

CCA-1494

YU ISSN 0011-1643

UDC 541

Original Scientific Paper

Structure and Properties of Small Ring Propellanes by the IMO Method

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Received December 12, 1983

Small ring propellanes containing only three and four membered rings were studied by using the IMO (Iterative Maximum Overlap) method. In order to calculate their geometries, a new relationship between bond overlaps and bond lengths for propellane central bonds was obtained. The calculated geometries, along with bond lengths and bond angles, for the first time contain all the dihedral angles between different rings. The hybridization parameters, strain and central bond energies were calculated in order to discuss their chemical stability, and it was shown that the smallest member [1.1.1]propellane is the most stable molecule in this series.

INTRODUCTION

Compounds containing very highly strained bonds have been of considerable interest for some time. A very interesting class of such compounds are propellanes. [*n.m.l*]propellanes¹ are tricyclic hydrocarbons in which the three rings are fused together at a common carbon-carbon conjoining bond, as shown schematically in Figure 1.

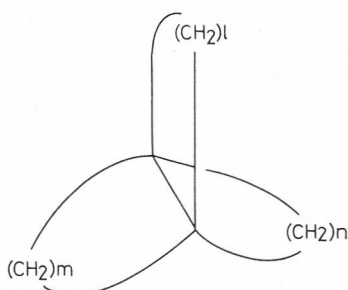


Figure 1. The propellane structure.

Propellanes with larger *n*, *m* and *l*, which contain only unstrained rings, are not particularly different from other saturated hydrocarbons. Propellanes with smaller *n*, *m* and *l* are more strained, and until relatively recently some of the most interesting ones were only characterized indirectly as fleeting intermediates in chemical reactions by trapping experiments. It has been suggested that the small ring propellanes containing only three and four

membered rings are strained to such an extent and, therefore, so unstable that they can not even be synthesised. However, recent syntheses^{2,3} of the remaining small ring propellanes show that these presumptions were not correct, and it has even been shown³ that the smallest member [1.1.1]propellane is the most stable.

The small ring propellanes considered in this paper, containing only three and four membered rings, are shown in Figure 2.

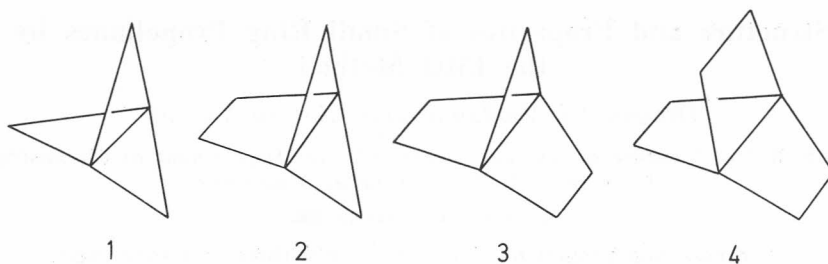


Figure 2. The small ring propellanes containing only three and four membered rings.

It is very interesting to apply the IMO (Iterative Maximum Overlap) method to these kind of molecules. Until now this method has been found very useful for discussion of many molecular properties for various strained hydrocarbons⁴⁻⁹. It should prove very useful to calculate hybrid functions of central (conjoining) bonds, *i. e.* the bonds between two inverted carbon atoms. The first reason for doing such calculations is that the nature of bonding at inverted carbon atoms is still not well understood. The second reason is the increased *p*-character of central bond hybrids. As the size of the rings in propellanes decreases, the hybrid exponents of the central bond hybrids increase and in the limiting case of [1.1.1]propellane should be sp^∞ , which implies that in this case we are dealing with pure (*p*) orbitals.

