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Stereochemistry in Substituted Cyclopentanes: An Approach to the Analysis by Proton NMR

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Abstract: A rationalization is suggested which can help organic chemists in realizing analyses of the relative stereochemistry of substituted cyclopentanes by proton NMR, through the coupling constants between vicinal hydrogens. Some useful generalizations, derived from the dihedral angles found for cyclopentane through a molecular mechanics program, are given.

In the course of our studies on the synthesis of natural products we were frequently faced with the problem of determining the relative stereochemistry of the intermediates. In recent years we prepared a number of intermediates containing a cyclopentane ring and we verified that these rings have certain particularities that bring considerable complexity to the problem when compared to other rings.

In a cyclohexane ring, the hydrogens are either axial or equatorial, forming with their neighbors dihedral angles of 60° or 180°, thus rendering the application of the Karplus equation[1] and some of its variations[2] a straightforward procedure to find out the stereochemistry of the products through the coupling constants between vicinal hydrogens which could be measured in the proton NMR spectrum. The problem can often be reduced to the use of average values for the coupling constants Jaa (axial-axial, ϕ = 180°, J = 8-10 Hz), Jae (axial-equatorial, ϕ = 60°, J = 2-6 Hz) and Jee (equatorial-equatorial, ϕ = 60°, J = 2-6 Hz). Moreover, there are usually only two relevant conformations for the cyclohexane ring (the two possible chair conformations) and often one of the conformations is obviously more stable than the other since a bulk substituent is more stable equatorial than axial.

1.1. relative conformation **a**

1.2. relative conformation **b**

Figure 1. Dihedral angles between a hydrogen and its two neighbors in a cyclohexane ring

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In a cyclopentane ring, however, the problem is far more complex. In most cases there are several possible conformations to the ring and the dihedral angles vary between wide limits. The analysis becomes much more difficult than in the case of the cyclohexane ring.

However, if due care is exercised in recognizing the limits usually implied in generalizations, it is possible to simplify the problem for the organic chemist, frequently interested only in the determination of the relative stereochemistry of a certain isomer.

A number of publications deal with several aspects of this problem.[3] Of particular interest is the paper by Sable and Steyn.[4] We were unable, however, to make out a clear procedure from the existing material and thus decided to seek for an alternative approach.

We commenced by determining the more stable conformations of cyclopentane itself through the computer program GMMX.[5] Two different conformers were found;[6] the dihedral angles between all vicinal hydrogens were determined, as well as the corresponding J *vic* values calculated by the program. These results were organized in **table 1** according to the following procedure:

1. Each line of the table contains the two dihedral angles (and the corresponding J *vic* values) that a certain hydrogen makes with the two hydrogens of the same neighboring carbon atom. Only the counterclockwise direction in the ring was considered, to avoid useless repetitions;
2. All the 20 sets of values were included, and no distinction was made between values from conformer 1 or from conformer 2. In this way, a wider range of possible values for these angles has been covered;
3. The different sets of dihedral angles values were separated in two groups according to the value of the *trans* dihedral angle:

   group a: *trans* dihedral angle above 120°; values shown in section **1.1** of the table;

   group b: *trans* dihedral angle below 120°; values shown in section **1.2** of the table;

   The difference ϕ *trans* - ϕ *cis* is always around 120°, as required by considerations about the bond angles in an sp^3-hybridized carbon atom. The reason for the negative sign of ϕ *cis* in section **1.2** will become evident in the subsequent discussion.
4. In **group a** the lines were ordered according to increasing values of the angles, while in **group b** they are in the reversed order. In this way the absolute values of ϕ *cis* on each line are approximately the same on each section of the table.

First of all, we will consider the reasons for the separation in groups **a** and **b**. *A certain hydrogen* can have both hydrogens of the neighboring carbon atom on the same side in a Newman projection, as in **figure 2.1**, or each hydrogen of the neighboring carbon atom on each side, as in **figure 2.2**. In the first case the *reference* hydrogen is, in relation to its two considered neighbors, in a position that is similar to an *axial* hydrogen in a cyclohexane ring,[9] and in the second case it is in a position similar to an *equatorial* hydrogen. *Group* **a** corresponds to a *relative conformation* **a**, where the reference hydrogen is on the same side of each of its two neighbors, like an axial hydrogen (**figure 2.1**), and *group* **b** corresponds to a *relative conformation* **b**, where the reference hydrogen is between its two neighbors, like an equatorial hydrogen (**figure 2.2**). The expression *relative conformation* is being used here to express the position of a certain hydrogen in relation to two of its neighbors, and should not be confused with the conformation of the ring as a whole.

