Short Communication

## Remarks on the anomalous polarity of 1,4-dioxan in photophysics and photochemistry

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1,4-dioxan is a very peculiar solvent. Although its static dielectric constant D, as measured on pure dioxan by conventional methods, is very low (around 2, *i.e.* similar to hydrocarbons like cyclohexane), it is a good solvent for polar and non-polar solutes.

In solvatochromic shift measurements, which are of importance in photophysics and photochemistry, it behaves in most cases like a polar solvent with a polarity (defined by the function $f(D) = 2(D - 1)/(2D + 1)$) similar to that of ether-type solvents. In a recent study [1] of the effects of dioxan on aniline absorption and fluorescence spectra it was suggested that the anomaly was the result of a specific association described by the formation of hydrogen bonds:
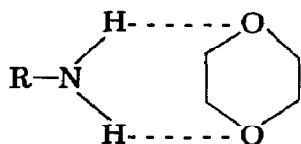
This suggestion must be contrasted with the earlier hypothesis [2] of "conformation polarization" in which it was proposed that dioxan derives its anomalous polarity from its stereoisomer boat form which is a polar molecule, in contrast with the more stable chair form which is non-polar. In the vicinity of polar solute molecules the solvent shell would consist mostly of the polar boat form as long as the increased dipole–dielectric stabilization outweighed the energy difference between the chair and the boat forms.

To decide between the two mechanisms, the effective $f(D)$ function of 1,4-dioxan was measured for the absorption solvatochromic shifts of a number of solute molecules (Table 1), some of which cannot form hydrogen bonds of the type suggested above. One example of a direct comparison, between indole and 1-methylindole, is shown in Fig. 1. This shows convincingly that hydrogen bonding of the type R—N—H . . . O—C— is not responsible for the dioxan anomaly. The same conclusion is reached from a comparison of other amino and *N*-dimethylamino derivatives.

TABLE 1

The effective polarity of 1,4-dioxan determined
from the solvatochromic shifts of the solutes

Solute	f(D)
Indole	0.81
1-methylindole	0.81
Michler's ketone	0.72
4-N-dimethylaminonitrosobenzene	0.80
2-nitroanisole	0.80
4-phenylbenzaldehyde	0.75
Benzophenone	0.68
Aniline	0.80
Theoretical value	0.40

The polarity is defined by the function $f(D)$
(see text).

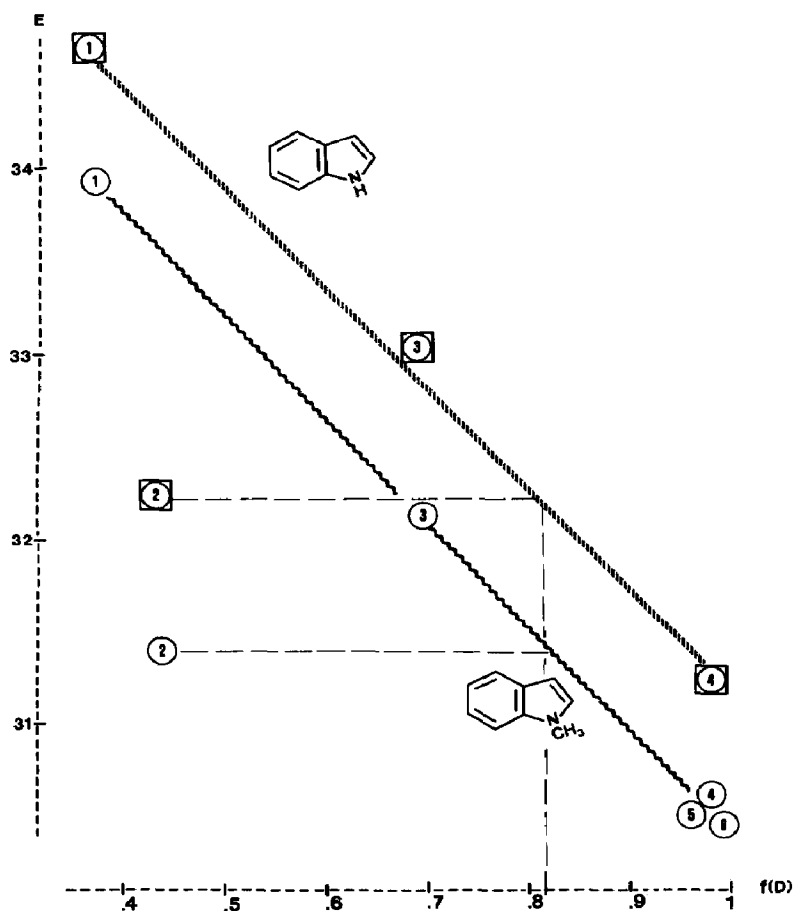

Fig. 1. Solvatochromic shifts of the first absorption bands of indole (□) and 1-methylindole
(○), illustrating the similar dioxan anomaly that occurs in both cases: 1, pentane; 2, 1,4-
dioxan; 3, diethyl ether; 4, acetonitrile; 5, n-butanol; 6, methanol. E is the energy of the
absorption maximum in units of 10^3 cm^{-1}.

An understanding of the mechanism of this well-documented anomalous polarity [3] of 1,4-dioxan is important for two reasons.

(1) When solvatochromic shifts are used to evaluate the excited state dipole moment of molecules of photochemical interest, it is incorrect to consider dioxan as a non-polar solvent of dielectric function $f(D) = 0.4$. Dipole moments determined in this way may be too small by up to a factor of 2.

(2) The effect of solvent polarity on photochemical reactivity is a subject of great importance [4]. Here again, it is wrong to consider dioxan as a non-polar solvent. Only the *observed* solvatochromic shifts are a useful guide to the ordering of electronic states of a molecule in different solvents.

If 1,4-dioxan derives its anomalous polarity from conformation polarization rather than from hydrogen bonding, the very general nature of this mechanism must be taken into account for all polar solutes. This is true not only for pure 1,4-dioxan but also for the frequently used solvent mixtures in which it is assumed to be the "non-polar" component.

1 G. Perichet, R. Chapelon and B. Pouyet, *J. Photochem.*, *13* (1980) 67.
2 M. B. Ledger and P. Suppan, *Spectrochim. Acta, Part A*, *23* (1967) 3007.
3 J. Hurwic, in A. D. Buckingham, E. Lippert and S. Bratos (eds.), *Organic Liquids*, Wiley, New York, 1978, p. 205.
4 R. D. Rauh and P. A. Leermakers, *J. Am. Chem. Soc.*, *90* (1968) 2246.