Solvent-induced Conformational Changes of 1,2-Dicyano- and -Dihalogeno-ethanes

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INTENSIVE investigations of internal rotation in molecules of type $X \cdot CH_2 \cdot CH_2 \cdot X$ (X = CN, Cl, etc.) have established[1,2] that an assemblage of such molecules can be effectively considered as a mixture of staggered *gauche-* and *trans*-isomers. Any molecular conformation may be designated by an angle ϕ with origin at the *cis*-form of C_{2v} symmetry, so that the *trans*-conformation with C_{2h} symmetry is defined by $\phi = 180°$. Several physical methods have shown that at a given temperature the liquid state has a greater *gauche* content than the gaseous state. This has been attributed by Watanabe *et al.*[3] to reaction-field stabilization of the polar *gauche*-isomer.

More generally *all* polar configurations will be stabilized by the reaction field and we can write the energy, $U(\phi)$, of the molecule in a dense medium as

$$U(\phi) = U_1(\phi) + U_2(\phi) \qquad (1)$$

where $U_2(\phi)$ is the potential function governing intramolecular rotation in the gaseous state and $U_2(\phi)$ is the potential energy of the molecule due to the neighbouring molecules. To a first approximation $U_2(\phi)$ can be evaluated from the Onsager reaction-field model[4] to give

$$U_2(\phi) = -\frac{\epsilon - 1}{2\epsilon + 1} \cdot \frac{\mu^2(\phi)}{a^3} \qquad (2)$$

where ϵ is the dielectric constant of the medium, μ is the dipole moment of the solute, and a is the "molecular radius".[4] For 1,2-dichloroethane the function $U_1(\phi)$ has the form[5] indicated (see Figure), and its analogues probably have potential functions of similar shape. Vector analysis of the molecular moment into two C–X group moments gives

$$U_2(\phi) = -k \cos^2 (\phi/2) \qquad (3)$$

where k is a positive constant for a given molecule and environment.
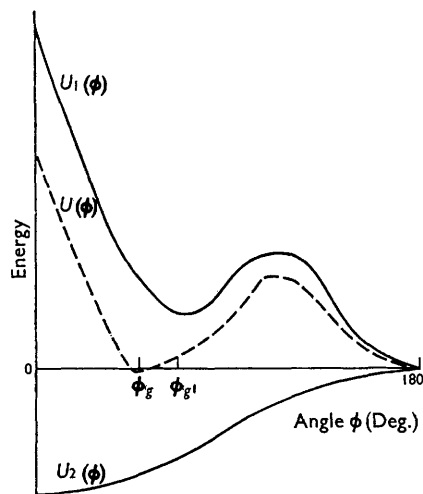
FIGURE

Potential energy curves for 1,2-disubstituted ethanes showing gauche-configurations at $\phi_{g_1}°$ and $\phi_g°$ in gaseous and dense media respectively. (The difference $\phi_{g_1} - \phi_g$ is exaggerated.)

Comparison of the potential functions $U(\phi)$ and $U_1(\phi)$ reveals, *inter alia*, that the angle ϕ_g specifying the *gauche*-conformation diminishes as the dielectric constant of the medium increases. We believe that this implication has received little attention and supporting evidence is now presented.

The molar Kerr constant ($_mK$) of 1,2-di-cyanoethane (dipole moment[6] 3·90 D) in benzene at 25° increases rapidly with increasing solute concentration. At infinite dilution the $_mK$ is $+21 \times 10^{-12}$, but this value is more than doubled at a solute concentration less than 2·5%. Comparison of the observed moment and $_mK$ with calculated values indicates about 75% of a *gauche*-isomer in which $\phi_g = 93°$. It is relevant that infrared studies below $-43·7°$ suggest an absence of the *trans*-conformer.[7] The larger $_mK$ at solute concentrations around 2·5% is consistent with a decrease of at least 2° in ϕ_g, accompanied by an increase in the *gauche*-population, as expected from the greater value of ϵ at this concentration. The slope of the graph of dielectric constant against solute concentration also increases[6] with increasing concentration, in agreement with the formation of a more polar *gauche*-form.

Similar nonlinear concentration-dependences of Kerr effects and dielectric constants are found in data[8] for 1,2-dichloroethane ($\mu = 1·47$ D) and 1,2-dibromoethane ($\mu = 0·93$ D) as solutes in carbon tetrachloride, again suggesting a decrease in the dihedral angles of their *gauche*-conformations. The lower polarities are probably responsible for concentration effects smaller than those found for 1,2-dicyanoethane.

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