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Crystal and Molecular Structure of 3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)- α -D-glucopyranose (TACEG)

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Crystals of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)- α -D-glucopyranose have hexagonal symmetry with cell dimensions $a = b = 8.524$ (1) and $c = 41.700$ (5) Å. Direct methods were used to solve the structure which was later refined by least-squares calculations to an R of 0.068. The cyano group was found to be *trans* or *exo* to the pyranose ring. The dioxolane ring is not planar and the pyranose ring has a skew conformation. Several criteria are presented for distinguishing between the four main conformations in six-membered rings.

Introduction

3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)- α -D-glucopyranose (TACEG) was one of the two principal compounds obtained by reactions of *cis*- α -acetoxyglycopyranosyl halides with metallic cyanides (Chacon-Fuertes, 1975). The crystal structure determination was carried out in order to establish the configuration at the dioxolane-2C atom and the conformation of the pyranose ring.

Coxon & Hall (1964) have studied this compound and other 1,2-*O*-alkylidene- α -D-glucopyranoses by PMR. They said that the *cis* fusion of a 1,2-cyclic acetal ring forces the D-glucopyranose ring to depart from the expected chair conformation; this is surprising since the bulky substituents are not in predominantly equatorial orientations. From the experimental and theoretical dihedral angles they proposed a skew boat conformation for the pyranose ring which has been

confirmed by the crystal structure determination of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]- α -D-glucopyranose (Heitmann, Richards & Schroeder, 1974). On the other hand, in a similar compound Trotter & Fawcett (1966) found a flattened chair conformation for this ring. In view of this controversy we have undertaken the present study. Moreover we have attempted to describe this kind of conformation quantitatively.

Experimental

Transparent crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanolic solution. The unit-cell parameters were obtained from the θ measurements of 32 reflexions.

Crystal data

$C_{15}H_{19}O_9N$, F.W. 357.3. Hexagonal; $a = b = 8.524$ (1), $c = 41.700$ (5) Å, $V = 2623.9$ Å³; $D_m = 1.34$, $D_x = 1.36$

g cm^{-3} , $Z=6$; space group $P6_1$; $\lambda(\text{Mo } K\alpha)=0.7107 \text{ \AA}$.

The density was determined by flotation in aqueous KI. The cell parameters and the intensities were measured on a Philips PW1100 four-circle automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

A triangular prismatic crystal of approximate dimensions $0.20 \times 0.20 \times 0.56 \text{ mm}$ was used to collect 1567 independent reflexions (ω scan mode) up to $\theta=25^\circ$. 304 reflexions had intensities less than the standard deviations and were considered unobserved. The data were corrected for Lorentz and polarization effects, put on an approximate absolute scale by means of a Wilson plot and reduced to normalized structure factors. An absorption correction was not applied.

Solution of the structure

The structure was solved by direct methods using *MULTAN 74* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An E map generated from the phase set (100 reflexions) with the highest combined figure of merit (2.04) located a small fragment of the molecule. Two cycles of tangent refinement showed the positions of 19 atoms. The remaining non-hydrogen atoms were located from a Fourier synthesis. At the beginning of this study space group $P6_1$ was assumed since the systematic absences of $00l$ with l odd suggested that the space group was either $P6_1$ or $P6_5$. From the structure determination we found that the absolute configuration was the expected D configuration of the sugar moiety and so space group $P6_1$ was considered as correct. Isotropic full-matrix least-squares followed by anisotropic block refinement reduced R to

0.084. A difference Fourier map revealed all the H atoms.

The weighting scheme was $\omega = K\omega_1\omega_2$ with $\omega_1 = 1/\sigma_f^2$ and $\omega_2 = 1/\sigma_s^2$ and σ_f , σ_s as follows:

$$\begin{aligned} \sigma_f &= (1.76 - 0.07|F_o|) & \text{if } 0 \leq |F_o| < 15.6 \\ \sigma_f &= (0.56 + 0.01|F_o|) & \text{if } 15.6 \leq |F_o| \\ \sigma_s &= (1.92 - 3.12s)^{1/2} & \text{if } 0.0 \leq s < 0.40 \\ \sigma_s &= (0.24 + 1.46s)^{1/2} & \text{if } 0.40 \leq s < 0.54 \\ \sigma_s &= (-3.68 + 8.50s)^{1/2} & \text{if } 0.54 \leq s, \end{aligned}$$