Table 1

1.1. group a

(relative conformation **a**)

line	angle		Jvic		rel. conf.
	ϕ *cis*	ϕ *trans*	J *cis*	J *trans*	
1	+6	+126	11.526	5.207	**a1**
2	+14	+133	10.954	6.797	
3	+17	+138	10.566	7.790	
4	+25	+144	9.499	9.145	
5	+33	+154	8.154	10.953	**a2**
6	+39	+158	6.951	11.649	
7	+40	+161	6.866	11.987	
8	+44	+164	5.933	12.349	
9	+46	+168	5.571	12.669	
10	+47	+168	5.334	12.729	

1.2. group b

(relative conformation **b**)

line	angle		Jvic		rel. conf.
	ϕ *cis*	ϕ *trans*	J *cis*	J *trans*	
1	-6	+113	11.507	2.634	**b1**
2	-13	+105	11.033	1.551	
3	-19	+101	10.423	1.039	
4	-24	+94	9.726	0.552	
5	-35	+85	7.796	0.354	**b2**
6	-37	+81	7.337	0.463	
7	-41	+79	6.486	0.571	
8	-43	+76	6.268	0.743	
9	-47	+74	5.404	0.969	
10	-47	+73	5.377	1.023	

2.1. relative conformation **a**

2.2. relative conformation **b**

Figure 2. Examples of dihedral angles between a hydrogen and its two neighbors in a cyclopentane ring

Figure 2 shows only one pair of angles for each case. If we consider all possible values of **table 1**, each one of the relative conformations corresponds to a wide range of values (ϕ *cis* varying from 6 to 47°), as can be seen in **figure 3**:


3.1. relative conformation **a** 3.2. relative conformation **b**

Figure 3. Range of possible angles for relative conformations **a** and **b**

The corresponding J values also spread over a wide range. It is thus convenient to separate each relative conformation in two, as already shown in **table 1**. The point chosen to make the separation is strongly suggested, in natural fashion, by the J values themselves.[10]

Conclusions

We think that the points below can be very useful in determining the relative stereochemistry of a substituted cyclopentane.

1. In **table 1** it can be seen that J *cis* is never below 5 Hz, while J *trans* varies from 0.3 to 13 Hz. When finding in a proton NMR spectrum a J *vic* value below 5 Hz, to assume this to be a J *trans*, subject to further verification, can be a valuable starting point.

This seems to be a particularly useful tool. We have examined J *vic* values of 30 different substituted cyclopentanes, most of them synthesized in our laboratory, and a few from the literature.[11] A total number of 38 values for J *cis* and 38 values for J *trans* were examined, and no significant exception to this rule was found, as can be seen in the graphs of **Figure 4**. Several J *cis* and J *trans* values given by Sable and Steyn[4] also confirm this as a useful rule; however, the reader is urged to read this paper, and also some related papers,[4,12] to become aware of the effect produced by strained systems and by the electronegativity of substituents.

