Non-anomalous Absolute Configuration of 1,5-Disubstituted 9,10-Dihydro-9,10-bridged Anthracenes

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Summary The disagreement between the absolute configuration of (−)-1,5-diamino-9,10-dihydro-9,10-ethenoanthracene determined by the Bijvoet *X*-ray method and by the exciton analysis of the c.d. spectrum derives from the use in that analysis of the origin-dependent dipole-length method for the calculation of the transition moments, whereas the employment of the origin-dependent dipole-velocity procedure affords a concordant configurational assignment.

UNTIL the recent report[1,2] of an anomalous class, consisting of the 1,5-disubstituted 9,10-dihydro-9,10-bridged anthracenes, the exciton analysis of the c.d. spectrum of a chiral molecule has been found to give invariably the same absolute configuration as the Bijvoet X-ray diffraction method. Examples† include bulbocapnine,[3,4] argemonine[5,6] caracurine-II,[7,8] (+)-2,2′-dihydroxy-1,1′-binaphthyl,[9,10] (−)-1,1′-bianthryl-2,2′-dicarboxylic acid,[11,12] (+)-*trans*-stilbene oxide,[13,14] (+)-[6]-helicene,[15,16] the (−)-$[\mathrm{As(cat)_3}]^-$ ion,[17,18] the (−)-$[\mathrm{Fe(phen)_3}]^{2+}$ ion,[19,20] and the (+)-$[\mathrm{Ni(phen)_2}]^{2+}$ ion.[21,22] In the cases where the coupling of the electric excitation moments of two or more chromophores is involved the particular location of the excitation moment in a chromophore is not critical for the exciton analysis of the c.d. spectrum, only the orientation of that moment in the chromophore being important.

However, the dissymmetric class of 1,5-disubstituted 9,10-dihydro-anthracenes (*e.g.* Figure 1), have no π-electron optical activity in the exciton approximation if it is assumed, as it often was in the early studies,[4,6,12] that the electric moment of a π-excitation in a benzenoid chromophore is located at the centre of the benzene ring. The c.d. spectra of (−)-1,5-diamino-9,10-dihydro-9,10-ethenoanthracene[1] and of (+)-2,7-diaminotriptycene,[2] each containing two aniline chromophores, have the exciton form, indicating that the barycentre of the electric moment of an aniline π-excitation is, in general, displaced from the centre of the benzene ring.

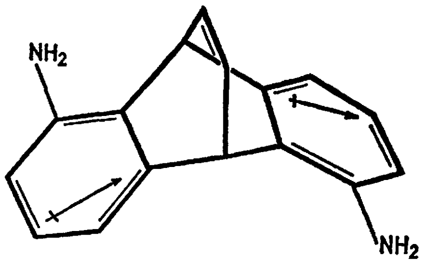

FIGURE 1. *The lower-frequency coupling mode, giving a negative rotational strength in* 9S,10S-1,5-*diamino*-9,10-*dihydro*-9,10-*ethenoanthracene, of the lowest-energy π-excitation of the two aniline chromophores calculated in the dipole-velocity representation.*

A re-examination of previous studies of aniline dimers, namely, the π-SCF calculations on calycanthine and caracurine-II[8] and a Hückel treatment of Tröger's base,[23] shows that the electric moment of the lowest-energy π-transition of aniline is displaced from the centre of the benzene ring towards the amino-substituent in the dipole-length representation but is shifted towards the *para*-carbon atom when calculated by the dipole-velocity procedure. The directions of the shifts depend solely on the length or velocity method adopted and are independent of the parameterisation and level of approximation. The magnitudes of the shifts are larger for the lower approximation and become substantial in the simple corresponding-carbanion model, which provides a paradigmatic contrast of the length with the velocity representation. In the corresponding-carbanion model[24] the lowest-energy π-excitation of aniline becomes an analogue of the transition of an electron from the non-bonding MO (I) to the lowest unoccupied MO (II) of the benzyl anion (Figure 2). The charge-densities of this transition show (Figure 3a) that the electric moment obtained by the dipole-length method is directed along the line joining the two *ortho*-carbon atoms, whereas the vectorial bond-order changes in the transition indicate (Figure 3b) that the electric moment of the dipole-velocity representation is directed along the line through the midpoints of the two *meta–para* carbon–carbon bonds.

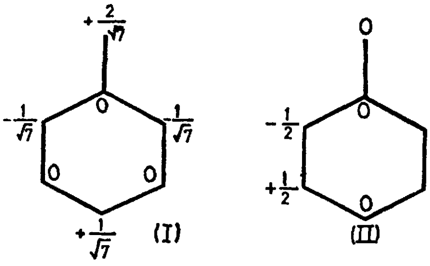

FIGURE 2. *The non-bonded MO, π_4* (I), *and the lowest unoccupied MO π_5* (II), *of the benzyl anion.*

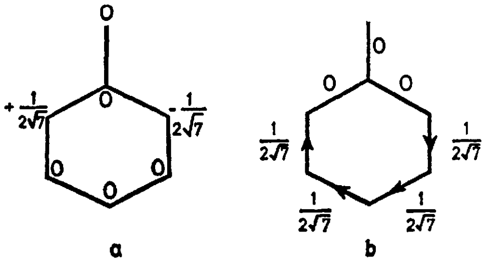

FIGURE 3. (a) *The charge density,* $C_{\mu4}C_{\mu5}$, *of the transition,* π_4 (I) → π_5 (II) *of the benzyl anion,* $C_{\mu n}$ *representing the atomic orbital coefficient of carbon atom,* μ, *in the molecular orbital,* π_n. (b) *The vectorial bond-order change,* $(C_{\mu4}C_{\nu5} - C_{\mu4}C_{\nu5})$, *of the benzyl anion transition,* π_4 (I) → π_5 (II), *representing the transitional charge momentum along the bond between the carbon atoms,* μ *and* ν.

The Coulombic coupling of the lowest-energy electric moment of the two aniline chromophores, obtained by the dipole-velocity method, gives a negative and a positive rotational strength at a lower and higher frequency, respectively, for the 9*S*,10*S*-configuration of 1,5-diamino-9,10-dihydro-9,10-ethenoanthracene (Figure 1), as is observed[1] for the (−)-isomer, in agreement with the X-ray configurational assignment.[1] The exciton c.d. analysis employing the aniline excitation moments calculated by the dipole-length formalism assigns to the (−)-isomer the enantiomeric 9*R*,10*R*-configuration,[1] and it provides a crucial example of the long-suspected hazard of the use of the dipole-length procedure in the calculation of rotational strengths.

Gorin, *et al.*[25] pointed out that rotational strengths calculated from inevitably-inexact wavefunctions by the dipole-length method are, in general, origin-dependent. Moffitt showed[26] that origin-independent rotational strengths are ensured by working consistently in the dipole-velocity representation.[27] The sum-rule for rotational strengths is violated in the dipole-velocity, but not in

† References to the X-ray determination of the configuration of a given molecule, or to a chemical correlation based on a Bijvoet standard, and to the corresponding exciton c.d. analysis are cited in the corresponding serial order.

the dipole-length procedure.[28] In stereochemical applications the loss of the sum-rule is expected to be generally less of a hazard than origin-dependency, since the signs and the frequency-order of the bands in the c.d. spectrum are of primary concern in those applications. The theoretical reproduction of the magnitudes of the observed rotational strengths, although strongly confirmatory of a c.d. analysis, has not as yet proved to be the decisive element in a configurational assignment.

(*Received*, 13*th February* 1973; *Com*. 200.)

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