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A Hückel Molecular Orbital Approach to Stereochemical Problems based on the Variation of the Coulomb Integral

By

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The simple Hückel molecular orbital method was applied to explain energy differences between isomers and conformers of a number of saturated hydrocarbons. First the energies of the various known forms of n-butane, cyclohexane and cyclopentane were matched by varying the Coulomb integral α according to the non-neighbor interactions by which a given carbon orbital is affected. The parameters obtained in this way were then applied to more complex saturated hydrocarbons. Good agreement with experiment was obtained whenever data were available. Extra resonance integrals (β) between non-neighbor atoms were not introduced.

La simple méthode des orbitales moléculaires de Hückel a été utilisée à interpréter les différences d'énergie entre les isomères et les conformères d'un grand nombre d'hydrocarbures saturés. Les paramètres nécessaires ont été obtenus à partir des énergies connues du butane normal, du cyclohexane et du cyclopentane en variant l'intégrale Coulombienne, α, selon les interactions entre atomes non-contigus qui affectent un carbone donné. Les paramètres ainsi obtenus ont été ensuite appliqués aux cas des hydrocarbures saturés plus complexes. L'accord avec l'expérience est très satisfaisant dans tous les cas où des données expérimentales sont disponibles. On n'a pas introduit d'intégrales de résonance (β) entre atomes non-contigus.

Die einfache Hückelmethode wurde zur Berechnung von Energiedifferenzen zwischen verschiedenen Konformationen bzw. Isomeren von gesättigten Kohlenwasserstoffen benützt. Dabei wurden zunächst die Coulombintegrale der verschiedenen Formen von n-Butan, Cyclohexan und Cyclopentan justiert. Anschließend wurden die so gewonnenen Parameter bei der Berechnung weiterer Verbindungen verwendet, wobei die Übereinstimmung mit experimentellen Daten, soweit diese vorlagen, als gut zu bezeichnen war. Eigene Resonanzintegrale für nicht benachbarte Atome wurden nicht eingeführt.

Introduction

In a recent paper Hoffmann [9] made an attempt to correlate a great number of facts of organic stereochemistry by using the simple Hückel molecular orbital approximation. He used a very simple parametrization originally proposed by Mulliken [19] taking the valence state ionization potential for a given atom as the Coulomb integral and the arithmetic mean of the Coulomb integrals of two atoms forming a bond multiplied by the overlap integral and an empirical constant as the resonance integral. He used the valence-state ionization potentials given by Skinner and Pritchard [25, 31].

This simple scheme has the great merit of being universally applicable to all types of molecules and it had a partial success in interpreting certain stereochemical facts thanks to a very rapid computer program making it possible to

carry out calculations for a great number of geometrical arrangements for each compound.

Conformational problems are recognized to be those of non-neighbor or long distance interactions between non "chemically" bonded atoms so the heart of the problem is how to represent best these interactions. Hoffmann's method consists in doing this by introducing resonance integrals between non-neighbors and this is indeed the most natural approach.

It occurred to us, however, that it may not be the best one. Since we wish to remain within the framework of the Hückel method we have to ask what are the changes that undergo the Coulomb integrals (α) and the resonance integrals (β) in going from one stereoisomer to the another or one conformation to the other. Now, if we think of the non-neighbor β as quantities roughly proportional to overlap integrals they are seen to be very small and they may not represent the greater part of the interaction between non-neighbor atoms. On the other hand if we explicit the Hamiltonian we have for a Coulomb integral related to an atomic orbital p, with the usual notations

$$\alpha_p = \int \chi_p(u) \, H^{\text{Core}} \chi_p(u) \, d\tau_u$$
$$= (T:pp) + (p:pp) + \sum_{q \neq p} (q:pp)$$

or, by the GOEPPERT-MAYER and SKLAR approximation [6]

$$\alpha_p = W_{2p} - \sum_{q \neq p} [(pp \mid qq) + (q:pp)]$$

where all monocentric terms are contained in W_{2p} and all atomic orbitals are considered. Both the $(pp \mid qq)$ and the $(q:pp)$ are functions of distance, undergo appreciable changes when the distances are altered and the former remain important at distances where the overlap integrals are negligible. It can be shown, on the other hand that, in the Pariser and Parr approximation [20] the resonance integrals may be considered as properties of one given link only (see [10]).

