Relationships between the Torsion Angles in Seven-membered Rings

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A relationship between torsional angles in seven-membered rings has been proved by its application to several experimental and theoretically computed geometries. This general formula, with two phase angles, is reduced to that proposed by Flapper and Romers, with a single phase angle, when only conformations belonging to symmetrical pathways are considered. However, for distorted conformations the general formula provides far better results.

A GENERAL formula relating the intracyclic torsion angles of a puckered n-membered-ring (hereafter n-ring) was recently deduced[1] by assuming infinitesimal normal displacements from a planar reference conformation.† The particular expressions for the cyclopentane and cyclohexane rings are equivalent to the empirical ones proposed previously.[2,3] However, the expression for the cycloheptane ring differs from that given by Flapper and Romers.[4]

In the present work the two reported relationships between the torsion angles of the cycloheptane ring are compared and applied to the analysis of a set of 7-ring geometries determined by X-ray and electron diffraction or calculated by molecular mechanics methods. The relationship proposed by Flapper and Romers,[4] with a single phase angle, represents in fact a particular case of the more general expression, with two phase angles, discussed below.[1] Although both formulae give the same results when considering conformations belonging to symmetrical paths, introduction of the second phase angle parameter enables the general relationship to describe highly distorted geometries for which the Flapper and Romers expression is not obeyed.

Relationships between the Torsional Angles.—Relationship (1) between the intracyclic torsion angles of the cycloheptane ring was deduced[1] for infinitesimal out-of-plane displacements of the carbon atoms from a planar regular heptagonal conformation. The quantities

$$\theta_{j,j+1} = \theta_2\cos[\phi_2 + \pi/2 + 2\pi(2j - 1)/7] +$$
$$\theta_3\cos[\phi_3 + \pi/2 + 3\pi(2j - 1)/7]; \quad j = 1,2,\ldots,7 \quad (1)$$

θ_2 and θ_3 measure the amplitudes (θ_2 and $\theta_3 \geqslant 0$) and ϕ_2 and ϕ_3 the phase angles ($0 \leqslant \phi_2, \phi_3 \leqslant 2\pi$) of the puckering.

Terms on the right hand side of (1) represent two normal conformational pathways for cycloheptane, so that any puckered conformation can be expressed as a linear combination of another two, each from a normal path.

The terms $\theta_2\cos[\phi_2 + \pi/2 + 2\pi(2j - 1)/7]$ and $\theta_3\cos[\phi_3 + \pi/2 + 3\pi(2j - 1)/7]$ give, respectively, the boat–twist-boat, B–TB, and the chair–twist-chair, C–TC,

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† Cano *et al.* have applied a finite Fourier expansion model to the analysis of the conformation parameters of n-membered rings (F. H. Cano, C. Foces-Foces, and S. García-Blanco, *Acta Crystallogr.*, 1978, **A34**, S91). Their relationship between the torsion angles differs from that deduced in ref. 1 for a regular polygon in the first two additional terms of the Fourier expansion which, in general, would be negligible.

pathways. In both cases, conformers with C_s symmetry correspond to phase angles ϕ_2 or ϕ_3 equal to $n(2\pi/7)$ (boat or ring-inverted chair) and to $(n + 1/2)(2\pi/7)$ (ring-inverted boat or chair). Conformers with C_2 symmetry appear for $(n + 1/4)(2\pi/7)$ (ring-inverted twist-boat or twist-chair), and for $(n + 3/4)(2\pi/7)$ (twist-boat or ring-inverted twist-chair). The first two symmetrical conformations of each normal pathway are depicted in the Figure where B(1) and C'(1) denote, respectively, a boat and a ring-inverted chair with a mirror plane through atom 1 and bisecting bond 4–5. TB'(7) and TC(5) designate a ring-inverted twist-boat and a twist-chair with a dyad running through atom 7 and the midpoint of bond 3–4, for the former, and through atom 5 and the centre of bond 1–2 in the latter. The complete sets of symmetrical conformations belonging to each of the normal paths are given in Table 1.

