Absolute Configuration of (−)-1,5-Disubstituted 9,10-Dihydro-9,10-etheno- or -ethano-anthracenes. Comparison of *X*-Ray and Circular Dichroism Studies

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Summary The absolute configurations of (−)-1,5-disubstituted 9,10-dihydro-9,10-etheno- or -ethano-anthracenes as indicated by c.d. spectral analysis are not consistent with those determined by the current *X*-ray method; this work provides an additional example to the accumulated results that the rigorous exciton theoretical analysis of c.d. spectra does not agree with the Bijvoet method of *X*-ray crystal analysis.

The determination of the absolute configurations deduced by the *X*-ray fluorescence technique of Bijvoet[1,2] is generally accepted as entirely reliable. We have found[3] that the absolute configurations indicated by the exciton analysis of the c.d. spectra are not always in agreement with those determined by the Bijvoet method.[2] Investigations to compare these two methods have been continued and the same situation is found in the series of etheno- or ethano-anthracenes. The optically active title compounds were synthesized and resolved and their c.d. spectra recorded; typical spectra are shown in Figure 1.

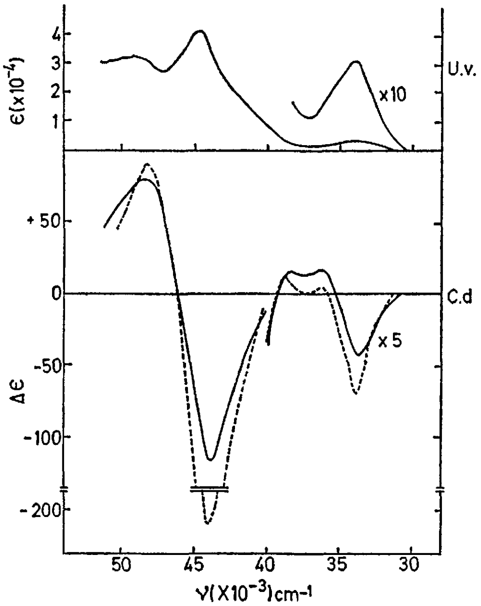

Figure 1. *The u.v.* (*top*) *and c.d.* (*bottom*) *spectra of* (−)-1,5-*diamino*-9,10-*dihydro*-9,10-*ethenoanthracene in methanol. Solid line at room temperature and dotted line at* −120 °C *by a JASCO J*-20 *spectropolarimeter.*

The u.v. and c.d. bands in the 34,000—36,500 cm^{-1} region are attributed to the coupled states of the $^1B_{2u}$-type levels of the aniline chromophore, the polarization being perpendicular (short-axis in monosubstituted benzenes) to the C-1—C-4 and C-5—C-8 lines, respectively. The strongest bands at 44,000—50,000 cm^{-1} correspond to the $^1E_{1u}$ states of the same polarization direction. These assignments are based on convincing theoretical and experimental studies of the spectra of substituted benzenes and triptycenes.[4]

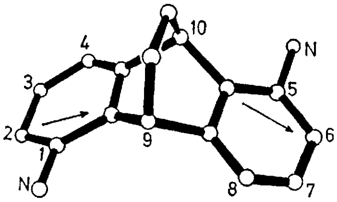

Figure 2. *The absolute configuration of* (−)-1,5-*diamino*-9,10-*dihydro*-9,10-*ethenoanthracene determined as* 9R,10R *by the c.d. spectral analysis. Arrows indicate positions and directions of transition moments in this treatment. The absolute configuration of this compound has been shown by Bijvoet* X-*ray analysis to be* 9S,10S.

The chirality of the present system originates in the displacement of the transition moment of the aniline chromophore; it can be deduced theoretically by the calculation of the transition densities[5] with the LCAO SCF MO CI of aniline.[6] The exciton coupling is evaluated by the dipole–dipole or by the point-charge approximation, and the parallel arrangement of the short-axis polarized transition moments will give the lower energy state. The rotational strength is estimated by the standard procedure.[7] The negative rotation for the lower energy band of the short-axis polarized band pair suggests that the absolute configuration should be as shown in Figure 2.

Similar c.d. spectral patterns have been observed with other molecules having other substituents, *e.g.*, nitro-, methoxy-, and carboxy-groups, and will be published elsewhere. The influence of the $^1B_{1u}$-type levels, which exists between the $^1B_{2u}$ and the short-axis polarized[1] $^1E_{1u}$ states, on the optical rotation is most prominent for weak substituents such as methyl and protonated amino-groups. The $^1B_{2u}$ levels of the latter are coupled with the $^1B_{1u}$-type states and reversal of the sign of the rotational strengths has been observed.

On the other hand, the *X*-ray crystal structure analysis has been performed on (−)-1,5-diamino-9,10-ethenoanthracene dihydrobromide monohydrate. The crystals are monoclinic, space group $P2_1$, $a = 8{\cdot}63$, $b = 8{\cdot}00$, $c = 12{\cdot}34$ Å, $\beta = 97{\cdot}78°$, $Z = 2$, $D_m = 1{\cdot}62$ and $D_c = 1{\cdot}65$ g cm^{-3}. Three-dimensional diffraction data were collected on Hilger-Watt four-circle diffractometer by using Cu-K_α radiation. The structure was solved by the heavy-atom method, and least-squares refinement has so far reduced R to 0·13 for 1733 independent reflections. The absolute configuration was determined with the Bijvoet method for 50 Friedel's pairs, and it gave the absolute configuration as the *antipode* of Figure 2, *i.e.*, as $9S,10S$. The chemical correlation of the absolute configuration with (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide is described *in* the following communication.

This disagreement between *X*-ray and c.d. methods for some compounds is a matter for serious concern. The fundamental theory of *X*-ray scattering and circular dichroism has been examined in detail and the full accounts of these investigations will be published elsewhere.[8]

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