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BOND ANGLE DISTORTION OF C_3CZCC_3 FRAGMENTS (Z = C, N, P, S, O, Si) BY CZC OPENING AND SYMMETRICAL C_3C- DISTORTION. ANALYSIS OF CRYSTALLOGRAPHIC DATA BY PERTURBATION OF SYMMETRY DISTORTION COORDINATES.

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ABSTRACT.- The framework distortion of C_3CZCC_3 fragments is largely controlled by local strain release. It is not limited to the C_3C- tilt previously mentioned in other compounds. We show a very significant opening of angle CZC and an important symmetrical distortion of C_3C- groups by expansion (Z = NO, S, O) or compression (Z = C, NH, NMe, NS, P, Si). We discuss the effect upon the apparent size of tertiary groups.

In congested systems, interactions between substituent groups lead a molecule to search for stable shapes by specific mechanisms of *rotation* and of *framework distortion.* These mechanisms are the foundation stone for the idea of "apparent" or "relative" size of groups described according to their volume, shape and positioning.

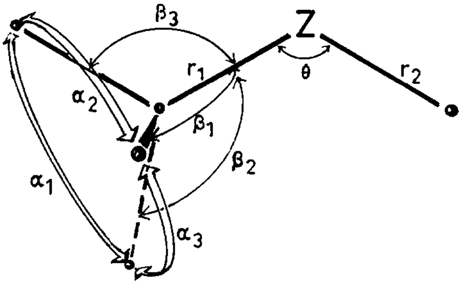
When neighboring interactions dominate, the resulting geometry seems difficult to predict and requires a case by case analysis (1).

For some congested systems, the situation may be different. The energies linked to the different constraints could be distributed in a fragment in a precise and transferable manner, particularly affecting certain structural elements. It is not enough to analyze the geometry in terms of internal coordinates in order to test this hypothesis. *We have studied the shape of fragments with the aid of local symmetry functions and with reference to little substituted compounds.*

The quantitative results were carried out by analyzing 239 -C_3CZCC_3- fragments from the Cambridge Crystallographic Data Base (2). The fragments are either acyclic or part of a 6 atom cycle. Indeed, we observed spectroscopic, UV, IR, NMR anomalies in both cyclic and acyclic series for various compounds with this type of fragment. These seem to indicate the existence of specific distortions despite the diversity of the Z atoms.

METHODS : Local symmetry functions and LOSIR concept

The shape is analyzed by reference to more symmetric ideal structures (C_{3v} symmetry of C_3C- groups, C_{2v} symmetry of the CZC unit) and with the help of local symmetry distortion coordinates (3). Some reveal the discrepancy from C_{3v} and C_{2v} symmetries of C_3C- and CZC units (coordinates S_2 and S_5, fig.1, for example). Others correspond to symmetry maintenance (S_1, S_3, S_4, fig.1). These latter may also reveal the system's response to certain structural strains if we compare their values with those of little substituted compounds $CH_3Z\ CH_3$ (S_1,S_3), CH_4 (S_4), $CH_3\ CH_2\ Z$ (CC)...



$S_1 = r_1+r_2$

$S_2 = r_1-r_2$

$S_3 = \Theta$

$S_4 = \alpha_1+\alpha_2+\alpha_3-\beta_1-\beta_2-\beta_3$

$S_5 = 2\beta_1-\beta_2-\beta_3$

Fig.1 5 of the 19 symmetry distortion coordinates of $-C_3CZCC_3-$ fragment.

With our method we measure the distortions of real shapes as compared to Low Strain Ideal References (LOSIR). These idealized structures have ideal symmetries (3) and standard parameters, i.e. distances and angles of little substituted compounds.

CRYSTALLOGRAPHIC DATA ANALYSIS

Despite the enormous heterogeneity in the nature of the Z substructure, *certain fairly pronounced regularities are discernable.* The relative perturbation of the bond angles with regard to the LOSIRs is far greater than that of the bond lengths.

Bond lengths

Mean bond lengths CZ (S_1) and CC are approximately the same in LOSIRs and in corresponding C_3CZCC_3 fragments. The difference between the two CZ distances can be large, affecting the C_{2v} symmetry of the unit CZC (S_2 coordinate), but it is not on an average more than 2% of the CZ distance.

Bond angles

When compared with the LOSIRs, angle perturbation is both systematic and large. *It is not confined to the tilt of the tBu mentioned previously in other series of compounds (4).* It includes three basic elements.