The two terms on the right hand side of (1) provide conformations with the same definite symmetry element for $\phi_3 = n\pi/14$, with n an integer, and $\phi_2 = 3\phi_3$ or $\phi_2 = 3\phi_3 + \pi$, as can be deduced from inspection of Table 1. *E.g.* for the phase angles $\phi_3 = \pi/14$, $\phi_2 = 3\pi/14$, and $\phi_2 = 17\pi/14$ the respective conformations TC(5), TB(5), and TB'(5) are obtained, all with a dyad running through atom 5 and the centre of bond 1–2. Substitution of the above relations between ϕ_2 and ϕ_3 in expression (1) leads to the simplified equation (2) with only a phase angle ϕ.

$$\theta_{j,j+1} = \theta_2\cos[3\phi + p\pi/2 + 2\pi(2j - 1)/7] +$$
$$\theta_3\cos[\phi + \pi/2 + 3\pi(2j - 1)/7]; \quad p = 1,3 \quad (2)$$

Conformations with a definite symmetry element are generated from (2) if, for the corresponding ϕ value, the θ_2 and θ_3 values are varied. Alternatively, symmetrical conformational pathways result if, for given sets of θ_2 and θ_3 values, the ϕ value is changed.

A remarkable difference between expressions (1) and (2) is that, whilst with (1), for $0 \leqslant \phi_2$(or ϕ_3) $\leqslant 2\pi$ all the B–TB (or C–TC) conformations appear only once, the expression (2), for $0 \leqslant \phi \leqslant 2\pi$, also gives all the C–TC conformations once but repeats the family of the B–TB conformations three times.

Another relationship between the torsion angles of cycloheptane was proposed[4] as the Fourier expansion (3) between the torsion angle θ_i and the phase angle Δ.

$$\theta_i = A\sin\phi_j + B\sin3\phi_j + C\sin5\phi_j + D\sin7\phi_j; \quad \phi_j =$$
$$\Delta/2 + 2\pi j/7; \quad j = 0,1,\ldots,6; \quad i = 2j + 4, \bmod 7 \quad (3)$$

TABLE 1

Normal conformational pathways of cycloheptane

$\phi_3,^a$ ϕ_2^{b}	0	$\pi/14$	$2\pi/14$	$3\pi/14$	$4\pi/14$	$5\pi/14$	$6\pi/14$	$\pi/2$
C–TC	C'(1)	TC(5)	C(2)	TC'(6)	C'(3)	TC(7)	C(4)	TC'(1)
B–TB	B(1)	TB'(7)	B'(6)	TB(5)	B(4)	TB'(3)	B'(2)	TB(1)
$\phi_3,^a$ ϕ_2^{b}	$\pi/2$	$8\pi/14$	$9\pi/14$	$10\pi/14$	$11\pi/14$	$12\pi/14$	$13\pi/14$	π
C–TC	TC'(1)	C'(5)	TC(2)	C(6)	TC'(3)	C'(7)	TC(4)	C(1)
B–TB	TB(1)	B(7)	TB'(6)	B'(5)	TB(4)	B(3)	TB'(2)	B'(1)
$\phi_3,^a$ ϕ_2^{b}	π	$15\pi/14$	$16\pi/14$	$17\pi/14$	$18\pi14$	$19\pi/14$	$20\pi/14$	$3\pi/2$
C–TC	C(1)	TC'(5)	C'(2)	TC(6)	C(3)	TC'(7)	C'(4)	TC(1)
B–TB	B'(1)	TB(7)	TB'(6)	B(6)	TB'(5)	B'(4)	TB(3)	TB'(1)
$\phi_3,^a$ ϕ_2^{b}	$3\pi/2$	$22\pi/14$	$23\pi/14$	$24\pi/14$	$25\pi/14$	$26\pi/14$	$27\pi/14$	2π
C–TC	TC(1)	C(5)	TC'(2)	C'(6)	TC(3)	C(7)	TC'(4)	C'(1)
B–TB	TB'(1)	B'(7)	TB(6)	B(5)	TB'(4)	B'(3)	TB(2)	B'(1)

^{a} C–TC itinerary. ^{b} B–TB itinerary.