OUTLINE OF THE IMO METHOD

We give here a brief outline of the Iterative Maximum Overlap Method (IMO) and of the details available⁴⁻⁹. The aim of the method is to construct a set of local hybrid orbitals of the form

$$\Psi_{Aj} = a_{Aj} (2s)_A + (1 - a_{Aj}^2)^{1/2} (2p)_{Aj} \quad (1)$$

where A denotes the carbon atom in question and *j* refers to a direction in space of the $(2p)_{Aj}$ and consequently Ψ_{Aj} orbitals. The orthonormality conditions⁹ provide a set of the following relationships:

$$a_{Ai} a_{Aj} + (1 - a_{Ai}^2)^{1/2} (1 - a_{Aj}^2)^{1/2} \cos \Theta_{ij} = \delta_{ij} \quad (2)$$

where Θ_{ij} is the angle between the symmetry axes of the hybrid orbitals Ψ_{Ai} and Ψ_{Aj} , *i. e.* the interhybrid angle, and δ_{ij} is Kronecker delta. The sum of all bond overlap integrals is maximized by the variation of a_{Ai} 's

$$E_b = k_{CC} \sum_{C-C} S_{CC} + k_{CH} \sum_{C-H} S_{CH} \quad (3)$$

where k_{CC} and k_{CH} are scaling factors⁶.

The linear relations between bond distances and overlap integrals are proposed^{4,7}:

$$d(\text{C—C}) = -1.166 S_{\text{CC}}^{\sigma}(b) - 2.278 S_{\text{CC}}^{\pi}(b) + 2.298 \quad (\text{\AA}) \quad (4)$$

$$d(\text{C—H}) = -0.869 S_{\text{CH}} + 1.726 \quad (\text{\AA}) \quad (5)$$

The dependence of (b) is according to equation (1) when two such hybrid orbitals overlap in space, *i. e.* the σ - and π -part of inplane overlap associated with the bent bond. Using these relations in iterative procedure the consistent molecular geometry can be obtained.

Relationships for calculation of instantaneous bond dissociation energies⁸ and molecular strain energies⁹ have been established:

$$E(\text{C—C})_{\text{IBD}} = 372.3 S_{\text{CC}} - 143.7 \quad (\text{kcal/mol}) \quad (6)$$

$$E_{\text{S}} = 18.9 \sum_{\text{C—C}} S_{\text{C—C}}^{\sigma} + 1110.1 \sum_{\text{C=C}} S_{\text{C=C}}^{\pi}(b) - 11.7 \sum_{\text{C—C}} S_{\text{C=C}}^{\sigma+\pi} + 211.5 \sum_{\text{C=C}} S_{\text{C—C}}^{\pi} \\ (b) + 13.2 n_{\text{CC}} \quad (\text{kcal/mol}) \quad (7)$$

where n_{CC} is the number of CC bonds in the molecule. For three membered rings the constant parameter that multiplies the sum of π -overlaps of single CC bonds in equation (7), has the separate value of 189.1⁹. It is also possible to calculate heats of formations of molecules⁴, proton chemical shifts⁶ and spin-spin coupling constants⁶.

BOND OVERLAP-BOND LENGTH RELATIONSHIP FOR CENTRAL BONDS

In order to apply the IMO method to small ring propellanes we had to add an extension to the method. Namely, we could not use equation (4) for calculation of central bond distances. It is a well known fact that the nature of bonding at inverted^{1,10} carbon atoms is problematical, and it can be said to be different from usual CC bonding in organic chemistry. It is obviously difficult to describe the bond between a pair of inverted carbon atoms in traditional terms. Thus, we required a new relationship between central bond distances and central bond overlaps. We obtained that relationship in the following way.

The difference between calculated strain energies of small ring propellanes³ and related bicyclo alkanes¹¹ should correspond to the dissociation energies of central bonds. Having the bond dissociation energies, we can then calculate the corresponding bond overlaps by using the relationship between instantaneous bond dissociation energies and bond overlaps (equation (6)). A plot of calculated bond overlaps *vs.* MNDO calculated distances of central bonds³ shows a linear relationship. The procedure is shown in Table I and in Figure 3 and the relationship obtained is:

$$d_{\text{CB}} = -0.264 S_{\text{CB}} + 1.741 \quad (\text{\AA}) \quad (8)$$

Index CB is used to denote the central bond. This relationship is obtained in quite a qualitative manner, but this can also be said for used calculated values of strained energies. For evaluation of this relationship we used MNDO calculated bond lengths because they seem to be more reasonable than the bond lengths at the 6-31 G* and 4-31 G SCF level³.

