Tetrahedron Vol. 48, No. 35, pp. 7131-7144, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

A Revised Nomenclature for the Ring Conformation and a Note on the Conformational Distance in Cyclododecane

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(*Received in Japan* 6 *April* 1992)

Key Words: ring nomenclature; conformational space search; conformational distance; cycloalkane; molecular mechanics

Abstract: *The need for keeping track of a large number of unique conformers of medium to large cycloalkanes, which are recently being 'discovered' by computational conformational space search, prompted us to improve the nomenclature for cycloalkanes conformation and to re-establish one-to-one correspondence between the name and structure. A revision of the Dale nomenclature is proposed which is capable of distinguishing all of the significant energy minima produced so far by computation. The nomenclature can also be used advantageously to interpret the segmental characters of torsion angle patterns of a ring backbone and to assess 'closeness' among conformations in the conformational space. In this context, Saunders' conformational distances have been evaluated for a few conformers and saddle points of cyclododecane.*

INTRODUCTION

A large number of new conformational isomers have been 'discovered' and will continue to be so for medium to larger cycloalkanes as more and more new algorithms are developed in recent years for computational conformational space search. [1] One problem that arose from the wide-spread computer search is that we must deal with a number of conformers differing only marginally in energy and structure. However, the existing two systematic nomenclatures for cycloalkanes, namely the labeling scheme by Hendrickson [2] and the dividing notation by Dale, [3] are found insufficient to accommodate all the new conformers.

In the Hendrickson scheme, every cyclic conformer is premised to have at least one C_2 axis or plane of symmetry, so that all the conformers are basically categorized into twisted or non-twisted groups. Then, taking a horizontal view of the structure, one composes a name by combining chair (C) and boat (B) labels. A character T is attached at the top of name if the structure belongs to twisted group. This scheme is, however, suitable only to 5- to 8-membered cycloalkanes. Recently, Raber and co-workers [4] proposed to add a new

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label S to denote skewed form when they expanded this scheme to cyclononane. In addition to the ambiguous distinction between twist and skew (for example, cyclononane conformers labeled as SCC and SBB apparently have a C_2 axis and those labeled as TCTC and SBC have no symmetry elements), this scheme totally fails for larger cycloalkanes.

Dale's method regards a cyclic structure as a polygon composed of corners and sides, and aligns the length of side (number of bonds) in series to give an integer. This method is more generally applicable and appropriate to produce top-view drawings of conformations. Symmetric conformations produce 'symmetric' integer. Dale defined a corner by two consecutive gauche bonds. When the gauche bonds are of the same sign (GG and G'G'), the corner is called 'genuine', while it is called 'pseudo' when the signs are opposite (GG' and G'G).[5] Dale first used only the genuine corner to divide a side, but later Trotter and co-workers[6] proposed to include pseudo corner as the side divider as well, and mark the side length with a prime (') when the side is flanked by at least one pseudo corner. However, in the Trotter's modification, it is difficult to know where and how many pseudo corners exist on a primed side. Bernardinelli and Gerdil[7] defined a 'fused' corner for a gauche bond flanked by anti bonds on both sides (AGA). They did not consider to use pseudo corner as the side divider.

In spite of these modifications, none of them covers all the patterns of bond rotation sequences along the endocyclic bonds as shown in Table 1. In addition to this disadvantage, two more critical problems can be identified in the original and modified Dale nomenclatures: (1) the frequent occurrence of identical names for different energy minima, and (2) the inability to regenerate the structure from the name.

In this paper, we propose a revised Dale nomenclature applicable to virtually all of the significant conformers of medium to large cycloalkanes. Merits of previous nomenclatures are retained and the one-to-one correspondence between energy minima and its name has been achieved. This nomenclature has been used in our laboratory for the past few years with no serious problem having been found. Advantages and limitations will be illustrated below by using cyclododecane and cycloheptadecane.

Table 1. Dale-Type Representations of Dihedral Angle Patterns

Pattern	Dale[3]	Bernardinelli[7]	Trotter[6]	Present study
-GAGGAG-	33	33	33	33
-GAGG'GAG-	313	313	-	3'1'3
-GAGGG'G'AG-	323	323	323	323
-GAGAG-	-	3*3	-	3*3
-GAGG'AG-	-	-	3'3'	3'3
-GAGGGAG-	-	-	-	313
-GG'GG'-	-	-	-	-

DEFINITIONS

First we note that the familiar anti/gauche notations, which are the basis of our nomenclature, have been rather subjectively classified. For purely technical reasons, the anti and gauche angles are defined, rigorously albeit temporarily, as follows:

$0 \geq \omega > 120$	G : positive gauche
$0 > \omega > -120$	G' : negative gauche
$120 \leq \lvert\omega\rvert \leq 180$	A : anti

The corners, division marks and sides in the Dale nomenclature are re-defined as follows:

1. A gauche bond itself or the meeting point of two contiguous gauche bonds is the corner.
1-1. Two contiguous gauche bonds of the same sign comprise a 'genuine corner' and is not given any division mark.
1-2. Two contiguous gauche bonds of opposite sign flanked by at least one anti bond is the 'pseudo corner' and marked with a prime (').
1-3. A gauche bond flanked by two anti bonds forms a 'fused corner', which is marked with an asterisk (*). This gauche bond is counted twice when determining the lengths of both sides.

Provision 1-2 for the presence of at least one anti bond for the pseudo corner is required in order to treat the partial sequence GGG'G': the central GG' portion of this sequence should not be defined as a pseudo corner but as a side of length 2. Otherwise, this part will become two sides, each having a length 1, causing the name unnecessarily long.

2. Sides are comprised of anti bonds.
2-1. The length of a side is represented by an integer equal to the number of bonds between both corners. In principle, a side consists of several anti bonds and two gauche bonds at both ends.
2-2. Exceptions are the sides of lengths 1 and 2, which do not contain anti bond as shown below.

	Side pattern	
Side length	*syn-end* type	*anti-end* type
1	G, G'	-
2	GG', G'G	-
3	GAG, G'AG'	GAG', G'AG
4	GAAG', G'AAG	GAAG, G'AAG'
5	GAAAG, G'AAAG'	GAAAG', G'AAAG
:	:	:

Note that there are two types of sides; one is the '*syn-end*' pattern wherein the terminal gauche bonds direct themselves to the same directions from a plane defined by anti bonds, such as GAG, GAAG' or GAAAG. This type of side is naturally favored in cyclic structures and actually can be seen must often. On the other hand, the other type wherein the two gauche termini point to opposite directions each other from the average A_n plane, such as GAG', GAAG or GAAAG', rarely appears in cyclic structures. Conformations containing this pattern, especially in the sides of odd lengths, is unstable. We call this unfavorable type as the '*anti-end*', and actually this pattern is forbidden in *small* cyclic molecules. Conformers containing the *anti-end* pattern sometimes emerge in larger cycloalkanes.

2-3. The length of a side with the *anti-end* pattern is underlined.

This last definition can be only provisional because of some technical complications. The naming process is not seriously perturbed if the rule 2-3 is neglected. Nevertheless, inclusion of this rule ensures complete decoding process from the conformer's name even in highly flexible cyclic structures containing either type of sides.

The representation 3'1'3 of a pattern GAGG'GAG shown in Table 1 is notably different from the previous expression 313. According to Dale's original scheme, 313 should have corresponded to the short helical structure GAGGGAG. However, he considered this partial structure energetically so unfavorable that it rarely appears, and used this nomenclature (313) to the pattern GAGG'GAG, which was seen often in mediume rings. Contrary to his intent, the short helix pattern GAGGGAG is stable and does show up often in low-energy forms of large rings (see DISCUSSION). For example, the global minimum of cycloheptadecane contains this segment pattern (see EXAMPLES). Hence it is definitely necessary to clearly distinguish 313 (GAGGGAG) from 3'1'3 (GAGG'GAG).

The only pattern that our nomenclature cannot properly process is GG'GG' (Tab. 1). While this pattern often occurs in smaller rings like chair cyclohexane, any conformation of medium to large cycloalkanes containing this pattern must be so strained that they cannot be significant (*vide infra*).

PRACTICE

In naming a cyclic conformation, the ring is divided into sides at every gauche bond, the division point marked according to the rules given above, and the series of characters consisting of integers, primes and asterisks are permuted so that the smallest integer series results. In deciding the last series, corner is preferred to pseudo corner and the latter to fused corner. Finally, the series is bracketed with [ ] to complete a name. Note that the size of ring is equal to the sum of the integers subtracted by the number of asterisks if any.