These considerations lead us to make an attempt to assess conformational problems by a method based on the variation of α without introducing extra β for representing non-neighbor interactions.

Outline of the method

The simple Hückel method was applied to the case of saturated hydrocarbons [29, 30] in two different approximations.

The cruder one, labelled "C" approximation disregarded not only the hydrogen $1s$ orbitals but also those carbon sp^3 hybrides which are bonded to a hydrogen atom. Thus the molecular orbital is simply a linear combination of those carbon sp^3 orbitals which establish the carbon — carbon bonds (Fig. 1; ref. 5). The calculation process is, of course, the same as what is currently used in π electronic systems.

In the other approximation, called the "H" approximation all carbon sp^3 orbitals and hydrogen $1s$ orbitals were introduced.

FUKUI, KATO and YONEZAWA [5] and KLOPMAN [13, 14, 15] have later shown that these simple methods have a surprising success in computing heats of

formation and ionization potentials of saturated hydrocarbons. Naturally, agreement with experiment depends on the choice of the parameters entering the related secular equations.

In the "C" approximation there is only one parameter whose determination is causing problems. This is the choice of the resonance integral $\beta' = m\beta$ for the interaction between two hybrids belonging to the same carbon atom. (β is the resonance integral between two hybrid orbitals directly bonded together.) Yoshizumi [33] determined m from the experimental values of the dipole moments of halogen substituted paraffins and obtained that $m^2 = 0.12$.

Fukui, Kato and Yonezawa took the positive square root, $+ 0.34$ but later Klopman has shown that a better and almost perfect agreement is reached with the experimental ionization potentials and heats of formation simultaneously, for normal, branched and cyclic paraffins if m is given the negative sign. Klopman was able to show too that introducing a parameter for representing this $2 - 3$ interaction is actually equivalent to introducing the $1 - 4$ interaction instead, the respective secular determinants being identical [14, 15] (Fig. 1).
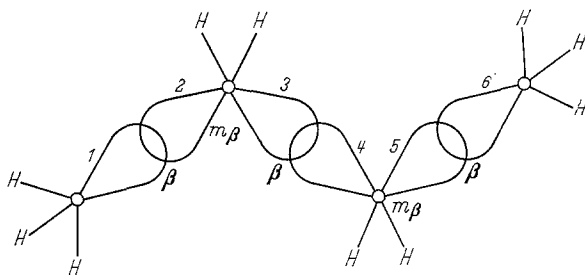

Fig. 1. Carbon sp^3 hybridized orbitals in n-butane

In the "H" approximation several parameters are needed. Here too we preferred using Klopman's parameters rather than Sandorfy's [29] and Fukui's [5] earlier values for reasons similar to those mentioned above. The parameters needed are for 1,4 interactions of $C - C - C$, $C - C - H$ and $H - C - H$ types equal to $m\beta$, $d\beta$ and $p\beta$ respectively; $\beta_{C-H} = t\beta$ and $\alpha_H = \alpha_C + n\beta$.

Their numerical values given by Klopman are:

$$m = - 0.3305 \qquad t = 1.2375$$
$$d = - 0.1101 \qquad n = 0.4049$$
$$p = - 0.0806$$

We adopted these values in our calculations using the "H" approximation and we took $m = - 0.35$ when using the "C" approximation. Our β was $\beta_{C-C} = 39.036$ Kcal/mole in both approximations, essentially the same as Klopman's, obtained from the experimental heats of formation of methane and ethane [14].

This basic parametrization does not enable us to differenciate among different conformations of the same compound since this requires taking into account interactions more distant than $1 - 4$ (see Fig. 1). We achieved this by varying α as described in the following section.

n-Butane and cyclohexane

We first tried to match the experimental total energies and barriers to internal rotation in the case of n-butane since this molecule is taken as a reference compound in many conformational problems and the method of solving molecules into n-butane systems, originated by TURNER [32] has been followed by many authors [4, 7].