TABLE I

Estimated Instantaneous Bond Dissociation Energies (E_{CB}), Bond Lengths (d_{CB}) and Bond Overlaps (S_{CB}) using Strain Energies (E_s) of Propellanes and Related Bicyclo-alkanes

Molecule	Strain energies E_s /kcal/mol		Central bond		
	[<i>n.m.l.</i>]propellanes ³	bicyclo[<i>n.m.l.</i>]alkanes ¹⁰	$\frac{E_{CB}}{\text{kcal/mol}}$	$\frac{d_{CB}}{\text{Å}}$	S_{CB} ⁸
1	103	92.2	10.8	1.631	0.415
2	106	41.2	64.8	1.596	0.560
3	108	16.1	91.9	1.571	0.633

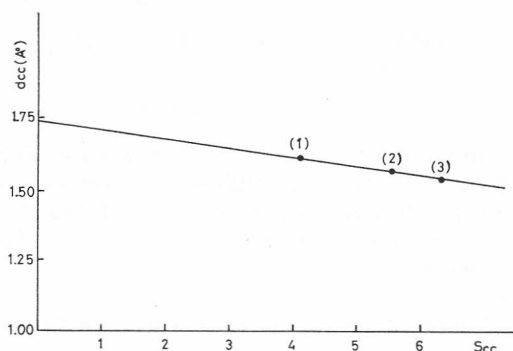
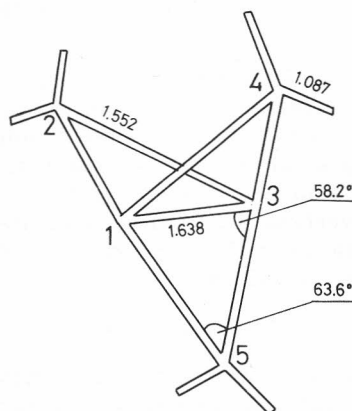


Figure 3. The dependence of central bond lengths in small ring propellanes upon the bond overlaps.

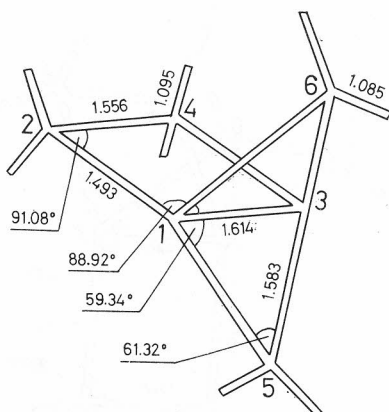
RESULTS AND DISCUSSION

Calculated geometries (bond lengths, bond angles and dihedral angles) and hybridization parameters along with deviation and interhybrid angles of **1**, **2**, **3** and **4** are given in Figures 4–7 and in Tables II–V.



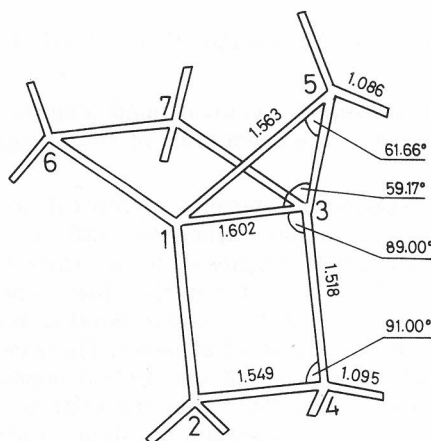
DIHEDRAL ANGLE BETWEEN THREE MEMBERED RINGS-120°

Figure 4. Geometry of [1.1.1]propellane. Bond lengths are given in Å.



DIHEDRAL ANGLE BETWEEN THREE MEMBERED RINGS -116.28°

Figure 5. Geometry of [2.1.1]propellane. Bond lengths are given in Å.



DIHEDRAL ANGLE BETWEEN FOUR MEMBERED RINGS -123.76°

Figure 6. Geometry of [2.2.1]propellane. Bond lengths are given in Å.