Figure 1 demonstrates how one of the cyclododecane conformers (No. 5 in Tab. 2 below) is named by the original Dale nomenclature and its three modifications including ours. The original nomenclature regards the right half of this form a side of length 9, hence failed to convey any information on the bond rotation indices on this side. The Bernardinelli procedure may at first sight appear acceptable, but actually contains two problems. First, it gave a different rotation index (for the 93° bond) due to contradicting definitions between theirs and ours. Second, this nomenclature has no provision for the pseudo corner. A critical problem in the Trotter modification is that the number of primes in the name does not agree with that of pseudo corners. The suitability of our modification is best illustrated by its ability to regenerate the unique sequence of bond rotation indices back from the nomenclature. Thus, for the case of [333'4*] given in Fig. 1, the process is as follows. We begin with the first side of length 3.

i) Start with G and construct the side of length 3.	GAG
ii) The second side of length 3 is connected with the first through a genuine corner.	GAGGAG
iii) Same as above for the third side.	GAGGAGGAG
iv) The fourth side of length 4 is connected with the third through a pseudo corner. The default pattern of the side of length 4 has the gauche of opposite sign at the other end.	GAGGAGGAGG'AAG
v) The last corner is a fused one and connected to the first side. Remove the redundant G.	GAGGAGGAGG'AA(G)

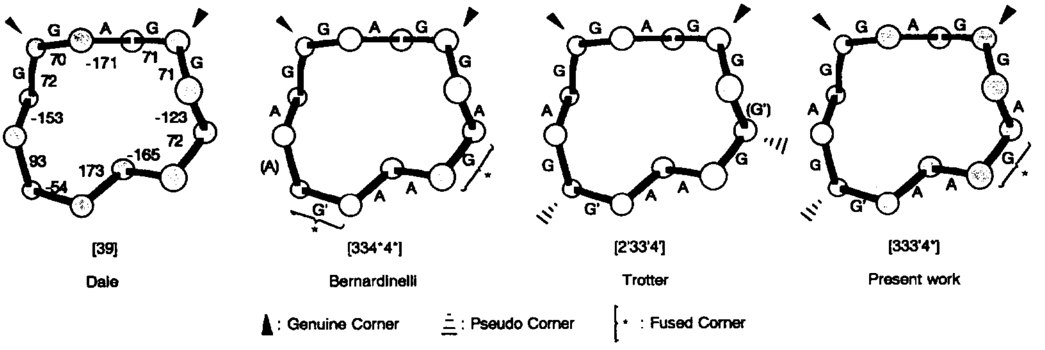

Fig.1 Application of the original Dale nomenclature and its three modifications including ours to the 5th most stable conformer of cyclododecane. Three types of corners as well as bond rotation indices (A, G and G') that can be deduced back from the nomenclature are given on the bonds.

EXAMPLES

Cyclododecane

Table 2 lists conformers of cyclododecane within 8 kcal/mol from the global energy-minimum [3333] conformer, [8-10] as generated by CONFLEX3 program based on 'down-stream and filling-up' algorithm [11] and using MM2 [12] as the minimizer. These 46 conformers completely agree with those recently generated by Saunders who used his stochastic search algorithm in the most exhaustive manner. [13] Note that all of these are distinguishable by our nomenclature, except for two minor cases, which turned out to be chemically insignificant as mentioned below.

Exceptions are Nos. 4/6 (bold-faced in Tab. 2), and Nos. 10/18 (also bold-faced), wherein the conformers are given the same name, [2343] and [333'3'], respectively. Within these pairs, torsional isomerism does exists computationally but is practically meaningless, as shown in detail in Table 3. We first note that, in terms of dihedral angles, these pairs are so close that acquires the same name as well as bond rotation indices. They are identified as different conformers because they have no imaginary frequency and the energy differences are greater than the identity criteria (*ca.* 0.01 kcal/mol). According to MM2 analysis, however, they convert into each other over very low barriers. Fig. 2(a) shows how the [2343] conformers, No. 4 and No. 6, interconvert by slight rotation of C1-C2 and C8-C9 bonds across the chiral saddle point (one imaginary frequency) lying 0.43 kcal/mol above No.4 and 0.04 kcal/mol above No. 6 conformer. Similarly, Fig. 2(b) shows the interconversion pathway between the [333'3'] conformers, No.10 and No. 18. The saddle point was found by driving C1-C2 and C10-C11 bonds to lie 1.16 kcal/mol above No.10 and 0.01 kcal/mol above No.18 conformer.

In order to evaluate how close these stationary points are on their torsional energy surfaces, we find that Saunders' *conformational distance* [13] is a convenient index. Conformational distance is defined as follows:

Table 2. Modified Dale Nomenclature for Low-Energy Conformers of Cyclododecane

No.	Nomenclature [a]	MM2 Steric E (kcal/mol)	Rel. E (kcal/mol)
1	[3333][b]	20.61	0.00
2	[2334][c]	21.68	1.07
3	[1'434']	22.35	1.74
4	**[2343]**[d]	**23.08**	**2.47**
5	[333'4*]	23.22	2.61
6	**[2343]**	**23.48**	**2.87**
7	[13'31'4']	23.91	3.30
8	[133'1'4']	24.05	3.44
9	[1'344']	24.11	3.50
10	**[333'3']**	**24.48**	**3.87**
11	[23'4'3]	25.13	4.52
12	[2424][d]	25.23	4.62
13	[23'3'4]	25.32	4.71
14	[343*4*]	25.39	4.78
15	[143'4']	25.43	4.82
16	[13'44']	25.44	4.83
17	[1331'4']	25.57	4.96
18	**[333'3']**	**25.63**	**5.02**
19	[1353]	26.07	5.46
20	[33'33']	26.12	5.51
21	[1'425']	26.17	5.56
22	[1323'3]	26.47	5.86
23	[2325]	26.67	6.06
24	[2232'3]	26.69	6.08
25	[1'323*4']	26.71	6.10
26	[22323']	26.73	6.12
27	[1'313'4']	26.95	6.34
28	[13'233]	26.99	6.38
29	[1'4'3'4']	27.00	6.39
30	[4'4'4']	27.09	6.48
31	[2244]	27.11	6.50
32	[44'$\underline{4}$']	27.12	6.51
33	[2323*3]	27.19	6.58
34	[1'5'1'5']	27.30	6.69
35	[23'34']	27.31	6.70
36	[2'33'4]	27.35	6.74
37	[2'3'34]	27.41	6.80
38	[1'33*33']	27.57	6.96
39	[1'32'3'3]	27.58	6.97
40	[23'34']	28.06	7.45
41	[13*33*4']	28.15	7.54
42	[1'4'4*4']	28.27	7.66
43	[1'4'25]	28.35	7.74
44	[13'4'$\underline{4}$']	28.37	7.76
45	[1233*$\underline{4}$']	28.49	7.88
46	[1344]	28.60	7.99

[a] A side with an *anti-end* pattern is underlined. [b] Refs. 8-10. [c] Refs. 9, 10. [d] Ref. 9.

$$\sqrt{\sum_{i=1}^{N} (\omega_i^{A} - \omega_i^{B})^2 / N}$$

where ω_i^A and ω_i^B are the i-th corresponding dihedral angles for the pair of stationary points under comparison, A and B, respectively, and N is the total number of dihedral angles on the ring. According to this definition, the saddle point for [2343] (Fig. 2a) is separated by 9.8° from No. 4 and 4.1° from No. 6 conformer, respectively. The sum of these distances (13.9°) almost agrees with the distance between No. 4 and No. 6 (13.6°, see conformational distance of Tab. 3), indicating that the saddle point is situated almost exactly along the vector connecting these conformers in the conformational space. Similarly, the saddle point for [333'3'] can be considered to be away from No. 10 by 16.5° and from No. 18 by 3.1°. Again, the sum (19.6°) is very close the distance between No. 10 and No. 18 conformers (18.7°).

Close inspection of the optimized geometries revealed that the isomerism within these pairs of energy minima arises from the different dispositions between internal hydrogen atoms which approach to within 2.0 Å. This rare isomerism has actually been noted sometime ago in some annulenes [14] and may be called as the 'internal crowding isomerism.' However, it seems very likely that the present cases are artifacts resulting from particular balance between hardness of atoms and torsional barrier heights in the force field used. In fact, when these structures were re-optimized with MM3 [15] which is claimed to have softer *van der* Waals and tighter torsion parameters for sp^3-carbon and hydrogen compared with MM2, each conformer pair merged into a single [2343] and [333'3'] conformer, respectively. [16]

Conformers Nos. 32 [44'$\underline{4}$'], 44 [13'4'$\underline{4}$'] and 45 [1233*$\underline{4}$'] contain an *anti-end* pattern in the side of length 4, which makes these forms highly unstable (Tab. 2). Note that this pattern appears only on near the shortest and/or flanked with pseudo or fused corners. [17] This tendency is retained in larger cycloalkanes (see next example).

Table 3. Comparison of Endocyclic Dihedral Angles and Conformational Distances of Indistinguishable and Distinguishable Conformers of Cyclododecane

