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THE OPTICAL ACTIVITY OF THE H-STRETCHING VIBRATIONAL MODES OF CALYCANTHINE AND IRCD DETERMINATIONS OF ABSOLUTE CONFIGURATION

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Summary: The infrared circular dichroism (IRCD) due to the H-stretching vibrational modes of calycanthine originates principally from chromophore-substituent coupling and not from the degenerate interchromophore coupling mechanism particular to dissymmetric dimers. The general non-degenerate mechanism provides a procedure for the determination of absolute configuration from the IRCD associated with a localised characteristic vibrational mode.

Absolute stereochemical configuration from electronic optical activity was first determined non-empirically for calycanthine,[1] the assignment being subsequently supported by a Bijvoet anomalous X-ray diffraction study,[2] and by extensions of the electronic CD spectrum and of the method of analysis.[3] In a dissymmetric dimer, such as calycanthine (Figure) and other natural products[4] and biaryls,[5] an electronic excitation with a given energy in each monomer chromophore Coulombically couple to one another, giving two resultant transitions with oppositely-signed rotational strengths, separated by the exciton splitting energy. The observable expected from this mechanism is a pair of oppositely-signed CD bands with a common magnitude, centred on the monomer transition frequency, and with a sign-order along the frequency ordinate reflecting the particular absolute configuration of the dimer.[1] The exciton CD couplets are generally observed in the electronic CD spectra of dissymmetric dimers, and are widely used for non-empirical configurational determinations.[4-6]

Infrared absorption bands at a characteristic group frequency are due to an electric-dipole vibrational transition largely localised in a particular group of atoms, i.e., in a vibrational chromophore, so that a CD couplet associated with each group IR absorption is expected in the IRCD spectrum of a dissymmetric dimer. Over the IR region of the H-stretching modes it is found that calycanthine and other dimer systems give generally a single CD absorption at a characteristic group frequency, and not an exciton CD couplet (Figure). A calculation by the standard procedure[4-6] of the rotational strengths and the frequency-splitting of the exciton CD couplet expected from the Coulombic coupling of the two N-H stretching modes of calycanthine, based upon the observed isotropic absorption intensity of the mode at 3448 cm^{-1} (Figure), gives the rotational strengths ± 4.8×10^{-4} Debye Bohr magneton (dβM), with the negative higher in frequency than the positive strength by 0.70 cm^{-1}. Since the frequency interval is small relative to the spectral band-pass of the IRCD instrument (7 cm^{-1} for a 1mm slit-width) and the band width of the N-H stretching IRCD absorption (32 cm^{-1}), the mutual cancellation of the oppositely-signed rotational strengths is so extensive that the CD couplet is not observable. Analogous factors account for the absence of an exciton CD couplet associated with any of the C-H stretching modes (Fig).