This expression is equivalent to formula (2) provided $C = D = 0$. Actually, expressions $C\sin5\phi_j$ and $D\sin7\phi_j$ do not represent physically meaningful conformations and are only small correction terms in (3) (*cf.* ref. 4). Expressions (3) and (2), with $A \geqslant 0$, give the same results provided that relationships (4) hold with $p = 3$ for

$$\theta_3 = A, \, \theta_2 = |B|, \, \phi = \pi - \Delta/2 \quad (4)$$

$B > 0$ and $p = 1$ for $B < 0$ [p defined in equation (2)].

Direct comparison of equations (3) and (1) shows that the first and second terms on the right hand side of (3) are equivalent to the second and the first terms on the right hand side of (1), respectively, provided that (5)—(8) hold. Therefore, the equivalence of (1) and (3) requires

C'(1)   TC(5)

B(1)   TB'(7)

S(1)   TS(4)

H(1)   TH(4)

C_s and C_2 forms in the symmetrical pathways of cycloheptane

$$A = \theta_3; \, \phi_3 + \Delta/2 = \pi \text{ or } 3\pi \quad (5)$$
$$A = -\theta_3; \, \phi_3 + \Delta/2 = 2\pi \quad (6)$$
$$B = \theta_2; \, \phi_2 + 3\Delta/2 = 2\pi, \, 4\pi, \text{ or } 6\pi \quad (7)$$
$$B = -\theta_2; \, \phi_2 + 3\Delta/2 = \pi, \, 3\pi, \, 5\pi, \text{ or } 7\pi \quad (8)$$

the fulfilment of the relationships (9) between ϕ_2 and ϕ_3,

$$3\phi_3 - \phi_2 = -\pi, \, \pi, \, 3\pi, \text{ or } 5\pi \quad (9)$$

when A and B have the same sign, and (10) if they have

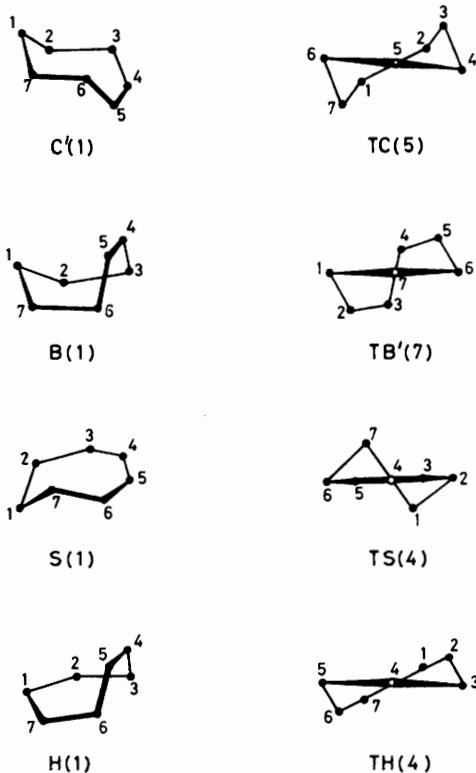$$3\phi_3 - \phi_2 = 0, \, 2\pi, \text{ or } 4\pi \quad (10)$$

different signs.

In summary, expressions (1) and (3), with $C = D = 0$, are fully equivalent for the analysis of symmetrical conformations or, more exactly, of those conformations belonging to symmetrical pathways. In these cases only a phase angle is needed and (1) reduces to (2) or (3). However, to analyse highly distorted 7-rings two phase angles are required and the general expression (1) must be used.

