Ultrasonic Relaxation and the Chair–Boat Equilibrium in Some Substituted 1,3-Dioxans

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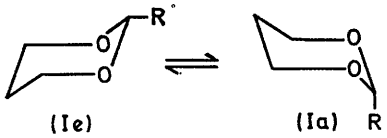
Summary Ultrasonic relaxation has been observed in a number of alkyl-substituted 1,3-dioxans: relaxation of the 2-alkyl derivatives has been attributed to ring inversion, whilst the relaxation found in 2,2,4- and 2,2-substituted derivatives is considered to be the result of the perturbation of a chair–boat equilibrium.

IN an ultrasonic absorption study of liquid alkyl derivatives of 1,3-dioxan over the temperature range −30° to +90° and frequency range 5—105 MHz, relaxation has been observed in 2-alkyl-1,3-dioxans (alkyl = Me, Et, Pr^n, Pr^i, or Bu^n). The relaxation process is of an intramolecular nature (the relaxation frequency was found to be independent of concentration) and has been attributed to perturbation of the equilibrium between the equatorial (1e) and axial (1a) chair isomers:—



(1e) (1a)

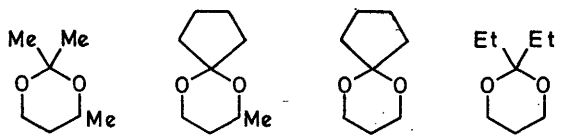
Preliminary examination of the ultrasonic data indicates that the relaxation frequency for the ring inversion process

is *ca.* 10—20 MHz at 80°, which corresponds to an energy barrier of 30 kJ mole^{-1} for the less stable → more stable inversion process. The maximum absorption per unit wavelength is *ca.* $1{\cdot}6 \times 10^{-3}$.

No relaxation was observed in the 4-methyl homologues of the above molecules. In the stable conformers of these molecules both substituents are equatorial and ring inversion produces a considerable steric synaxial interaction[1] resulting in such a large energy difference between the conformers that virtually all the molecules are diequatorial. This may account for the absence of relaxation, or, alternatively, the inversion barrier may be too high (>50 kJ mole^{-1}).

It is surprising, therefore, that an ultrasonic relaxation has been observed in 2,2,4-trimethyl-1,3-dioxan (II) and 4-methyl-1,3-dioxan-2-spiro-cyclopentane (III). Even more remarkable is the relaxation we have now observed in 1,3-dioxan-2-spiro-cyclopentane (IV) and 2,2-diethyl-1,3-dioxan (V) which cannot be due to ring inversion since the equilibrium between both chair forms is isodynamic because of the symmetry of the substituents with respect to the dioxan ring.

The symmetrical disposition of the cyclopentane ring is indicated by the n.m.r. spectrum of 5,5-dimethyl-1,3-dioxan-2-spiro-cyclopentane which shows a singlet methyl peak at room temperature and two identical methyl peaks below the coalescence temperature which are indicative of equal populations of the two chair forms. The observed relaxation is due to an intramolecular process and in the present molecules it must arise from the perturbation of a conformational equilibrium in which there is an enthalpy difference between the two forms.[2,3]



(II) (III) (IV) (V)

According to current theories of ring inversion,[4] the chair-to-chair inversion proceeds *via* a half-chair transition state, through a number of flexible forms of which the twist–boat conformers correspond to troughs in the potential energy diagram.

On the basis of the symmetry of (IV) and (V) and the similar relaxation frequencies of (II), (III), and (IV) we therefore attribute the relaxations observed in these molecules to a perturbation of the equilibrium between the chair and boat forms.

The relaxation frequencies of (II), (III), and (IV) are *ca.* 10—20 MHz at −15° which indicate a much faster process than the ring inversions in (I). These frequencies correspond to an activation energy† between the less stable and more stable forms of *ca.* 21 kJ mole^{-1} which is the expected order of energy difference between the half-chair and the boat forms.[4,5] For these molecules the maximum absorption per wavelength is $3{\cdot}5 \times 10^{-6}$. The barriers for the chair-to-chair ring-inversion in spirodioxans are *ca.* 35 kJ/mole.[6]

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† The barriers were estimated from the Arrhenius equation using a pre-exponential factor of 10^{12}.

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