Optical Activity of Characteristic Vibrational Modes and Absolute Configuration

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Summary The observed vibrational circular dichroism (c.d.) due to the symmetric and the antisymmetric N–H stretching modes of (*R*)-(+)- and (*S*)-(−)-2,2′-diamino-1,1′-binaphthyl originates principally from non-degenerate chromophore-substituent coupling and not from the degenerate coupling mechanism particular to dissymmetric dimers; the general non-degenerate mechanism provides a procedure for the determination of absolute configuration from the c.d. associated with a localised characteristic vibrational mode.

ABSOLUTE configuration from electronic optical activity was first determined non-empirically for dissymmetric dimers.[1] An electronic excitation with a given energy in each monomer chromophore of such dimers Coulombically couples to the other, giving two resultant transitions with oppositely-signed rotational strengths, separated by the exciton splitting energy. The observable signal expected from this mechanism is a pair of oppositely-signed c.d. 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 c.d. couplets are generally observed in the electronic c.d. spectra of dissymmetric dimers, and are widely employed for non-empirical configurational assignments.[2,3]

As the i.r. bands at a characteristic group frequency are attributed to an allowed electric dipole transition localised in a particular group of atoms, *i.e.* a vibrational chromophore, a c.d. couplet associated with each group frequency i.r. absorption is expected in the vibrational c.d. spectra of a dissymmetric dimer. Over the i.r. region of the H-stretching modes it is found that the dimeric natural products[1,2] and chiral biaryls[4,5] give generally a single c.d. absorption at a characteristic group frequency and not an exciton c.d. couplet (Figure 1). Calculations[1-5] of the rotational strength and frequency-splitting of the exciton c.d. couplet expected for the symmetric, ν_s, and the antisymmetric, ν_a, N–H stretching modes in (*R*)-(+)-2,2′-diamino-1,1′-binaphthyl (**1**) from the intensity data for these modes in the corresponding monomer,[6] 2-naphthylamine, show that the exciton frequency-splitting is small, 0·41 and 0·06 cm^{-1} for the ν_s and ν_a modes, respectively. As the splitting is small relative to the spectral band-pass of the i.r.c.d. instrument (7 cm^{-1} for 1 mm slit-width) and the band-width of the ν_s and ν_a absorption (22 and 34 cm^{-1}, respectively), the extent of the mutual cancellation of the oppositely-signed rotational strengths is larger for the vibrational exciton couplets than has been found for the corresponding electronic couplets.[1-5]

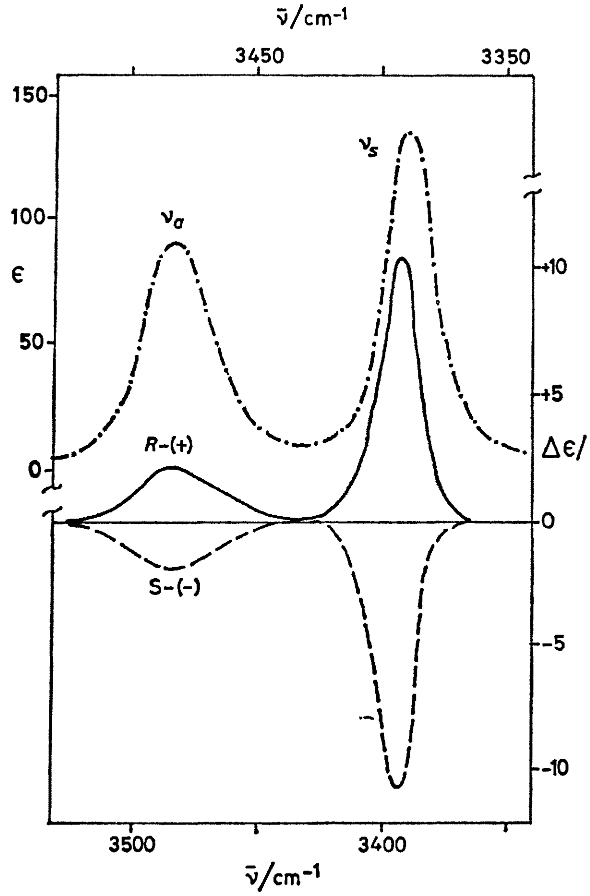
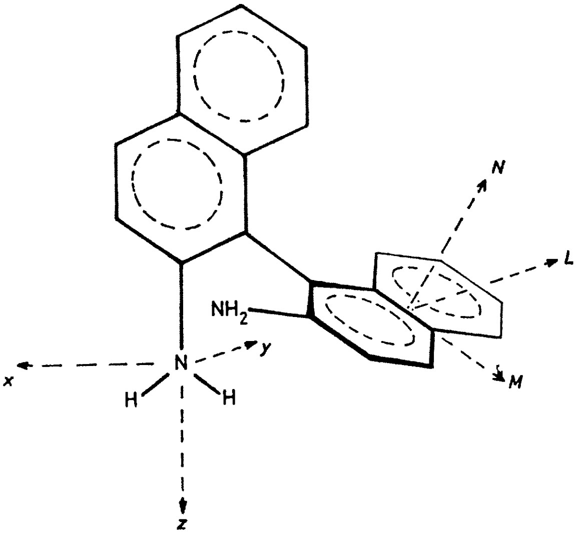


FIGURE 1. The absorption spectrum (upper curve) and circular dichroism (lower curves) of (*R*)-(+)- (full line) and (*S*)-(−)-2,2′-diamino-1,1′-binaphthyl (broken line) in carbon tetrachloride solution over the N–H stretching mode range.

