Absolute Configuration of (—)-Stilbenediamine

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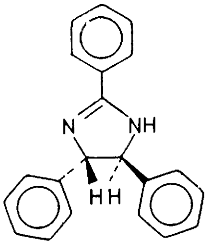
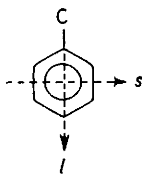
Summary The c.d. spectra of the zinc(II) complexes of (—)-stilbenediamine [(—)-1,2-diphenylethane-1,2-diamine] indicate that this ligand has the (*S*,*S*)-configuration, contrary to recent (*R*,*R*)-assignments.

Lifschitz and Bos[1] resolved stilbenediamine (stien) and isolated a cobalt(III) complex, (+)-$[Co(l\text{-stien})_3]^{3+}$, which exhibits a positive o.r.d. anomaly near 500 nm. As the more stable *lel*-isomers[2] of the tris-chelate complexes formed by cobalt(III) with (*S*)- or (*S*,*S*)-1,2-diamines also give a positive Cotton effect near 500 nm, the (*S*,*S*)-configuration was assigned[3] to (—)-stilbenediamine. More recent work suggests a contrary assignment on two main grounds.[4,5] Firstly, (—)-$[Co(l\text{-stien})_3]^{3+}$ is thermodynamically more stable than the (+)-isomer in methanol solution, implying that these are the *lel* and the *ob* isomers, respectively, of a (*R*,*R*)-1,2-diamine. Secondly, (—)-stilbenediamine is a hydrolysis product of (—)-isoamarine (I) which gives an exciton c.d. spectrum similar to that of (*R*,*R*)-(+)-*trans*-



(I)



(II)

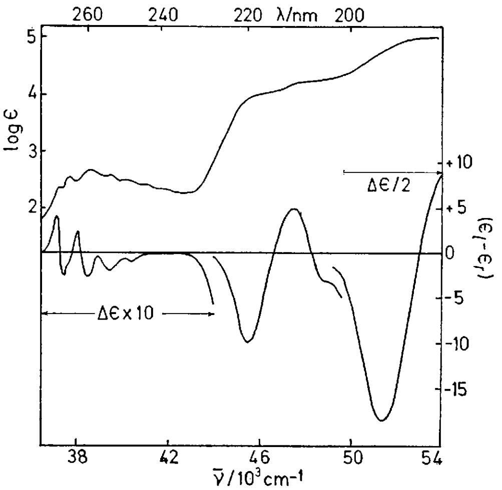


Figure 1. *The absorption spectrum (upper curve) and c.d. spectrum (lower curve) of* $[Zn(l\text{-stien})]^{2+}$ *in methanol.*

stilbene oxide[6], suggesting the (R,R)-configuration for (I) and (−)-stilbenediamine.

Although isoamarine and *trans*-stilbene oxide are spectroscopically similar in that each contains two adjacent and chirally disposed alkylphenyl chromophores, the presence of an additional benzamidine chromophore in (I) limits the analogy. In order to assess the significance of this limitation we have examined the c.d. spectrum of the mono- and bis-chelate complexes of zinc(II) with (−)-stilbenediamine. The spectra of the two complexes are similar in band-positions and signs, the main difference being that the isotropic and c.d. intensities are twice as large for the bis- as for the mono-chelate complex (Figure 1). Thus the c.d. arises principally from the electronic interactions between the two alkylphenyl chromophores of a given ligand in the bis-chelate complex as in [Zn(1-stien)]$^{2+}$, the interactions being closely analogous to those obtaining in *trans*-stilbene oxide. However, the c.d. spectrum of (R,R)-(+)-stilbene oxide[6] is virtually enantiomorphous to that of [Zn(1-stien)]$^{2+}$ (Figure 1), suggesting the (S,S)-configuration for the ligand in this complex (Figure 2), contrary to the recent configurational assignments.[4,5]

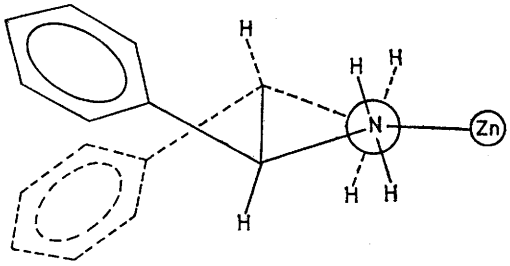


FIGURE 2. *The preferred* δ*-conformation of a* (S,S)-(−)-*stilbenediamine chelate ring in* [Zn(1-stien)]$^{2+}$.

Of the several c.d. spectra here considered those of the zinc(II) complexes of (−)-stilbenediamine are the better resolved in the 260 nm region of the ${}^1L_b$ transition of the alkylphenyl chromophore where the first two members of the 0–0+900 cm^{-1} progression exhibit weak-coupling exciton-splitting (Figure 1). The 260 nm ${}^1L_b$ transition and the 215 nm ${}^1L_a$ transition of an alkylbenzene are short- and long-axis polarised, respectively, in the frame (II) of the chromophore.[7] The Coulombic coupling of the ${}^1L_b$ moments of the two alkylphenyl groups in a monochelate complex of (S,S)-stilbenediamine (Figure 2) is expected to give in the 36—42kK region a positive c.d. band followed by a negative c.d. absorption at higher frequency, the pattern being repeated for each vibronic component in the weak-coupling case. For the corresponding coupling of the two ${}^1L_a$ moments a negative c.d. band followed by a positive c.d. absorption at higher frequency is expected in the 44—49kK region. These expectations, which correspond to the observed c.d. of [Zn(1-stien)]$^{2+}$ (Figure 1), hold whether the chelate ring is planar, has the puckered λ-conformation with di-axial phenyl substituents, or has the preferred[2] δ-conformation with di-equatorial substituents (Figure 2). The expectations are based on the assumption of the (S,S)-configuration for (−)-stilbenediamine and, in the case of the coupling of the ${}^1L_b$ moments, that the plane of each benzene ring is perpendicular, or nearly so, to the mean plane of the chelate ring, as models indicate.

The (S,S)-configuration of (−)-stilbenediamine requires the same configuration for (−)-isoamarine, from which the ligand is derived by hydrolysis. The adventitious isomorphisms between the c.d. spectra of (−)-isoamarine and (R,R)-(+)-*trans*-stilbene oxide[6] consist of a positive c.d. band followed by a negative c.d. absorption at higher frequency in the ${}^1L_a$ region, 42—49kK, and the same pattern in the ${}^1B_a$ region, 49—54kK, the ${}^1L_b$ c.d. absorption being unresolved in both cases. In (S,S)-(−)-isoamarine (I) the long-axis polarised ${}^1L_a$ transition of the benzamidine chromophore[8] at 44kK interacts coulombically with the totally-symmetric A-coupling mode of the ${}^1L_a$ moments of the two alkylphenyl groups, which has a positive rotational strength, but not with the lower-energy B-coupling mode, which has a negative rotational strength. The interaction generates two A-modes in the C-2 group of (I), one with the major dipole and positive rotational strength at lower energy, and the other with minor strengths at higher energy. If the frequency-interval between the two A-modes resulting from the secondary interaction is appreciably larger than that between the A- and B-mode of the primary coupling of the alkylphenyl chromophores, the order of a negative and then a positive c.d. band at higher frequency expected in the ${}^1L_a$ region, and also in the ${}^1B_a$ region, for the two-chromophore model of (S,S)-(−)-stilbenediamine is reversed in the three-chromophore model for (S,S)-(−)-isoamarine (I).

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