MOLECULAR COMFORMATION OF THE CYCLOHEPTANE RING IN THE SOLID STATE

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ABSTRACT. The conformations adopted by cycloheptane derivatives in the solid state are described and parameterized. The effects of the molecular environment on the geometry and conformation of the ring have been elucidated based on X-ray diffraction structural data. The boat conformation is seldom observed in the boat/twist boat pseudorotational sequence of these derivatives. Some inadequately assigned conformations in the literature have been revised.

INTRODUCTION

The cycloheptane carbon framework constitutes the major structural unit in a rapidly rising number of naturally occurring compounds, particularly in the perhyroazulenic sesquiterpenoids (Figure 1a). Some of these compounds are known to function as metabolites. The way in which a given sesquiterpenoid act is undoubtedly a function of its total structure. While the conformation of cyclopentane and cyclohexane derivatives have been extensively examined [1-10] those of cycloheptane derivatives have not been subjected to such extensive and comparative analyses.

It is known that several conformational differences exist between the higher symmetry cyclohexane and the relatively lower symmetry cycloheptane [11]. For instance, cyclohexane has one chair form, while the more flexible cycloheptane has a family of chair forms that are readily interconvertible by pseudorotation. Among the chair forms in the latter sequence, the twist chair with a C_2 axis of symmetry and a chair with a C_s plane of symmetry are symmetrical, with the former thought to be most stable, and the latter the least stable in the pseudorotation sequence. However, like cyclohexane, the cycloheptane chair forms are also thought to be capable of undergoing a conformational flip into a series of higher energy boat forms. The boat series is normally made of flexible forms interconvertible by pseudorotation. In this sequence, a twist boat form with a C_2 axis of symmetry is judged the most stable, while the boat form with a C_s plane of symmetry is the least stable.

However, in the literature, some conflict exists about the possible conformations of some cycloheptane derivatives in the solid state, For example, Sekita *et al.* [12] attributed a boat conformation to the cycloheptane ring of the compound bromomexicanin-E, while McPhail and Sim [13], assigned a conformation midway between the twist chair and chair form to the same ring. The relationship between the conformation of the same ring and the stereochemistry of fusion of a five membered ring to the cycloheptane derivative has also been a subject of some discussion in the literature. Hendrickson [11] proposed that *cis* fusion of a five membered ring to the cycloheptane ring is most favoured at bond A in the twist chair form (Figure 1b), while *trans* fusion takes place at either bond B or C (Figure 1b). McPhail and Sim [13] from studying the structures of six cycloheptane derivatives demonstrated that in euparotin bromoacetate (H7, Chart 1) the *cis* fused cyclopentene and *trans* fused γ-lactone are found at bonds of the D and B types respectively, but the authors erroneously (as shown

later) proposed that in the closely related compounds solstitalian (H8, Chart 1) and bromodihydroisophoto-santonic lactone acetate (H9, Chart 1), the *cis* fused five membered rings are found at bonds of the A type.

The present study was therefore carried out to resolve the above conflicts, and attempt to decipher factors that determine the various conformations adopted by the cycloheptane ring derivatives. Consequently, we have examined the conformations of various carboxylic cycloheptane ring in 29 molecular environments in terms of some geometric and conformational parameters [1,3,13]. Some previous conformational assignments in the literature have been revised.