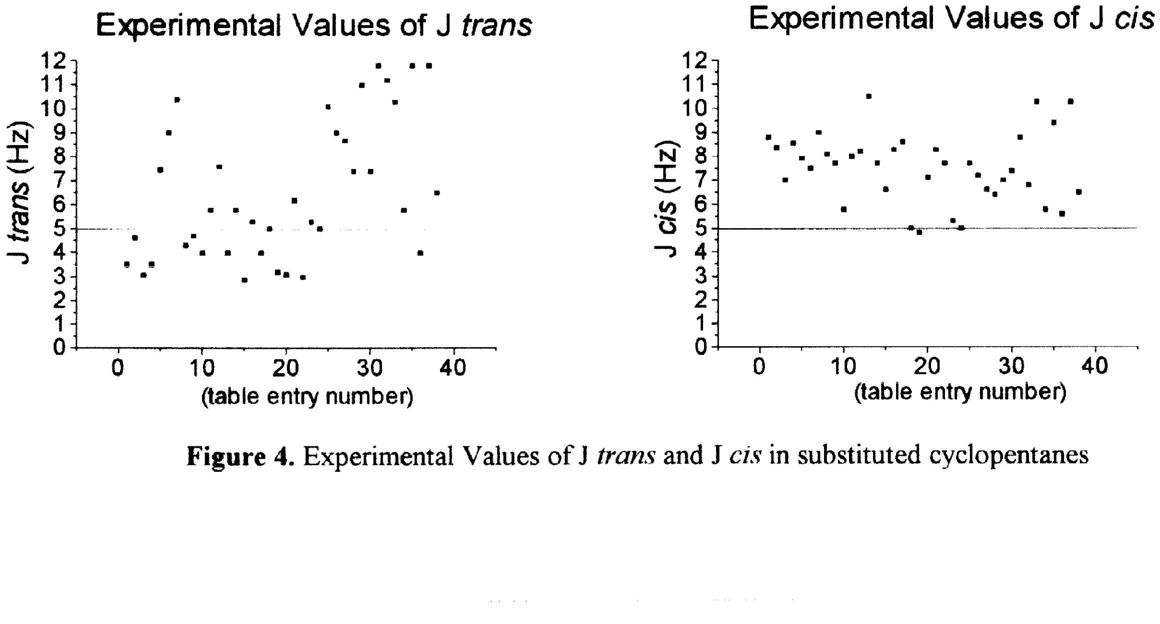


Figure 4. Experimental Values of J *trans* and J *cis* in substituted cyclopentanes

It seems that the main limitation to the strength of this rule is that J *vic* values below 5 Hz are relatively uncommon, even for J *trans*.

2. While in a cyclohexane ring hydrogens are either axial or equatorial (and thus have only two possible relative conformations in relation to its neighbors), in a cyclopentane ring it is convenient to consider *four* possibilities, each one representing a relatively narrow range of dihedral angles and J values.

Relative Conformation a1 (figure 5.1): the reference hydrogen is axial-like and the dihedral angle with its *cis* neighbor is small (6 to 25°); J *cis* is between 9 and 12 Hz, while J *trans* is in the range 5-9 Hz. In the limit between this and the following relative conformation (**a2**), J *cis* ≈ J *trans* ≈ 9 Hz.

Relative Conformation a2 (figure 5.2): the reference hydrogen is also axial-like, but the dihedral angle with its *cis* neighbor is larger (30 to 47°); J *cis* is now in the range 5-8 Hz, while J *trans* is larger (10-13 Hz). Obviously, in the limit between this relative conformation and the preceding one (**a1**), J *cis* trends to equal J *trans* (*ca.* 9 Hz).

Relative Conformation b1 (figure 5.3): here the reference hydrogen is equatorial-like and the dihedral angle with its *cis* neighbor is small (6 to 25°). J *cis* and J *trans* have opposite values in the range of possible variations: J *cis* is between 9 and 12 Hz, and J *trans* is between 0.5 and 3 Hz.

Relative Conformation b2 (figure 5.4): as in the previous case, the reference hydrogen is equatorial-like, but the dihedral angle with its *cis* neighbor is larger (30 to 47°). J *cis* drops to the range 5-8 Hz, while J *trans* keeps up in low values (0-1Hz).

5.1. Relative conformation **a1**

5.2. Relative conformation **a2**

5.3. Relative conformation **b1**

5.4. Relative conformation **b2**

Figure 5. Relative conformations of a reference hydrogen in relation to its two neighbors in a 5-membered ring

3. Another remarkable conclusion that can be drawn from **table 1** is that J *cis* is almost always larger than J *trans*. The only inversion occurs in the case of the relative conformation **a2**. The importance of this point can be realized by examining an example in which J *cis* = J *trans* = 5 Hz. One can take as highly probable that in this case there are two stable conformers of the 5-membered ring: in one of them the considered hydrogens have the relative conformation **a2**, and in the other, the relative conformation **b2** (see examples).

Nowadays one of the fastest procedures to determine the relative stereochemistry of a compound from its proton NMR plain spectrum is to compare the J *vic* values from the spectrum to the calculated values (obtainable from molecular mechanics programs like GMMX, which takes into account the several possible conformers and produces average values according to Boltzmann distribution law).