The band areas of an electronic exciton c.d. couplet are not generally equal,[1-5] owing to the superposition of optical activity originating by the non-degenerate 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 single c.d. absorption is observed at the transition frequency with a sign reflecting the particular enantiomeric disposition of the substituents relative to the chromophore in the molecule. The vibrational c.d. accessible with an i.r.c.d. instrument employing a conventional black-body radiation source, which limits the attainable spectral band-pass, is mainly that originating from the non-degenerate coupling mechanism (Figure 1).

For the ν_s N–H stretching mode of the (*R*)-(+)-diamine (**1**) the non-degenerate interaction which accounts for the major part (+9·9 × 10^{-4} Debye Bohr magneton, dβ_M) of the observed rotational strength (+16·7 × 10^{-4} dβ_M) consists of the Coulombic coupling of the *z*-polarized dipole transition moment of the amino group substituted into one naphthalene nucleus with the dipole induced by the radiation field in the other naphthalene nucleus (Figure 2). The induced dipole has components along the *L*, *M*, and *N* axes of the naphthalene nucleus, each with a magnitude proportional to the corresponding principal component of the polarizability tensor at the transition frequency. At zero frequency, the values of the principal components are,[8] $\alpha_L = 21{\cdot}8$, $\alpha_M = 16{\cdot}6$, and $\alpha_N = 11{\cdot}3$ Å^3. Correction to the N—H stretching frequency region increases each of these values by 0·2%, which is negligible relative to the error limits of the values.[8] An extension of the non-degenerate coupling treatment[7] from cylindrical to rhombic anisotropy in the perturbing substituent affords the expression (1) for



(1)

FIGURE 2. The *R*-configuration of (+)-2,2′-diamino-1,1′-binaphthyl and the vibrational chromophore co-ordinate frame (*X*,*Y*,*Z*) for the symmetric N—H stretching mode with the principal axes (*L*,*M*,*N*) of the naphthalene polarizability tensor. The dihedral angle between the molecular planes of the naphthalene nuclei is taken as (π/2), on a time and molecule average, and each NH$_2$ group is assumed to be coplanar with the nucleus into which it is substituted, on the same average basis.

the main contribution to the rotational strength of the ν_s N—H stretching mode fundamental, R_{01} (S), in the (*R*)-(+)-diamine (**1**).

$$R_{01}(\mathrm{S}) = \pi\bar{\upsilon}_{01}D_{01}[3XYZ(\alpha_{\mathrm{L}}-(3/4)\alpha_{\mathrm{M}}-(1/4)\alpha_{\mathrm{N}})-(\sqrt{3}/4)Y(3Z^2-R^2)(\alpha_{\mathrm{M}}-\alpha_{\mathrm{N}})]R^{-5} \tag{1}$$

In equation (1), $\bar{\upsilon}_{01}$ and D_{01} refer to the wavenumber (3389 cm^{-1}) and dipole strength ($8{\cdot}10 \times 10^{-3}$ square Debye) of the 0—1 ν_s absorption, and X,Y,Z to the Cartesian coordinates of the centre of one naphthalene nucleus in a frame with the nitrogen atom of the NH_2 group substituted into the other nucleus as its origin, at a separation R (Figure 2).

Equation (1) is strictly applicable to (*R*)-(+)-2-amino-1,1′-binaphthyl, giving the calculated ν_s N—H stretching rotational strength, $R_{01}(\mathrm{S}) = +5 \times 10^{-4}\,\mathrm{d}\beta_{\mathrm{M}}$, compared with twice that value for the (*R*)-(+)-diamine (**1**). Additional non-degenerate contributions to $R_{01}(\mathrm{S})$ arise in the latter case from the coupling of the ν_s transition dipole of one NH_2 group with, firstly, the ν_a dipole of the other NH_2 group and, secondly, the induced dipole of that NH_2 group proportional to the polarizability anisotropy. The additional contributions are positive for R_{01} (S) of the (*R*)-(+)-diamine (**1**) but are smaller by an order of magnitude than that afforded by equation (1).

Analogues of equation (1) for other characteristic group vibrational modes in a chiral molecule provide a general method for the determination of absolute configuration non-empirically from the vibrational c.d. produced by the non-degenerate coupling mechanism. The absolute configurations of a range of chiral biaryls have been established by chemical correlations based upon a Bijvoet *X*-ray crystal structure determination,[9,10] as well as by the electronic c.d. couplet method,[4,5] and the vibrational c.d. at the characteristic H-stretching frequencies of these biaryls provides a check of the procedure proposed.

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