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# CONFORMATIONAL DYNAMICS : ASSOCIATION OF CORRELATED AND NON-CORRELATED ROTATIONS OF METHOXY GROUPS IN ANOMERIC STRUCTURES. CONVERGENCE OF A THEORETICAL STUDY OF 2,2-DIMETHOXYPROPANE AND OF SOME CRYSTALLOGRAPHIC DATA OF ACYCLIC ANALOGUES OF PYRANOSES.

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ABSTRACT. *For anomeric acyclic structures, a peripheral interconversion pathway in several steps with correlated and non correlated relative rotations of the two alkoxy groups of the 2,2-dimethoxy propane-like fragments is favoured. One cannot oversimplify the evaluation of interconversion energy of such complex processes. The final geometry and the dynamics of the system depend on competition or cooperative contributions due to non bonded steric terms and the usual stereodependent anomeric effect.*

The transmission of conformational effects triggered by two interacting chemical rotors (1-4) arouses great interest. Correlated disrotation and conrotation or stepwise non correlated rotations has proven most useful for interpreting experimental effects in which the size of two interacting alkyl groups appears smaller than the expected values for such highly strained systems. Moreover, bending relaxation (5) can act in parallel either as a dominant element or simply accompany rotational relaxation. Thus, the balance between relaxation mechanisms is complex.

In this paper, we report on the conformational dynamics of anomeric systems (6), which are considered to be controlled principally by electronic effects. The quantitative results were carried out by analyzing 85 X-ray structures from the Cambridge data base (7) which have a common C-O-C-O-C fragment. Using these data we have been able to propose a new stepwise interconversion mechanism involving correlated and non correlated rotation of the alkoxy groups.

## MECHANISM OF INTERCONVERSION OF CONFORMERS OF $C_2$ SYMMETRY.

As previously reported by Dunitz and Bürgi (8) a set of X-ray crystallographic structures tend to concentrate at minima on the energy surface. Thus 52% of the acyclic structural fragments $C_1O_2C_3O_4C_5$ adopt a structure which is doubly anomeric and thus has the $C_2$ symmetry in the crystalline state. Both torsional angles $\Phi_1$ ($C_1O_2C_3O_4$) and $\Phi_2$ ($O_2C_3O_4C_5$) are close to 60°. The other fragments have different symmetry ($C_{2v}$,$C_s$,C).

There are no structural fragments corresponding to the central part of the conformational space where $\Phi_1$ and $\Phi_2$ are close to zero (Figure 1); this space is therefore an energy maximum.

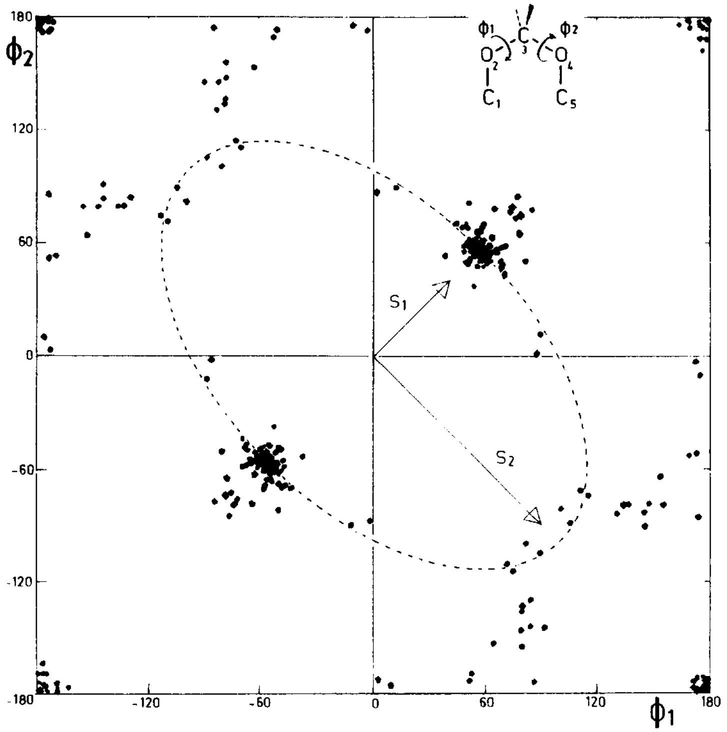

Fig.1 - Conformational crystallographic data of acyclic C-O-C-O-C fragments.

