Communications to the Editor

Torsionally Distorted Olefins. Resolution of *cis*- and *trans*-4,4'-Bi-1,1',2,2',3,3'-hexahydrophenanthrylidene

Sir:

Only few examples are known of optically active stereoisomers of alkenes bearing no chiral centers.[1] In principle both the cis as well as the trans form of olefins should be capable of existence as stable optically active stereoisomers, provided bulky substituents cause a permanent out-of-plane distortion of the double bond. This expectation has now been realized by the synthesis and resolution of *dl-cis-* (II) and *dl-trans-*4,4'-bi-1,1',2,2',3,3'-hexahydrophenanthrylidene (III) using a novel method of resolution (as applied to olefins).

When 4.1 g (21 mmol) of 4-keto-1,2,3,4-tetrahydrophenanthrene (I)[2] in 25 ml of dry THF was added, under nitrogen, to the black suspension resulting from mixing 6.5 g of $TiCl_3$ and 0.75 g of $LiAlH_4$ in 20 ml of THF, an immediate reaction occured.[3] The resulting mixture was stirred and heated for 4 h under reflux and after a normal workup 4.0 g of an oil could be isolated. The apolar fraction of the complex reaction mixture consisted of 0.80 g of colorless crystalline olefins, separable into cis (II, mp 192–193 °C) and trans isomers (III, mp 234–235 °C) via preparative TLC (deactivated alumina) (Scheme I).[4]

The structures of both olefins are based upon the following observations. Correct elemental analysis of both olefins and spectral data in agreement with structures II and III were obtained. The olefins II and III were reconverted into starting ketone I by oxidation using RuO_4. Hydrogenation of either olefin gave the same dihydro product (5% Pd/C, 3 atm H_2, ethanol solution). Both olefins showed the expected C_2 symmetry in their ^{13}C NMR spectra. Assignment of the cis configuration to the lower melting isomer (II) is based upon the 100-MHz ^1H NMR spectra and the UV spectra. In the cis isomer an upfield shift was observed for protons in the 5,5' ,6,6',7,7',8,8' positions. (ABCD system, δ 6.36, 6.48, 6.70, and 6.86). These protons are influenced by the shielding zones of the aromatic rings, indicating a helix-like shape of this isomer. In the 100-MHz ^1H NMR spectrum of the trans isomer a multiplet was observed for the protons in the 5,5',6,6',7,7', 8,8',9,9',10,10' positions (δ 7.1–7.8). A multiplet at δ 8.2 is probably due to the protons in the 5,5' positions, deshielded as a result of steric interaction.[5]

A hypsochromic shift is observed for the low energy band in the UV spectrum of the cis isomer (II) compared to that of the trans isomer (III) (Figure 1 and 2). This effect is well known for the *cis*- and *trans*-di-1-naphthylstilbene system.[6] The structural relationship of II and III was clearly demonstrated by the slow isomerization of either pure cis- or pure trans isomer to a cis–trans mixture.
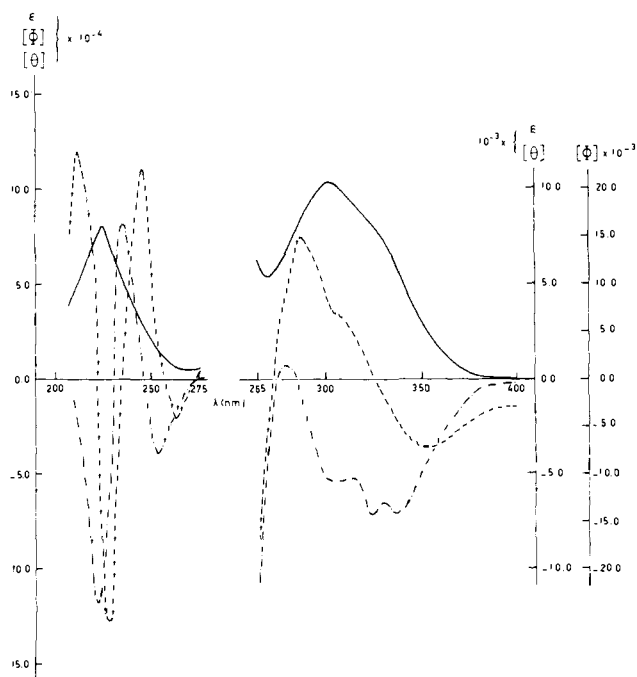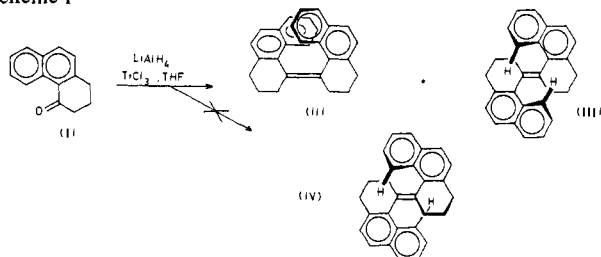
Scheme I