The atomic numbering scheme used is shown in Figure 1a for a typical sesquiterpenoid. Schematic representations of the twist chair, chair and twist boat forms as proposed by Hendrickson [11], are shown in Figure 1b, 1c, and 1d, respectively. The various kinds of bonds with respect to the symmetry elements (C_2 or C_s) of the rings are labelled A to D, and A' to C' for symmetry related equivalents in Figure 1.
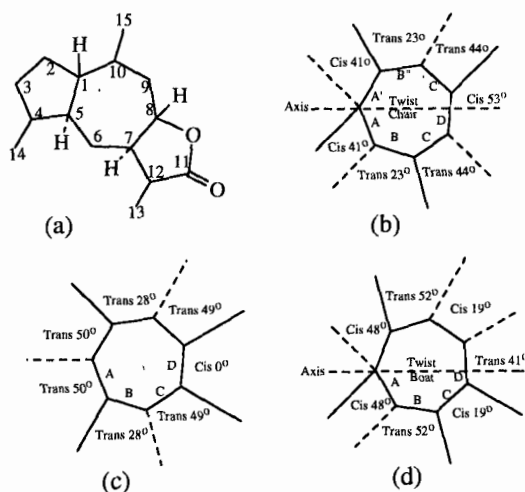

Figure 1.   (a) Atomic numbering scheme used for a cycloheptane ring with two fused 5-membered rings; Schematic representations of (b) twist chair (c) chair (d) twist boat conformations of cycloheptane illustrating preferred stereochemistry of 5-membered ring fusion. (After Hendrickson [11]).

EXPERIMENTAL

Data for calculation. Primary structural data for molecules containing cycloheptane derivatives were obtained from X-ray analyses with R_f values not exceeding 15%.

Asymmetric parameters. Asymmetric parameters (ΔC_2 and ΔC_s) were calculated using the expressions defined by Duax and Co-workers [1] and described in our earlier papers [4,5] in this series. For the ideal chair, $\Delta C_s = 0$, while for the ideal twist chair $\Delta C_2 = 0$. Similarly, for the ideal boat $\Delta C_s = 0$ and for the twist boat $\Delta C_2 = 0$.

Conformational parameters Σ_2 *and* Σ_s. The parameters Σ_2 and Σ_s proposed by McPhail and Sim [13] are measures of the deviation of the ring conformation from C_2 and C_s symmetry. They have been estimated in this study using the expressions:

$$\Sigma_2 = /\omega_1 - \omega_6/ + /\omega_2 - \omega_5/ + /\omega_3 - \omega_4/;$$

$$\Sigma_s = /\omega_1 + \omega_7/ + /\omega_2 + \omega_6/ + /\omega_3 + \omega_5/ + /\omega_4/$$

where ω_1 to ω_7 are the endocyclic torsion angles of the rings as illustrated in Figure 2. Each pair of angles within the modulus sign is a symmetry pair in terms of both the sign and magnitude of the torsion angles. For ideal forms both Σ_2 (for twist chair or twist boat) and Σ_s (for chair or boat) are zero.
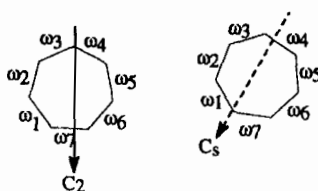

Figure 2.   Sketches showing symmetry pairs of endocyclic torsion angles (ω_1 to ω_7) used in calculating the conformation parameters Σ_2 and Σ_s. (After McPhail and Sim [13]).

Definition of the conformations. The conformations are described in the text as chair, twist chair, boat or twist boat depending on the sign sequence of the endocyclic torsion angles, and the estimated conformational parameters ΔC_s, ΔC_2, Σ_2 and Σ_s. According to Bucourt [13] simplified topological convention in terms of the sign sequence of endocyclic torsion angles are shown in Figure 3 for the various forms. In the figure, the conventional notation reflects dispositions of the perspective views as indicated in the sketches. For the twist chair and twist boat conformers, the views are along the axis and this accounts for the way their conventional notations are oriented.
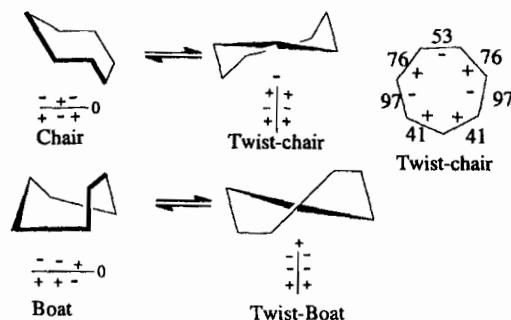

Figure 3.   Topological conventions of sign sequences of the endocyclic torsion angles in the various conformations. (After Bucourt [3]).