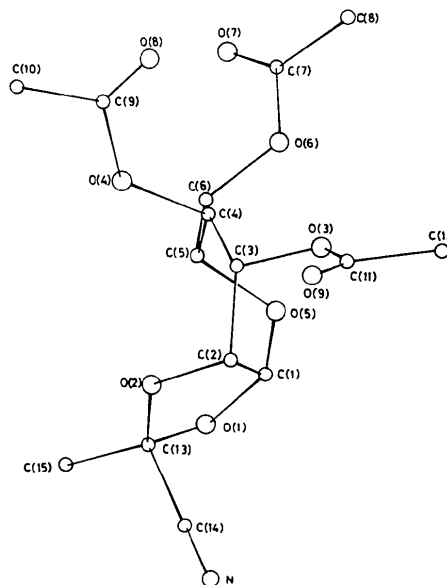


Fig. 1. A perspective view of the molecule showing the conformation and the numbering system.

Table 1. *Final positional* ($\times 10^4$) *and thermal parameters and their standard deviations for the heavy atoms*

Anisotropic temperature factors are expressed as $-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j$ and are multiplied by 10^3 .

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	6845 (6)	6579 (6)	-2306 (1)	74 (3)	67 (3)	45 (2)	50 (2)	-3 (2)	-6 (2)
O(2)	5570 (5)	8323 (5)	-2265 (1)	58 (2)	58 (2)	41 (2)	37 (2)	-6 (2)	-1 (2)
O(3)	5933 (5)	8384 (5)	-1398 (1)	54 (2)	69 (3)	36 (2)	38 (2)	-3 (2)	-3 (2)
O(4)	8595 (5)	12176 (5)	-1885 (1)	54 (2)	46 (2)	53 (2)	30 (2)	-6 (2)	-4 (2)
O(5)	8486 (5)	7886 (5)	-1842 (1)	47 (2)	42 (2)	48 (2)	25 (2)	-6 (2)	0 (2)
O(6)	11489 (5)	10588 (5)	-1505 (1)	39 (2)	48 (2)	60 (3)	18 (2)	-5 (2)	9 (2)
O(7)	14385 (7)	12760 (8)	-1539 (1)	57 (3)	94 (4)	103 (4)	-3 (3)	-18 (3)	16 (3)
O(8)	11019 (7)	13887 (6)	-1580 (1)	100 (4)	55 (3)	95 (4)	35 (3)	-39 (3)	-13 (3)
O(9)	3255 (6)	8243 (6)	-1372 (1)	53 (3)	86 (3)	98 (3)	44 (3)	19 (2)	13 (3)
N	2467 (9)	4111 (10)	-2515 (2)	84 (4)	102 (5)	104 (6)	22 (4)	-9 (4)	-33 (4)
C(1)	6750 (8)	6833 (7)	-1962 (0)	57 (4)	46 (3)	36 (3)	30 (3)	-3 (3)	-4 (3)
C(2)	5534 (8)	7697 (7)	-1935 (1)	46 (3)	54 (4)	34 (3)	24 (3)	-1 (3)	2 (3)
C(3)	6282 (7)	9265 (8)	-1700 (1)	42 (3)	54 (4)	36 (3)	28 (3)	-1 (2)	1 (3)
C(4)	8325 (7)	10548 (7)	-1721 (1)	46 (3)	43 (3)	33 (3)	27 (3)	-5 (2)	-2 (2)
C(5)	9277 (7)	9745 (8)	-1911 (1)	45 (3)	48 (3)	35 (3)	27 (3)	-7 (3)	-3 (3)
C(6)	11269 (8)	10617 (8)	-1843 (2)	50 (3)	63 (4)	44 (4)	34 (3)	4 (3)	4 (3)
C(7)	13089 (9)	11753 (9)	-1376 (2)	53 (4)	53 (4)	84 (5)	16 (3)	-8 (4)	3 (4)
C(8)	13001 (12)	11661 (12)	-1014 (2)	94 (6)	96 (7)	56 (5)	38 (5)	-37 (4)	-5 (4)
C(9)	9969 (9)	13788 (8)	-1780 (2)	60 (4)	45 (3)	71 (4)	33 (3)	2 (3)	-1 (3)
C(10)	10114 (11)	15306 (9)	-1954 (2)	94 (5)	46 (4)	99 (6)	38 (4)	-13 (5)	1 (4)
C(11)	4311 (8)	7864 (9)	-1257 (1)	38 (3)	57 (4)	56 (4)	25 (3)	4 (3)	-19 (3)
C(12)	4063 (11)	6763 (12)	-962 (2)	90 (5)	101 (6)	37 (4)	45 (5)	17 (3)	11 (4)
C(13)	5702 (8)	7071 (8)	-2458 (1)	62 (4)	62 (4)	41 (3)	40 (3)	-2 (3)	0 (3)
C(14)	3850 (9)	5375 (9)	-2493 (2)	67 (4)	75 (4)	44 (4)	34 (4)	0 (3)	-15 (3)
C(15)	6445 (10)	7876 (10)	-2782 (2)	80 (5)	80 (5)	60 (4)	50 (4)	11 (4)	9 (4)