Formula (3) [or (2)] generates symmetrical conformations for $\Delta = n\pi/7$, (or $\phi = n\pi/14$), which will belong to C–TC or B–TB families depending on the value of the ratio A/B (or θ_3/θ_2). The chair conformations C(i) appear for $\infty > A/B > 0.8$ and $-2.25 > A/B > -\infty$ whilst the boat ones B(i) are generated for $0.8 > A/B > -2.25$. Changes from chair to boat take place through the hinge H(i) and sofa S(i) conformations which are depicted in the Figure together with the twist-hinge TH(i) and twist-sofa TS(i) ones. The H, TH, S, and TS families are obtained for A/B values of 0.8, 1.0, −2.25, and −2.8 respectively. Therefore the intervals for the A/B ratio, where the TC and TB conformations are generated, differ somewhat from the aforementioned ones for the C and B conformations and, as a consequence, the S/TS family does not appear for $B = -0.61 A$ as assumed in ref. 4.

Analysis of puckered 7-rings by means of equations (1) and (3) requires the determination of the corresponding parameter values from the seven intracyclic torsion angles. The θ_2, θ_3, ϕ_2, and ϕ_3 values in (1) can be computed by using the procedure given in ref. 1. Formula (1) can be rewritten as (11) where the coefficients are

$$\theta_{j, j+1} = \sum_{m=2}^{3} [A_m(\theta_m\cos\phi_m) + B_m(\theta_m\sin\phi_m)] \quad (11)$$

given by (12). The unknowns, $\theta_m\cos\phi_m$ and $\theta_m\sin\phi_m$,

$$A_m = -\sin[m\pi(2j-1)/7], \quad B_m = \\ -\cos[m\pi(2j-1)/7] \quad (12)$$

can be determined from the experimental $\theta_{j,j+1}$ values by solving the linear equation system (11) by a least-squares method. In the case of (3) the set of A—D and Δ parameter values can be obtained by a trial-and-error method. For each Δ value linear regression is performed until the best fit between the experimental and the calculated values of the torsion angles is achieved.

RESULTS

A number of 7-rings have been analysed using equations (1) and (3) as a practical test on the reliability of these expressions. Fits to formula (3) were made both with and without the constraint $C = D = 0$. The geometries examined were taken from molecular mechanics computations and from X-ray or electron diffraction analysis.

The selected geometries from molecular mechanics computations were those reported by Flapper and Romers (Table 1 of ref. 4) and by Bocian and Strauss (Table 3 of ref. 5). The former authors report 24 predicted geometries, computed using several force-fields, for the four symmetrical forms C, TC, B, and TB of cycloheptane. The second authors have calculated six geometries for nearly symmetrical forms of cycloheptane, five for 1,3-dioxepan and six for oxepan.

The analysed geometries from electron diffraction correspond to cycloheptane [6] and oxepan.[7] The torsion angles have been reported for the forms TC and C of cycloheptane (Figure 5 in ref. 6) and for two TC forms of oxepan (Figure 6 in ref. 7).

The X-ray diffraction data analysed are those previously discussed by Flapper and Romers,[4] together with others from recent reports. The whole set comprises 46 7-ring geometries of the following 30 compounds (the indication (nx) means n different reported geometries):