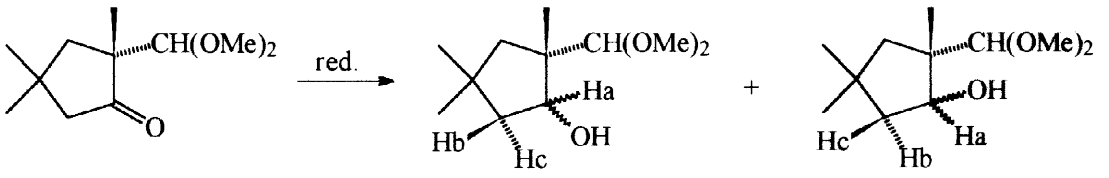
As shown by the following examples, however, the precision limitations of the calculations can bring considerable uncertainty to the conclusions. In cases where a cyclopentane ring is the subject in question, the above considerations can help the chemist to detect and correct mistakes, leading to more reliable results.

Examples

Two examples will be given to show how these rules can be applied to find the relative stereochemistry of isomeric substituted cyclopentanes.

Example 1

Compounds **1.1** and **1.2** were obtained by reduction of the corresponding ketone.[13, 14] They were, clearly, stereoisomers.



1.1
Ha: 3.92δ (t, 1H, J=5Hz)

1.2
Ha: 4.04δ (dd, 1H, J_1=7.7Hz, J_2=10.1Hz)

In this case, one of the asymmetric centers bears no hydrogen atoms; **Ha**, however, is easy to identify and Jab and Jac could be measured easily:

Experimental values

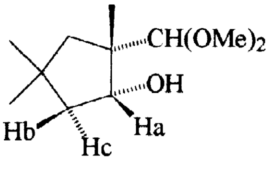
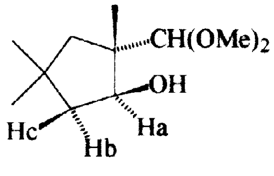
	1.1	**1.2**
Jab	5.0 Hz	7.7 Hz
Jac	5.0 Hz	10.1 Hz

By the J values shown in **figure 5** one should conclude that isomer **1.1** has stable conformers in which the relative conformation of **Ha**, **Hb** and **Hc** are **a2** and **b2**; this is the only combination of relative conformations that can give 5 Hz for both Jab and Jac.

Isomer **1.2**, on the other hand, has stable conformers in which the relative conformations of **Ha**, **Hb** and **Hc** are **a1** and/or **a2**; relative conformations **b1** and **b2** cannot give important contribution, because J *trans* would then become smaller.

Feeding GMMX with the two structures **1** ***cis*** and **1** ***trans***, the following results were obtained:

Table 2

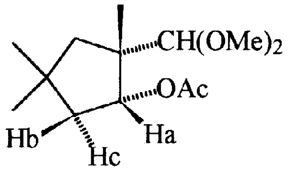
	 **1** ***cis***				 **1** ***trans***	
Ring conformer	1	2	3	4	1	2
Population (%)	51.9	45.7	1.4	0.9	68.3	31.7
Energy (kcal/mole)	29.2	29.3	31.4	31.7	27.1	27.5
Dihedral angle Ha-Hb	-38	-37	37	42	41	42
Jab (*cis*)	5.0	5.0	7.6	6.8	6.9	6.8
Dihedral angle Ha-Hc	79	79	157	160	160	160
Jac (*trans*)	1.7	1.7	9.3	9.8	9.8	9.9
Relative conformation Ha-Hb-Hc (see **table 1**)	**b2**	**b2**	**a2**	**a2**	**a2**	**a2**
Boltzmann averaged Jab (*cis*)	5.1				6.9	
Boltzmann averaged Jac (*trans*)	1.9				9.8	

It is clear that **1** ***cis*** shows the relative conformations **b2** and **a2**, exactly as foreseen for isomer **1.1**, while **1** ***trans*** shows only conformation **a2**, as foreseen for isomer **1.2**. **1.1** is, then, the *cis* isomer and **1.2** is the *trans* isomer. This conclusion was fully confirmed by NOE experiments[13, 14] and by the following **example 2**.

