

Table 4. Configuration coordinate parameters

Material	$\Delta(\text{cm}^3/\text{mol})$	R	β
Phenanthrene			
in crystal	- 3.7	1.01	1.4
in PMMA	- 1.0	1.00	0.53
in hexane	- 3.1	1.00	0.016
Anthracene			
in crystal	- 10.2	1.00	1.1
in PMMA	- 3.3	1.01	0.27
in hexane	- 9.2	1.00	1.7×10^{-3}
in methanol	- 7.4	1.00	2.9×10^{-3}
in glycerol	- 5.7	1.02	0.18

Δ , β and R for phenanthrene and anthracene in various media. The decrease in volume of the system upon electronic excitation, Δ , depends strongly on the medium. There is a balance among several factors: the increase in dipole moment of the molecule upon electronic excitation, the polarizability of the surrounding medium and the compressibility of the medium. The crystal has a larger polarizability than the PMMA or the hexane, while the hexane has a much larger compressibility than the crystal of PMMA. The balance of these factors gives the resultant value of Δ . The effect of compressibility can be seen in the data for anthracene in hexane, methanol and glycerol. The relative compressions of the solvents in 10 kbar are 0.31/0.25/0.12. The excited state of anthracene (1L_a) has a much larger dipole moment than the excited state of phenanthrene (1L_b). The ratio of the Δ values for the two molecules are: in the crystal 2.7, in PMMA 3.3, and in hexane 3.2.

β is largest for the most rigid medium, the crystal; smaller by a factor of three for PMMA; and smaller by two orders of magnitude in hexane. For anthracene the β s are in the ratio 1/1.7/100 for hexane/methanol/glycerol. The viscosities of the three solvents are in the ratio 1/1.7/1200. There is a clear relationship between the stiffness of the medium and the coupling to the solute molecule.

For these and other $\pi-\pi^*$ excitations $R \simeq 1.0$. This is not necessarily general. For impurities in alkali halides values of R ranging from 0.5 to 1.5 have been observed.

In addition to studies on aromatic hydrocarbons in various environments²⁰, this analysis has been successfully applied to purine and pyrimidine bases and the corresponding nucleosides in the crystal, in neutral aqueous solution and in acidic and basic solution²¹. It appears to be a powerful method for characterizing electronic excitations.

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APPENDIX

The theme of this paper is the effect of pressure on electronic energy levels in solids, and resulting chemical reactivity. However, there is also a very extensive area of research involving the effect of pressure on chemical reactivity in solution. This has generally been limited to pressures in the range of 5–10 kbar, but since organic liquids compress 16–20 per cent in 5 kbar and 25–30 per cent in 10 kbar, significant results can be expected. These studies fall into two general areas: the inducing of new chemical reactions or the enhancement of yield in chemical reactions, and studies of the effect of pressure on reaction rate in order to elucidate the mechanisms of reactions. A general review of the area is given by Weale^{1A}. Important contributions for both organic and inorganic systems have been made by Osugi and co-workers^{2A–6A}. A recent paper by Dauben and Kozikowski^{7A} is a particularly nice example of the use of pressure to overcome stereochemical resistance to reaction.

Physical-organic chemistry at high pressure has been reviewed by LeNoble^{8A} and by Eckert^{9A}, both of whom have made important contributions. Johnson, Eyring and Stover^{10A} discuss pressure effects on rate processes in biological systems.

The basic approach to physical-organic chemistry in this area is to start from an equation for the reaction velocity constant:

$$k = (k_B T/h) \exp(-\Delta G^\ddagger/RT) \quad (\text{A1})$$

where k_B is Boltzmann's constant, h is Planck's constant, T the temperature