The ellipsoidal curve in Figure 1 indicates correlated movement between conformations. Although we cannot as yet indicate a sequence ordering reflecting a gradual distortion of the fragments, this may be possible when even larger numbers of structures become available. Nevertheless we feel that it is possible at this stage to propose the existence of a pathway involving peripheral interconversion between conformers of $C_2$ symmetry (broken line, Figure 1). This pathway avoids the constrained structure ($\Phi_1 = \Phi_2 = 0$).

The theoretical potential energy surface was also calculated for 2,2-dimethoxypropane as a model system using the INDO method, which compares well with previous work (9).

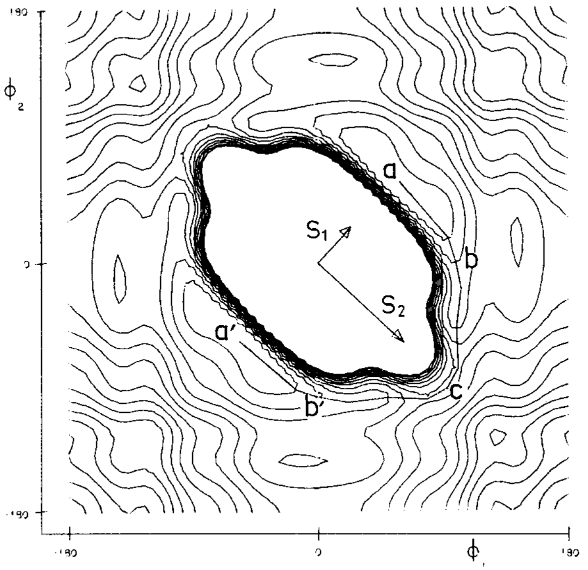

Fig.2 - 2,2-Dimethoxypropane. Theoretical Conformational map. Separation of lines 0.627 kcal $mol^{-1}$. Central part omitted.

The conformational map (Figure 2) shows :

(i) an impossible conversion of the two $C_2$ conformers by a correlated conrotation (component $S_1 = (\Phi_1 + \Phi_2)/\sqrt{2}$).

(ii) a preferred pathway operating by the following multistep interconversion (a → b → c → b' → a').

This overall mechanism (Figure 3) is a conrotation which results from several steps,

- a correlated disrotation (a → b) brings one of the Me groups into a position ($\Phi_1$ = 100°) where there is a weak interaction with the other Me group.
- a stepwise non correlated rotation (b → b') where the second Me group is initially (b → c) blocked in a position mimimizing interaction ($\Phi_2$ = 100°) and then the first Me group moves alone (c → b') in the opposite direction.
- a final correlated disrotation (b' → a') ends the interconversion.

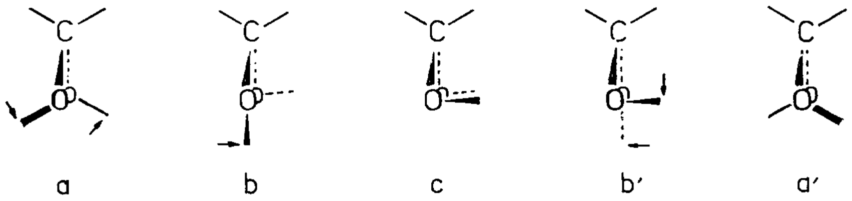

Fig.3 - Interconversion pathway involving several steps : correlated disrotations (a → b and b' → a'), non correlated (b → c and c → b').

## ELECTRONIC AND STERIC FACTORS

The existence of a "through space directing effect" could explain the high energy areas around conformations $\Phi_1 = \Phi_2 = 0°$ (9 $kcal.mol^{-1}$) and $\Phi_1 = \Phi_2 = 120°$ (4.8 $kcal.mol^{-1}$). These "forbidden" areas also correspond to maxima in the internal rotational barrier while the most stable conformers of $C_2$ symmetry also correspond to minima. The small interconversion energy (1.58 $kcal.mol^{-1}$) compares well with the torsional energy around a single C-O bond (1.072 and 3.100 $kcal.mol^{-1}$ for $CH_3OH$ and $CH_3OCH_3$ (10)). The rotational effect alone is insufficient to justify this small interconversion energy;there is also a contribution from the change in bond angles which diminishes the barrier by a factor of two (3 to 1.58 $kcal.mol^{-1}$).

We thus suggest that one of the -OMe groups by rotating induces a similar rotation of the other distant rotor. The transmission of the effect from one group to the other could take place through the minimization of both non-bonded steric interactions and of anomeric torsional energies.

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