Tetrahedron Letters No.15, pp. 1383-1386, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE RELATIONS BETWEEN TORSIONAL AND VALENCY ANGLES OF CYCLOPENTANE

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(Received 1 February 1967)

In 1960 Hendrickson (1) computed the energies of various cyclopentane conformers as a function of geometric parameters, i.a. torsional and valency angles. The aim of the present note is to correlate the results of his calculations with the conclusions of Pitzer et al. (2,3) concerning the pseudo-rotation of cyclopentane. Pitzer et al. described the cyclopentane ring as having a certain degree of puckering which rotates around the ring and which is associated with a phase angle P. Their calculations are based upon the assumption that the displacement z_j of the j th atom from the plane of the unpuckered ring can be written as

$$z_j = \sqrt{\frac{2}{5}}\, q \cos\left\{2\left(P + \frac{2\pi j}{5}\right)\right\} \quad (1)$$

where q is the amplitude of the puckering. Their calculations are restricted to such values of P for which the molecule has C_s or C_2 symmetry and the authors argued that the energy depends largely on the value of q (the degree of puckering) and only slightly on P; i.e. the potential barrier in the pseudo-rotation circuit is very small.

It was thought worthwhile to have at our disposal relations which afford all torsional angles φ_j and valency angles ϑ_j as a function of P given a certain degree of puckering (consult Fig. 1a for the numbering of the various angles). We plotted Hendrickson's corrected values (4) for φ_j against those for ϑ_{j+i} ($i = 1,2,3,4$).(Fig. 1b) and found that in the region where the total energy is constant, the torsional angles are related by

$$\varphi_j = \underline{a} \sin\left(P + \frac{4\pi j}{5}\right) ; \quad j = 1,2....5 \quad (2)$$

The constant $\underline{a}$ is the amplitude of the vibrational angular motion depicted in Fig. 1b. A similar plot of ϑ_j versus ϑ_{j+i} reveals that ϑ_j can be expressed as

$$\vartheta_j = \tau + b \sin\left\{2\left(P + \frac{4\pi j}{5}\right) + \delta\right\}; \quad j = 1,2...5 \quad (3)$$

in the same region, indicating that the valency angles ''vibrate'' between the values $\tau - b$ and $\tau + b$. The phase lag can be evaluated from a plot of ϑ_j versus φ_j (Fig. 1c). Noting that the cyclopentane ring has C_s symmetry for P = 0 when $\varphi_5 = 0$ and $\vartheta_1 = \vartheta_5$, it follows that $\delta = 7/10\pi$ or $-3/10\pi$. The plots depicted in Fig. 1 are Lissajous curves and clearly demonstrate that the angular motions have a vibrational character in the region of minimum energy. The parameters a, τ and b (based upon Hendrickson's calculations) have respective values of 44°, 104° and 2.5°.

The following conclusions can be drawn:

1°. Up to $\varphi_1 = 40.0°$ the table published by Hendrickson (4) represents a large part of the pseudo-rotation itinerary of one cyclopentane model, whereas the other entries correspond to a number of cyclopentane models differing in degree of puckering at a certain point of the rotational pathway.

2°. Throughout the pseudo-rotation circuit (by varying P between 0 and 2π) $10C_s$ or envelope forms and 10 C_2 or half-chair forms are met. Torsional angle φ_j about bond $C_j - C_{j+1}$ as well as valency angle ϑ_{j+3} attain their maximum values when a two-fold rotation axis passes through C_{j+3} and the midpoint of $C_j - C_{j+1}$. Torsional angle φ_j is zero and valency angle ϑ_{j+3} attains its minimum value when a mirror-plane goes through C_{j+3} and is perpendicular to the line $C_j - C_{j+1}$ in its midpoint.

3°. Experimental knowledge of two torsional angles is sufficient for calculation of all other angular magnitudes.

