,4*S*)-**23**) *and (–)-(1S,2R,4S)-Spiro[5,6-dimethylidenebicyclo[2.2.1]heptane-2,2'-oxirane]* ((–)-(1*S*,2*R*,4*S*)-**24**). $(CH_3)_3SOI$ (347 mg, 15.7 mmol) was added portionwise to a stirred suspension of NaH (57 mg, 2.4 mmol) in anh. DMSO (2 ml) under Ar. After stirring at 20° until the end of H_2 evolution, the mixture was cooled to 10° and (–)-(1*S*,4*S*)-**12** [7] (200 mg, 1.49 mmol) in anh. DMSO (1 ml) was added slowly (15 min). After stirring at 20° for 2 h and then at 60–70° for 1 h, the mixture was cooled to 0°, and H_2O (25 ml) was added dropwise. The mixture was extracted with pentane (15 ml, 4 times). The org. extracts were combined, washed with H_2O (30 ml, 3 times), and dried ($MgSO_4$). The solvent was evaporated and the residue separated and purified by HPLC on silica gel (1 × 25 cm, AcOEt/hexane 6:94) yielding 50 mg (23%) of (–)-(1*S*,2*R*,4*S*)-**24** and 64 mg (29%) of (–)-(1*S*,2*S*,4*S*)-**23**.

(–)-(1*S*,2*S*,4*S*)-**23**: Colourless oil. $[\alpha]_{589}^{25} = -134$, $[\alpha]_{578}^{25} = -140$, $[\alpha]_{546}^{25} = -159$, $[\alpha]_{436}^{25} = -275$, $[\alpha]_{365}^{25} = -423$ (*c* = 11.7, $CHCl_3$). UV (isooctane): 237 (sh, 8670), 247 (9440), 255 (sh, 6070). CD (*c* = 0.068, isooctane): 212 (+1.2), 222 (0), 242 (–2.0). CD (*c* = 0.088, 95% EtOH): 215 (+0.93), 226 (0), 243 (–0.95). See also [38]. IR ($CHCl_3$): 1720, 1640, 880. ^{1}H-NMR (360 MHz, $CDCl_3$; relative [Eu(dpm)$_3$]-induced shifts in brackets): 5.36 (br. *s*, H of CH_2=C(5) *trans* to C(6) [2]); 5.27 (br. *s*, H of CH_2=C(5) *cis* to C(6) [7]); 4.94 (br. *s*, H of CH_2=C(6) *cis* to C(5) [9], H of CH_2=C(6) *trans* to C(5) [12]); 2.97, 2.79 (2*d*, ^2J = 5, CH_2(2') [100]); 2.94 (*ddd*, ^3J(H–C(4), H_{exo}–C(3)) = 4.5, ^3J(H–C(4), H_{anti}–C(7)) = 3.4, ^3J(H–C(4), H_{syn}–C(7)) = 1.5, H–C(4) [28]); 2.44 (*tm*, ^3J(H–C(1), CH_2(7)) = 1.5, H–C(1) [73]); 2.14 (*dd*, ^2J = 13, ^3J = 4.5, H_{exo}–C(3) [49]); 1.78 (*dt*, ^2J = 10, ^3J = 1.5, H_{syn}–C(7) [40]); 1.66 (*dddd*, 2*J* = 10, ^3J = 1.5, 3.4, ^4J(H_{endo}–C(3), H_{anti}–C(7)) = 3.5, H_{anti}–C(7) [30]); 1.46 (*dd*, ^2J = 13, ^2J = 13, ^4J = 3.5, H_{endo}–C(3) [68]). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 150.4 (*s*, C(5)); 146.2 (*s*, C(6)); 103.7 (*t*, ^1J(C,H) = 156, CH_2=C(6)); 100.9 (*t*, ^1J(C,H) = 156, CH_2=C(5)); 64.6 (*s*, C(2)); 54.3 (*td*, ^1J(C,H) = 176, ^3J(C,H) = 6, C(3')); 50.9 (*d*, ^1J(C,H) = 168, C(1)); 45.6 (*d*, ^1J(C,H) = 168, C(4)); 38.8 (*td*, ^1J(C,H) = 138, ^3J(C,H) = 8, C(7)); 36.7 (*t*, ^1J(C,H) = 134, C(3)). MS (70 eV): 148 (11, M^+), 133 (5), 120 (16), 105 (36), 91 (100).

