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SOME NEW ASPECTS IN THE CONFORMATIONAL ANALYSIS OF RIGID SYSTEMS

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In recent years many data have been accumulated demonstrating that the strain in polycyclic ring systems (originating either from non bonded interactions of substituents or from a change in hybridisation at one site of the molecule) may be relieved by alteration of bond angles[1]. In turn this leads to conformational changes which - in special cases - can be detected by physical and/or chemical properties. For a description of this phenomenon[2,3] the term "conformational transmission" has been coined: It means propagation of bond angle distortion within the molecular frame, i.e. angle deformation induced at one site of the molecule causes a corresponding angle deformation at another more or less remote site.

Our studies are concerned with systems where a partial compensation of a bond angle distortion is caused by an alteration of a torsional angle (at the same site) leaving all other bond and torsional angles (and of course bond lengths) unchanged. This can only be the case if the system is rigid and contains at least one single bond about which torsion occurs. [2.2] metacyclophane ($\underline{1}$) seems to fulfill these requirements: it consists of a rigid tenmembered-ring-system connecting two benzene rings which in addition furnish a powerful tool for detecting changes in molecular geometry via the ^{1}H-NMR chemical shifts of the intraanular aryl protons. Recently[4] it has been demonstrated that the rather unusual location of their resonance absorption can be satisfactorily explained in terms of ring current theory: taking into account the puckered topology of the aromatic rings, no further assumptions are necessary for a quantitative interpretation. Therefore even subtle conformational changes should be reflected by the shift of these protons.

Introduction of substituents in positions 1 and 10 of 1 may give rise to a variation of the bond angle α (cf. fig. 1). In order to maintain the integrity of all other bond angles and of the bond lengths, the torsional angle has to change for geometrical reasons only. This corresponds to a rotation of the bonds C-1 — C-15 (C-10 — C-11) around an axis passing through C-1 and C-10. Simultaneously an inward or outward rotation of the aromatic ring concerned is caused by this operation^5 - depending on whether the value of α is increased or decreased.

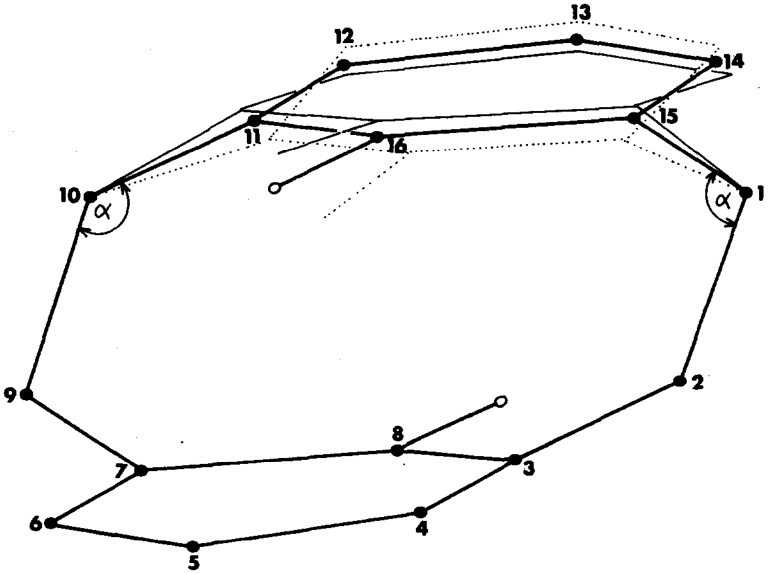
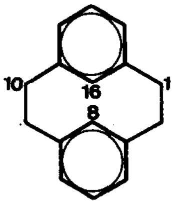
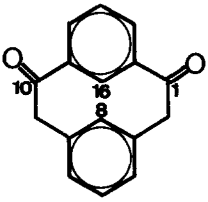


Fig.1

The torsion of one aromatic ring relative to the other should be reflected in the ^1H-NMR-spectrum. If one of the benzene rings is turned inwards, its intraanular proton should undergo an upfield shift. The opposite, namely an outward turn, results in a downfield shift. Thus, according to these assumptions we postulate the conformations as indicated by fig. 2 for 1,10-dioxo [2.2] metacyclophane (2) ($\alpha > 110^\circ$, $\delta_{H-8} = 5.8$ ppm, $\delta_{H-16} = 4.3$ ppm) and its bis-propylenthioketal (3) ($\alpha < 110^\circ$, $\delta_{H-8} = 3.8$ ppm, $\delta_{H-16} = 6.5$ ppm)[6].



1



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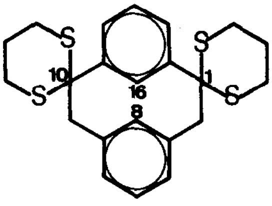

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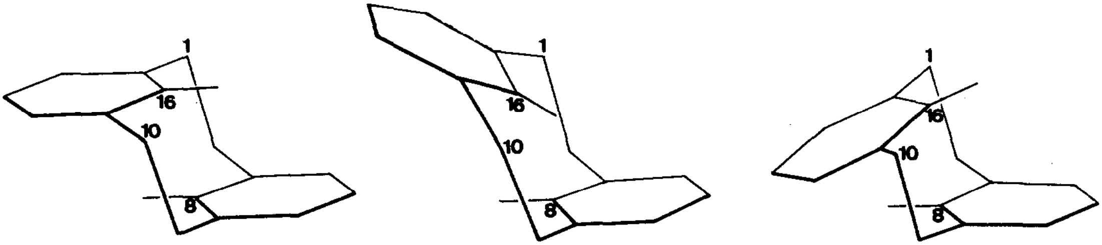

Fig.2

As the proximity of the intraanular protons may not exceed a critical value, secondary effects lead to the expected discrepancy between the calculated and observed shift of the proton being turned inwards.

By means of this concept many observations that have not been well understood now can be explained; e.g. the extraordinary chemical shift of the proton on C-8 in 1,10-dithia [2.2] metacyclophane[7]. Notwithstanding the fact that the length of the C-S bond exceeds that of the C-C bond and that the sulfur atoms may exercise some influence on the NMR-spectrum, a satisfactory interpretation of the chemical shift of the intraanular arylprotons can only be given by taking into account that the angle α (C-S-C) differs from 110°. In analogy to 2 this implies a rotation of one benzene ring towards the center of the system, which is reflected in the downfield shift of the C-8 proton.

If there are different substituents in positions 1 and 10 (e.g. 1-oxo [2.2] metacyclophane)[8] a displacement of the intraanular aryl proton takes place not only along the y- and z-axis, but also in the x-direction. Consequently, the σ-bond frame of this kind of [2.2] metacyclophane lacks any symmetry element.

Detailed aspects of these phenomena in this and other suitable molecular systems will be published elsewhere.

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