The experimental potential curve is shown in Fig. 2 taken from MISLOW (ref. [18] p. 37) as a function of the torsional angle, with the energy of the trans conformation taken as zero*.

The energy of the gauche form is experimentally known to be 0.8 — 0.9 kcal/mole higher than that of the trans and the energy of the eclipsed form by 4.4 — 6.1 kcal/mole (see refs. [11, 22]). Now using the "C" approximation it was easy to follow this potential curve in varying only the Coulomb integral, α, of the two
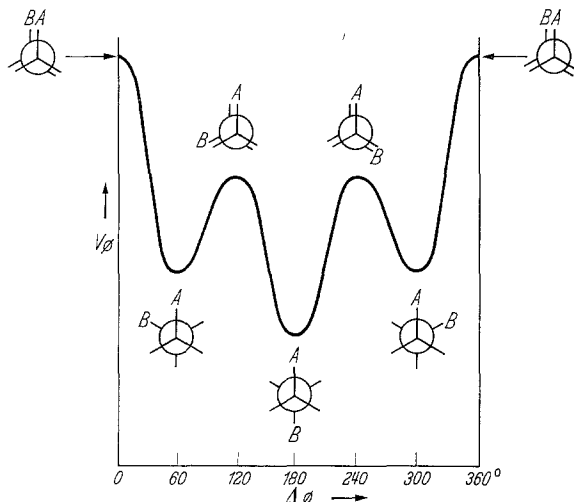
Fig. 2. Torsional strain $(V\varphi)$ as a function of angular displacement $(\varDelta\varphi)$ in molecules of type $A - CX_2 - CX_2 - B$

end sp^3 orbitals (1 and 6) without introducing extra βs. The C — C part of the heat of formation of trans-n-butane is, subtracting the energies of the ten C — H bonds (this quantity being considered as a constant for all molecules) $10 \cdot (-98.214$ kcal/mole), $E_{C-C} = -239.29$ kcal/mole $= 6.1299\,\beta$.

In order to lower this value by 0.9 kcal/mole $= 0.0231\,\beta$ we needed a supplement equal to $\alpha' = -0.0116\,\beta$ to the Coulomb integrals related to orbitals 1 and 6. At $\alpha' = -0.0456\,\beta$ we obtained the height of the barrier for internal rotation trans $\rightarrow$ gauche (3.5 kcal/mole), and at $\alpha' = -0.0573\,\beta - (-0.0797\,\beta)$ the energy of the eclipsed form (4.4 — 6.1 kcal/mole).

So it is seen that by a variation of α we can match the potential curve of n-butane. One may ask if we are not to modify as well the α in 2 and 5 since these two must vary at the same time as 1 and 6. However, since these modifications concern the diagonal terms in the secular determinant it does make no difference

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* We are very indebted to Professor K. MISLOW and to W. A. BENJAMIN, Inc. for the permission of reproducing Figs. 2 and 3.

if we give one extra α' to a given term or $\alpha'/2$ to two terms. It is hoped that the empirical adjustment of α will allow for the small $1 - 5$ type interactions too and that it will cover the changes in the mutual repulsion of the nuclei as well.

The same calculation was made with the "H" approximation. The same α' as were used with the "C" approximation are again able to match the maxima and the minima of the potential curve. Alternatively we may give an $\alpha' = -0.0033 \beta$ to the hydrogen $1s$ orbitals obtaining the same results.