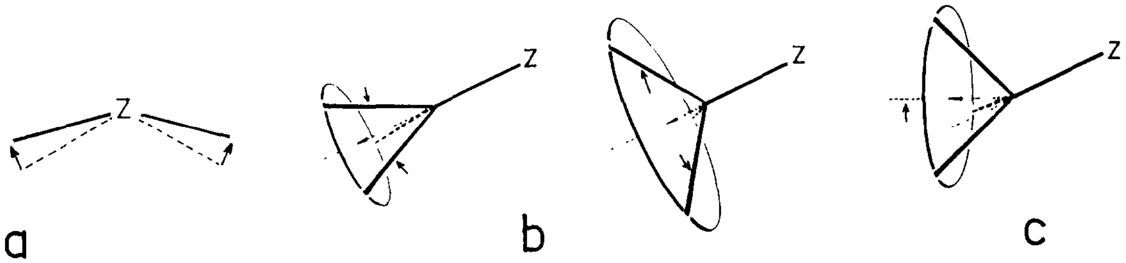


Fig.2 Bond angle distortion by CZC opening (a), compression or dilatation (b), rocking (c).

a) The mean bond angle CZC is consistently about 4° ($Z = C_{sp}2$, cyclic fragment) to 12° (Z = Si, acyclic fragment) greater than its value in little substituted compounds.

b) The CC_3 group is distorted by a symmetrical compression or dilatation. In the acyclic series, tertiary groups are compressed. This is shown by a negative S_4 coordinate. In the cyclic series, there is compression for Z = C, NH, NMe and NS but dilatation for Z = NO, O and S. This latter is shown by a positive S_4 coordinate (Table I).

c) The approximate threefold axis of the tertiary CC_3 group does not point in the direction of the CZ bond but systematically deviates from it (S_5 rocking coordinate). There is an obvious similarity to the Methyl tilt in MeOH, $MeNH_2$, MeNO (5).

	Acyclic fragment		Cyclic fragment	
Z	Csp^2	P	Csp^3	NO
S_2 (Å)	0.022	0.019	0.025	0.001
S_3 (degrees)	5.2	9.0	7.5	11.0
S_4 (degrees)	-10.5	-8.8	-5.1	+ 5.1
S_5 (degrees)	6.9	11.0	11.7	5.9

Table I : Selected average values of the perturbation from LOSIRs of some S_i coordinates.

APPARENT SIZE OF TERTIARY GROUPS - CROWDING AND STRAIN RELEASE

The real size of simple molecules is predictable. The real size of highly substituted molecules can be calculated and predicted by means of the study presented here. Indeed *the distortion of fragments* C_3CZCC_3 *is large, multiform and well defined.*

Knowledge of these distortions makes it possible to tackle, with greater success than formerly, the apparent sizes of tertiary groups. This can bring about a better understanding of the variations of reactivity and of rotation barriers in series of increasingly crowded compounds.

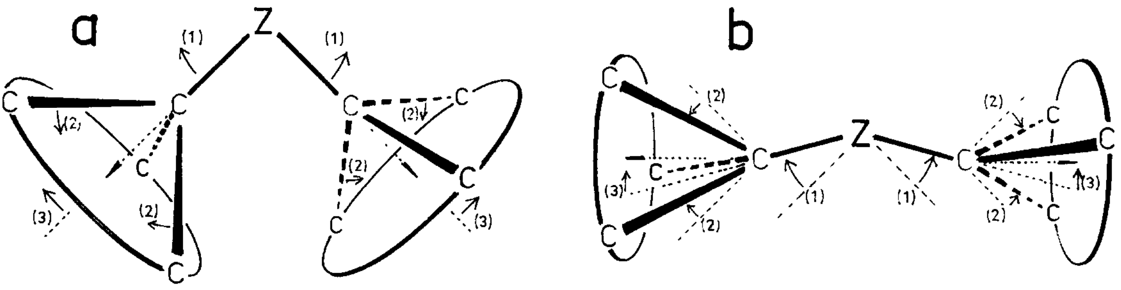


Fig.3 The interaction between geminal tertiary groups is modified (b compared to LOSIR a) by opening the central angle (1) symmetrical distortion (2) and the rocking of CC_3 groups (3).

This study shows, in particular, that *the mechanism of correlated rotation of groups* C_3C in C_3CZCC_3 (6) *is not the only one to minimize* the interactions of tertiary groups both between themselves and with their neighbors and, thus, the *apparent size* of these groups. The overall strain release implies this rotation as well as the framework distortion.

Among framework distortions, correlated rotation and angle opening are particularly significant. They are not observed in little substituted compounds. They can be linked to the *crowding effect* in the series studied, and we can conclude that these two distortion elements are the main factors for change in apparent size.

Tilt and symmetrical compression exist in little substituted compounds. The Methyl group tilt (Me OH ... (5)) has been attributed to bond-bond repulsion interactions. In crowded compounds, the atom-atom repulsion interactions 1-4 and 1-5 are larger than the bond-bond repulsion interactions and act in the same direction. Although we learn a good deal from the regularity trends of the various structural distortions, it is premature to assess the electronic and steric contributions to the adaptative shaping processes.

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