4°. It is not possible to choose , τ and b independently. A certain degree of puckering i.e. a given value of a implies a corresponding pair τ, b. Substituting eqs. (2) and (3) in Pitzer and Donath's (3) geometrical relations:

$$\cos\varphi_2 = \left[\cos\vartheta_2\,(\cos\vartheta_3 - 1) - \sin 1/2\,\vartheta_3\,(1 - 2\sin 1/2\,\vartheta_3)\right] \Big/ \sin\vartheta_2\,\sin\vartheta_3,$$

$$\cos\varphi_1 = \left[\cos\vartheta_2\,\cos\vartheta_1 + \sin 1/2\,\vartheta_3\right] \Big/ \sin\vartheta_2 .\,\sin\vartheta_1,$$

a set of equations is obtained from which τ and b can be solved (Fig. 2).

In following papers of this series (5,6) we will show that the spread in a, τ and b, even for substituted cyclopentane rings occurring in steroids, is small. In steroids we can make use of a ''standard'' ring D with a precision of about 1°. For the weighted average of the calculated <u>a</u> value of the five membered ring in 11 steroids (6) or steroid-like compounds we find 46.7° ± 0.7°. The standard torsional angles of ring in the two symmetrical forms are compared below with theoretical values for a free cyclopentane ring:

	C_2 - form			C_s - form		
	exp[6]	theor[1,4]	theor[3]	exp[6]	theor[1,4]	theor[3]
φ_1	+ 46.7	+ 44.0	+ 48.2	+ 44.4	+ 41.8	+ 45.8
φ_2	- 37.8	- 35.5	- 38.8	- 44.4	- 41.8	- 45.8
φ_3	+ 14.4	+ 13.7	+ 15.1	+ 27.4	+ 26.0	+ 28.7
φ_4	+ 14.4	+ 13.7	+ 15.1	0	0	0
φ_5	- 37.8	- 35.5	- 38.8	- 27.4	- 26.0	- 28.7

The authors thank Prof. Havinga for his interest during this investigation.

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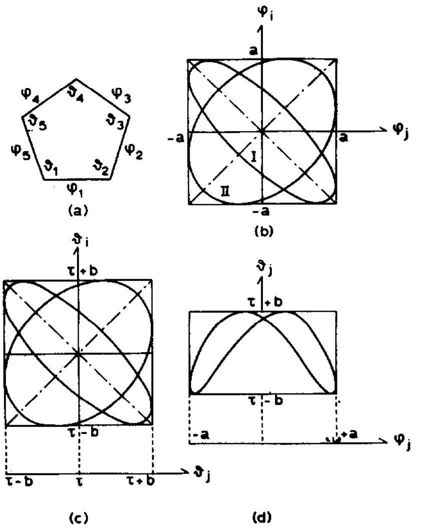

Fig. 1. a) Numbering of torsional and valency angles in cyclopentane; b) Plots of φ_j vs φ_i; c) Plots of ϑ_j vs ϑ_i; d) Plot of φ_j vs ϑ_j.

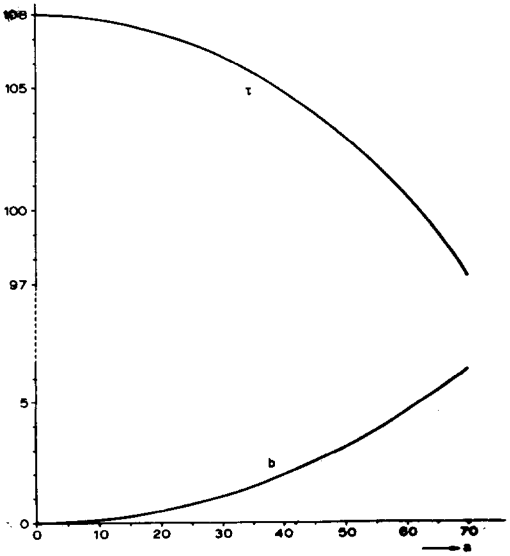

Fig. 2. Plot of τ and b vs. a.