

Angular Dependence of the U.V. Absorption Maximum Wavelength in Exciton Coupling Systems

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It is shown from the u.v. data for various bis[*p*-dimethylamino]benzoates] that in exciton coupling systems if the angle between two electric transition moments is larger than 90° , the u.v. λ_{\max} is shifted to longer wavelengths relative to that of the mono[*p*-dimethylamino]benzoate], while if the angle is less than 90° , the u.v. λ_{\max} is shifted to shorter wavelengths.

The c.d. exciton chirality method has been extensively used to determine the structures of various organic compounds on a non-empirical basis.¹ When two identical *para*-substituted benzoate chromophores couple with each other, the c.d. spectrum exhibits split Cotton effects of opposite signs which

are characteristic of exciton coupling systems. On the other hand, the u.v. spectrum shows no such change; the u.v. curve merely looks like a single absorption band of double intensity. However, careful examination of the u.v. spectra led to the following generalisation that in exciton coupling systems,

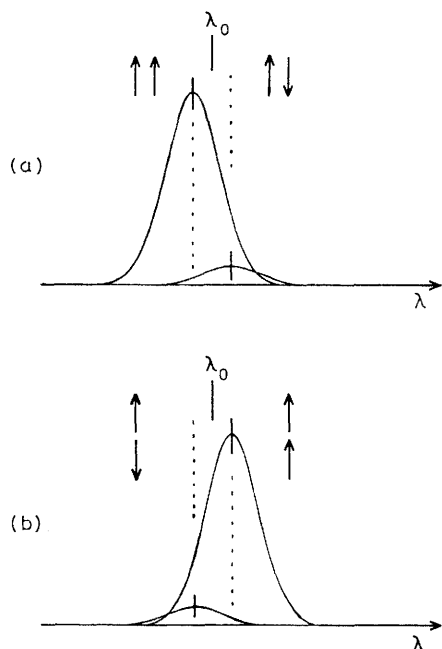


Figure 1. Angular dependence of the u.v. λ_{\max} for exciton coupling systems; when the angle θ between the two transition dipole moments (indicated by arrows) is less than 90° [as in (a), $\theta = 0^\circ$], the u.v. spectrum exhibits a blue shift relative to that of the mono chromophore (λ_0). On the other hand, an angle larger than 90° [as in (b), $\theta = 180^\circ$] leads to a red shift.

if the angle between two electric transition moments is larger than 90° , the u.v. λ_{\max} is shifted to longer wavelengths relative to that of the single chromophore. If the angle is less than 90° , the u.v. λ_{\max} is shifted to shorter wavelengths.†

For example, in the case of the (*p*-dimethylamino)benzoate chromophore, the λ_{\max} of the monobenzoate (1) is 311.0 nm (Table 1). The u.v. spectrum of the binary system (1*R*,2*S*,3*R*,4*S*)-bornane-2,3-diyl bis[*p*-dimethylamino)benzoate] (2), in which the angle between the two transition moments is *ca.* 40° , exhibits a blue shift of 6.1 nm (λ_{\max} 304.9 nm, Table 1). On the other hand, the u.v. spectrum of 5 α -cholestane-2 β ,3 α -diyl bis[*p*-dimethylamino)benzoate] (19) with an angle of 180° shows a red shift of 3.8 nm (314.8 nm, Table 1).

The present results can be theoretically interpreted on the basis of the exciton coupling mechanism, as follows:‡ if the angle between the two transition moments is *ca.* 0° , the out-of-

† In some special cases, similar results have been found: for 1,1'-bianthryl derivatives: (a) G. M. Badger, R. J. Drewer, and G. E. Lewis, *J. Chem. Soc.*, 1962, 4268; (b) S. F. Mason, in 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' ed. G. Sznatzke, Heyden, London, 1967, Ch. 4; (c) for (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene, a binary system composed of two anthracene chromophores, N. Harada, Y. Takuma, and H. Uda, *J. Am. Chem. Soc.*, 1978, **100**, 4029.

‡ The energy (*E*) and dipole strength (*D*) of exciton coupling binary systems are formulated:¹

$$\alpha\text{-state, } E^\alpha = E_a - V_{ij}, \quad D^\alpha = \frac{1}{2}(\mu_{i0a} - \mu_{j0a})^2$$

$$\beta\text{-state, } E^\beta = E_a + V_{ij}, \quad D^\beta = \frac{1}{2}(\mu_{i0a} + \mu_{j0a})^2$$

where E_a is excitation energy for the $0 \rightarrow a$ transition, V_{ij} is the interaction energy, and μ_{i0a} and μ_{j0a} are the electric transition moment vectors of chromophores *i* and *j*, respectively. The ratio of two dipole strengths is formulated (see also footnote †, ref. b)

$$D^\alpha/D^\beta = (1 - \cos \theta)/(1 + \cos \theta)$$

where θ is the angle between two transition moments μ_{i0a} and μ_{j0a} . When $\theta = 90^\circ$, $D^\alpha/D^\beta = 1$; therefore, no shift of λ_{\max} is observable.