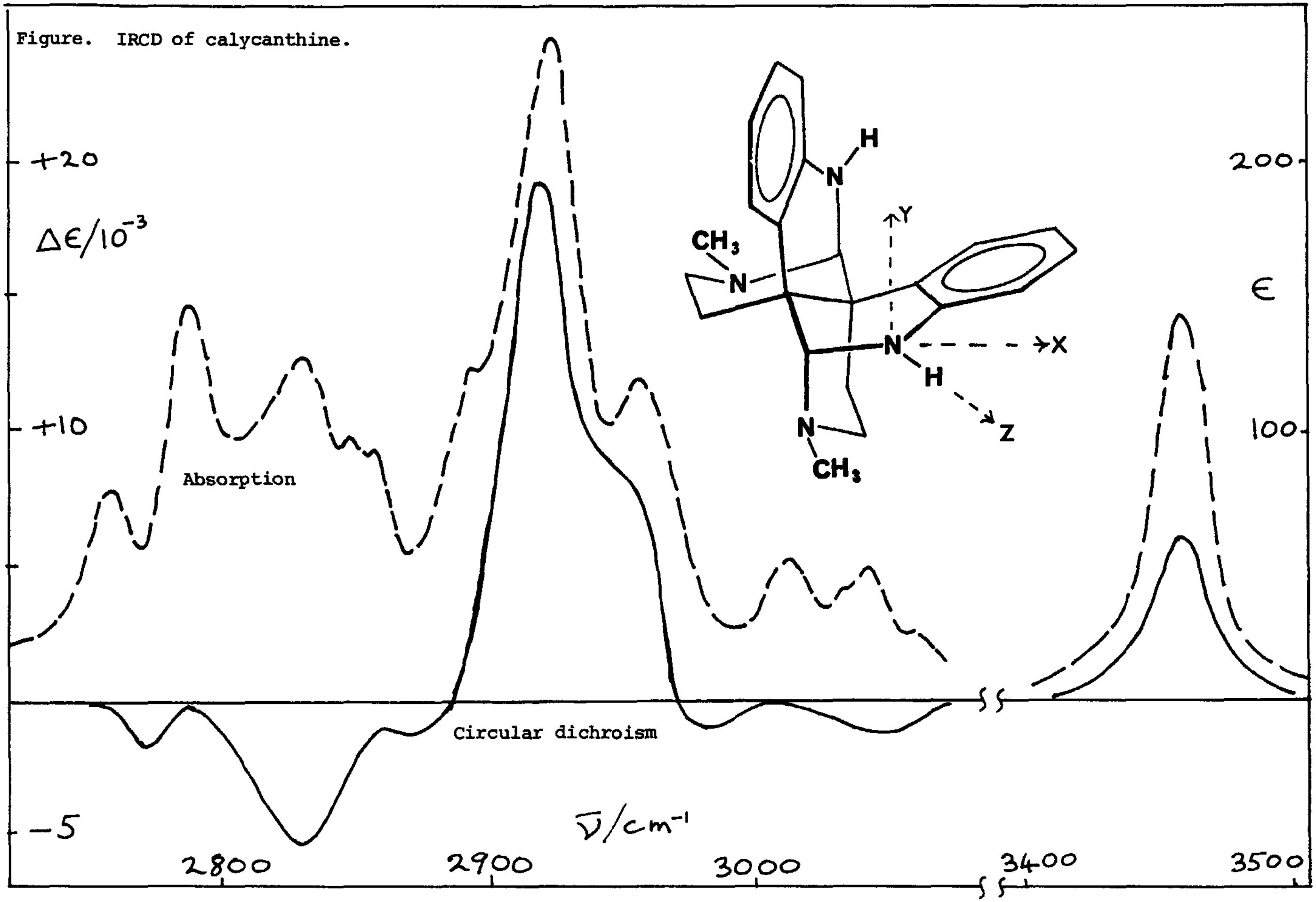
The band areas of an electronic exciton CD couplet are not generally equal,[4-6] owing to the superposition of optical activity originating from the non-degenerate substituent-chromophore coupling mechanism, which is not confined to dissymmetric dimers. According to the latter mechanism,[7] the rotational strength of an electric dipole transition derives from the Coulombic coupling of the chromophore transition dipole with an electric dipole or dipoles induced non-resonantly by the radiation field in other groups of the chiral molecule. The corresponding observable is a single CD absorption at the chromophore transition frequency with a sign reflecting the particular enantiomeric disposition of the substituents relative to the chromophore in the optical isomer studied.

For the N-H stretching mode of calycanthine, the non-degenerate interaction which accounts for the major part ($+1.1 \times 10^{-3}$ $d\beta_M$) of the observed rotational strength ($+1.4 \times 10^{-3}$ $d\beta_M$) consists in the Coulombic coupling of the Z-polarized dipole transition moment of the N-H group substituted into one benzene ring with a dipole induced by the radiation field in the other benzene nucleus (Figure). Taking the benzene ring to have cylindrical symmetry, the induced dipole has one component directed parallel to the cylinder axis, proportional to $\alpha_{\parallel}$, and other, proportional to $\alpha_{\perp}$, directed in the molecular plane, and the effective moment contributing to the vibrational CD is proportional to the anisotropy, $(\alpha_{\parallel} - \alpha_{\perp}) = \beta\bar{\alpha}$, where $\bar{\alpha}$ represents the mean polarizability and β the anisotropy factor.[7] The polarizability anisotropy of benzene at zero frequency has the value,[8] $\beta\bar{\alpha} = -5.62(\text{Å})^3$, and a correction to the transition frequency of the N-H stretching mode involves a negligible increase in the value by 0.2%. For the two N-H groups of calycanthine, the total rotational strength, R_{01}, at the fundamental stretching mode wavenumber, $\bar{\nu}_{01}$, is given by the expression, taken over for a vibrational chromophore in a chiral molecule from that for the corresponding electronic case,[7]