where s is $\sin \theta/\lambda$ and $K=0.60$.

Further cycles of anisotropic refinement of the heavy atoms with the H atoms treated isotropically (Hamil-

Table 2. Fractional coordinates ($\times 10^3$), thermal parameters ($\times 10^2$) and bond distances (\AA) for the hydrogen atoms

	x	y	z	U	C-H
H(1)	611 (8)	552 (9)	-185 (1)	5 (2)	1.08 (6)
H(2)	425 (8)	668 (9)	-188 (2)	5 (2)	1.03 (5)
H(3)	571 (8)	979 (8)	-171 (1)	3 (2)	0.82 (8)
H(4)	885 (8)	1088 (8)	-154 (2)	8 (2)	0.86 (6)
H(5)	925 (7)	998 (8)	-214 (1)	5 (2)	0.97 (5)
H(6a)	1200 (8)	1202 (9)	-194 (2)	6 (2)	1.11 (7)
H(6b)	1170 (7)	989 (8)	-193 (1)	4 (2)	0.94 (8)
H(8a)	1252 (22)	1239 (20)	-92 (4)	20 (6)	0.98 (21)
H(8b)	1272 (16)	1048 (16)	-94 (3)	10 (4)	0.97 (14)
H(8c)	1412 (15)	1223 (14)	-94 (3)	9 (4)	0.88 (11)
H(10a)	891 (16)	1510 (16)	-198 (3)	14 (4)	0.96 (14)
H(10b)	1066 (13)	1632 (13)	-188 (2)	9 (3)	0.80 (9)
H(10c)	991 (14)	1517 (13)	-219 (2)	14 (3)	0.98 (10)
H(12a)	327 (14)	521 (14)	-100 (2)	18 (3)	1.16 (10)
H(12b)	511 (16)	725 (16)	-82 (3)	10 (4)	0.98 (12)
H(12c)	327 (16)	657 (17)	-88 (3)	13 (4)	0.70 (13)
H(15a)	548 (14)	791 (14)	-287 (2)	7 (3)	0.92 (13)
H(15b)	757 (8)	885 (8)	-275 (2)	7 (2)	0.91 (5)
H(15c)	650 (11)	690 (10)	-289 (2)	10 (3)	0.96 (10)

Table 3. Bond distances (\AA) and angles ($^\circ$) and their standard deviations for the heavy atoms