RESULTS AND DISCUSSION

Geometric $\Sigma / \omega /$ and conformation parameters (ΔC_s, ΔC_2, Σ_2 and Σ_s) for some cycloheptane ring derivatives (H1 to H19) in the chair / twist chair forms are shown in Table 1a, while the corresponding endocyclic torsion angles are given in Table 1b. Table 2a presents a listing of the geometric and conformational parameters for rings (H21 to H29) in the boat/twist boat family of conformations, with the endocyclic torsion angles correspondingly listed in Table 2b. It is quite evident from the values of $\Sigma / \omega /$ that the rings in the chair/twist chair conformations are more puckered (with a mean $\Sigma / \omega / = 425^0$) than those in the boat/twist boat forms (mean $\Sigma / \omega / = 324^0$). Chart 1 shows the molecular environments of the various cycloheptane derivatives examined in this study.

Table 1a.   Conformation and geometric parameters for some cycloheptane ring derivatives in the chair/twist chair forms.

Compd. Code	Σ_2	Σ_s	ΔC_2	ΔC_s	$\Sigma /\omega /$	Approx. Symmetry of torsion angles	Ref.
H1	82	13	40.2	5.5	421	$C_s(6)$	(16)
H2	7.5	100.3	3.0	36.5	454	$C_2(6)$	(16)
H3	7.4	99.7	2.5	36.2	459	$C_2(6)$	(16)
H4	29	61	11.9	22.4	401	$C_2(7)$	(17)
H5	100	20	39.3	7.3	433	$C_s(9)$	(14)
H6	74	22	34.6	7.4	422	$C_s(7)$	(18)
H7	32	107	12.7	39.4	407	$C_2(8)$	(13)
H8	19	79	6.9	28.9	454	$C_2(8)$	(13)
H9	19	49	7.3	22.1	446	$C_2(8)$	(13)
H10	22	97	7.6	33	426	$C_2(8)$	(13)
H11	40	92	18.9	31.3	420	$C_2(8)$	(13)
H12	62	40	25.7	13.7	405	$C_s(6)$	(12, 13)
H13	56	37	21.7	14.7	348	$C_s(7)$	(15)
H14	30	62.2	13.0	22.5	462	$C_2(1)$	(19)
H15	95	8	37.3	4.1	426	$C_s(8)$	(20)
H16	28	77	9.7	27.4	437	$C_2(10)$	(21)
H17	27.4	71.0	12.6	24.1	398	$C_2(10)$	(22)
H18	62	48	21.7	16.8	431	$C_s(1)$	(23)
H19	102	10	40.5	4.4	427	$C_s(1)$	(24)
H20	42.1	73.5	17.0	19.7	448	$C_2(9)$	(32)

The relative conformations of the rings in the chair/twist chair family (H1-H20) are displayed in Tables 1a and Figure 4. The cycloheptene derivatives fused to two 5-membered rings (H1, H6 and H13) all adopt the chair conformation. The methylene cycloheptene ring represented in this study by the derivatives H5, H8, H10, H14, H16, H19 and H23 has received some attention in the literature [14]. Thus, while molecular mechanics calculations for a series of chair and twist chair conformers indicate that the most stable form of an isolated methylene cycloheptane is a twist chair, in which a C_2 axis of the ring passes through the carbon atom adjacent to that bearing the exocyclic methylene group, the rings in H5, H19 and H23 adopt conformations different from the twist chair. Both H5 and H19 adopt the chair conformation while H23 adopts a twist boat conformation. The latter conformation may be due to constraints arising from the double *cis* fusion of the two 5-membered rings in H23 to bonds, which are in a 1,3-relationship. The relative positions of the C_2 axis (for the twist

chair) and mirror plane C_s (for the chair) for the fused methylene cycloheptene do not necessarily follow the pattern prescribed by molecular mechanics for the free ring. Thus, while the C_2 axis of the ring in H14, H16 and the mirror plane in H19 pass through the required carbon atom, these symmetry elements in H5, H8 and H10 do not pass through the expected carbon atom. It would appear that for the fused ring, other intramolecular constraints may influence the relative position of the symmetry element in the methylene cycloheptane.

