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A MOLECULAR MECHANICS STUDY OF NEW MOLECULES CONTAINING INVERTED CARBONS
SMALL-RING GEMINANES AND [n.1.1]PROPELLANES WITH $n>4$[1]

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The optimum geometry, steric energy and heat of formation of new molecules containing inverted carbons, i.e., small-ring geminanes and [n.1.1]propellanes with $n>4$, has been calculated on the basis of molecular mechanics. Three molecules under investigation exhibit unsymmetrical pairs of inverted carbons and in four of them an isolated inverted carbon is present. The calculated strain in the molecules seems not to be big enough to preclude their syntheses.

An inverted carbon is a carbon atom having all substituents in one hemisphere. Due to the highly unusual properties of the bond formed by such atoms, the molecules forming them are the subject of numerous investigations in spite of the fact that only few examples of this kind have been synthesized. In his recent review on the topic Wiberg[2] has given eight molecules 1 - 7, 9 possessing inverted carbons and tricyclo[2.2.2.$0^{1,4}$]octane 8 as a limiting case. With the exception of bicyclobutane 1 all other cited molecules are [k.1.m]propellanes of a general formula 10 involving a pair of symmetrical inverted carbons each (with $k<5$ and at least one cyclopropane ring, i.e., $m = 1$). Recently, we have carried out a molecular mechanics study[3] of larger [k.1.m]propellanes


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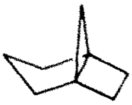
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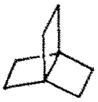
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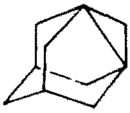
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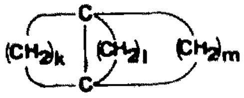

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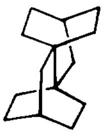
with k, l, m equal to 2, 3, 4[4]. A subsequent attempt to extend the calculations to smaller propellanes with k, l, m equal to 1, 2, 3[5] proved unsuccessful due tothe lack of some parameters involved.During this study four important questions have arisen : Are there propellanes possessing medium and large rings exhibiting inverted carbons ? Are there other types of molecules possessing inverted carbons ? Is there a possibility of existence of an asymmetric pair of inverted carbons [6,7] ? and Is there a possibility of existence of a single inverted carbon in a molecule ? The positive answers to these questions will be discussed in the present paper as well as some properties of the new hypothetical molecules 13 - 22 (most of which possess inverted carbons) which have been analysed by means of molecular mechanics[3] using the program KNOW[8] with the standard MM2 parametrization[9]. The method has been shown to yield very accurate values of steric energy E_s and heat of formation HOF for molecules with standard geometry[3] but its application to highly strained systems requires some justification. It should be stressed first that the main purpose of the present report is to attract attention of organic chemists to the systems under investigation. Secondly, semiquantitative information on the molecules containing inverted carbons seems to be of value and we believe that the molecular mechanics with the standard MM2 parametrzation can yield such an information concerning E_s and HOF values as well as the one concerning geometrical parameters (see ref. 10 and 11 for the successful applications of this kind to molecules containing planarized and planar cyclohexane rings and to some saturated cage compounds of the general formula $C_{12}H_{12}$). The results of the calculations presented below seem to indicate that these interesting molecules should not exhibit excessive strain and, thus, their syntheses seem plausible. On the other hand, the future results of experimental studies of small-ring geminanes and [n.1.1]propellanes with $n>4$ after their syntheses will provide a final check of the applicability of the MM2 method to such systems and will enable refinement of the parameters used.

GEMINANES

In 1980 Paquette[12] reported the syntheses of the molecules 11, 12 which can be considered as a fusion of two identical bicyclic systems and he called them [2.2.2]- and [3.2.1]geminanes.



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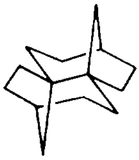

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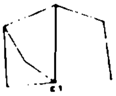
If one extends his definition to include the fusion of smaller rings and/or that of different bicyclic systems then the tetracyclic molecules 14 - 22 can be analysed and it turns out that most of them as well as tricyclo[3.1.1.0.^{1,4}]heptane 13 possess inverted carbons.

