Table 2. $\Delta\bar{V}_{AB}$ for bianthrones

Compound	ΔV_{AB}, cm³/mol Pressure, kbar		
	60	90	120
BA in PMMA	−0.9	− 0.7	− 0.5
2,2′-DMBA in PMMA	− 1.1	− 0.7	− 0.3
2,2′-DRBA in PMMA	− 0.9	− 0.8	− 0.7
4,4′-DMBA in PMMA		− 0.4	
BA in PS	− 0.8	− 0.3	

to point out that for xanthylidenanthrone, which undergoes a similar transformation, the molar polarizations of the B and A forms have the ratio $P_B/P_A = 2.3$[18]. The smaller decrease in E_D with density in PS compared with PMMA may be associated with its smaller dielectric constant ($\varepsilon_{PS} = 2.6$ and $\varepsilon_{PMMA} = 3.5$), and thus with a weaker solute–solvent interaction.

This is, then, a pressure-induced electronic transition of a type which can only be produced by light or heat under ordinary pressures. There is preliminary evidence that similar transitions occur at high pressure in some spiropyrans and perhaps in some stilbenes also.

ANALYSIS OF CONFIGURATION COORDINATE PARAMETERS

The configuration coordinate analysis discussed at the beginning of this paper can be used as a basis for characterizing a wide variety of electronic excitations. In the course of its derivation, equations were developed for the shift of the optical absorption (or emission) peak with pressure and the change of half-width. These can conveniently be written:

$$(\delta h\nu)_a = pR\Delta + p^2\frac{(R-1)}{2\omega^2} + \frac{R^2\Delta^2}{2}(\omega^2 - \omega_0^2) \tag{5}$$

$$(\delta h\nu)_e = \frac{p\Delta}{R} + \frac{p^2(R-1)}{2\omega^2R^2} - \frac{\Delta^2}{2}(\omega^2 - \omega_0^2) \tag{6}$$

$$\delta(E_{1/2})_a = N\left[\left|\omega R\Delta + \frac{p(R-1)}{\omega}\right| - \left|\omega_0 R\Delta\right|\right] \tag{7}$$

$$\delta(E_{1/2})_e = N\left[\left|\frac{\omega\Delta}{R^{1/2}} + \frac{p(R-1)}{\omega R^{3/2}}\right| - \left|\frac{\omega_0\Delta}{R^{1/2}}\right|\right] \tag{8}$$

Here $h\nu$ represents the energy of the peak maximum, $E_{1/2}$ the peak width at half height and δ the change in the value of the quantity between pressure p and 1 atm (effectively zero pressure). Δ, the displacement along the configuration coordinate of the excited state potential well with respect to the ground state well, could be considered as the change in volume of the system upon excitation of an electron, at least if the normal mode in question is the breathing vibration of the system. The potential wells are considered as harmonic with force constants ω^2 and ω'^2. $R = (\omega'/\omega)^2$, and $N = (8kT\ln 2)^{1/2}$ for Gaussian peaks at ordinary temperatures. ω^2 is considered to be pressure dependent, and ω_0^2 is the value at 1 atm. It is assumed that R is constant or at least varies slowly with pressure compared with ω^2. This

seems reasonable and no available data justify a more complex pressure dependence.

In general, the shift of the optical absorption or emission peak with pressure can be expressed within the accuracy of most data as a quadratic function of pressure. The change of half-width may be linear or quadratic in pressure. This gives six or eight measured coefficients to determine R, Δ, and the pressure dependence of ω^2. (For some systems ω^2 may be independent of pressure; for others, a reasonable assumption may be that it is coupled to the bulk modulus of the crystal or solvent, e.g. in the form $\omega^2 = \beta(-\partial p/\partial V)$, which defines a dimensionless β.) In any case, the three parameters are considerably overdetermined if accurate peak shift and half-width change data are available for both absorption and emission. This gives the opportunity to calculate them from several combinations of the coefficients, and provides a test of the consistency of the data and the applicability of the configuration coordinate model. It is, of course, necessary that the emission occur from the same state as that to which the electron is excited, with no intersystem crossing. Otherwise, additional parameters are needed and the redundancy may disappear. Problems in measurement and calculation of half-widths under pressure have been discussed in some detail elsewhere[19].

As indicated above, one would use various combinations of absorption and fluorescence data to calculate Δ, R and the pressure dependence of ω^2. Four such methods used in this laboratory include:

(1) A method based on absorption data only, using the linear and quadratic coefficients from fitting the peak shift data and a linear term from the change of half-width with pressure.

(2) A similar calculation using emission data only.

(3) A combination of absorption and emission data, using the linear coefficients for peak shift of the absorption and emission peaks and the change of half-width of (say) the absorption peak. This method emphasizes the low-pressure data.

(4) A calculation using only the shifts of absorption and emission peaks which does not involve any half-width data.

Table 3. Configuration coordinate parameters for phenanthrene crystal

Method	Δ	R	β
1	3.7	1.01	1.4
2	− 3.8	0.99	1.7
3	− 3.8	1.00	1.3
4	− 3.8	1.01	1.6

This analysis has been applied successfully to a number of systems[20,21]. We discuss only a representative set of data here. In *Table 3* we exhibit results for phenanthrene in the crystal. The agreement among the methods is very good, which lends considerable credence to the analysis.

In *Table 4* we compare values for the configuration coordinate parameters