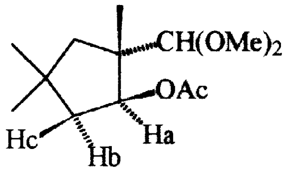
It should be remarked that in this case, as it happens in a number of cases, direct comparison of experimental J values to Boltzmann averaged calculated values is not very much conclusive; the value for calculated J *trans* (1.9 Hz) is too far from the experimental (5.0 Hz), which brings uncertainty to conclusions. By examining **table 2**, it is possible to see that this large difference in averaged J values could be the result of a very small error in the calculated values of energy of conformers: an error below ±4% in energy calculations could result in a difference of Boltzmann averaged J *trans* value of 3 Hz, which could bring the calculated value of 1.9 Hz to match the experimental (5.0 Hz), without large change in calculated J *cis* value. It seems that the molecular mechanics programs can find the stable conformations, angles and J values with a high degree of confidence; Boltzmann averaged J values, however, are not as much reliable because small errors in energy calculations can result in large differences of population of the several conformers and, consequently, in the averaged J values in certain cases.

Example 2

Compounds **2.1** and **2.2** are the acetates corresponding to **1.1** and **1.2**:



2.1



2.2

In this case the Boltzmann averaged J values match quite well the experimental values, so it is not really necessary to proceed a detailed analysis of the conformations as in **example 1**:

Experimental values

	2.1	**2.2**
Jab	4.8 Hz	7.2 Hz
Jac	3.2 Hz	9.0 Hz

Calculated values

	2.1	**2.2**
Jab	5.4 Hz	6.5 Hz
Jac	3.2 Hz	8.7 Hz

However, this example has many differences as compared to the previous case, and some more detailed considerations can be illustrative.

One of the experimental J values for compound **2.1**, 3.2 Hz, is well below 5 Hz and should, thus, correspond to a J *trans* value (according to "rule" number 1); the other value (4.8 Hz) would then be a J *cis*, which leads to the conclusion that the main conformers of the ring should be those corresponding to relative conformations (for **Ha**, **Hb**, **Hc**) **a2** and **b2** (the only conformations where J *cis* drops to ~ 5 Hz), possibly with predominance of **b2** (to bring J *trans* to a value below the arithmetic mean between 10-13 and 0-1 Hz).

Table 3 shows calculated values for compound **2.1**, confirming the above argumentation.

Table 3

Ring conformer	Population (%)	Energy	Dihedral angle Ha-Hb	Jab (*cis*)	Dihedral angle Ha-Hc	Jac (*trans*)	Relative conformation Ha-Hb-Hc
1	48.0	29.0	-38	4.9	78	1.7	**b2**
2	10.7	29.9	40	7.1	160	9.8	**a2**
3	8.9	30.0	-38	5.0	80	1.6	**b2**
4	6.7	30.1	38	7.3	158	9.6	**a2**
5	6.2	30.2	-37	5.1	79	1.6	**b2**
6	6.0	30.2	-35	5.3	81	1.6	**b2**
7	3.7	30.5	-37	5.1	79	1.6	**b2**
8	3.4	30.6	-37	5.1	79	1.6	**b2**
9	3.0	30.6	-37	5.1	80	1.6	**b2**
10	1.8	30.9	-37	5.0	79	1.7	**b2**
11	1.4	31.1	40	7.0	160	9.9	**a2**
12	0.5	31.7	-38	4.9	78	1.7	**b2**

Isomer **2.2**, with a relatively high value for J *trans* (regardless any previous considerations, J *trans* cannot be below 7.2 Hz), has main relative conformations **a1** and/or **a2** with only minor (if any) contribution of relative conformations **b1** and/or **b2**. An interesting point is that if 7.2 Hz is assumed to be a J *trans*, then **a1/b1** would be more likely to explain the value 9.0 Hz for a supposed J *cis*; on the contrary, if 9.0 Hz is assumed to be a J *trans*, the relative conformations that would best explain the supposed J *cis* value of 7.2 Hz would be **a2/b2**.

Again, the calculated values for compound **2.2**, summarized in **table 4**, are in accordance with the considerations.