		Bond													Conformational
Nomenc.	Conf. No.	1	2	3	4	5	6	7	8	9	10	11	12	1	Distance [a]
[2324]	4	-164.3	-52.1	50.8	-158.7	158.7	-50.8	-52.1	-164.3	-71.0	-83.2	83.2	71.0		
	6	180.0	52.4	56.9	-129.6	148.4	-68.5	-69.0	-170.0	-62.5	-68.5	83.7	64.1		
	dif.(|4-6|)	15.7	0.3	6.1	29.1	10.3	17.7	16.9	5.7	8.5	14.7	0.5	6.9		13.6
[333'3']	10	-172.7	78.7	-88.5	143.2	-88.5	78.7	-172.7	76.1	70.2	-130.6	70.2	76.1		
	18	-142.3	78.5	-100.5	170.5	-100.5	78.5	-142.3	73.1	75.0	-165.9	75.0	73.1		
	dif.(|10-18|)	30.4	0.2	12.0	27.3	12.0	0.2	30.4	3.0	4.8	35.3	4.8	3.0		18.7
[333'4*]	5	-122.8	71.6	-165.0	172.7	-54.3	93.1	-152.6	72.3	70.1	-171.3	70.9	70.5		
	dif.(|5-10|)	49.9	7.1	76.5	29.5	34.2	14.4	20.1	3.8	0.1	40.7	0.7	5.6		32.6

[a] Conformational distance is defined as root-mean-square average of dihedral angle differences. See text.