Calculated bond lengths of **1**, **2** and **3** are in agreement with MNDO calculations³. The central bond lengths have slightly higher values but the trend is the same. This could be an indication that the assumptions made in the evaluation of the relation between central bond distances and central bond overlaps (equation (8)) are not incorrect. These bond lengths lie in the upper part of reported distances between two inverted carbon atoms in various propellans, 1.55—1.64^{10,12-16}. Calculated central bond lengths of 1.638 in **1**, 1.614 in **2**, 1.602 in **3** and 1.588 in **4** show that these bonds are considerably longer than usual CC single bonds. It seems that as the size of the rings increases the central bond lengths decrease to a normal values of CC bonds, or are

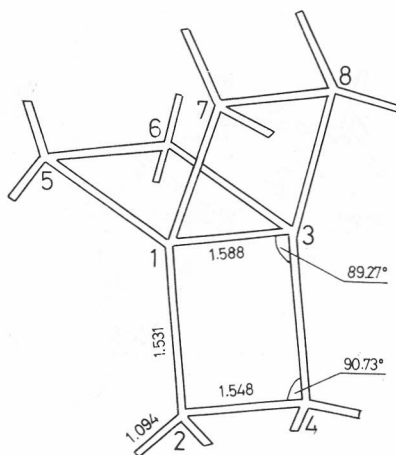
DIHEDRAL ANGLE BETWEEN FOUR MEMBERED RINGS -120°

Figure 7. Geometry of [2.2.2]propellane. Bond lengths are given in Å.

slightly stretched (1.57 Å in [3.2.1]propellane¹⁰ and 1.574 Å in [3.1.1]propellane derivative¹⁷).

It is very interesting to compare central bond lengths, their instantaneous bond dissociation energies and strain energies of four propellanes. The results are shown in Table VI.

Instantaneous bond dissociation energies of central bonds were calculated by using equation (6) as is customary when the IMO method is used. These energies are much lower than the energies of usual single CC bonds in organic chemistry. Only the central bond in **4** has the dissociation energy which is close to the usual values. In **2** and **3**, the central bond is very weak and in **1** it seems that the bond has no strength whatsoever. However, the central bond in **1** is in actual fact much stronger than the central bonds in the other small ring propellanes. It has been suggested^{2,3} that the central bond in **3** may well have negative bond energy. Now it is known (*J. Michl et al*³) that [1.1.1]propellane is isolable and far more stable than [2.1.1]propellane³, [2.2.1]propellane², [2.2.2]propellane¹⁸ and even more than [3.2.1]propellane¹⁹. This can be explained in terms of the strain relief upon rupture of the central bond³, which is vastly different in the four propellanes. It is huge in case of **4** and **3** because the related bicyclo alkanes contain only five and six membered rings and, therefore, have a very small strain. In the case of **2**, it is smaller what could indicate that this molecule is more stable than the previous two. The strain relief in the case of **1** is very small and this can be the reason why this molecule is far more stable than the others. However, if we look at our calculated values of strain energies (Table VI), it turns out that not only is the strain relief responsible for such behavior, but also the strain itself. The strain energy of **1** is the smallest and this also could be the reason for its higher stability. It should be noted here, that IMO calculated strain energies give only the qualitative picture. The agreement with calculated values at the 6-31 G* level of the SCF theory is very bad in the case of **1** and **2**, and not too bad in the case of **3**

and **4** (Table VI). We can also say that **2** should be more stable than **3** and **4**, since its strain energy is smaller, which is in agreement with the suggestion of Walker, Wiberg and Michl². However later, Michl *et al.*³ reported that only [1.1.1]propellane is more stable than the others, including [2.1.1]propellane and that the stability of **2** can be compared with the stability of **3**.

When speaking about central bonds in small ring propellanes, it is very useful to discuss their hybridization parameters and directions of hybrids. The central bond is formed from hybrid orbitals with very large hybrid exponents. In **4** the central bond is formed from two $sp^{5.6}$, in **3** from two $sp^{8.7}$, in **2** from two $sp^{14.7}$ and in **1** from two $sp^{53.8}$ hybrid orbitals (Tables II—V). This means that the p -character of these hybrids is strongly pronounced. The (p) orbitals participate in central bond hybrids, denoted as Ψ_{13} in Tables II—V, with the following amounts: 0.920 in **4**, 0.947 in **3**, 0.968 in **2** and 0.991 in **1**. In the limiting case of **1**, we can easily talk about pure (p) orbitals forming the central bond. In the case of **1** and **4** (D_{3h} symmetry is assumed) central bond hybrids are directed to one another along the bond line. In the case of **2**, the central bond hybrids lie in the plane of the four membered ring, outside of the ring and are directed to one another forming the deviation angle with the bond line of 0.6° (Figure 5). This deviation angle is responsible for deviation from D_{3h} symmetry so that the dihedral angle (120° in **1**) between two three membered