We went on applying our scheme of α variation to cyclohexane. For cyclohexane there are the following conformations: "chair", "boat" and "twist" or "skew boat". The energy differences are, if the energy of the chair form is taken for zero, 5.5 kcal/mole (twist) (Fig. 3) [12] and the energy of the boat form has been calculated as 1.6 kcal/mole more than the energy of the twist form [8]. Using the
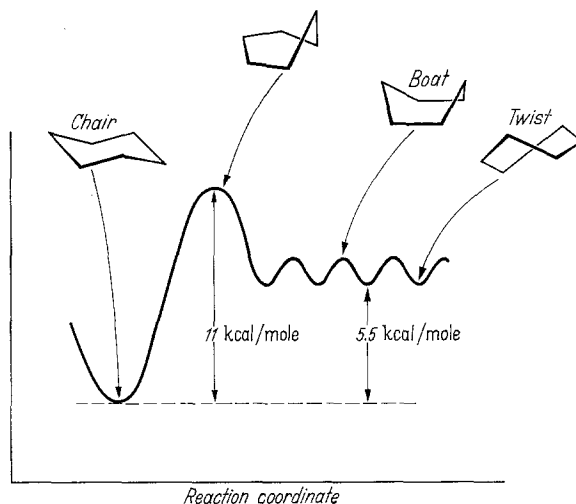
Fig. 3. Torsional isomerism in cyclohexane

"C" approximation we matched the 7.1 kcal/mole of the boat form in using $\alpha' = -0.046 \beta$. As to the skew boat form we have to change all the α since in this form all relations between diagonally placed carbons are the same, and different from those in the chair form. -0.0117β was needed for obtaining 5.5 kcal/mole (Fig. 3. Ref. [18], p. 77).

A similar treatment may be carried through with the "H" approximation. For the more complex molecules we only used the "C" approximation. It is seen that, other things being equal, the total energies vary in a near linear way with the value of α. We used these empirical α values in our calculations related to more complex molecules.

Application to other Saturated Hydrocarbons

Using the parameters obtained from the treatment of n-butane and cyclohexane we treated a number of other conformational problems.

Methylcyclohexane is known to have two conformations, equatorial and axial, while the cyclohexane ring itself has the chair form in both cases. In the axial

conformation the methyl group is in such a position that the $C_{methyl} - C_{ring}$ bond axis makes a dihedral angle of 60° with the two $C - C$ bonds which are its second neighbors. This situation is analogous to the one present in the gauche form of n-butane and therefore we applied the $\alpha' = -0.0116\,\beta$ correction to the appropriate orbitals in order to represent $1 - 6$ type interactions (see the figures in the Appendix) $(\alpha'_{14} = 2 \cdot (-0.0116\,\beta);\ \alpha'_4 = \alpha'_9 = -0.116\,\beta$ since C_{14} is implied in two $1 - 6$ type interactions).

In the equatorial form we have trans relationships instead of the gauche ones, and no extra parameters were applied.

In this manner we obtained almost exactly the experimental energy difference between the axial and equatorial forms, 1.8 kcal/mole, the latter being more stable.

Similar success has been achieved with the dimethylcyclohexanes. The results are shown in the table.

For one isomer, the cis-1,3 (axial, axial) dimethylcyclohexane, we needed a new parameter to represent the extranuclear interaction between the two methyl groups which are on the same side of the ring. A value of $\alpha' = -0.0486\,\beta$ was needed to match the experimental energy difference -5.4 kcal/mole between the cis-1,3 (axial, axial) and cis-1,3 (equatorial, equatorial) forms and we used this parameter in other cases where similar interactions occur. (*Cis-syn-cis* perhydrophenanthrene and *cis-syn-cis* perhydroanthracene).

We applied the same technique to decalines, perhydrophenanthrenes and perhydroanthracenes. In each case if an orbital is engaged in n $(1 - 6)$ type interactions it was given a parameter $\alpha' = n\,(-0.0116\,\beta)$. All these are compiled in Tab. 1 and compared with experimental results when available.

The experimental data were taken from Rossini's et al. compilation [26] for cyclohexane and cyclopentane derivatives and from Eliel and al. [4] for decaline (p. 231), perhydroanthracene and perhydrophenanthrene derivatives (p. 233 to 236). For the latter two categories of molecules the experimentally determined order of stabilities is the same as what we obtained in our calculations.
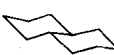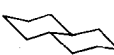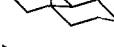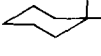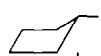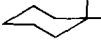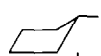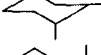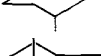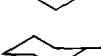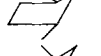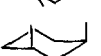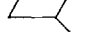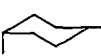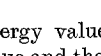
In order to carry out similar calculations on cyclopentane derivatives and steroids we need parameters for the cyclopentane ring.