Table 1b.   Endocyclic torsion angles of some cycloheptane ring derivatives in the chair/twist chair conformation.

Compd.	Torsion angle (deg.)						
Code	C1 - C5	C5 - C6	C6 - C7	C7 - C8	C8 - C9	C9 - C10	C10 - C1
H1	76	-66	69	-85	60	4	-61
H2	-95.1	39.8	38.4	-83.8	93.7	-44	68.9
H3	-94.1	37.8	40.8	-91.5	71.5	-49.9	73.3
H4	-84	62	-18	-31	62	-68	76
H5	-64	-3	68	-90	67	-62	79
H6	64	-82	64	-57	76	-73	6
H7	25	-63	102	-41	-42	85	-49
H8	51	-74	88	-35	-45	92	-69
H9	63	-78	79	-31	-42	81	-72
H10	44	-59	84	-37	-43	90	-69
H11	-36	59	-81	32	53	-98	61
H12	-36	68	-82	19	60	-86	51
H13	29	-52	74	-93	69	-30	-1
H14	49.3	-90.7	74.6	-60.9	75.3	-82.4	28.3
H15	-4	-63	86	-66	65	-79	63
H16	79	-69	57	-75	89	-40	-28
H17	-77	60.6	-36.0	58.7	-81.2	31.6	52.9
H18	-76	87	-51	-23	65	-64	65
H19	62	-87	68	3	-68	80	-59
H20	-65.6	56.6	-79.3	83.6	-25.3	-51.2	86.1

Table 2a.   Conformation and geometric parameters for some cycloheptane ring derivatives in the boat/ twist boat forms.

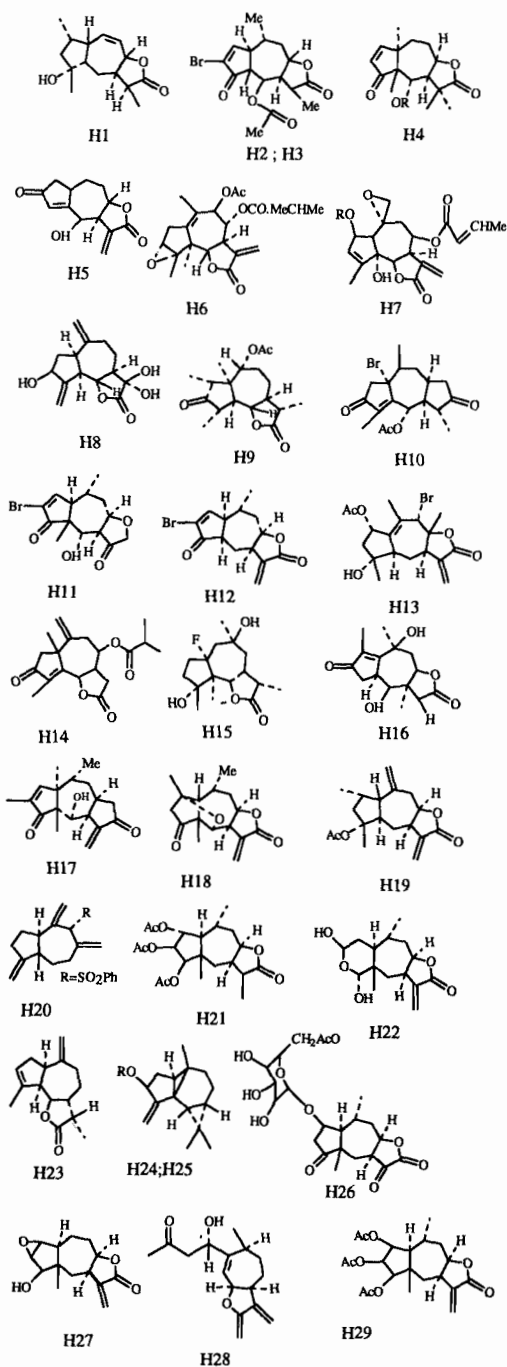| Compd.						Approx. symmetry of	
Code	Σ_2	Σ_s	ΔC_2	ΔC_s	$\Sigma|\omega|$	torsion angles	Ref.
H21	17.7	48.9	6.1	20.2	335	$C_2(10)$	(25)
H22	25.1	47.7	8.5	19.2	330	$C_2(10)$	(25)
H23	11.7	59.4	4.0	18.4	329	$C_2(10)$	(26)
H24	60.4	52.5	30.5	21.5	334	$C_s(10)$	(27)
H25	70.2	57.7	34.6	25.8	346	$C_s(10)$	(27)
H26	8	54	2.8	21.2	323	$C_2(10)$	(28)
H27	33.9	46.4	12.1	16.1	326	$C_2(10)$	(29)
H28	30	58	12.1	19.9	295	$C_2(9)$	(30)
H29	31	69.3	11.1	26.1	302	$C_s(10)$	(31)

