# The Non-alternating Ground-state Conformations of some Simple Eclipsed Carbon–Carbon and Nitrogen–Carbon Bonds. X-Ray Crystallographic Evidence and Molecular Mechanics Calculations

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Some simple carbon–carbon and nitrogen–carbon bonds which have eclipsed ground-state conformations are shown to be non-alternating, from structural information in the Cambridge Crystallographic Data Base or from molecular mechanics calculations.

The preferred conformations of simple carbon–carbon and nitrogen–carbon bonds are expected to be alternating in their Newman projection. Substituents are alternately attached to the front F or back B atom terminal of the bond in a progression round 360° of the projection, see **1**. Some time ago, Hounshell, Dougherty and Mislow suggested[1] that in certain circumstances some highly strained molecules might have a ground state with a non-alternating bond and presented molecular mechanics calculations and indirect experimental evidence that the indicated bonds in **2** and **3** are examples.


1   **2**   **3**
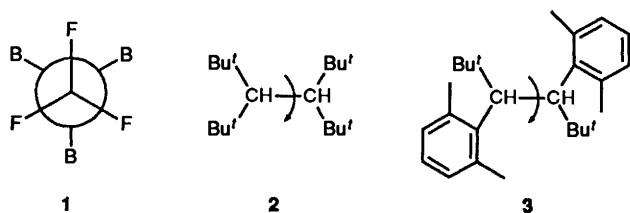
They discussed other structural types that might be propitious and pointed out that beyond ground states, 'eclipsed' rotational transition states in unsymmetrical molecules should provide further examples. All three pairs of substituents will not eclipse simultaneously because of disymmetry, so between the closely spaced successive eclipses, conformations that are non-alternating will be found, as **4** with X and K eclipsed is followed by non-alternating **5**.

4   **5**   **6**
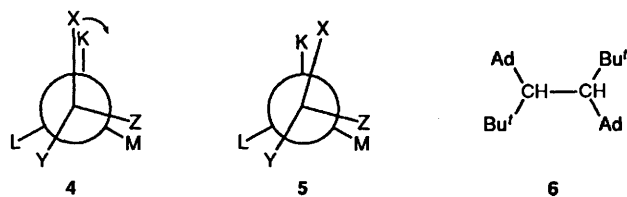
Osawa's more recent molecular mechanics calculations[2] for **3**, and crystal structure determination[3] for a close analogue **6** (Ad = 1-adamantyl) showed that the structure is in fact alternating.

Recently I presented molecular mechanics calculations and indirect NMR evidence that the central bond in 1,1,2-tri-*tert*-butylethane is eclipsed and non-alternating,[4] see **7** and suggested that these two features should be quite common in molecules with fragments of the type R^1CH_2–CHR^2R^3 (**8**) where groups R are demanding of space. The consequent opening up of the R^2–C–R^3 and the closing down of the H–C–H bond angle make non-alternation the natural accompaniment of eclipsing, see **9**.

Evidence in support of this postulate could be expected from

7   **9**   **11**
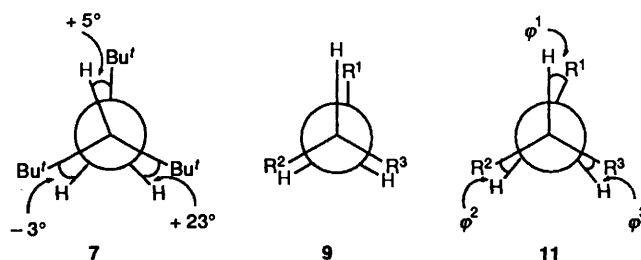
crystal structure, and Watson and I recently reported[5] an analysis of fifteen crystal structure determinations[6] of molecules containing the structural fragment RCH_2CH_2–$CH(CR_3)CR_3$ (**10**) [groups R (not = H) need not be identical]. We found that in twelve of these cases the conformation is eclipsed or nearly so; specifically the eclipsing sum[5] $\Sigma = |\varphi_1| + |\varphi_2| + |\varphi_3|$ in **11** = <60°, so average torsional angles are less than 20°. For alternating bonds all φ values have the same sign whereas non-alternating bonds have φ values of different sign. The sign of φ is positive when the front to back progression is clockwise, and negative otherwise, see **7**.