Figure 1. UV(—), ORD (- - -), and CD (-·-) spectra of cis-olefin II.

Both *dl*-cis and *dl*-trans olefins could be resolved using HPLC techniques by employing an alumina column impregnated with (+)-TAPA.[7] Partial resolution of the cis isomer was achieved (d-(+)-II: $[\alpha]^{22}_{578}$ +88° c 1.60 × 10^{-3}, n-hexane). In addition the trans isomer could be resolved completely (l-(−)-III: $[\alpha]^{22}_{578}$ −508° c 3.14 × 10^{-3}, n-hexane). The ORD and CD spectra of II (Figure 1) and of III (Figure 2) showed large rotations and ellipticities.

Recently published CD data and calculations on rotational strength indicate torsion of the olefin chromophore as the dominant contribution in determining the sign of the Cotton effects.[9] However, in this case the entire conjugated system rather than an isolated twisted olefin chromophore must be involved in the interpretation of the spectra. Important features to be taken into considerations are: The direction of the principal C_2 axes. Note that in the cis olefin this axis is perpendicular to a plane through the π-orbitals of the double bond, while in the trans olefin the C_2 axis lies in the plane of the π-orbitals of the double bond (we realize that it is awkward to speak of a "plane" through the twisted olefin π-orbitals). Thus the relations between the transition moments and the C_2 axes in the two olefins differ. This must be evident in the spectra. Whether true exciton splitting is present cannot at this time be answered unequivocally. To a first approximation the fact that we are dealing with a conjugated system would argue against it.

The trans isomer could in principle exist in two diastereomeric forms; one *dl*-trans (III) and one non-dissymetric form (IV). The resolution of the trans olefin is proof of the structure as III and not IV. The partial stereoselectivity of the reductive dimerization of I, resulting in the formation of *dl*-trans olefin (III) only, might give an indication about the structure of the intermediate Ti complex.[10] Stereoselective formation of the cis isomer (II) could also be achieved: reaction of I under the
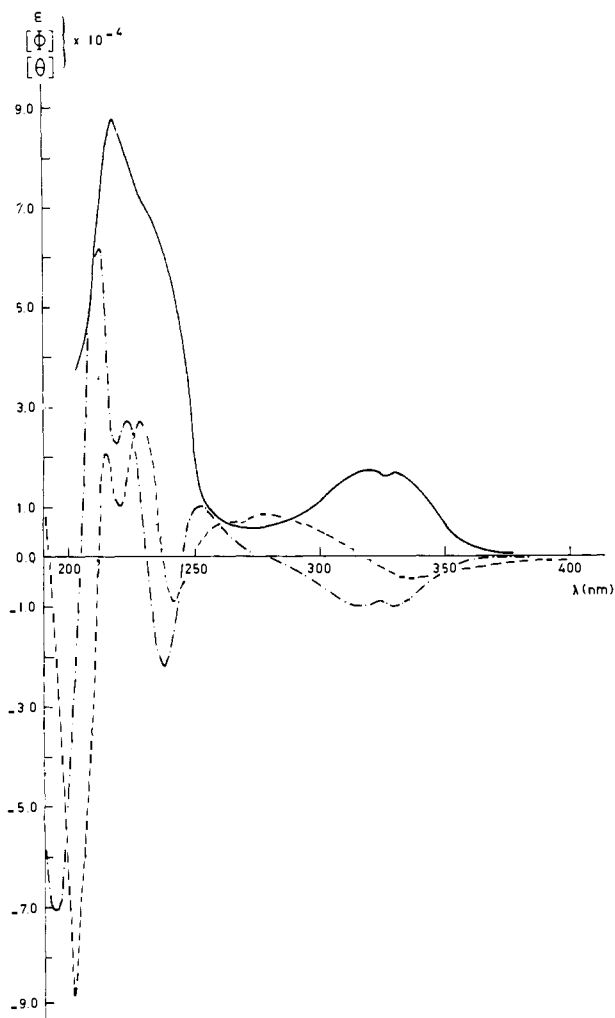
Figure 2. UV (—), ORD (- - -), and CD (---) spectra of trans-olefin III.