(1) Calcium cycloheptane carboxylate pentahydrate [8] (4x)
(2) 1-Dimethylphosphono-1-hydroxycycloheptane [9] (2x)
(3) 4,4-Dichloro-2a-aza-A-homo-5β-cholestan-3-one [10] (2x)
(4) N-Methylrhoeagenine iodide [11]
(5) Buxenine-G dihydrobromide, (2x), and dihydroiodide [12]
(6) 2-Chlorotropone–cycloheptatriene adduct [13] (3x)
(7) Radiatin [14]
(8) N-Deacetyl-N-methylcolchicine [15]
(9) 7,8,9,10-Tetrachloropentacyclo[8.4.2.2²,⁷.0¹,⁹.0²,⁸]octadeca-4,12-diene [16] (2x)
(10) 8-Carboxy-1-hydroxy-2-oxobicyclo[3.2.2]non-6-ene-9,4-carbolactone [17] (2x)
(11) 2-Methoxy-3-methyl-7-phenyl-9,10,11-trihydro-4H-cyclohepta[f]quinolinone [18]
(12) Cephalotaxine p-bromobenzoate [19]
(13) 3,6-Spirodicycloheptylidene-1,2,4,5-oxacyclohexane [20]
(14) 17β-Hydroxy-8(9—10β)abeo-estr-4-en-3,10-dione [21]
(15) Bromoindole derivative of 3β-methoxy-21-keto-Δ¹³-serratene [22]
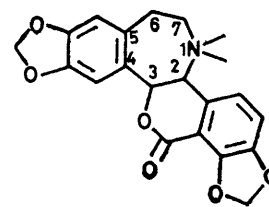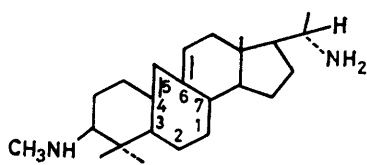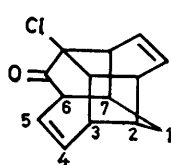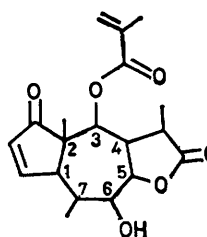(16) Bis-(1,4-diazacycloheptane)–copper(II) nitrate hemihydrate [23] (4x)
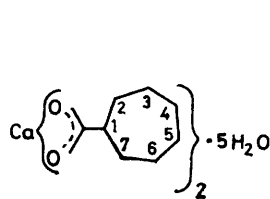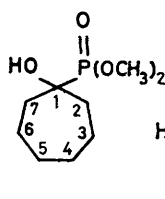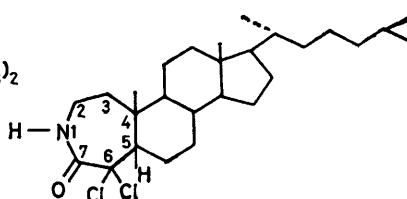
(1)   (2)   (3)   (4)
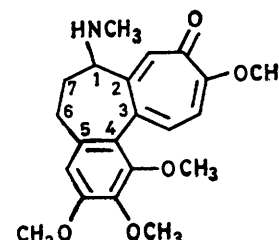
(5)   (6)   (7)   (8)

(9)   (10)   (11)   (12)

TABLE 2

Results obtained for the fits to formulas (1) and (3) of the torsion angles of certain distorted 7-rings