Table 1. The angle between two electric transition moments, and the observed u.v. λ_{\max} data for a number of bis[*p*-dimethylamino)benzoates].

Compound and angle ^a	λ_{\max} /nm	Solvent ^b
Monobenzoate		
(1) Cholest-5-en-3 β -yl	311.0	1% D/E
40° (1,2-dibenzoate)		
(2) (1 <i>R</i> ,2 <i>S</i> ,3 <i>R</i> ,4 <i>S</i>)-bornane-2,3-diyl	304.9	E
70° (1,2-dibenzoate)		
(3) 5 α -Cholestane-2 β ,3 β -diyl	307 ^c	E
(4) 5 α -Cholestane-2 α ,3 α -diyl	308 ^c	E
(5) Cholest-5-ene-3 β ,4 β -diyl	308 ^c	E
(6) Cholest-5-ene-3 α ,4 α -diyl	309.4	E
70° (1,4-dibenzoate)		
(7) 5 α -Cholestane-3 β ,6 β -diyl	309 ^c	E
(8) 5 α -Hydroxycholestane-3 β ,6 β -diyl	309.3	E
(9) Cholest-4-ene-3 β ,6 β -diyl	310.0	E
(10) 5 α -Cholestane-3 β ,6 α -diyl	310 ^c	E
70° (1,6-dibenzoate)		
(11) 5 α -Androstane-3 β ,11 β -diyl	310 ^c	10% D/E
(12) 5 α -Pregnane-3 β ,11 α -diyl	310 ^c	E
70° (1,8-dibenzoate)		
(13) D-Homo-5 α -androstane-3 β ,15 β -diyl	310 ^c	E
90° (1,3-dibenzoate)		
(14) (1 <i>R</i> ,5 <i>S</i> ,6 <i>S</i>)-Spiro[4.4]nonane-1,6-diyl	310.5 ^d	E
(15) (1 <i>R</i> ,1' <i>S</i> ,2 <i>S</i>)-2,2'-Spirobi-indane-1,1'-diyl ^e	310.9	E
110° (1,5-dibenzoate)		
(16) 5 α -Cholestane-3 β ,7 β -diyl	310 ^c	E
(17) 5 α -Cholestane-3 β ,7 α -diyl	310 ^c	E
180° (1,3-dibenzoate)		
(18) (1 <i>R</i> ,1' <i>R</i> ,2 <i>S</i>)-2,2'-Spirobi-indane-1,1'-diyl ^e	313.9	E
180° (1,2-dibenzoate)		
(19) 5 α -Cholestane-2 β ,3 α -diyl	314.8	E

^a The angles were roughly estimated from molecular models. ^b D: dioxan, E: ethanol. ^c Taken from ref. 4. ^d Taken from ref. 5. ^e The stereochemistry of these compounds was independently established by n.m.r. spectroscopy (see ref. 2).

phase combination of the two transition moment vectors is energetically more stable than the in-phase combination [Figure 1(a)]. The in-phase combination at shorter wavelengths gives rise to a more intense absorption band, because the u.v. intensity is proportional to the square of the sum of the vectors. However, the out-of-phase combination at longer wavelengths gives rise to a weak absorption band. Therefore, summation of the two curves results in a blue shift of the u.v. λ_{\max} . If the angle is *ca.* 180° , the order of the energy levels is reversed; the state with the in-phase combination is more stable than the state with the out-of-phase combination [Figure 1(b)]. As a result, an intense absorption band is located at longer wavelengths while a weak band is at shorter wavelengths; summation of the two curves results in a red shift.

The u.v. data for pertinent bis[*p*-dimethylamino)benzoates] with various angles and interchromophoric distances are listed in Table 1. As the angle increases, the u.v. λ_{\max} gradually shifts to longer wavelengths; around 90° , the observed shifts are small, in agreement with the theoretical expectation.‡ Provided the angle remains unchanged, a dibenzoate system with a longer interchromophoric distance exhibits a smaller shift because of weak exciton interaction. The data listed in Table 1 are in agreement with the present postulation based on the exciton theory. From u.v. data of exciton coupling systems, in general, one can determine whether the angle

between two transition moments is greater or less than 90° ,[§] while c.d. data enable one to determine the absolute relationship between the direction of two transition moments. This method was successfully used for structure determination as discussed in the following communication.²

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§ From the theoretical viewpoint, the present theory does not hold for some isolated cases, *e.g.*, hypothetical 1,1'-binaphthyls with the dihedral angle larger than *ca.* 110° because of sign inversion³ of the interaction energy V_{ij} . However, it does hold for actual 1,1'-binaphthyls which have the dihedral angle of *ca.* $70-90^\circ$.

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