The crystallographic demonstration of non-alternating conformations in some of the compounds studied, and in the analogous series R^1CH_2–NR^2R^3 (**12**), and molecular mechanics calculations[7] of other compounds which might be expected to show the same phenomenon, are now reported.

Results and Discussion

The three hydrogen atoms of the fragment **7** could be identified in the crystal structures of ten of the twelve molecules of type **10** reported[5] to have eclipsed conformations, these ten being **13**, **14a–d**, and **15–19**. Five of these ten are non-alternating and five are alternating and Table 1 shows this along with the eclipsing sum for each example.

For the five alternating bonds, eclipsing appears less marked than for the non-alternating bonds as implied in the introduction, Σ having a value of 40.1° on average whereas the average of the non-alternating cases is 26.0°. The effect is small, however, with average dihedral angles different by less than 5° between the two sets.
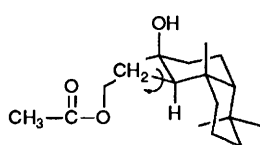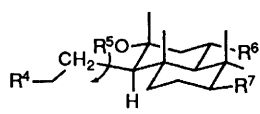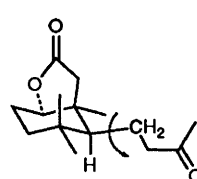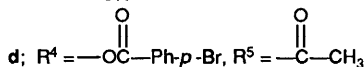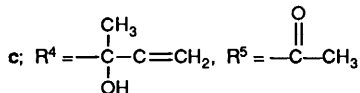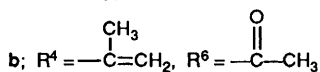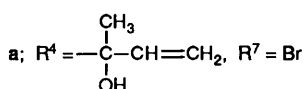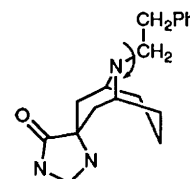
It is more significant that the group R^1 of structure **8** more nearly eclipses hydrogen in the non-alternating than in the alternating bonds, which helps the H–C–H projection fit inside the R^2–C–R^3 projection. The R^1–C–C–H dihedral in the non-alternating cases varies from 2.4° to 8.6° averaging 5.4°, while for the alternating cases the range is 8.6°–15.1° with the average 12.3°.

Of the thirteen examples in the Data base with structures containing carbon–nitrogen bonds of type **12**, where NR^2R^3 is

Table 1 Eclipsed molecules of types **8** and **12** with alternating or non-alternating bonds

Compound	Eclipsing sum Σ or $\psi\Sigma/°$	Dihedral angles $\varphi/°$	Alternating (A) or non-alternating (NA)	Ref.
13	13.2	−2.8, −6.9, +3.5	NA	6(a)
16	36.2	−8.6, −12.9, +3.5	NA	6(g)
14b	43.9	−7.2, −6.8, ±29.9	NA	6(i)
14c	14.3	−2.4, −8.0, +3.9	NA	6(b)
17	22.3	−5.8, −13.7, ±2.8	NA	6(d)
14a	34.7	+8.6, +19.4, +6.7	A	6(f)
14d	44.5	−12.2, −7.6, −24.7	A	6(e)
15	33.9	+13.1, +13.1, +7.7	A	6(e]
18	39.6	−12.3, −13.8, −13.5	A	6(h)
19	48.0	−15.1, −28.0, −4.9	A	6(k)
20ᵃ	19.8	+4.0,ᵇ +12.2, −3.6	NA	8
	28.3	+3.4,ᵇ +20.1, −4.0	NA	8

ᵃ Two independent molecules in the unit cell. R¹ putatively eclipses the nitrogen lone pair. ᵇ Calculated assuming the lone pair splits the external C–N–C angle.

13

14 Rⁿ = H except for:

a; R⁴ = —C(CH₃)(OH)—CH=CH₂, R⁷ = Br

b; R⁴ = —C(CH₃)=CH₂, R⁶ = —C(=O)—CH₃

c; R⁴ = —C(CH₃)(OH)—C=CH₂, R⁵ = —C(=O)—CH₃

d; R⁴ = —OC(=O)—Ph-p-Br, R⁵ = —C(=O)—CH₃

15

16

17

18

19

20

part of a ring, only one structure **20** shows eclipsed bonds with Σ = 19.8° or 28.3° in the two molecules of the unit cell.[8] In both molecules the bond is non-alternating.