Cyclopentane is known to have two conformations, the "envelope" form, in which one carbon atom projects out of the plane of the other four; the "half-chair" form, in which three neighboring carbon atoms lie in one plane, while the other two are twisted in such a way, that one lies above and the other below the plane (these carbons are equidistant from this plane. See figures in the table). In the "envelope" form there are five $1 - 6$ type interactions one of which corresponds to an eclipsed situation, two to a nearly gauche situation and two to an intermediate situation. The parameters used to match the experimental heat of formation were, in the same order,

$$\alpha' = -0.046\,\beta, \qquad 0 \quad \text{and} \quad -0.0128\,\beta\,.$$

The "half-chair" form is in the present case considered as approching the ideal equally staggered form, and all the $1 - 6$ interactions are taken as approximately equal. The parameter needed would then be $\alpha' = -0.0143\,\beta$.

Table

Cyclohexanes

	E calc.	ΔE calc.	E exp.	ΔE exp.
chair	1661.43		1661.79	
skew-boat	1655.95	5.48		5.5
boat	1654.31	1.63		1.6

Methyl cyclohexanes

	E calc.	ΔE calc.	E exp.	ΔE exp.
equatorial	1940.63		1941.71	
axial	1938.84	1.79		1.8

Dimethyl cyclohexanes

	E calc.	ΔE calc.	E exp.	ΔE exp.
1,1	2220.05		2219.97	
1,2 e,e	2218.96		2219.95	
1,2 e,a	2217.17		2217.99	
1,2 a,a	2216.27			
1,3 e,a	2218.05		2219.10	
1,3 e,e	2219.85		2221.06	
1,3 a,a	2214.31	5.5		5.4
1,4 e,e	2219.85		2221.03	
1,4 e,a	2218.05		2219.12	
1,4 a,a	2216.25			

Decalines

	E calc.	ΔE calc.	ΔE exp.
trans	2677.09		
cis	2674.38	2.71	˙2.7
trans 9-méthyl	2954.95		
cis 9-méthyl	2954.01	0.93	0.5

Cyclopentanes

	E calc.	E exp.
envelope	1378.89	1378.83
puckered	1378.85	1378.83

Methyl- and Dimethyl-cyclopentanes

		E calc.	E exp.
1	e	1658.10	1658.40
1,1		1937.49	1938.10
1,2 e,e		1937.33	1937.80
1,2 a,e		1935.51	1936.07
1,3 e,e		1937.31	1937.60
1,3 e,α		1935.51	1937.06

All energy values are given in kcal/mole. $\Delta(E - E')$ is the difference between a given energy value and the one immediately following it in the table except in the case of perhydro phenanthrenes and perhydroanthracenes where it means the difference between the given energy value and the energy of _trans-anti-trans_ perhydrophenanthrene and _trans-syn-trans_ perhydroanthracene respectively.

In methyl and dimethylcyclopentanes [1, 2] and in steroids [3] the cyclopentane ring is present in the envelope form. Two types of bonds can be recognized in this form. They are classical axial and equatorial bonds, *a* and *e* as found in cyclohexane, and the so-called bisectional bonds, which both form an angle of 54°44′ with the plane. If the 1-position is taken as the tip of the envelope, then the 1,1-, 1,2- and 2,5- (that is 1,3-)-dimethylcyclopentanes will present the same types of interactions as 1,1-, 1,2-, and 1,3-dimethylcyclohexanes, as we

Table (continued)