Chart 1. Structural formulae of compounds discussed showing the molecular environments of the cycloheptane derivatives.

Table 2b.   Endocyclic torsion angles of some cycloheptane ring derivatives in the boat/twist boat
conformation.

Compd. Code	Torsion angle (deg.)						
	C1 - C5	C5 - C6	C6 - C7	C7 - C8	C8 - C9	C9 - C10	C10 - C1
H21	-72.0	-13.7	71.7	-19.9	-64.5	44.5	48.5
H22	-61.3	-21.4	72.5	-12.0	70.8	48.9	42.7
H23	-60.4	-21.1	75.0	-17.9	-65.8	46.0	42.9
H24	78.5	-42.6	-2.8	42.7	-55.0	-42.0	70.9
H25	77.5	-45.5	-3.7	44.8	-62.6	-34.8	76.9
H26	-70	-11	67	-15	-68	47	45
H27	-69.2	-19.4	65.0	-4.1	-74.7	40.4	53.5
H28	3	57	-11	-64	49	37	-74
H29	-69	-19.4	65	-4.1	-74.7	40.1	30.1

In general, a preponderance of 1,3-non-bonded interactions among substituents on the cycloheptane derivatives over 1,4-non-bonded interactions leads to a preference of conformations in the chair/twist chair family to those in the boat/twist boat forms. The chair/twist chair sequence also appears preferred when there are equal numbers of 1,3 and 1,4-non-bonded interactions on the cycloheptane ring derivative. Within the chair/twist chair family, it is not easy to decipher any distinctive factor which determines what conformation in the series the ring adopts. The conformation of bromomexicanin-E (H12) in this sequence requires a revision. The cycloheptane ring derivative in H12 was earlier assigned a boat conformation [12] and later changed to a conformation midway between the chair and the twist chair forms [13]. Examination of the symmetry parameters in the Table 1a for H12, and the correlation diagrams (Figure 4a and 4b) reflecting the possibility of interconversion by pseudorotation, shows that the ring H12 adopts a conformation closer to the twist chair form than the chair form.
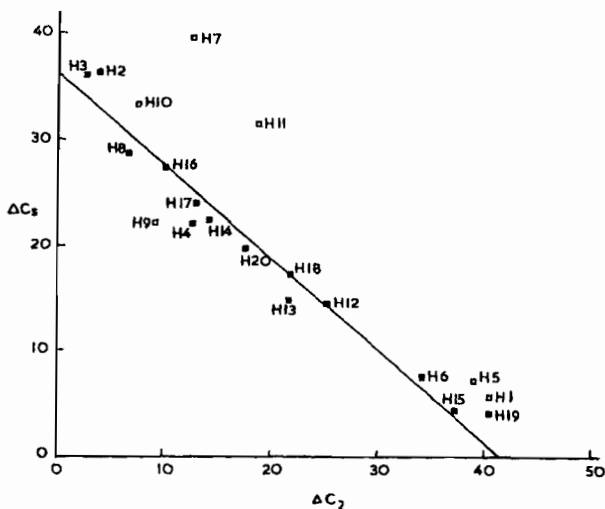