All these examples show that non-alternation is a fairly regular feature of eclipsed bonds, not always present, but more likely to occur the more bonds are eclipsed.* Questions arise whether a bond may have two conformational minima near to eclipsed, one of which is alternating, the other non-alternating,

with a barrier to their interconversion according to the usual rules of conformational equilibria, and whether the non-alternating conformation is in any way a consequence of the crystal lattice. To investigate these points and to further explore the occurrence of non-alternating conformations in similar molecules I carried out molecular mechanics calculations of some structures using Allinger's MM3 program,[7] which predicts gas-phase structures. The experimentally determined bond conformation in **14a** and the calculated gas-phase bond conformations are close as can be seen in **21** and **22**, both non-
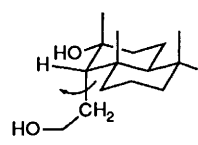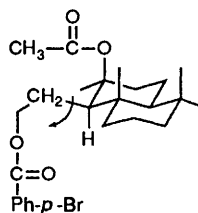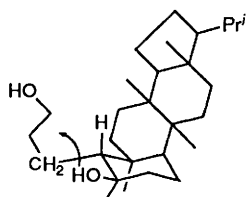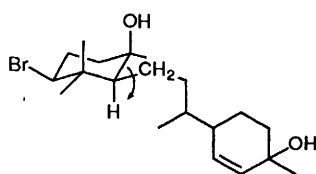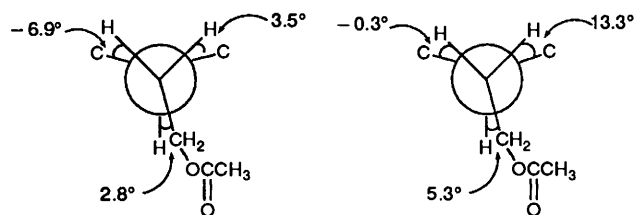
21   **22**

alternating, but the calculated conformation **22** is within one degree of alternating.

I used the dihedral drive option of the MM3 program to seek the alternating minima for **14a** and other non-alternating ones, and found illusory versions of these when coarse convergence limits were used in the calculation. With finer convergence limits a conformational minimum very close to **22** was arrived at from various directions.

I calculated other molecules with bonds of the type **8** for which no experimental evidence is available and in some

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* I am aware that bonds not perfectly eclipsed (Σ = 0) are not eclipsed at all pedantically, but because of distortions to bond angles, perfect eclipsing is unlikely.

molecules (**23** and **24**) found eclipsed non-alternating structures to be the most stable. No stable alternating conformations of such molecules could be found by calculation and the barrier to interconverting enantiomeric non-alternating conformations of such compounds through the perfectly eclipsed is not significantly above the convergence limit of 0.0001 kcal mol^{-1}. The analogues **25**, and **26** with only two flanking methyl groups
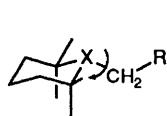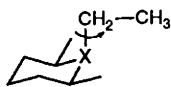

23 X = N, CH; R = Me, Bu^t
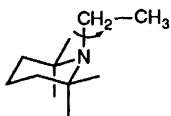
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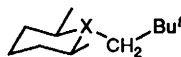
25 X = N, CH

26 X = N, CH

are less markedly eclipsed and alternating. It is nonetheless remarkable that such simple molecules have a bond with a near-to-eclipsed preferred conformation.

Such calculations of known and unknown eclipsed conformations suggest that lattice forces are not a significant cause of eclipsing. They also suggest that using hydrogen atom positions from crystal structures, the basis of the present experimental demonstration of non-alternating bonds, is not tendentious, which is reasonable, since the crystallographic uncertainty is in the hydrogen position along the C–H bond vector, not laterally.

I conclude that ground-state non-alternating conformations are a real phenomenon for eclipsed bonds of type **8**, particularly likely when eclipsing is most marked. Non-alternation is a consequence of H–C–H and R^1–C–R^3 bond angles being, respectively, less than and greater than the ideal tetrahedral value and is no more than the fitting of the projection of the first inside that of the second, which is more probable the more R^1 of **8** is eclipsed. Conformational minima are quite well defined but are determined by long-range R^1–R^2, R^3 interactions so that conformations near the minima with exact eclipsing of groups R with hydrogen atoms are not maxima in the potential energy diagram. Non-alternation seems to be an insignificant consequence of eclipsing of bonds of type **8**.

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