Table 4

Ring conformer	Population (%)	Energy	Dihedral angle Ha-Hb	Jab (*cis*)	Dihedral angle Ha-Hc	Jac (*trans*)	Relative conformation Ha-Hb-Hc
1	30.2	28.8	42	6.8	160	9.9	**a2**
2	13.3	29.2	42	6.7	161	9.9	**a2**
3	10.6	29.8	42	6.8	160	9.8	**a2**
4	6.4	29.7	-38	4.8	78	1.7	**b2**
5	5.9	29.7	43	6.7	162	10.1	**a2**
6	5.5	29.8	40	7.0	160	9.8	**a2**
7	4.1	29.9	40	7.1	158	9.5	**a2**
8	2.6	30.2	43	6.7	163	10.1	**a2**
9	2.5	30.2	43	6.7	163	10.1	**a2**
10	2.5	30.2	43	6.7	162	10.1	**a2**
11	2.4	30.3	-39	4.8	77	1.8	**b2**
12	2.2	30.3	42	6.8	162	10.1	**a2**
13	2.0	30.4	43	6.6	162	10.1	**a2**
14	1.9	30.4	42	6.7	161	9.9	**a2**
15	1.8	30.4	43	6.6	162	10.0	**a2**
16	1.1	30.7	-39	4.8	78	1.8	**b2**
17	1.0	30.8	-35	5.3	82	1.4	**b2**
18	1.0	30.8	-35	5.4	83	1.4	**b2**
19	0.7	31.0	-37	5.0	79	1.6	**b2**
20	0.6	31.1	-35	5.4	83	1.4	**b2**
21	0.5	31.2	-30	6.2	88	1.2	**b2**
22	0.4	31.3	-36	5.2	80	1.6	**b2**
23	0.4	31.4	-35	5.3	82	1.4	**b2**
24	0.4	31.4	-33	5.7	85	1.3	**b2**

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5. GMMX, version 1.5, Serena Software, P. O. Box 3076, Bloomington, IN 474-2-3076.
6. The conformation of cyclopentane was studied by several authors;[8] conclusions that an envelope, half-chair and planar conformations were or not possible have been drawn, as well as conclusions about pseudorotation.[7] We should remark that these conclusions have no direct connection with the problem studied in this paper, except maybe for the fact that the half-chair is generally regarded as a main possible conformation. Our aim in this paper is to determine the *range* of possible values for the dihedral angles between vicinal hydrogens in a cyclopentane ring, the corresponding J *vic* values, and provide a suggestion for the rationalization of the wide range through some simple rules. As the half-chair conformation already contains a wide range of possible dihedral angles, considerations about the existence or not of other conformations would have little effect. We have determined the conformations considered in this paper by using the default values of the GMMX program; we have also verified that the results obtained depend on the particular conformation (structure) which is fed to the program. The differences, however, had no effect in the conclusions drawn here, so this aspect was ignored in favor of simplicity.
7. Under a practical point of view, pseudorotation is a process by which a conformation of a cyclopentane is transformed into another conformation through rotation about σ bonds. As far as all stable conformers are being taken into account, the existence or not of pseudorotation has no effect in average dihedral angles or in average J values. We should, however, note that the GMMX program found two conformers for cyclopentane as a result of the symmetry of the molecule. One should understand that each conformer, in fact, represents five conformers (the five possible conformers that can be obtained by keeping the structure and just changing the numbering of the carbon atoms); if one intends to calculate the J values for the cyclopentane itself, all those conformations should be taken into account. On the other hand, considering that this paper deals with *relative stereochemistry* in substituted cyclopentanes, it becomes clear that the compounds in question are not symmetrical, and this problem has no longer any meaning: each possible conformer, obtained

through pseudorotation or not, will be a different conformer, and should be found and taken into account by the molecular mechanics program.

8. For example: Saebф, S.; Cordell, F. R.; Boggs, J. E. *J. Mol. Structure* **1983**, *104*, 221-232, and references cited therein; Esteban, A. L.; Galache, M. P.; Diez, E.; Altona, C.; Smits, G. F. *J. Mol. Structure* **1986**, *142*, 379-382.
9. There is a remarkable difference between cyclohexane and cyclopentane rings in this respect: in cyclohexane an axial hydrogen has its neighbors both on the same side, irrespective of the neighboring carbon atom chosen to compare. One can choose the hydrogens on the carbon atom on the right side (clockwise in the ring) or in the left side of the carbon atom bearing the reference hydrogen, and the result will be the same (**figure 6**):