Figure 4a.   Correlated variation in principal asymmetry parameters ΔC_s and ΔC_2 for cyclo-heptane derivatives in the chair and twist chair conformations. The equation of the line is: $\Delta C_s = 16.44 - 0.896 \, \Delta C_2$ (n = 13, r^2 = 0.96). The points ($\square$) were not included in the least squares fit.
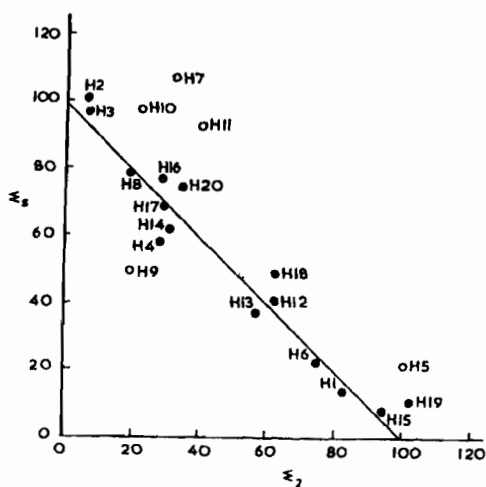
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Figure 4b. Correlated variation in the conformation parameters Σ_s and Σ_2 for cycloheptane derivatives in the chair/twist chair conformations.The equation of the line is: $\Sigma_s = 99.44 - 0.974 \, \Sigma_2$ ($n = 14$, $r^2 = 0.95$). The points ($\circ$) were not included in the least squares fit.

Comparison of C_2 [1], Figure 4a with Figure 4b, and Figure 5a with Figure 5b shows that the conformation parameters C_s and Σ_s and Σ_2 proposed by McPhail and Sim [13] give similar conformational information for these rings in the solid state. Thus, any of these parameters may be used to specify the ring conformation with a possibility of obtaining information on the pseudorotational sequences of the two families.
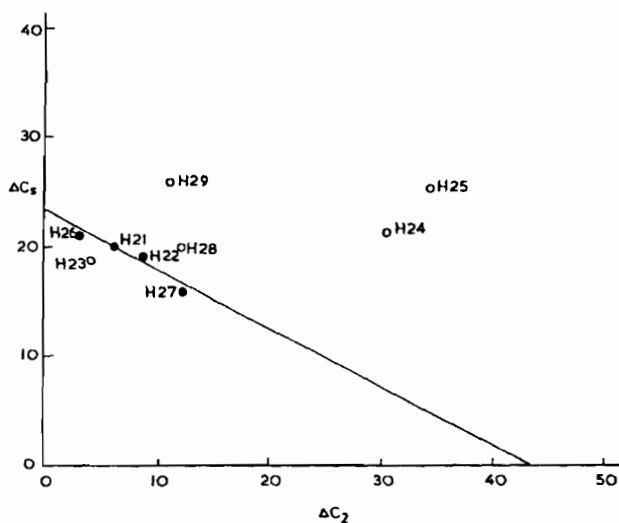