The optimum geometry, heat of formation, HOF, and steric energy, E_s, have been calculated using the molecular mechanics[3] program KNOW[8] with the standard MM2 parametrzation[9] for the molecules 13 - 22. The lengths of the bridgehead-bridgehead bond d_{12}, E_s and HOF values and the distance d_i from the plane going through the bridging neighbours of an inverted carbon atom to this



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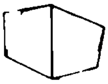

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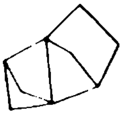

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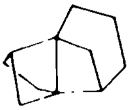
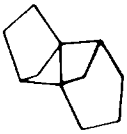
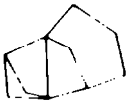


cis-21



trans-21



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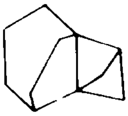

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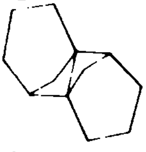
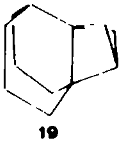
cis-22



trans-22



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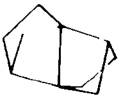
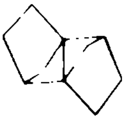


cis-20



trans-20

same atom are collected in the Table. For the molecules 21 - 22 two stable conformers very close in energy, trans-1 and trans-2, have been found. Despite the attempts, no other stable conforers have been detected for the molecules under investigation.

Table

The calculated values of the bridgehead-bridgehead bond lengths d_{12}, of the inverticity distances d_i, and those of steric energy E_s and heat of formation HOF for tricycloheptane 13 and the geminanes 14 - 22

Molecule	d_{12} in pm	d_i in pm	E_s in kcal/mol	HOF in kcal/mol
13	174.5	15.1	120.88	91.22
14	177.4	33.0, 33.0	174.28	144.58
15	174.4	16.1, 25.0	142.28	106.17
16	173.3	6.2, 20.5	139.19	96.67
17	161.9	0.9	125.23	82.71
18	157.5	-	119.50	70.56
19	155.9	-	114.32	58.97
cis-20	162.9	3.8, 3.8	105.26	62.74
trans-20	171.4	8.7, 8.9	108.73	66.21
cis-21	157.9	-	98.12	49.18
trans1-21	170.5	1.4, 3.8	107.21	58.27
trans2-21	171.1	8.5	107.23	58.30
cis-22	157.8	-	88.14	32.79
trans1-22	171.1	6.3	108.57	53.22
trans2-22	171.0	-	108.58	53.23

The following conclusions can be drawn from the data :

1. The molecules 13 - 16, cis- and trans-20, two stable conformers of 21, and one conformer of 22 possess inverted carbons.
2. Because of the symmetry of the systems there are symmetrical pairs of inverted carbons in the molecules 14 and cis- and trans-20. The corresponding unsymmetrical pairs are present in the molecules 13, 15, 16 and trans-21, while in the molecules trans2-21 and trans1-22 an isolated inverted carbon is present. In the molecule 17 one of the bridgehead carbons represents a limiting case similar to that found in the molecule 8, i.e. the carbon atom and its three bridging neighbours lie approximately in a plane.
3. As concerns their structures and the trends exhibited by bridgehead-bridgehead bond lengths and E_s and HOF values, the molecules 13 - 22 fall into three classes. The first one consists only of one molecule 13, the second one is formed by the molecules 14 - 19, in which the rings involved are enlarged in only one bicycle and the third class consists of the molecules 20 - 22, in which the ring enlargement is introduced in both bicycles, thus enabling cis and trans isomerism.

The molecules 14 - 19 exhibit regular trends in E_s, HOF, d_{12} values and the degree of inverticity as measured as $d_i$values for a given inverted carbon i. For obvious reasons, the E_s, HOF and d_{12} values decease when larger rings are involved. At the same time the corresponding $d_i$values diminish, too.