Adduct (1:1) of (–)-(1*S*,2*S*,4*S*)-**23** with ethylenetetracarbonitrile (TCNE): m.p. 208°. Anal. calc. for $C_{16}H_{12}N_4O$ (276.30): C 69.56, H 4.38; found: C 69.73, H 4.44.

*(–)-(1S,2R,4S)-***24**: Colourless oil. $[\alpha]_{589}^{25} = -130$, $[\alpha]_{578}^{25} = -136$, $[\alpha]_{546}^{25} = -156$, $[\alpha]_{436}^{25} = -278$, $[\alpha]_{365}^{25} = -442$ (*c* = 5.3, $CHCl_3$). UV (isooctane): 237 (sh, 8400), 244 (8950), 253 (sh, 5950). CD (*c* = 0.064, isooctane): 233 (+0.66), 241 (+0.5). CD (*c* = 0.045, 95% EtOH): 235 (+0.61). See also [38]. IR ($CHCl_3$): 3030, 1245, 905. ^{1}H-NMR (360 MHz, C_6D_6; relative [Eu(dpm)$_3$]-induced shifts in brackets): 5.32 (br. *s*, H of CH_2=C(6) *cis* to C(5) [15]); 5.28 (br. *s*, H of CH_2=C(5) *cis* to C(6) [12]); 4.91 (br. *s*, H of CH_2=C(5) *trans* to C(6) [11]); 4.86 (br. *s*, H of CH_2=C(6) *trans* to C(5) [20]); 2.76 (*ddd*, ^3J = 4.5, 2.3, 1.5, H–C(4) [16]); 2.69, 2.60 (2*d*, ^2J = 5, CH_2(2') [100]); 2.40 (*dd*, ^3J = 1.6, 1.5, H–C(1) [60]); 1.93 (*ddd*, ^2J = 9.5, ^3J = 1.6, 1.5, H_{syn}–C(7) [29]); 1.91 (*dd*, ^2J = 13, ^3J = 4.5, H_{exo}–C(3) [56]); 1.70 (*dd*, ^2J = 13, ^4J(H_{endo}–C(3), H_{anti}–C(7)) = 2.5, H_{endo}–C(3) [43]); 1.44 (*dddd*, ^2J = 9.5, ^3J = 1.5, 2.3, ^4J = 2.5, H_{anti}–C(7) [15]). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 150.5 (*s*, C(5)); 147.0 (*s*, C(6)); 103.2 (*t*, ^1J(C,H) = 161, CH_2=C(6)); 101.1 (*t*, ^1J(C,H) = 160, CH_2=C(5)); 65.7 (*s*, C(2)); 52.8 (*d*, ^1J(C,H) = 150, C(1)); 50.7 (*t*, ^1J(C,H) = 177, ^3J(C,H) < 4, C(3')); 45.5 (*d*, ^1J(C,H) = 150, C(4)); 38.5 (*tm*, ^1J(C,H) = 139, ^3J(C,H) = 8, C(7)); 37.7 (*t*, ^1J(C,H) = 135, C(3)).

Adduct (1:1) of (–)-(1*S*,2*R*,4*S*)-**24** with TCNE: m.p. 177°. MS (70 eV): 276 (32, M^+), 220 (29), 156 (41), 91 (100). Anal. calc. for $C_{16}H_{12}N_4O$ (276.30): C 69.56, H 4.38; found: C 69.80, H 4.18.

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