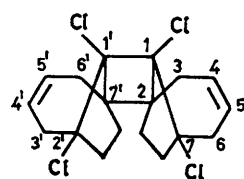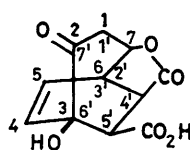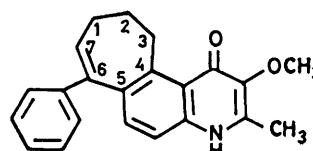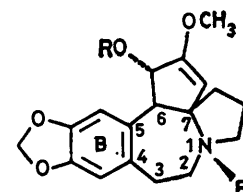| Compound [a]	θ_{12} [b]	θ_{23} [b]	θ_{34} [b]	θ_{45} [b]	θ_{56} [b]	θ_{67} [b]	θ_{71} [b]	σ [c,d]	A,[e] θ_3 [f]	B,[e] θ_2 [f]	Δ,[e] ϕ_3 [f]	ϕ_2 [f]
(1a)	46.0	−69.0	76.0	−26.0	−41.0	71.0	−53.0	(3.3)				
	0.6	−4.8	4.1	0.1	2.8	−3.4	4.4	3.4	74.9	29.9	701.4	
	−0.1	−0.1	0.4	1.1	1.3	1.0	0.4	0.8	75.0	30.1	192.0	22.3
(1b)	18.0	54.0	−60.0	−12.0	59.0	−18.0	−41.0	(4.3)				
	−1.9	5.2	−4.9	5.7	−5.8	2.9	1.3	4.3	13.9	57.7	371.0	
	0.3	0.8	0.6	0.0	−0.6	−0.8	−0.4	0.6	15.1	57.7	18.1	163.2
(2)	−65.0	88.6	−69.8	−1.0	73.0	−95.0	74.0	(3.0)				
	5.4	−1.3	3.1	−0.8	−0.1	−5.2	3.7	3.4	97.4	31.5	360.1	
	3.0	3.0	1.2	−0.9	−1.9	−0.9	1.3	2.0	97.5	31.6	358.3	185.0
(3a)	39.0	−86.0	45.0	39.0	−75.0	30.0	−2.0	(4.1)				
	2.8	−6.9	2.0	−5.5	3.9	−5.2	−1.1	4.3	52.3	51.5	26.2	
	−1.5	−1.8	−1.9	−1.6	−1.2	−1.0	−1.1	1.5	52.6	51.5	172.9	318.6
(3b)	42.0	−86.0	46.0	37.0	−73.0	30.0	−6.0	(5.3)				
	4.2	−7.8	3.6	−6.2	5.1	−7.2	−1.6	5.5	53.8	49.4	26.2	
	−1.4	−1.2	−1.2	−1.4	−1.6	−1.7	−1.6	1.4	54.3	49.5	174.4	318.0
(4)	49.8	−66.4	61.4	−6.3	−59.1	85.1	−60.5	(5.0)				
	−3.8	6.7	−4.6	0.9	−1.0	9.6	−3.8	5.2	79.4	28.6	715.0	
	−0.3	−1.0	−0.6	0.7	1.9	2.1	1.1	1.3	79.5	29.0	178.8	17.4
(5)	103.0	−61.0	19.0	−7.0	9.0	23.0	−75.0	(4.6)				
	3.3	4.7	3.9	−8.8	7.5	−0.4	0.8	5.1	71.6	−28.4	699.4	
	3.6	2.9	1.2	−0.2	−0.3	1.1	2.8	2.1	71.8	28.7	194.3	202.5
(6)	−34.6	31.5	−43.5	7.7	55.6	−104.1	80.1	(20.9)				
	2.6	29.6	−42.8	16.0	2.4	−7.2	−7.7	21.0	73.1	−27.8	419.1	
	2.0	0.9	−1.6	−3.8	−3.9	−1.8	0.8	2.4	76.4	33.9	347.3	236.3
(7)	−82.4	61.4	−17.1	−33.8	64.2	−64.3	71.5	4.9				
	−9.8	1.2	1.4	0.9	−3.0	8.0	0.8	5.0	83.8	13.2	394.0	
	−2.6	−2.6	−0.7	1.7	2.7	1.7	−0.7	2.0	83.9	14.4	345.1	105.5
(8)	−80.8	4.5	53.8	−4.2	−71.1	41.3	48.3	(3.8)				
	−6.2	3.7	0.8	−3.5	2.9	−7.2	1.2	4.2	17.4	70.4	231.0	
	−1.5	0.2	0.8	0.0	−1.7	−3.0	−2.9	1.8	18.2	70.4	47.7	14.5
(9a)	94.6	−59.7	17.2	1.2	−13.6	43.5	−78.7	(2.7)				
	3.1	−0.7	−2.5	2.9	−3.3	0.8	4.1	2.8	75.3	−18.6	710.3	
	2.3	0.7	−1.0	−1.4	−0.4	1.5	2.7	1.6	75.3	18.7	183.4	202.3
(9b)	81.8	−38.0	8.3	−4.9	−12.7	64.6	−108.4	(3.8)				
	−5.8	−2.5	5.4	−4.9	3.2	−0.2	−4.5	4.2	78.7	−26.9	14.0	
	−4.1	−2.3	0.3	1.6	0.8	−1.7	−3.9	2.5	78.7	27.1	175.5	152.0
(10a)	29.5	49.7	−79.2	2.9	69.5	−34.0	−37.0	(4.9)				
	−2.5	3.4	−7.2	6.7	−4.6	6.4	−0.8	5.0	18.5	66.8	362.0	
	−0.5	−1.4	−1.1	0.2	1.5	1.8	0.9	1.2	19.7	66.8	19.5	176.6
(10b)	−37.0	86.8	−89.5	16.9	64.2	−71.5	29.5	(8.9)				
	−5.4	13.0	−7.3	6.6	−8.6	10.1	−9.0	8.9	73.6	47.3	354.5	
	−0.6	1.1	1.9	1.2	−0.5	−1.8	−1.9	1.4	74.4	47.6	11.3	181.4
(11)	38.1	46.2	−81.1	12.2	40.4	1.7	−69.0	(4.7)				
	−9.0	2.4	−7.5	3.2	0.1	−4.0	3.4	5.1	24.1	64.4	127.5	
	−3.3	−3.3	−2.1	−0.5	0.2	−0.5	−2.0	2.1	24.9	64.4	101.2	169.5
(12)	−52.9	−39.5	70.3	0.4	−49.8	3.0	75.0	(3.0)				
	−4.2	4.4	−2.7	2.9	1.8	0.2	4.1	3.2	16.7	68.4	487.0	
	0.2	0.0	0.5	1.3	1.9	1.7	0.9	1.1	17.2	68.4	310.7	349.8