above conditions, but in the presence of $(-)$-*trans*-2,3-methylenedioxybutane as solvent gave cis-isomer II as the only olefinic product. This product was nevertheless optically inactive.

Some additional aspects of the structures of the cis and trans olefins need to be mentioned. The structure of II resembles that of a heptahelicene (more accurately a tetrahydroheptahelicene) with a double bond replacing an aromatic ring. The olefin III has a double helix structure and resembles a double pentahelicene with a double bond replacing two aromatic rings.[11a] Both chiral as well as achiral double helix structures have been reported in the helicene case.[11b] The role of π-bond torsion has been the subject of many investigations,[1,9] although almost all of the attention has been focused on *trans*-cyclooctene. NMR studies connected with π-bond torsion have been reported for systems such as bisfluorenylidene and bianthrone, but no stable enantiomers have been obtained thus far.[12] To our knowledge, olefins II and III represent the first instance in which a *dl*-cis and *dl*-trans form of one inherently dissymmetric olefin have been isolated and resolved into enantiomers.

The isomerization and racemizations of II and III may furnish further information about the torsional distortion in both olefins. This complex series of interconversions will be the subject of further investigations.

References and Notes

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(4) In the case of II and III, only one of the possible enantiomers is shown in Scheme I.
(5) In the 100-MHz ^{1}H NMR spectra of both *cis*-II and *trans*-III isomers, multiplets were observed for the protons in the 1,1′,2,2′,3,3′ positions. (II: δ 1.7–3.1; III: δ 1.6, 2.2, and 2.7). For the cis isomer an AB system was observed for the protons in the 9,9′,10,10′ positions.
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(7) The first report of the use of (+)-TAPA[8a] in chromatographic separation of optical isomers is due to Klemm et al.[8b] Gil-Av et al.[8c] have recently reported its use in HPLC for the resolution of helicenes. We have applied the technique independently to the resolution of heterohelicenes.[8d]
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(10) Dreiding models of the intermediate Ti complexes as suggested by McMurry and co-workers[3] indicate that, in going from the precursors of III and IV to the olefins, the formation of IV is disfavored due to steric hindrance.
(11) (a) Whether we view II as an "open helicene", a "chiral and rigid stilbene", or a novel helical conjugated π-system is a matter of semantics. (b) R. Martin, *Angew. Chem.*, **86**, 727 (1974); W. H. Laarhoven and Th. J. H. M. Cuppen, *Tetrahedron Lett.*, 163 (1971); R. H. Martin, Ch. Eyndels, and N. Defay, *ibid.*, 2731 (1972).
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Synthesis and Spectral Data of a Stable, Optically Active 1,2-Dioxetane

Sir:

Some years ago the synthesis and structure proof of the stable 1,2-dioxetane, derived from adamantylideneadamantane,[1] was reported. Subsequently this molecule has been studied in considerable detail.[2] Using the same olefin moiety, we have now prepared and characterized an *optically active* 1,2-dioxetane.[3]

In addition to the criteria we enumerated for the successful synthesis of the adamantylideneadamantane-1,2-dioxetane[1] (electron-rich olefin; avoidance of "ene" reaction and no steric hindrance), stereochemical considerations played a crucial role in our present synthetic strategy. (i) The possible difficulties in resolving a 1,2-dioxetane made us decide to prepare an optically active (and if possible optically pure) olefin, as precursor of the 1,2-dioxetane. (ii) Condition i requires either the synthesis of an olefin with a functional group allowing resolution, or the synthesis of an optically active olefin precursor. (iii) The position and nature of the substituent, which imparts chirality