TABLE II

[1.1.1]propellane **1**

Hybrids	Overlaps	Interhybrid angles	Deviation angles
		degrees	degrees
$\Psi_{13} = sp^{53.81}$	$S_{13}\sigma = 0.387$	$\Theta_{312} = 95.46$	$\delta_{13} = 0.0$
$\Psi_{12} = sp^{2.10}$	$S_{13}\pi = 0.0$	$\Theta_{215} = 119.12$	$\delta_{12} = 37.31$
$\Psi_{21} = sp^{2.86}$	$S_{12}\sigma = 0.560$	$\Theta_{123} = 105.46$	$\delta_{21} = 20.66$
$\Psi_{2H} = sp^{2.40}$	$S_{12}\pi = 0.041$		
	$S_{2H} = 0.736$		

TABLE III

[2.1.1]propellane **2**

Hybrids	Overlaps	Interhybrid angles	Deviation angles
		degrees	degrees
$\Psi_{13} = sp^{14.74}$	$S_{13}\sigma = 0.476$	$\Theta_{312} = 101.31$	$\delta_{13} = 0.57$
$\Psi_{12} = sp^{1.77}$	$S_{13}\pi = 0.0$	$\Theta_{315} = 99.53$	$\delta_{15} = 40.49$
$\Psi_{21} = sp^{3.18}$	$S_{21}\sigma = 0.678$	$\Theta_{124} = 107.50$	$\delta_{12} = 11.82$
$\Psi_{24} = sp^{3.48}$	$S_{12}\pi = 0.006$	$\Theta_{351} = 104.38$	$\delta_{51} = 21.52$
$\Psi_{15} = sp^{2.48}$	$S_{24}\sigma = 0.628$	$\Theta_{516} = 113.80$	$\delta_{21} = 8.97$
$\Psi_{51} = sp^{4.03}$	$S_{24}\pi = 0.003$	$\Theta_{215} = 118.56$	$\delta_{24} = 7.44$
$\Psi_{2H} = sp^{2.72}$	$S_{15}\sigma = 0.525$		
$\Psi_{5H} = sp^{2.32}$	$S_{15}\pi = 0.045$		
	$S_{2H} = 0.726$		
	$S_{5H} = 0.738$		

TABLE IV
 [2.2.1]propellane 3

Hybrids	Overlaps	Deviation angles	
		degrees	
$\Psi_{13} = sp^{8.66}$	$S_{13}^{\sigma} = 0.513$	$Q_{312} = 101.31$	$\delta_{13} = 11.51$
$\Psi_{12} = sp^{2.12}$	$S_{13}^{\pi} = 0.009$	$Q_{315} = 99.53$	$\delta_{15} = 30.35$
$\Psi_{21} = sp^{3.37}$	$S_{12}^{\sigma} = 0.641$	$Q_{124} = 107.50$	$\delta_{12} = 20.15$
$\Psi_{24} = sp^{3.30}$	$S_{12}^{\pi} = 0.014$	$Q_{351} = 104.38$	$\delta_{51} = 21.71$
$\Psi_{15} = sp^{2.91}$	$S_{24}^{\sigma} = 0.639$	$Q_{516} = 113.80$	$\delta_{21} = 11.90$
$\Psi_{51} = sp^{3.88}$	$S_{24}^{\pi} = 0.001$	$Q_{215} = 118.56$	$\delta_{24} = 4.61$
$\Psi_{2H} = sp^{2.72}$	$S_{15}^{\sigma} = 0.557$		
$\Psi_{5H} = sp^{2.39}$	$S_{15}^{\pi} = 0.037$		
	$S_{2H} = 0.727$		
	$S_{5H} = 0.736$		

 TABLE V
 [2.2.2]propellane 4

Hybrids	Overlaps	Interhybrid angles	Deviation angles
		degrees	degrees
$\Psi_{13} = sp^{5.55}$	$S_{15}^{\sigma} = 0.577$	$\Theta_{312} = 105.46$	$\delta_{13} = 0.0$
$\Psi_{12} = sp^{2.54}$	$S_{13}^{\pi} = 0.0$	$\Theta_{215} = 113.18$	$\delta_{12} = 16.20$
$\Psi_{21} = sp^{3.38}$	$S_{12}^{\sigma} = 0.638$	$\Theta_{124} = 107.40$	$\delta_{21} = 10.81$
$\Psi_{24} = sp^{3.31}$	$S_{12}^{\pi} = 0.010$		$\delta_{24} = 5.83$
$\Psi_{2H} = sp^{2.70}$	$S_{24}^{\sigma} = 0.639$		
	$S_{24}^{\pi} = 0.002$		
	$S_{2H} = 0.727$		