[a] First row: experimental torsion angles. Second row: results for the fits to formula (3) with $C = D = 0$. Third row: results for the fits to formula (1). [b] Experimental torsion angle in the first row and deviations between the experimental and the calculated torsion angles in the second and third rows. [c] Root mean square deviations $\sigma = [(1/7)\Sigma\{\theta_{ij}(\exp) - \theta_{ij}(calc)\}^2]^{\frac{1}{2}}$. [d] Values in parentheses correspond to the fits to formula (3) including terms $C\sin5\phi$ and $D\sin7\phi$. [e] Parameters in formula (3), (second row). [f] Parameters in formula (1), (third row).

(17) 1,6-anhydro-β-D-Glucopyranose [24]
(18) 1,6-anhydro-β-D-Mannofuranose [25]
(19) 1,6 : 2,3-dianhydro-β-D-Gulopyranose [26] (2x)
(20) Pseudoguaianolide autumnolide [27]
(21) Tetramethylenephosphoric acid [28]
(22) 3-N-Methylamino-3-phenylbicyclo[3.2.1]octan-2-one hydrochloride [29]
(23) Veatchine [30]
(24) and (25) 1-Hydroxy-5-acetoxy- and 1,6-diacetoxy-10α-bromobicyclo[4.3.1]dec-3-ene [31]
(26) Cleomeolide [32]
(27) 1-Cyanotricyclo[3.3.0.0^{2,8}]octa-3,6-diene [33]
(28) Dodecachlorotetracyclo[7.2.1.0^{2,8}.0^{5,12}]dodeca-3,6,10-triene [34] (2x)
(29) ε-Caprolactam [35]
(30) exo-12-Methoxy-10-oxo-11-azatricyclo[6.4.1.0^{2,7}]trideca-2,4,6-triene [36]

Among the 46 X-ray geometries there are 16 corresponding to compounds (1)—(12), whose torsion angles are fitted to formula (3) giving root mean square deviations, σ, greater than the average of 2.6°. The results obtained for fits of the torsion angles of these geometries to formulas (1) and (3), with $C = D = 0$, are listed in Table 2. For the remaining experimental and theoretical geometries only average σ values will be discussed. Therefore no tables with the results of the fits for these geometries will be given here but they can be obtained, upon request, from E.D.

DISCUSSION

Relationship (1) between the torsion angles of the cycloheptane ring was deduced by assuming infinitesimal displacements from planarity of atoms in a regular heptagon.[1] Therefore, for general 7-rings, deviations

from (1) must be expected due to the finite puckering effect and to the fact that, with the exception of the cycloheptane molecule, the planar conformations differ from a regular heptagon.