Perhydrophenanthrenes

I E calc. 3658.16

trans–anti–trans

Perhydrophenanthrenes

II a E calc. 3655.50 ΔE calc. 2.66

cis–syn–trans

Perhydrophenanthrenes

II b E calc. 3655.49 ΔE calc. 2.67

cis–anti–trans

Perhydrophenanthrenes

III E calc. 3653.68 ΔE calc. 4.47

cis–anti–cis

Perhydrophenanthrenes

IV E calc. 3650.87 ΔE calc. 7.29

cis–syn–cis

Perhydrophenanthrenes

V E calc. 3648.41 ΔE calc. 9.74

trans–syn–trans

Perhydroanthracenes

I E calc. 3659.04

trans–syn–trans

Perhydroanthracenes

II E calc. 3656.35 ΔE calc. 2.69

cis–anti–trans

Perhydroanthracenes

III E calc. 3653.64 ΔE calc. 5.40

cis–anti–cis

Perhydroanthracenes

IV E calc. 3653.57 ΔE calc. 5.47 ΔE exp. 5.39

trans–anti–trans

Perhydroanthracenes

V E calc. 3651.72 ΔE calc. 7.31

cis–syn–cis

Cholestanes

5 α E calc. 7141.23

Cholestanes

5 β E calc. 7140.32 ΔE calc. 0.91

are in presence of the same types of bonds, that is essentially equatorial and axial bonds.

We applied the method described above to 5 α-cholestane and 5 β-cholestane. The side chain was taken to be *trans* ([4] p. 261).

The agreement with experimental data in the case of methyl and dimethyl-cyclopentane is good. The results are summarized in the table.

The secular determinants for a few typical molecules are given in the Appendix.

Discussion

The method we used in the calculations reported in this paper is, naturally, a crude and wholly empirical one. It has, however, surprising success in correlating a very great number of experimental data related to isomers and conformers in paraffinic hydrocarbons.

If we look for the reasons that a parametrization based only on experimental heats of formation of the different forms of *n*-butane, cyclohexane and cyclopentane is able to account for similar properties of so many of their derivatives we have to conclude that these basic units are only slightly perturbed when they form part of more complex hydrocarbons.

Another point that energes is the possibility of representing several interactions by only one empirically chosen parameter in the simple Hückel molecular orbital method. It is useful to remember, in this connection, the observation made by KLOPMAN [14] that introducing a parameter in order to represent $2 - 3$ interactions in the approximation we used is tantamount of representing $1 - 4$ interactions. Our method was based on the inclusion of parameters representing $1 - 6$ type interactions and — until only the total energy of the ground state is sought — this seems to represent adequately the whole set of $1 - 6$, $2 - 5$, $1 - 5$ and more distant interactions. Also interactions between CH_2 or CH_3 groups may be represented by a parameter given to the carbon only.

The choice of the Coulomb integral, α, as a quantity to vary according to non-neighbor interactions rather than introducing "long distance" βs seems to be qualitatively justified by the presence of two-center integrals between non-neighbors in the theoretical expression of α.

PITZER and CATALANO [23] made an attempt to explain non-neighbor interactions as being principally an electron correlation effect, using dispersion force formulation. (For further developments see references [16, 17, 21, 23, 27, 28, 34]) More recently POPLE and SANTRY [24] — in a perturbation treatment of the factors causing delocalization in saturated hydrocarbons — gave reasons to believe that dispersion forces may account for only a part of the non-neighbor interaction energy. We believe that a variation of α may, at least partly cover dispersion force effects since we may regard α dependant on the mutual polarisabilities of the atoms in a given molecule.

In our opinion, although the procedure we used is lacking deeper justification at this stage, in view of its success in treating many conformational problems it may be considered as a useful empirical tool. It may represent, for example, a possible way to obtaining the electronic densities at different points of a given molecule.

Appendix
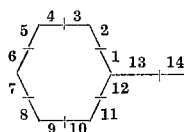
Methylcyclohexane Equatorial Conformation

y	1	0	0	0	0	0	0	0	0	0	m	m	0
1	y	m	0	0	0	0	0	0	0	0	0	0	0
0	m	y	1	0	0	0	0	0	0	0	0	0	0
0	0	1	y	m	0	0	0	0	0	0	0	0	0
0	0	0	m	y	1	0	0	0	0	0	0	0	0
0	0	0	0	1	y	m	0	0	0	0	0	0	0
0	0	0	0	0	m	y	1	0	0	0	0	0	0
0	0	0	0	0	0	1	y	m	0	0	0	0	0
0	0	0	0	0	0	0	m	y	1	0	0	0	0
0	0	0	0	0	0	0	0	1	y	m	0	0	0
0	0	0	0	0	0	0	0	0	m	y	1	0	0
m	0	0	0	0	0	0	0	0	0	1	y	m	0
m	0	0	0	0	0	0	0	0	0	0	m	y	1
0	0	0	0	0	0	0	0	0	0	0	0	1	y