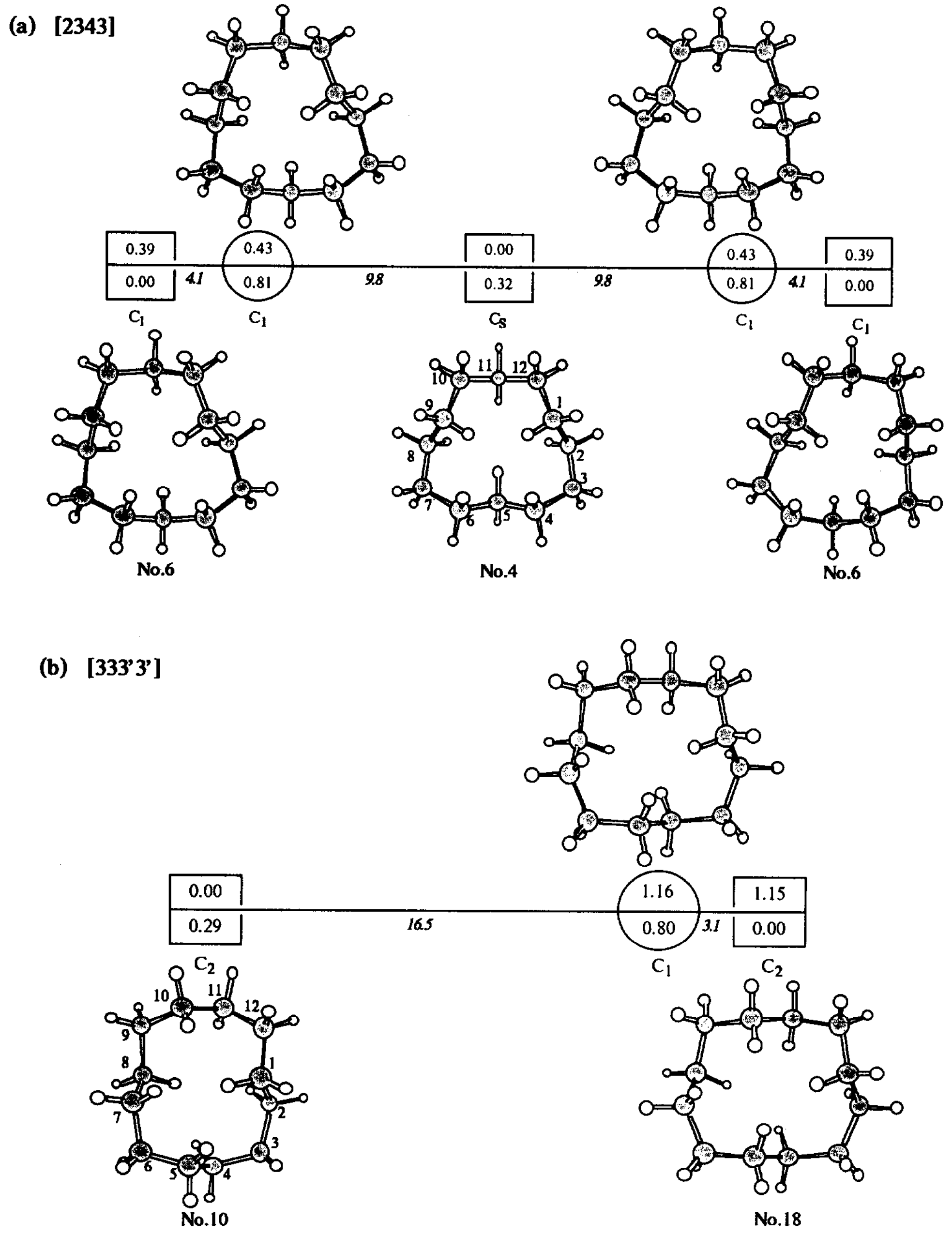

Fig. 2 Conformational interconversion pathways (a)between [2343] conformers Nos. 4 and 6, and (b)between [333'3'] conformers Nos. 10 and 18 of cyclododecane on the MM2 energy surface. Energy-minimum structures are drawn below the center line, with relative steric energy(upper entry) and free energy(lower entry, 25°C) inside a square along the center line. Point group is given below the square. Similarly, saddle points are drawn above the center line, with energy values inside and point group below a circle. Free energies are derived by including vibrational analysis using BIGSTRN-3 program.[21] The italic numbers under the center line are 'conformational distance' in degrees between the minimum and saddle point calculated according to the definition of Saunders.[13]

Cycloheptadecane

Recently, we reported that the all of 262 conformers of cycloheptadecane within 3 kcal/mol from the global minimum was found by using CONFLEX3. [1b] All of these agrees with the Saunders' conformers. [18] As shown in Table 4, the 69 low-energy conformers within 2 kcal/mol from the global minimum can be given unique names by our nomenclature. While Saunders and co-workers presented the global minimum of cycloheptadecane as [133433] by using Dale's nomenclature, we assigned [13434*3]. Figure 3 illustrates the difference in dividing points between theirs and ours. They misassigned the AGA and the helical segment. [19]

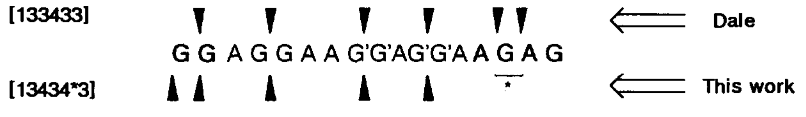

Fig.3 Consequence of corner deviding of the 17 endocyclic rotaion indices in the global minimum of cycloheptadecane based on Dale's nomenclature (upper) and ours (below).

In contrast to cyclododecane, the *anti-end* patterns often appear in the significantly populating conformers of cycloheptadecane and this is responsible for a duplication for No.21 and No.36 conformers (bold-faced in Tab. 4). Note that the apparently unfavorable No. 21 containing the *anti-end* side pattern turned out to be more stable than No. 36. This fact indicates that, in such a large ring, distortions which would have been serious in smaller ring can be absorbed. These are conformers which are different only in the side pattern type. In spite of the increased flexibility, it is possible to extract the sequence of bond notations in the ring conformation from the name if the underlining is appropriately given.

Table 4. Modified Dale Nomenclature for 69 Low-energy Conformers of Cycloheptadecane

No.	Nomenclature [a]	MM2 Steric E (kcal/mol)	Rel. E (kcal/mol)
1	[13434*3]	19.09	0.00
2	[33434]	19.11	0.02
3	[1331333]	19.47	0.38
4	[34*344]	19.48	0.39
5	[1'4*445]	19.68	0.59
6	[34*4'4*4]	19.75	0.66
7	[3434*4']	19.76	0.67
8	[34*44*4]	19.86	0.77
9	[34*4*35]	19.90	0.81
10	[3444*4*]	19.97	0.88
11	[1334'33]	20.02	0.93
12	[1334*43]	20.12	1.03
13	[3434'4*]	20.15	1.06
14	[34'34*4]	20.17	1.08
15	[33*$\underline{4}$35]	20.22	1.13
16	[34*44'4*]	20.26	1.17
17	[13535]	20.30	1.21
18	[33344]	20.30	1.21