Figure 5a. Correlated variation in principal asymmetry parameters ΔC_s and ΔC_2 for cycloheptane derivatives in the boat and twist boat conformations. The equation of the line is: $\Delta C_s = 23.18 - 0.543\Delta C_2$ ($n = 4$, $r^2 = 0.93$).
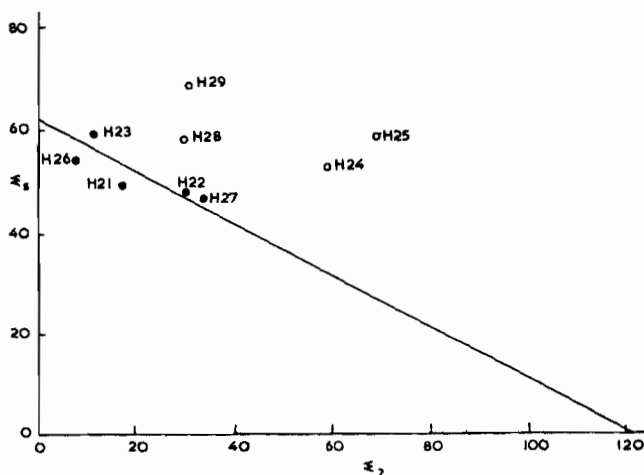
Figure 5b. Correlated variation in the conformation parameters Σ_s and Σ_2 for cycloheptane derivatives in the boat and twist boat conformations. The equation of the line is: $\Sigma_s = 62.00 - 0.516\ \Sigma_2$ (n = 4, r^2 = 0.69).

In Figures 5a and 5b, and Tables 2a and 2b, the relative conformations of rings in the boat/twist boat series are presented. It is evident that the twist boat form is the predominant form, as can be seen from Figures 5a and 5b. There is clearly a clustering of the points towards the twist boat end of the pseudorotation interconversion line, suggesting the much higher stability of the twist boat form over the boat form. The conformations in this sequence seem to be adopted when there is, on the ring derivative, a relatively higher preponderance of 1,4-non-bonded interactions over 1,3-non-bonded interactions (generally in a ratio greater than 2:1, respectively). The derivative H23 appears an exception to this rule. However, the twist boat conformation is probably imposed on this ring by the unusual double cis fusion of two 5-membered rings at the B and D types of bond (Figure 1). In fact, it is only in the twist boat that bonds B and D can have the same fusion stereochemistry in the same derivative (Figure 1). The cycloheptene (H28) fused to only one 5-membered ring adopts the twist boat form unlike the derivatives (H1, H6 and H13) fused to two 5-membered rings which adopt the chair conformation. However, in H28, there is clearly a preponderance of 1,4-non-bonded interactions over 1,3-non-bonded interactions. Only (H24 and H25) in the set studied have the characteristics of the boat form. Even then, the corresponding points in Figures 5a and 5b deviate significantly from the pseudorotation interconversion line. This would suggest that the rings are forced to adopt a particular boat form, possibly by special constraints imposed by the presence of two highly strained cyclopropane rings.

Several of the conformations in the boat/twist boat sequence were inadequately described in the literature. Thus, H21, H22, H28 and H29 were described essentially as distorted boat forms and boat respectively. The sign sequence of the torsion angles in Table 2b, together with Figures 5a and 5b show that these are more of twist boat forms than boat forms. The ring H23 was described as adopting the twist chair conformation, while from this study it is clearly seen to belong to the twist boat form. Examination of the values of the torsion angles in Tables 1b and 2b shows that while the chair and boat forms tend towards the monoplanar form [3], the twist chair tends towards the 1,2-diplanar form and the twist boat towards the 1,3-diplanar form.