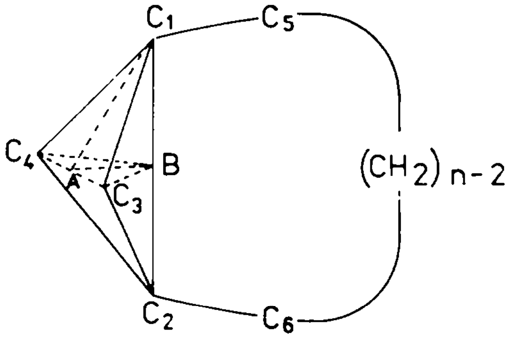
The pattern of changes differs when going to the third class of the molecules 20 - 22. There, for the trans-molecules the arrangement is so unfavourable that the E_s and d_{12} values change very little on rings enlargement, while, consequently, the HOF values diminish at the same time. On the other hand, the cis-molecules are more stable and less strined than the trans ones and the corresponding d_{12}, E_s and HOF values are lower than the values for the trans-molecules and they decrease on the enlargement of the rings involved.

4. As expected, the ring enlargement in the same bicycle releases strain less effectively than the corresponding enlargements in both bicycles, i.e., the E_s value for 17 is bigger than that for cis-20 and the values for 18 and 19 are bigger than the corresponding values for cis-21 and cis-22, respectively. On the other hand, the bridgehead-bridgehead distances d_{12} in the same series 17 - 19 are lower than these in the series 20 - 22 showing that the strain in the molecules is not localized in the bonds.

5. The strain in the molecules under investigation seems to be not big enough to preclude their syntheses.

[n.1.1] PROPELLANES WITH n>4

As stated above, bicyclobutane 1 and the small-ring propellanes 2 - 7 and 9 are the only known systems in which inverted carbons are present. Searching for propellanes possessing medium and large rings and exhibiting inverted carbons let us consider [n.1.1]propellane shown schematically in the Figure. The following simplifying assumptions have to be made : a. all bonds within cyclopropane rings are equal. b. The bond C1C5 (and the C2C6 one) lie in the C1AC2 bisecting the angle between cyclopropane rings. c. The angle C2C1C5 is equal to 120°. d. The value of the angle C3C1C4 is equal to 95° (taken from the [1.1.1]propellane structure analysis[13]).



Under these assumptions the value of the AC1B angle can be calculated from the relation :

$$\cos(AC1B) = \frac{1}{2\cos(C3C1C4/2)} = 0.7401$$

Then, the angle AC1B + C2C1C5 equal to ca. 167° is less than 180°, thus, the C1 atom (and, by symmetry, the C2 one) is inverted. The limiting case corresponding to the value of 180° for the AC1B + C2C1C5 angle can be achieved for a rather unusual value of 133° of the angle AC1B or for the value of 85° for the angle C3C1C4. The last value is considerably lower than the lowest reported value of 91° forced by additional bridges found for the angle between the cyclopropane rings in [n.1.1]propellanes [14]. By even a simpler reasoning one can prove that for [n.2.2]propellanes the corresponding value of AC1B + C2C1C5 angle is bigger than 180°, i.e., the bridgehead carbon atoms in the last molecules are not inverted. No analogous simple reasoning can be carried out for [n.2.1]propellanes for n>4 but it seems that should represent the limiting case for which the three neighbouring atoms lie in a plane with the corresponding bridgehead carbon or very close to it. No [n.1.1]propellanes are known for n>4 although the molecules with n = 5 or more should be considerably less strained than [4.1.1]- and [3.1.1]propellanes, derivatives of which are known[2]. To have an insight into the energetics of the systems, an estimation of the steric energy E_s and heat of formation HOF has been performed by means of the same method as that used previously for the molecule 13 and the geminanes 14 - 22. As for the molecules 13 - 22 it has been found that the calculated values of HOF and E_s (32.8 and 21.9 kcal/mol, respectively) seem to indicate that the strain in the [n.1.1] propellane with n>4 is not big enough to preclude synthesis of [5.1.1] propellane and the higher members of the series.

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