 TABLE VI
 Dissociation Energies, Central Bond Lengths and Strain Energies of Small Ring Propellanes

Molecule	Distances of central bonds ^a	Central bond dissociation energies ^a	IMO strain energies ^a	Calculated strain energies
	Å	kcal/mol	kcal/mol	kcal/mol
1	1.638	0.4	67.8	103 ^b
2	1.614	33.6	71.1	106 ^b
3	1.602	50.6	96.2	108 ^b
4	1.588	71.2	88.9	73.28 ^c —90 ^d

^a This work

^b SCF 6—31 G*, 4—31 G for 3 Ref. 3.

^c Force field calculations, E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Amer. Chem. Soc.* **95** (1973) 8005

^d M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.* **94** (1972) 4191

rings is 116.3° . Similarly in **3**, the central bond hybrids lie in the plane of three membered ring and are directed to each other outside of the ring forming the deviation angle with the bond line of 11.5° (Figure 6). Such a large deviation angle is responsible for the increase of the dihedral angle between two four membered rings from 120° in **4** to 123.8° in **3**.

Newton and Schulman²⁰ have made *ab initio* calculations of [1.1.1]propellane and according to these calculations the central bond is formed from two sp^4 hybrid orbitals directed away from one another and having zero overlap population. There is also recent experimental evidence stating that there exists absence of residual electron density along the central bond in [3.1.1]-propellane derivative¹⁷, what is in agreement with the Newton and Schulman general kind of description. However speaking about the hybrid orbitals in [1.1.1]propellane, there are three $sp^{2.1}$ hybrids on the inverted carbon atom which leaves almost pure (*p*) orbital available for forming in this case the σ bond. According to orthonormality conditions, this provides a hybrid orbital with a very large hybrid exponent $sp^{53.8}$ (Table II).

CONCLUSION

The crucial point in the IMO method is that the hybrids are constrained in order to satisfy the empirical bond lengths-bond overlap correlations. We have evaluated a similar correlation valid for small ring propellane central bonds (equation (8)). Calculated geometries of small ring propellanes show satisfactory agreement with some other more sophisticated methods of calculation, such as the MNDO method³. The IMO approach gives consistent geometries, so it was possible to calculate the dihedral angles in less symmetric propellanes (**2** and **3**) which contain both three and four membered rings.

The calculations of strain energies show that the smallest member [1.1.1]-propellane is the most stable, *i. e.* it's strain energy is the smallest. It is suggested that this could be, besides the strain relief, another reason for it's relatively high chemical stability.

The investigation of electron density distribution and deformation (difference) density distribution in small ring propellanes would be very helpful in understanding their stability and the nature of bonding at inverted carbon atoms. These calculations are currently under way.

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SAŽETAK

Strukturni parametri i svojstva malih propelana dobiveni primjenom IMO metode

Dragan Lj. Vučković i Ljubica Vujisić

Primjenom iterativne metode maksimalnog prekrivanja (IMO) proučavani su neki propelani koji sadrže tročlane i četveročlane prstene. Da bi se mogla izračunati njihova geometrija, uvedena je nova relacija između integrala prekrivanja i duljina centralnih veza propelana. U tu svrhu korišteni su teorijski strukturni parametri koji se mogu naći u literaturi. Izračunane IMO-geometrije, pored duljina veza i kutova među vezama, sadrže i sve diedarske kutove, pa su tako po prvi puta dani svi strukturni parametri tih zanimljivih molekulskih sustava. Svojstva koja slijede iz elektronske strukture prodiskutirana su s pomoću izračunanih parametara hibridizacije. Dane su energije napetosti i energije centralnih veza da bi se s pomoću njih mogla odrediti stabilnost tih spojeva. Proizlazi da je najstabilnija molekula najmanji član ove serije ([1.1.1]propelan).