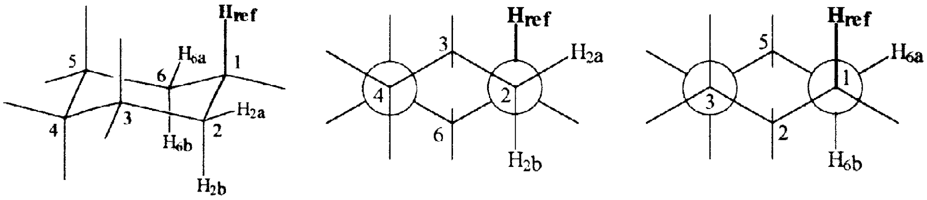
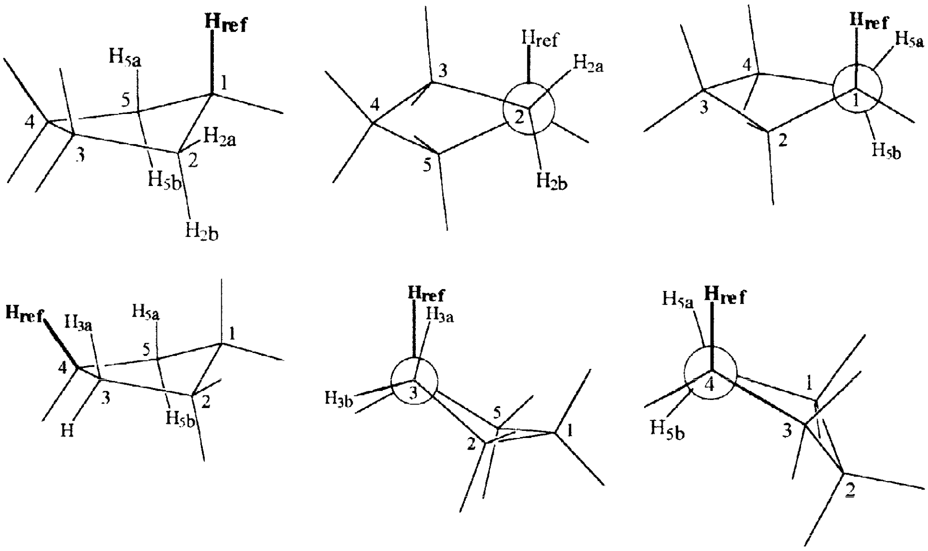


Figure 6

In cyclopentane this is true only for four of the ring carbon atoms. There is one carbon atom bearing a reference hydrogen which will belong to the relative conformation **a** when compared to two of its neighbors and will belong to the relative conformation **b** when compared to the other two neighbors (**figure 7**):



The example is for reference hydrogen in carbon atom 1, but the situation is similar for the reference hydrogen in carbon atoms 2,3 or 5.

Unique case (reference hydrogen in carbon atom 4).

Figure 7

It is important to reaffirm, however, that this occurs only with the hydrogens of *one* of the ring carbon atoms (in each conformer of the cyclopentane). For the other *four* carbon atoms the situation is similar to the cyclohexane, *i.e.*, a hydrogen of relative conformation **a** in relation to its neighbors on the right side has also a relative conformation **a** in relation to its neighbors on the left side.

10. In **section 1.1** of **table 1**, J *cis* is larger than J *trans* in the first entries (corresponding to low values of ϕ *cis*) but finally J *cis* becomes smaller than J *trans*. It is natural to choose the inversion point to separate the two relative conformations. In **section 1.2** of **table 1**, J *trans* decreases at first, then increases; again, it is natural to choose the minimum as the appropriate point for separate (this occurs around ϕ *trans* = 90°). The graphs of **figure 8** show the main points of the above argumentation in a more eloquent fashion.

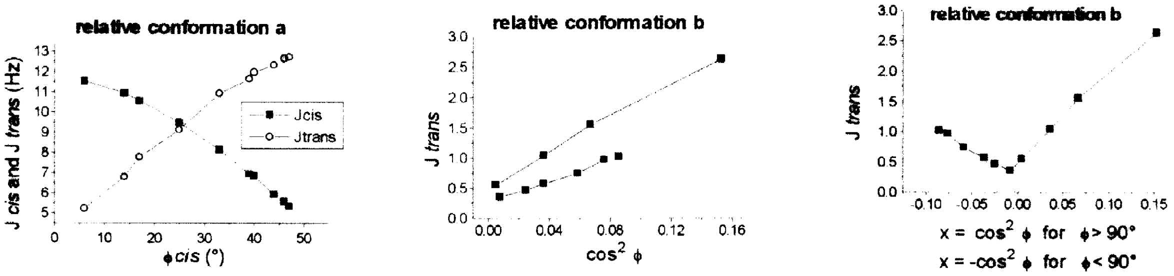


Figure 8

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