19	[13*4*353]	20.32	1.23
20	[13343'3]	20.38	1.29
21	**[13*$\underline{4}$34*$\underline{4}$']**	**20.41**	**1.32**
22	[3434*$\underline{4}$]	20.42	1.33
23	[3344$\underline{4}$*]	20.46	1.37
24	[344*4*4]	20.53	1.44
25	[133*$\underline{4}$'43]	20.54	1.45
26	[13344*3]	20.54	1.45
27	[3536']	20.57	1.48
28	[1'4*436]	20.58	1.49
29	[33*$\underline{4}$*34*4*]	20.58	1.49
30	[3$\underline{4}$*4'4*4]	20.58	1.49
31	[3344'4*]	20.59	1.50
32	[13*3443]	20.59	1.50
33	[13313'4*3]	20.61	1.52
34	[134*4'4*3]	20.65	1.56
35	[13'3343]	20.67	1.58
36	**[13*434*4']**	**20.68**	**1.59**
37	[34'3*$\underline{4}$'4]	20.68	1.59
38	[334'4*4]	20.69	1.60
39	[13*4*33*4*3]	20.70	1.61
40	[3434$\underline{4}$*]	20.73	1.64
41	[1334'$\underline{4}$*3]	20.74	1.65
42	[23444]	20.75	1.66
43	[1343'$\underline{4}$*3]	20.75	1.66
44	[3*4*345]	20.76	1.67
45	[13*$\underline{4}$*31'4*4']	20.76	1.67
46	[1343*$\underline{4}$'3]	20.76	1.67
47	[344*4'$\underline{4}$*]	20.77	1.68
48	[1334*34]	20.78	1.69
49	[33$\underline{4}$*33*$\underline{4}$*]	20.80	1.71
50	[1441'4*4']	20.81	1.72
51	[13*$\underline{3}$344']	20.82	1.73
52	[1'4*$\underline{4}$'45]	20.84	1.75
53	[343*4*3*$\underline{4}$*]	20.84	1.75
54	[24344]	20.87	1.78
55	[13*$\underline{4}$'4'4*3]	20.92	1.83
56	[13*44'4*3]	20.92	1.83
57	[13544]	20.94	1.85
58	[4*455]	20.94	1.85
59	[13*$\underline{4}$3'4*4']	20.97	1.88
60	[13*$\underline{4}$334']	20.99	1.90
61	[13*$\underline{4}$*33*$\underline{4}$*3]	21.00	1.91
62	[34'4*4'$\underline{4}$*]	21.00	1.91
63	[134'153]	21.01	1.92
64	[1444'4']	21.02	1.93
65	[34*4'4$\underline{4}$*]	21.03	1.93
66	[133'343]	21.05	1.96
67	[34*4'4'4*]	21.07	1.98
68	[34*34'4]	21.09	2.00
69	[33*4*3*4*4]	21.09	2.00

[a] A side with an *anti-end* pattern is underlined.

DISCUSSION

As advanced by himself, [5] Dale's nomenclature provides unique opportunities of inferring similarity among conformations. For example, [333'4*] (No. 5) and [333'3'] (No. 10) conformers of cyclododecane have the -333'- part in common, suggesting they lie close in the conformational space and may be readily interconvertible. Actually, as shown in Figure 4, the conversion of the -4*- part into -3'- involves rotation of only one bond from A to G, or the movement of a fused to pseudo corner. [20] The process could be 'realized' by constrained bond-driving technique implemented in BIGSTRN-3 [21] through a low-energy saddle point (C_1, Fig. 4).

It is interesting to note that the sum of conformational distances of these cyclododecane conformers along the saddle point (35.0°, Fig. 4) is only 2.4° longer than the 'direct' distance between the [333'4*] and [333'3'] conformers (32.6°, Tab. 3). For the three cases of conformational interconversion between 'close' conformers mentioned above, the total distance through the saddle point is always slightly longer than the direct distance between two conformers, and the difference seems to be proportional to the average of calculated barriers (Tab. 5). Systematic studies on the possible relationship in general conformational interconversions between barrier heights and the conformational distances will be interesting.

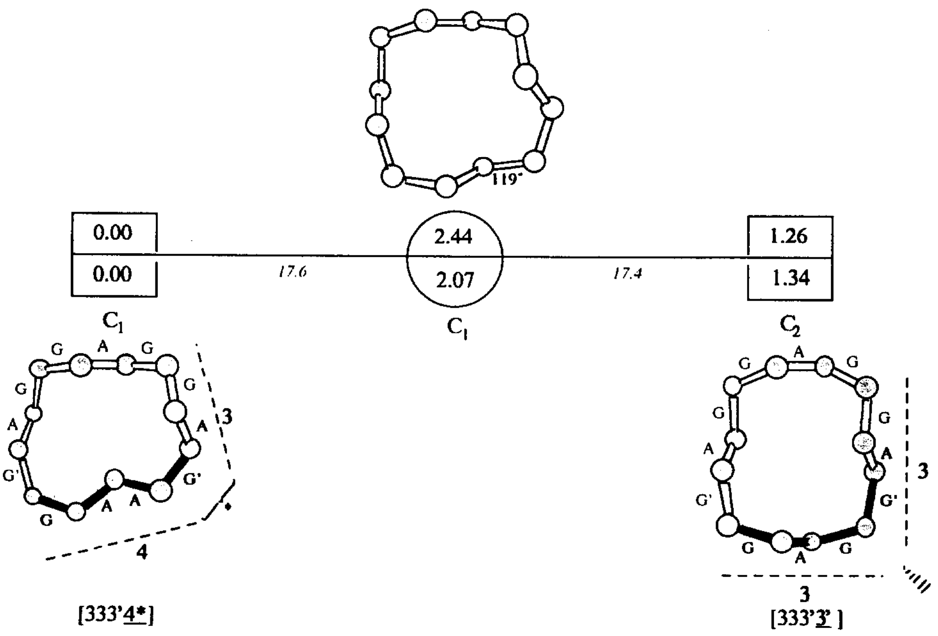

Fig.4 Conformational interconversion pathways between the No.5, [333'4*] and No.10, [333'3'] conformers of cyclododecane on the MM2 energy surface. A dashed wedge and an asterisk represent pseudo and fused corner, respectively. For other features, see caption of Fig.2.