Methylcyclohexane Axial Conformation

y	1	0	0	0	0	0	0	0	0	0	m	m	0
1	y	m	0	0	0	0	0	0	0	0	0	0	0
0	m	y	1	0	0	0	0	0	0	0	0	0	0
0	0	1	$y\text{-}a$	m	0	0	0	0	0	0	0	0	0
0	0	0	m	y	1	0	0	0	0	0	0	0	0
0	0	0	0	1	y	m	0	0	0	0	0	0	0
0	0	0	0	0	m	y	1	0	0	0	0	0	0
0	0	0	0	0	0	1	y	m	0	0	0	0	0
0	0	0	0	0	0	0	m	$y\text{-}a$	1	0	0	0	0
0	0	0	0	0	0	0	0	1	y	m	0	0	0
0	0	0	0	0	0	0	0	0	m	y	1	0	0
m	0	0	0	0	0	0	0	0	0	1	y	m	0
m	0	0	0	0	0	0	0	0	0	0	m	y	1
0	0	0	0	0	0	0	0	0	0	0	0	1	$y\text{-}b$

$a = 0.0116$ $b = 0.0232$

1,3 Dimethylcyclopentane Cis Conformation

y	1	0	0	0	0	0	0	m	m	0	0	0	0
1	$y\text{-}c$	m	0	0	0	0	0	0	0	0	0	0	0
0	m	$y\text{-}c$	1	0	0	0	0	0	0	0	0	0	0
0	0	1	y	m	0	0	0	0	0	0	0	m	0
0	0	0	m	$y\text{-}e$	1	0	0	0	0	0	0	m	0
0	0	0	0	1	y	m	0	0	0	0	0	0	0
0	0	0	0	0	m	$y\text{-}c$	1	0	0	0	0	0	0
0	0	0	0	0	0	1	$y\text{-}c$	m	0	0	0	0	0
0	0	0	0	0	0	0	m	y	1	0	0	0	0
m	0	0	0	0	0	0	0	1	$y\text{-}e$	m	0	0	0
m	0	0	0	0	0	0	0	0	m	y	1	0	0
0	0	0	0	0	0	0	0	0	0	1	y	0	0
0	0	0	m	m	0	0	0	0	0	0	0	y	1
0	0	0	0	0	0	0	0	0	0	0	0	1	y

$c = 0.0128$ $e = 0.046$

1,3 Dimethylcyclopentane Trans Conformation

$y\text{-}a$	1	0	0	0	0	0	0	m	m	0	0	0	0
1	$y\text{-}c$	m	0	0	0	0	0	0	0	0	0	0	0
0	m	$y\text{-}c$	1	0	0	0	0	0	0	0	0	0	0
0	0	1	y	m	0	0	0	0	0	0	0	m	0
0	0	0	m	$y\text{-}e$	1	0	0	0	0	0	0	m	0
0	0	0	0	1	y	m	0	0	0	0	0	0	0
0	0	0	0	0	m	$y\text{-}c$	1	0	0	0	0	0	0
0	0	0	0	0	0	1	$y\text{-}f$	m	0	0	0	0	0
0	0	0	0	0	0	0	m	y	1	0	0	0	0
m	0	0	0	0	0	0	0	1	$y\text{-}e$	m	0	0	0
m	0	0	0	0	0	0	0	0	m	y	1	0	0
0	0	0	0	0	0	0	0	0	0	1	y	0	0
0	0	0	m	m	0	0	0	0	0	0	0	y	1
0	0	0	0	0	0	0	0	0	0	0	0	1	$y\text{-}b$

$a = 0.0116$ $b = 0.0232$ $c = 0.0128$ $e = 0.046$
$f = 0.0244 = 0.0116 + 0.0128$

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