C(1)-O(1)	1.437 (4)	O(1)-C(1)-C(2)	104.0 (5)	C(7)-C(8)	1.509 (11)	O(6)-C(7)-C(8)	111.1 (6)
C(1)-O(5)	1.384 (6)	O(1)-C(1)-O(5)	109.3 (4)			O(7)-C(7)-C(8)	126.9 (6)
C(1)-C(2)	1.546 (11)	O(5)-C(1)-C(2)	114.8 (5)	C(9)-O(4)	1.357 (6)	C(9)-O(4)-C(4)	117.3 (5)
C(2)-O(2)	1.468 (7)	O(2)-C(2)-C(1)	102.0 (4)	C(9)-O(8)	1.195 (10)	O(4)-C(9)-O(8)	122.2 (6)
C(2)-C(3)	1.517 (8)	O(2)-C(2)-C(3)	111.2 (5)	C(9)-C(10)	1.434 (11)	O(4)-C(9)-C(10)	113.1 (6)
		C(1)-C(2)-C(3)	112.3 (5)			O(8)-C(9)-C(10)	124.5 (5)
C(3)-O(3)	1.422 (7)	O(3)-C(3)-C(2)	102.9 (5)	C(11)-O(3)	1.357 (8)	C(11)-O(3)-C(3)	117.8 (5)
C(3)-C(4)	1.527 (7)	O(3)-C(3)-C(4)	106.9 (5)	C(11)-O(9)	1.198 (10)	O(3)-C(11)-O(9)	121.3 (6)
		C(2)-C(3)-C(4)	114.9 (5)	C(11)-C(12)	1.497 (10)	O(3)-C(11)-C(12)	111.2 (7)
C(4)-O(4)	1.459 (8)	O(4)-C(4)-C(3)	106.8 (5)			O(9)-C(11)-C(12)	127.5 (6)
C(4)-C(5)	1.520 (10)	O(4)-C(4)-C(5)	108.6 (4)	C(13)-O(1)	1.393 (10)	C(13)-O(1)-C(1)	107.8 (5)
		C(3)-C(4)-C(5)	112.4 (5)	C(13)-O(2)	1.387 (9)	C(13)-O(2)-C(2)	105.1 (5)
C(5)-O(5)	1.407 (7)	O(5)-C(5)-C(4)	109.8 (4)	C(13)-C(14)	1.523 (8)	O(1)-C(13)-O(2)	107.6 (5)
C(5)-C(6)	1.500 (8)	O(5)-C(5)-C(6)	107.9 (6)	C(13)-C(15)	1.503 (9)	O(1)-C(13)-C(14)	107.9 (6)
		C(4)-C(5)-C(6)	113.9 (5)			O(1)-C(13)-C(15)	110.5 (5)
		C(5)-O(5)-C(1)	114.3 (5)			O(2)-C(13)-C(14)	110.0 (6)
C(6)-O(6)	1.423 (8)	C(5)-C(6)-O(6)	107.6 (5)			O(2)-C(13)-C(15)	110.5 (6)
C(7)-O(6)	1.335 (7)	C(7)-O(6)-C(6)	118.8 (5)			C(14)-C(13)-C(15)	110.3 (5)
C(7)-O(7)	1.213 (8)	O(6)-C(7)-O(7)	122.0 (7)	C(14)-N	1.135 (8)	C(13)-C(14)-N	179.0 (7)

Table 4. Main torsional angles around the bond defined by the central atoms

The method of calculating the torsional angles and their standard deviations is that given by Shmueli (1974; equation 9).

Pyranose ring		Dioxolane ring	
C(1)-C(2)-C(3)-C(4)	42.4 (6) $^\circ$	C(1)-C(2)-O(2)-C(13)	32.8 (4) $^\circ$
C(2)-C(3)-C(4)-C(5)	-14.9 (6)	C(2)-O(2)-C(13)-O(1)	-37.9 (5)
C(3)-C(4)-C(5)-O(5)	-38.7 (5)	O(2)-C(13)-O(1)-C(1)	26.5 (4)
C(4)-C(5)-O(5)-C(1)	69.7 (4)	C(13)-O(1)-C(1)-C(2)	-4.8 (4)
C(5)-O(5)-C(1)-C(2)	-39.8 (4)	O(1)-C(1)-C(2)-O(2)	-16.8 (4)
O(5)-C(1)-C(2)-C(3)	-16.5 (5)		
		Lateral angles	
O(5)-C(5)-C(6)-O(6)	-69.3 (6) $^\circ$	H(1)-C(1)-C(2)-H(2)	-18 (5) $^\circ$
C(4)-C(5)-C(6)-O(6)	52.8 (6)	H(2)-C(2)-C(3)-H(3)	-67 (6)
C(3)-O(3)-C(11)-O(9)	-5.0 (8)	H(3)-C(3)-C(4)-H(4)	95 (7)
C(4)-O(4)-C(9)-O(8)	6.0 (10)	H(4)-C(4)-C(5)-H(5)	-148 (5)
C(5)-C(6)-O(6)-C(7)	-159.0 (6)	H(5)-C(5)-C(6)-H(6a)	50 (6)
C(6)-O(7)-C(7)-O(7)	-4.3 (12)	H(5)-C(5)-C(6)-H(6b)	-74 (6)

