Synthesis, Circular Dichroism, and Absolute Configuration of Two Chiral Indanylideneindans

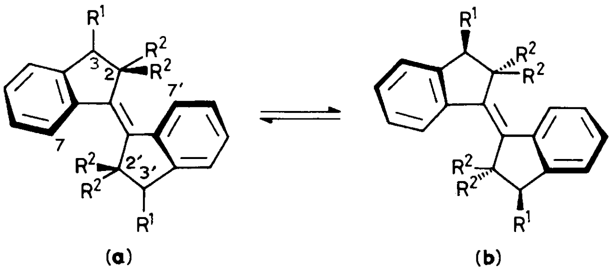
Volker Buss,*[a] **Lothar Simon,**[a] **and Peter Lemmen**[b]

[a] *Fachgebiet Theoretische Chemie der Universität, D 4100 Duisburg, Federal Republic of Germany*
[b] *Institut für Organische Chemie der Technischen Universität München, D 8046 Garching, Federal Republic of Germany*

Analysis of the temperature dependent circular dichroism spectra of the title compounds reveals *P*-helicity for the more stable conformer in agreement with ^{1}H n.m.r. data but contrary to force field calculations.

According to force field calculations[1] the two benzene rings in 1-(indan-1-ylidene)indan (**1**) are twisted out of the plane of the central double bond (point group C_2) in order to relieve strain in the five-membered rings and to allow a staggered orientation of the substituents at C-7 and C-2′ (C-7′ and C-2, respectively). Under achiral conditions the two enantiomers (**1a**) and (**1b**) cannot be distinguished. Chiral substitution, however, as in (**2**) and (**3**), should differentiate between the two possibilities with the result that the more stable conformer becomes more populated. In this communication we report direct spectroscopic evidence for the equilibrium between conformations (**a**) and (**b**), derive thermodynamic data, and assign absolute configurations.

The synthesis of the new compounds started with (*S*)-3-methylindan-1-one[2] which was coupled in the presence of a low-valent titanium salt[1] to yield (**2**). Methylation of (*S*)-



(1); $R^1 = R^2 = H$
(2); $R^1 = Me$, $R^2 = H$
(3); $R^1 = R^2 = Me$

3-methylindan-1-one gave (*R*)-2,2,3-trimethylindan-1-one[3] which was coupled to give (**3**).† The u.v. spectra of (**2**) and (**3**) (Figure 1) correspond closely to that of the parent compound (**1**) except that the vibrational fine structure is missing in (**3**). With their three-band system the spectra are quite similar in appearance to the u.v. spectrum of *trans*-stilbene[4] which suggests a similar composition of the excited states.

The circular dichroism (c.d.) spectrum of (**2**) (broad, negative bands at 330 and 290 nm, negative couplet at 245 nm) is strongly temperature dependent, the amplitudes of all bands increasing upon cooling. Assuming an equilibrium between the two chiral conformers and applying the method of Moscowitz, Wellman, and Djerassi[5] to evaluate the free energy difference very good linearity and convergence of the spectral data are obtained for a ΔG° value of 3.3 kJ/mol. This corresponds to *ca.* 80% of the more stable conformer at room temperature and *ca.* 96% at −150 °C .

The c.d. spectrum of (**3**) is similar to that of (**2**) but with amplitudes about four times as large. It is almost temperature independent indicating that the equilibrium between (**3a**) and (**3b**) is shifted strongly to one side. A thermodynamic analysis as for (**2**) was not possible; we took a lower limit for ΔG° to be 8 kJ/mol which corresponds to an equilibrium distribution of 97 : 3 at room temperature.

The spectra allow the assignment of absolute configurations to the different conformers. Consider the shape of the c.d. couplet centred at 245 nm. According to the results of different calculations on *trans*-stilbene[4,6] the *B*-band, which appears in the u.v. spectrum of (**2**) and (**3**) with a maximum at 238 nm, results from the in-phase coupling of the B_b-excitations of the benzene chromophores (Figure 2). This coupling mode has B_u-symmetry in the point group C_{2h} and *B*-symmetry in C_2. The out-of-phase coupling mode of symmetry A_g and *A*, respectively, is expected to occur at lower energy. The transition from the ground state to this mode is parity forbidden in C_{2h}. It is allowed, albeit with low intensity, in the twisted indanylideneindans with C_2-symmetry. From the fact that the rotatory strength of the intense high energy transition is negative while that of the low energy transition (not visible in the u.v.) is positive, we conclude that the more stable conformer has *P*-helicity, as in (**2a**) and (**3a**). The calculated rotatory strengths depend strongly on the inherent twist of the chromophore. In the exciton approximation[7] values of 280 and 580 × 10^{-55} S.I.U. are obtained for angles of 85 and 80°, respectively, between the C_2-axis and the plane of the benzene rings. The experimental values for the 250 nm band are *ca.* −665 (**2b**), 265 (**2a**), and 380 × 10^{-55} S.I.U. (**3a**), well within the results of the model.