The stereochemistry of ring fusion to the cycloheptane derivatives in the molecules studied is summarized for the various conformational forms in Table 3. For the twist chair forms (H4, H7, H8, H9, H10 and H11) the ring is cis fused only at bond A or D. This is in agreement with the proposal by Hendrickson [11]. However, it would appear that an A/D cis/cis fusion is not feasible in the twist chair conformation. Although most of the fusions at bonds B and C are trans as proposed by Hendrickson, a cis fusion at bond C is observed in H17, and the conformation though closer to the twist chair form, shows a significant deviation (ΔC_2 (10) = 12.6) from the ideal form. It is known that in some cases, a multiplicity of substituents or fused rings often, as in cyclohexane systems, causes ring conformation which are less favourable in the parent to become preferred [11]. This may be responsible for the cis fusion at bond C in H17. Similarly, a trans fusion is observed at bond D in H11 instead of the anticipated cis fusion. For solstitalian (H8) and bromodihydroisophotosantonic lactone acetate (H9), Mcphail and Sim [13] proposed that the cis fused 5-membered rings are found at bonds of the A type. It is obvious from Table 3, that these rings are fused at bonds of the D type, as in the related compound euparotin bromoacetate (H7). As can be seen from Table 1a (for H7, H8, and H9), the C_2 symmetry axis passes through the C8 carbon atom and bisects the C1 - C5 bond, which is a bond of the D type.

Table 3.   Stereochemistry of ring fusion* to the cycloheptane derivative.

Chair forms			Twist chair forms			Twist boat forms		
Ring code	Stereochemistry of fusion		Ring code	Stereochemistry of fusion		Ring code	Stereochemistry of fusion	
H1	B/B'	trans/trans	H2	B/B'	trans/trans	H21	B/C'	trans/cis
H5	B/C	trans/(-)[b]	H3	B/B'	trans/trans	H22	B/C'	trans/cis
H6	A/C	trans/(-)	H4	A/C'	cis/trans	H23	B/D	cis/cis
H12	B/B'	cis/cis	H7	B/D	trans/cis	H26	B/C'	trans/cis
H13	A'/C	trans/(-)	H8	B/D	trans/cis	H27	B/C'	trans/cis
H15	B/D	trans/cis	H9	B/D	trans/cis	H28	C'	cis
H18	A/D	trans/cis	H10	A/D	cis/(-)	H29	B/C'	trans/cis
H19	A/D	trans/cis	H11	A/D	cis/trans			
			H14	A/C	(-)/trans			
			H16	B/C	(-)/trans			
			H17	B/C'	trans/cis			
			H20	B	trans			

*Capital letters (A, B, C, and D) refer to bond types at which fusion takes place. [b](-) Refers to the presence of a double bond at ring junction.

From Figure 1c, the preferred fusion stereochemistry for the chair forms is a trans fusion at bonds of the type A, B or C, with cis fusion expected preferably at bond D. Generally, this is in agreement with Table 3. However, it is seen from the table that a B/B' cis fusion is possible as in H12. For the twist boat forms, cis fusion is expected at the A or C bond, while trans fusion is preferred at the B or D bond (Figure 1d). As can be seen also from Table 3, all observed C bond fusions are cis for the twist boat form, and most observed B bond fusions are trans as anticipated. However, an unexpected B/D ∝ -cis/cis fusion is observed in H23. It is not quite obvious why a B/D ∝ -cis/cis fusion pattern is adopted, but probably further strain arising from the presence of the C10 - alkene imposes the observed fusion stereochemistry on this ring.

CONCLUSION

Although the twist chair is estimated by energy calculations to be the most stable conformational form in the chair/twist chair pseudorotational sequence of cycloheptane, there is no high preponderance of the twist forms (eleven) over the chair forms (eight) among the derivatives reported in this study. On the other hand, the boat form is seldom observed in the boat/twist boat sequence, with the twist boat clearly the predominant form in this study. The stereochemistry of fusion of 5-membered rings to cycloheptane derivatives is generally in agreement with molecular energy calculations. However, multiplicity of substituents on the ring may force a different fusion stereochemistry from the expected one in the solid state.

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