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CONFORMATIONAL DISTORTIONS FROM LOCAL SYMMETRY IN CYCLIC AND ACYCLIC COMPOUNDS : CRYSTALLOGRAPHIC DATA ANALYSIS OF C_3CZCC_3 FRAGMENTS (Z = C, P, Si, N, S, O).

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ABSTRACT.- *The local conformational symmetry distortions of* C_3CZCC_3 *fragments versus standard reference are analyzed in a conformational* ϕ_1, ϕ_2 *mean torsion angle space. Local distortions induced by strain are interpreted as resulting from a conrotatory* ($\phi_1 \times \phi_2 > 0$ *quadrants 1 and 3) or a disrotatory relaxation process* ($\phi_1 \times \phi_2 < 0$ *quadrants 2 and 4). Impressive sectorization of acyclic fragments in quadrants 1 and 3 and cyclic ones (6 atom cycles) in quadrants 2 and 4 is reported.*

Symmetry distortion coordinates (1) are useful for describing a nuclear arrangement, thus regarded as a distorted version of a more symmetrical reference structure. Applied to various acyclic structural fragments (2), we shall point out, in this paper, their advantages both in cyclic and acyclic series.

This work deals with encumbered structures with a common C_3CZCC_3 fragment for which we,(3-4) with other contributors to the field, had determined various spectroscopic anomalies in IR, NMR (^{13}C, ^{17}O, ^{15}N) and UV. It was our objective to trace back these anomalies to the local geometries of the fragments.

The quantitative results were carried out by analyzing X Ray structures from the Cambridge Crystallographic Data Base (5) - 239 fragments ; Z = C, P, Si, N, S, O -. Only conformational aspects are considered in this paper.

I - CONFORMATIONAL SPACE AND LOCAL DISSYMETRY

In C_3CZCC_3 fragments, the six torsion angles ω_i (CCZC) generate six independent symmetry distortion coordinates.

The total conformational distortion is thus broken into these six S_i components, each preserving some of the symmetry elements of a reference structure considered free of any distortion. S_1 and S_2 describe distortion from C_{2v} local symmetry of the Z atom. The two dimensional conformational space built on these S_1 and S_2 symmetry coordinates, or by similarity, on the average Φ_1 and Φ_2 torsion angles, visualize discrepancies from the C_{2v} local symmetry. The remaining four coordinates S_i describe distortions of one rotor C_3C- from local C_{3v} symmetry.

$$\begin{array}{lcl} S_1 = (\Phi_1 + \Phi_2)/\sqrt{2} & & \Phi_1 = (\omega_1 + \omega_2 + \omega_3 - \Pi)/3 \\ & \text{with} & \\ S_2 = (\Phi_1 - \Phi_2)/\sqrt{2} & & \Phi_2 = (\omega_4 + \omega_5 + \omega_6 - \Pi)/3 \end{array}$$

The usual reference system chosen is the bistaggered form (two ω_i = 180°, the others = ± 60°) for which all the S_i and Φ_i coordinates are zero. This reference corresponds to the privileged form of little substituted acyclic CH_3ZCH_3 compounds as well as the classic chair of cyclohexanic compounds - intracyclic angles equal to 109°28'.

In highly substituted structures, constraints induce local dissymetries. These distortions with regard to the bistaggered symmetrical reference structure are used here to evaluate constraint effects. This method's promise is indicated by the drastic sectorization of the working space.

II - CONSTRAINED FRAGMENTS C_3CZCC_3 : QUADRANT SECTORIZATION

The most striking of our observations over a large population concern the way in which the points group themselves in the four quadrants of the Φ_1, Φ_2 conformational space (6). The fragment localization relation in (q_1, q_3) or in (q_2, q_4) induces a quadrant sectorization.