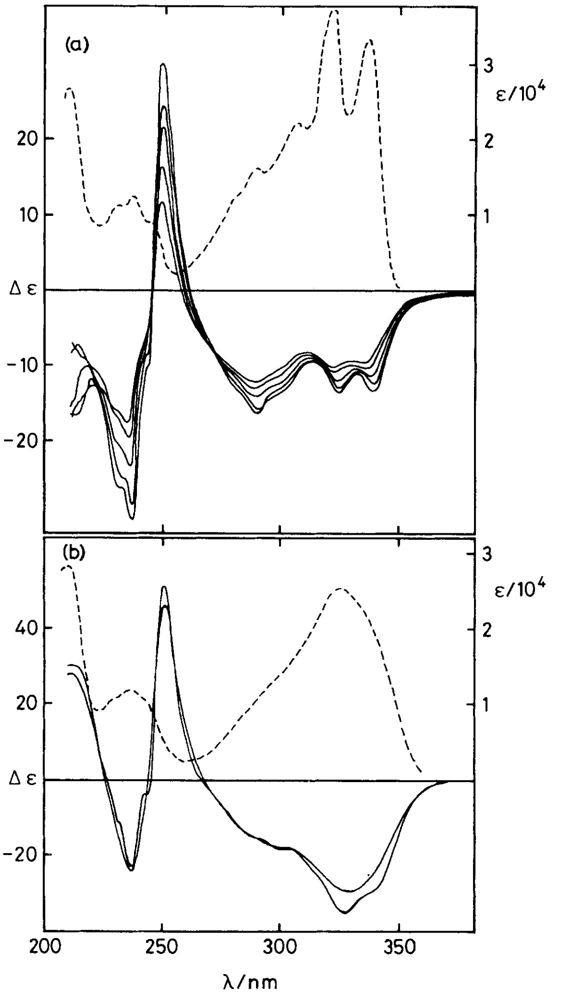


Figure 1. U.v. spectra (- - - -) and c.d. spectra (——) of (a) (**2**) and (b) (**3**) in isopentane. The five c.d. curves of (**2**) were measured at 0, −40, −80, −120, and −150 °C, the two curves of (**3**) at 0 and −150 °C. All spectra are corrected for volume contraction.

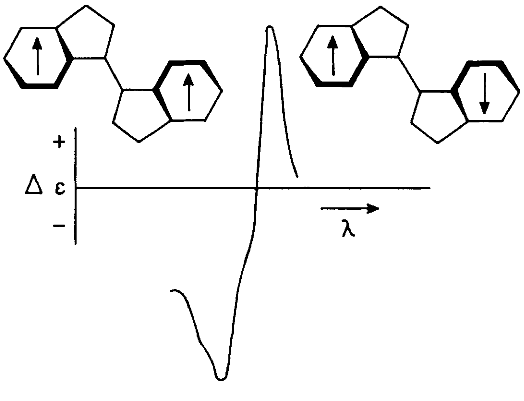


Figure 2. Origin of the c.d. couplet of (**2a**) and (**3a**) at 245 nm. On the high-energy side (left) the two benzene transitions couple in-phase to give a transition with high oscillator strength and negative rotatory strength. On the low-energy side (right) the out-of-phase coupling leads to low intensity in the u.v. and positive rotatory strength.

The negative sign of two long wavelength c.d. bands is also in accordance with *P*-helicity according to CNDO-calculations. These computations indicate, moreover, that the absorption at 290 nm has some of the character of an

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† All compounds gave analytical and spectral data in agreement with the assumed structures.

excitation from the double bond into the aromatic rings. It would thus correspond to one of the $^1G^-$ excitations which has been postulated by Beveridge and Jaffé[4] as a forbidden component of the *A* band in *trans*-stilbene.

Force field calculations agree only partly with our conclusions. As in the case of (**1**)[1] two energy minima with C_2 symmetry and opposite chiralities are found for (**2**) and (**3**) with the MMP1 force field.[8] The methyl groups at C-3 and C-3′ are equatorial in the conformers (**a**) and axial in (**b**). The diaxial conformations are found more stable by 0.5 and 5.8 kJ/mol for (**2**) and (**3**), respectively, in contrast to our interpretation of the c.d. spectra. Since, however, the ^{1}H n.m.r. spectrum of (**2**)‡ also indicates the preponderance of the diequatorial conformation (**2a**), we consider our assignment of the absolute configuration to be reliable.

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‡ After decoupling of the 3-CH_3 signal the 3 protons at C-2 and C-3 gave an ABX spectrum with δ_A 3.28 (2-H), δ_B 3.16(3-H), δ_X 2.55 (2-H), J_{AB} 7.9, J_{AX} −13.7, J_{BX} 5.2 Hz (200 MHz, C_6D_6). For a diaxial conformation one of the coupling constants (J_{BX}) should be *ca.* zero.

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