$$R_{01} = (\pi/2)\bar{\nu}_{01}D_{01}[\beta\bar{\alpha}(\bar{\nu}_{01})][Y(3Z^2-R^2)\sin 2\theta - 6XYZ\sin^2\theta]R^{-5} \qquad (1)$$

In equation (1), D_{01} refers to the dipole strength (7.81×10^{-3} square Debye) of the isotropic IR absorption at $\bar{\nu}_{01}$ (3448 cm^{-1}), and X,Y,Z, to the Cartesian coordinates of the centre of one benzene ring in a frame with the nitrogen atom of the N-H group substituted into the other nucleus as its origin, at a separation R (Figure). The X and the Y axes of the frame are so chosen that the cylinder axis of the benzene substituent lies parallel to the XZ-plane, thus reducing the angular variables to one, θ, the angle between the cylinder axis of the substituent and the Z-axis of the chromophore transition dipole direction.[7]

Figure. IRCD of calycanthine.



The evaluation of analogues of equation (1) for the groups in calycanthine other than the benzene nuclei shows that the latter dominate the rotational strength R_{01} of the N-H stretching mode, partly on account of the small polarizability anisotropies, $[(\beta\bar{\alpha}) = -0.12$, $+0.72\ (\text{Å})^3$, and zero, for the C-N, C-C, and C-H bond, respectively[9]], and partly because the contributions of the bonds making up the N-methylpiperidine rings of calycanthine largely cancel one another, leaving the aromatic ring contributions dominant. A similar but more complex analysis based upon the analogues of equation (1) accounts satisfactorily for the large positive CD at 2935 cm^{-1} and the weaker negative CD at 2845 cm^{-1} associated, respectively, with the antisymmetric and the symmetric stretching modes of the CH_2 groups.

The following principal conclusions emerge. Firstly, the vibrational CD associated with a characteristic group mode accessible with an IRCD instrument employing a conventional black-body radiation source is mainly that deriving from the general chromophore-substituent coupling mechanism. The dominance of that mechanism arises from the relatively weak dependence of the molecular or group electric-dipole polarizability upon the radiation frequency, $\bar{\nu}$, over the range from the rock-salt IR to the quartz UV region, i.e. $[\nu_o^{2} - \nu^{2}]^{-1}$, where $\bar{\nu}_o$ lies in the vacuum UV close to the ionisation frequency. In contrast the frequency-splitting of an exciton CD couplet is proportional to the corresponding dipole strength, which is typically larger by $\sim 10^3$ for electronic than vibrational transitions, as in the case of calycanthine where CD couplets are observed in the electronic but not in the vibrational CD spectrum. Secondly, a procedure for the determination of the absolute stereochemical configuration from the IRCD spectra of chiral molecules generally, not only dissymmetric dimers, is provided by analogues of equation (1) in the analysis of the generally-unique CD band associated with a given characteristic group-mode IR absorption. Thirdly, the chromophore-substituent coupling providing the major contributions to the IRCD derive from aromatic or other substituents with a large polarizability anisotropy.

The IRCD spectrum of calycanthine in $CDCl_3$ solution was measured with an IRCD spectrophotometer affording random noise less than $\Delta\varepsilon = 2 \times 10^{-4}$ peak to peak at the absorption maxima in the spectrum recorded (Figure). The design of the instrument is analogous to that of recently-described[10] IRCD spectrometers, with differences in the demodulation and signal processing systems which will be described elsewhere.

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