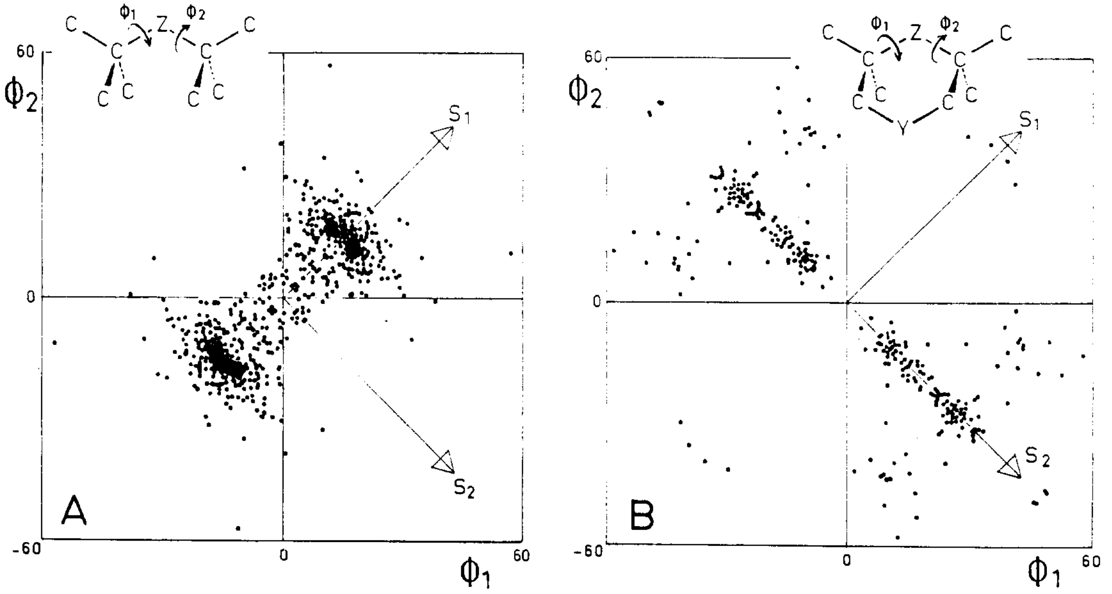

Fig. 1 - Quadrant sectorization A) acyclic fragments : sectorization in quadrants 1 and 3 (Φ_1 and Φ_2 of the same signs). B) cyclic fragments : sectorization in quadrants 2 and 4 (Φ_1 and Φ_2 of opposite signs).

When the fragment is acyclic (Fig. 1A), the representative points are inscribed in quadrants 1 and 3, corresponding to mean torsion angles Φ_1 and Φ_2 of the same sign. The corresponding structures are thus generated by conrotation (Fig. 2) from gear-clashed structures of local symmetry C_{2V} ($\Phi_1 = \Phi_2 = 0$). This observation was made by Nachbar, Johnson and Mislow (7) in a study of 23 CC_3CCC_3acyclic fragments. We generalize it here with a study of 148 C_3CZCC_3 acyclic fragments (Z = C,P,S). However, conrotation is rarely symmetrical (S_1) and includes a part - non dominant, of course - of component S_2. The resulting gear-meshed structures thus separate themselves from C_2 local symmetry.

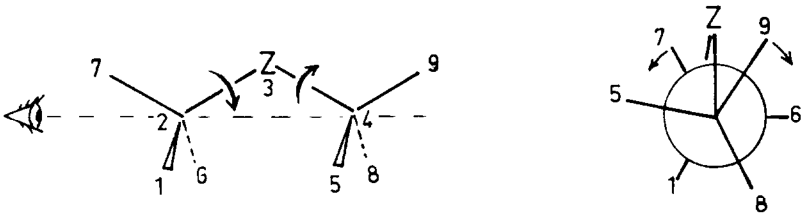

Fig. 2 - Limitation of strong interactions between synaxial alcoyl groups in standard gear-clashed geometry (C_{2v}) by symmetric conrotation leading to an intermeshed gear structure (C_2).

When the fragment is part of a six atom cycle (Fig. 1B), nearly all the representative Φ_1, Φ_2 points are inscribed in quadrants 2 and 4, corresponding to mean torsion angles of opposite signs. The corresponding structures are thus generated by disrotation from their chair structures. In these encumbered structures very flattened chair and boat forms are observed : the closing of the cycle introduces a specific element forbidding the process of conrotatory relaxation and consequently the twist forms (8). This radicalizes the location of cycles in q_2 q_4. Disrotation, often symmetrical (S_2), leads to local symmetry C_s structures, some of which have five atoms (12345) of the cycle in a planar location ($\Phi_i = 60°$).

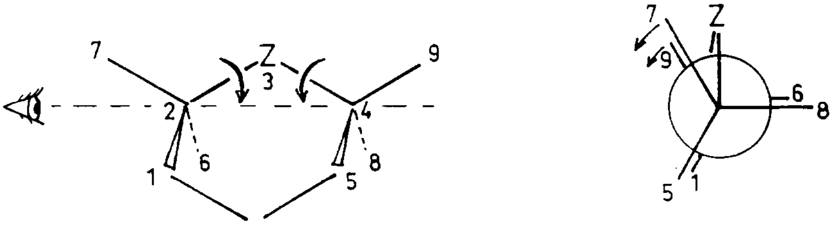

Fig. 3 - Limitation of strong interactions between synaxial alcoyl groups by symmetric disrotation leading to a less constrained gear-clashed structure (C_s).

Thus, disrotation transforms the standard constrained gear-clashed structure into another structure of the same type but less constrained (Fig. 3).

The mechanisms amplitude, estimated by the distance $d = \sqrt{\Phi_1^2 + \Phi_2^2}$, is very variable. Relaxations can be broader in cyclic series (8° to 58° for Z = C, 12° to 67° for Z = N) than in acyclic ones (4 to 30° for Z = P and 4 to 38° for Z = C). In both series, they are greater for $Z = Csp^2$ than for $Z = Csp^3$.

The interpretation of these broad rotational relaxation mechanisms brought out in this paper, for cyclic and acyclic series, supports some current views of the gear effect (9) used for interpreting the apparent diminishing size of the two C_3C- groups mutually drawn apart. Nonetheless, rotational relaxation is not the only mechanism affecting the geometry of these constrained structures.

The global dynamics and constraint aspects are, in fact, more complex. For instance, a valency relaxation greatly affects the size of C_3C groups also. The advantage of studying such a large data population is the ability to thereby distinguish broad tendencies concerning the relative roles of the various structural effects. To identify the relative roles of some other cooperative mechanisms, we are currently scrutinizing other parameters (valency angles and interatomic distances) of C_3CZCC_3 fragments.

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