For the cycloheptane molecule the torsion angles of the 30 symmetrical geometries [4,5] calculated by molecular mechanics methods can be satisfactorily fitted to formula (1). A maximum root mean square deviation σ of 2.2° and an average root mean square deviation $\bar{\sigma}$ of 0.8° result. The fits are better for the B and TB forms, $\bar{\sigma} = 0.2°$, than for the C and TC forms, $\bar{\sigma} = 1.2°$. For these latter forms, a similar $\bar{\sigma}$ value of 1.5° results for the torsion angles determined by electron diffraction. The same results are obtained for the fits to formula (3) with $C = D = 0$ (small differences appear for the geometries in ref. 5 because they are not absolutely symmetrical). However, when the constraint $C = D = 0$ is removed, far better fits are obtained. $\bar{\sigma}$ is $<0.1°$, showing that terms $C\sin5\phi$ and $D\sin7\phi$ in (3) are operative in the analysis of symmetrical conformations because they have the proper symmetry.

The introduction of heteroatoms in the cycloheptane ring causes worse fits of the torsion angles to formula (1) which must be attributed to the fact that the resulting planar conformations are not regular heptagons. Accordingly, the respective $\bar{\sigma}$ values of 0.9, 1.8, and 1.9° were obtained from the analysis of six conformations of cycloheptane, five of 1,3-dioxepan, and six of oxepan calculated by using the same force field.[5] Thus, the introduction of oxygen atoms in the ring doubles the $\bar{\sigma}$ value. For the fit of the torsion angles to formula (3) with $C = D = 0$, the respective $\bar{\sigma}$ values of 1.0, 2.3, and 4.8° result. These values are greater than those obtained with formula (1) due to the presence of distorted conformations (away from the symmetrical pathways), especially for the oxepan molecule. When the constraint $C = D = 0$ is removed the $\bar{\sigma}$ value for oxepan only decreases to 4.5° showing the fact that terms $C\sin 5\phi$ $D\sin 7\phi$ in (3) are inefficient in the analysis of distorted 7-rings. For the near symmetrical conformations of cycloheptane and 1,3-dioxepan these terms are operative and their $\bar{\sigma}$ values are reduced to 0.3 and 1.4°, respectively. Fits of the torsion angles of oxepan determined by electron diffraction for the two TC forms give $\bar{\sigma}$ values close to those mentioned above. For the fits to formulae (1) and (2), with and without the constraint $C = D = 0$ for the second, the respective $\bar{\sigma}$ values of 1.8, 4.7, and 4.3° were obtained.

The torsion angles determined by X-ray diffraction for the 46 7-ring geometries analysed in this work are far better fitted to formula (1), $\bar{\sigma}$ 1.3°, than to formula (3), $\bar{\sigma}$ 2.6°. The fit to formula (3) with $C = D = 0$ gives $\bar{\sigma}$ = 3.0°.

Most of the X-ray data correspond to 7-rings fused to other rings. Only compounds (1) and (2) contain isolated cycloheptane rings. The six conformations reported for these compounds follow the general behaviour giving $\bar{\sigma}$ values that differ by $<0.15°$ from the corresponding ones quoted above.

Among the 46 X-ray geometries there are 16 corresponding to compounds (1)—(12), whose torsion angles are fitted to formula (3), giving root mean square deviations $\bar{\sigma}$ 2.6°. Examination of the results obtained for the fits of the torsion angles of these 16 distorted geometries (Table 2) confirm the conclusions pointed out in the above study of the distorted geometries of oxepan. Comparison of the individual and of the root mean square deviations between the experimental and the calculated torsion angles shows that, for distorted geometries, much better fits are obtained by using formula (1), with two phase angles, than by using formula (3) $(C = D = 0)$, with only one phase angle. The respective $\bar{\sigma}$ values are 1.6 and 5.7°. Furthermore, similar fits are obtained when formula (3) is used either with the terms $C\sin5\phi$ and $D\sin7\phi$: $\bar{\sigma}$ 5.5°, or without, $\bar{\sigma}$ 5.7°. Inclusion of these terms gives rise to minute changes in the values of the A, B, and Δ parameters ($<0.2°$ for A and B and $<0.5°$ for Δ) and, likewise, the resulting values for C and D are smaller than 3°.

Compound (6) presents the most distorted of all the 7-rings analysed in this work. Its torsion angles, which are well fitted to the general relationship (1), σ 2.4°, do not obey the Flapper and Romers expression (3), σ 20.9°.

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