Table 5. Conformational Distances Involved in the Interconversion of Some of the Cyclododecane Conformers as Compared with MM2-Barriers.

Conformer		Distance (degree)				Barrier (kcal/mol)		
A	B	R1[a]	R2[b]	R3[c]	R1+R2-R3	$\Delta H_A^{\neq}$[d]	$\Delta H_B^{\neq}$[e]	$\Delta H_{av}^{\neq}$[f]
No. 4	No. 6	9.8	4.1	13.6	**0.3**	0.43	0.04	**0.23**
No. 10	No. 18	16.5	3.1	18.7	**0.9**	1.16	0.01	**0.58**
No. 5	No. 10	17.6	17.4	32.6	**2.4**	2.44	1.18	**1.81**

[a] Distance from conformer A to saddle point. [b] Distance from conformer B to saddle point. [c] Distance between conformer A and B. [d] Barrier height from conformer A. [e] Barrier height from conformer B. [f] $(\Delta H_A^{\neq}-\Delta H_B^{\neq})$ / 2.

The Dale nomenclature conveys several interesting features on the molecular geometry. (1) [13....3] is found frequently in Table 4. The arrangement of [..GAGGGAG..] corresponds to a part of helical structure and appears to represent a low-energy sequence in cyclic methylene chains. This observation is supported by our recent discovery of week attractive interaction in the GG (or G'G') sequence.[22] (2) There are lots of fused corners represented as [...3*4...], [...4*4...], *etc.* in cycloheptadecane conformer (Tab. 4). Fused corners, [...AGA...] are readily generated by rotating an inner anti bond in a long side to gauche. (3) Sides of lengths 3 and 4 most frequently appear. High abundance of the [...343...] and [...434...] suggests that a partial parallel motion in the diamond lattice (*e.g.*, the global minimum [3434] cyclotetradecane) must be a favored one. This expectation has been confirmed by our study on still larger cycloalkanes.[23]

Our nomenclature fails when an eclipsed bond appears, since *cis* bond index is ignored. In this case, Dale's notation for the transition state conformer, wherein the *cis* bond is defined as a one-bond side marked in italics,[24] can be appended to the present method. Actually, *cis* bond appears in the conformers of cycloheptane and cyclooctane, hence these two ring systems should better be represented by the Hendrickson scheme.[2] As the ring becomes larger, conformations of local segments will resemble acyclic chains in that *cis* bond will never occur, at least in the low-energy conformations. Recalling an other impossible case GG'GG' in our nomenclature, we should say that our nomenclature will work best for larger cyclic systems larger than cyclooctane.

Our success in establishing one-to-one correspondence between the name and conformation, makes it possible to generate all of the conformers simply by writing down all different names. In view of very large number of names that can be expected for medium to large cyclic systems, this kind of prediction will be useful only if we know some empirical criteria to judge the stability of a conformation by its name, with which we can screen potential candidates for geometry-optimization calculations. Application of our nomenclature method to such knowledge-based prediction of conformations of very large polymethylene chain molecule will be interesting, because information on the segmental bond indices can be experimentally obtained.[25]

We did not test extremely strained cycloalkanes, but they will not appear in chemical scene of large systems too often. Although we mentioned only cycloalkanes, the nomenclature and analysis mentioned above can be readily extended to other cyclic systems containing hetero atoms. Finally, our nomenclature evolved as a line notation suitable to incorporate into computer programs.

ACKNOWLEDGMENT

We thank Professor Eiji Ōsawa for facilities, financial supports, many useful discussions and untiring help in the preparation of manuscript.

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17 For instance, the shortest sides in No. 44 and No. 45 are both 1, which appears in our notation on the left end. Therefore, the *anti-end* pattern, if any, is likely to appear on the second or the last entry in the name.

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19. This conformer should be named [3437] if the original Dale nomenclature is strictly applied.

20. This is one of the Dale's elementary processes proposed for the cyclic interconversion. [24] This mechanism is also included in our bond flip mechanism for the elementary interconversion processes. See also refs. 1(a), 1(b), and 11.

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