ton, 1959) gave final weighted and unweighted R values of 0.065 and 0.068 respectively [$R_w = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}$, with $\langle w\Delta^2 \rangle$ showing no trends].

A difference Fourier synthesis calculated after refinement showed no residual electron density greater than $\pm 0.28 \text{ e \AA}^{-3}$.

The atomic scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962) and those for the H atoms from Stewart, Davidson & Simpson (1965).*

The positional and anisotropic thermal parameters of the heavy atoms are given in Table 1 and those of the H atoms, together with the C-H distances, in Table 2.

Results and discussion

A perspective view of the molecule and the numbering system is presented in Fig. 1. The bond distances and

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31897 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

angles for the heavy atoms, uncorrected for thermal vibration, are given in Table 3.

Taking into account the hypothetical values given by Kim & Jeffrey (1967) for the pyranose ring we found a similar mean value of 1.528 Å for the C–C distances while the C–O distance (1.400 Å) and the angle at the C atoms (112.8°) are respectively less than and greater than those given by Kim & Jeffrey (1967).

The main torsional angles are given in Table 4. The conformation of the pyranose ring is best described as skew, as predicted by Coxon & Hall (1964). Some flattening in the vicinity of the dioxolane fused ring has been observed. The angle between the plane defined by O(5), C(1), C(2) and C(4) and the plane defined by C(1), C(3), C(4) and C(5) is 29.2° and the deviations of the C(3), C(5), O(5) and C(2) atoms not used in the plane calculations are 0.542, –0.694, 0.634 and –0.575 Å respectively.

The only unusual bond distance in the dioxolane ring is C(2)–O(2), which is larger than normal (Riche & Pascard-Billy, 1975). The conformation of this ring has been studied with Altona's criterion. Thus, taking into account the torsional angles, the phase angle found is $\Delta = 17.8$ (4)°, which is midway between 36° for an envelope conformation and 0° for a twist-chair conformation. The maximum possible torsional angle is $\varphi_m = \pm 38.4^\circ$ and the internal consistency is 1.905 compared with the value of 1.618 given by Altona, Geise & Romers (1968).

The acetyl groups are planar within experimental errors. For the groups attached to C(3) and C(4) the dihedral angles defined by C(acetyl)–O–C(ring)–H are 30 (4) and 20 (5)°. Therefore the conformation is syn-periplanar (Klyne & Prelog, 1960). The conformation around the C(5)–C(6) bond is *gauche-gauche*, Table 4.

The packing of the molecules in the crystal is due solely to van der Waals forces.

A study of the distinctions between chair and boat conformations in six-membered rings has been carried out. At the beginning of this study two groups (pyranose and other six-membered rings) were con-

sidered. The following criteria were obtained and seem the most sensible for distinguishing between chair (C), half-chair (H), boat (B) and skew (S) conformations.

If φ_i is the torsional angle, we define:

$$\begin{aligned} \text{(I)} &= |\varphi_i - \varphi_{i+3}| \\ \text{(II)} &= \sum |\varphi_i - \varphi_{i+1}| \\ \text{(III)} &= \sum |\varphi_i| \\ \text{(IV)} &= \sum |\varphi_i - \varphi_{i+3}| \\ \text{(V)} &= \sum (|\varphi_i| - |\varphi_{i+1}|) \end{aligned}$$

For ideal conformations (Hendrickson, 1961; Bucourt, 1964) criterion (I) adopts the following values: (I)_C = 120, (I)_H = 75, (I)_B = (I)_S = 0°, but it is not exactly true for very distorted conformations, although the relation (I)_C > (I)_H > (I)_S > (I)_B still holds.

On the other hand, criterion (II) is exactly twice criterion (III) for chair and half-chair, approximately the same for boat and quite different for skew conformations. From this it is possible to distinguish the skew rings from other conformations.

Criterion (III) adopts the following ideal values: (III)_C = 360, (III)_H = 225, (III)_B = 240 and (III)_S = 274°. Considering experimental values the presence of a chair conformation is clearly indicated (see Table 5).

Moreover the relations (III) = (IV) for chair and half-chair but (III) ≠ (IV) for boat and skew conformations also exist.

The ideal values showed for criterion (V) are (V)_C = 0, (V)_H = 150, (V)_B = 240 and (V)_S = 152. We observed large deviations for strained chairs and, considering the similar values for skew and half-chair, this criterion seems useful for distinguishing boat conformations.

We have not observed significant differences between pyranose and other six-membered rings, thus Table 5 shows the mean values of the criteria with estimated standard deviations calculated as $s = [\sum (\bar{x} - x_i)^2 / N(N-1)]^{1/2}$, where \bar{x} is the mean value of x_i and N the number of values considered. Moreover the straining of each ring has been calculated as $\frac{1}{6} \sum (\varphi_{oi} - \varphi_{ci})^2$, where φ_{oi} and φ_{ci} are the ideal and experimental

Table 5. Mean values of the criteria defined in the text and the torsional angles

N is the number of rings used in the calculation of each conformation. All values are given in degrees. The e.s.d.'s are in parentheses.

Conformation	N	φ_i	(I)	(II)	(III)	(IV)	(V)	χ^2 range
Chair (a)	15	55 (1)	110 (1)	661 (9)	330 (4)	330 (4)	40 (9)	7–510
Half-chair (b)	11	3(1), 17(2), 49(2), 67(3)	67 (2)	404 (2)	202 (1)	202 (1)	127 (8)	20–266
Boat (c)	14	3(1), 59(1)	4 (1)	473 (13)	242 (6)	13 (3)	232 (7)	2–263
Skew (d)	4	29(3), 55(6)	23 (4)	349 (26)	225 (8)	69 (22)	150 (12)	57–568

(a) Cradwick & Sim (1971); Dobler & Dunitz (1964); Flippen & Gilardi (1974); Foces-Foces, Cano & García-Blanco (1976); Gilardi & Flippen (1974); Harrison, Hodder, Brewis & Halsall (1971); Leung & Marchessault (1974); Longchambon, Ohannesian, Avenel & Neuman (1975); Neuman, Gillier-Pandraud & Longchambon (1975); Panagiotopoulos (1974); Park, Kim & Jeffrey (1971); Perales & Lindley (1975); Webb & Becker (1967). (b) Berking & Seeman (1971); Coggon, Luhan & MacPhail (1973); Gibbons & Trotter (1972); Hackert & Jacobson (1971); Harrison *et al.* (1971); Huber & Hoppe (1965); Norton, Kartha & Lu (1964); Pilotti & Stensland (1972); Romers, Heykoop, Hesper & Geise (1966). (c) Aubry, Protas, Thong, Marraud & Néel (1973); Carrascal, Rodriguez, Valverde & Fayos (1975); Cradwick & Sim (1971); Destro, Filippini, Gramaccioli & Simonetta (1971); Fayos (1976); Filippini, Gramaccioli, Rovere & Simonetta (1972); Gibbons & Trotter (1972); Pointer, Wilford & Chui (1971); Tamura & Sim (1968). (d) Allen, Isaacs, Kennard & Motherwell (1973); Heitmann *et al.* (1974); Riche & Pascard-Billy (1975); present work.

torsional angles. We point out that although there has been no difficulty in assigning theoretical values in the 44 cases studied, some have quite large distortions from the ideal models.

We concluded that: (1) A six-membered ring adopts a skew conformation if $(II) \neq (III)$. (2) When $(II) \approx 2 \times (III)$ and $(III) \neq (IV)$ a boat conformation is present. (3) When $(II) = 2 \times (III)$ and $(III) = (IV)$, but (I) is greater than about 95° , a chair conformation is adopted. (4) When $(II) = 2 \times (III)$ and $(III) = (IV)$, and (I) is less than about 95° , the conformation is a half-chair.

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