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Note

Theoretical Studies on Small Ring Heteropropellanes. Oxapropellanes.*

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Oxa(1.1.1)propellane (2), dioxa(1.1.1)propellane (3), and trioxa(1.1.1)propellane (4) have been studied by means of *ab initio* SCF MO technique at 6-31G* level. The geometry optimization is carried out for these molecules and the parent hydrocarbon (1.1.1)propellane. The bond between the two bridgehead carbon atoms is predicted to be in (2) : 1.503 Å, (3) : 1.474 Å, and (4) : 1.456 Å. These are shorter than the calculated central bond (1.543 Å) in (1.1.1)propellane.

Small ring (*i.j.k*)propellanes ($i = 1, 2; j = 1, 2; k = 1, 2$) are highly strained tricyclic hydrocarbons of general formula $C_{2+n}H_{2n}$ ($n \geq 3$).¹⁻⁴ They may have been made years ago, but only relatively recently are recognized as propellanes, *i. e.* the tricyclic hydrocarbons in which the three rings are fused together at a common carbon-carbon conjoining bond.^{1,2} Heteropropellanes are of more recent date than the parent propellanes.⁵⁻⁸

Small ring oxa(*i.j.k*)propellanes ($i = 1, 2; j = 1, 2; k = 1, 2$) of general formula $C_{2+n-k}H_{2(n-k)}O_k$ ($k = 0, 1, \dots, n; n \geq 3$) are not as yet prepared. However, some larger oxapropellanes, such as oxa(3.2.1)propellane or dioxa(3.3.3)propellane, are known.^{5,6} Here we will consider only the smallest of the oxapropellanes: oxa(1.1.1)propellane, dioxa(1.1.1)propellane, and trioxa(1.1.1)propellane. Diagrams of these structures and the parent molecule (1.1.1)propellane are given in the Figure.

In the present work we are interested in the change of the length of the central carbon-carbon (C_1-C_3) bond that may happen on substitution of the $>CH_2$ group by oxygen in the propellane system. Various *ab initio* MO calculations that are reported in the literature found the C_1-C_3 bond in (1.1.1)propellane to be of a normal length (1.54 Å)^{9,10}, although each of the two bridgehead carbons, C_1 and C_3 , possess inverted configurations.¹² However, all *ab initio* MO calculations are not uniform in this respect, especially older computations. For example, Newton and Schulman¹¹ predicted the C_1-C_3 bond to be 1.60 Å. On the other hand the calculations performed by the IMO (Iterative Maximum Overlap) method^{13,14} predicted the central bond (1.1.1)-

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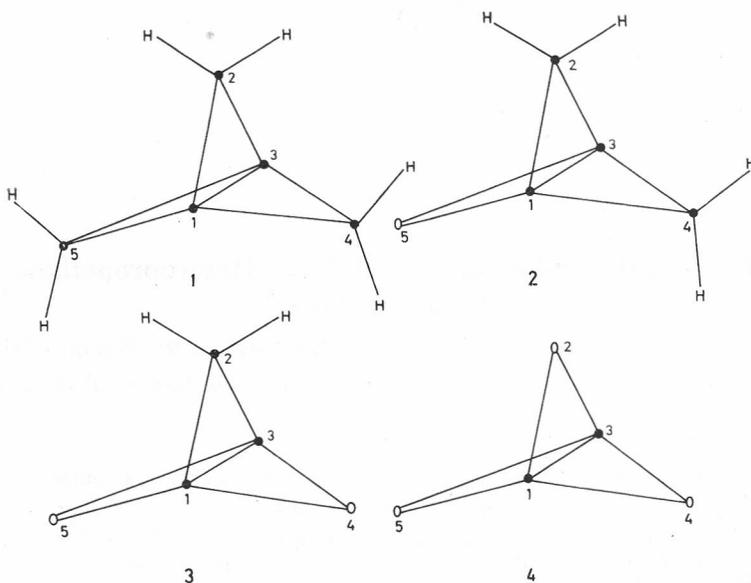


Figure. The structures of oxapropellanes under study

propellane to be much longer (1.638 Å).¹⁵ However, this result is not supported by the available experimental data. For example, it was found that the length of a central bond in (3.1.1)propellane is 1.55—1.57 Å.¹⁶ Perhaps this is the case when the IMO method, otherwise a very useful theoretical model, is less successful because of the unusual bonding situation in the molecule.

We performed on the systems in the Figure *ab initio* MO calculations in the RHF approximation using the Gaussian 80 technology.¹⁷ The standard Gaussian 80 (QCPE 937) programme was modified for the use on the Siemens 7760 Computer. The prime target of our study was the complete geometry optimization of oxapropellanes, which was carried out at the 4-31G* level and then the geometry refinement at the 6-31G* level.^{18,19} We first carried out calculation for (1.1.1)propellane (1) in order to check our adaptation of the Gaussian 80 programme. The obtained optimized geometry of (1.1.1)propellane is identical to that one reported by Wiberg¹⁰, the only difference being in the value for the C₁C₂C₃ angle. Our value (61.81°) is slightly bigger than the value obtained by Wiberg (59.11°)*. The total energy obtained for 1 in hartrees is -192.691061 and is identical to the value obtained by Wiberg (-192.691062 hartrees) with the 6-31G* basis set.

The next step was the complete geometry optimization for oxapropellanes at the 4-31G* level and then the 4-31G* optimized structures were partially optimized at the 6-31G* level. The calculated geometries of oxapropellanes together with the geometry of (1.1.1)propellane are given in Table I.

The total energies (in hartrees) of the optimized structures at the 6-31G* level are as follows: oxa(1.1.1)propellane: -228.480191, dioxo(1.1.1)propellane: -264.267511, and trioxo(1.1.1)propellane: -300.042596.

Our calculations show that the central C₁—C₃ bond in oxapropellanes becomes shorter on oxygen substitution. Thus, the bond length of the bridge-

* This is actually a misprint in Wiberg's paper.¹⁰

TABLE I
Optimized Geometries of Oxa(1.1.1)propellanes and the Parent Hydrocarbon(1.1.1)propellane

Compound*	Bond/Angle	Calculated value (Å, deg.)
1	C ₁ —C ₃	1.543
	C ₁ —C ₂	1.502
	C ₂ —H	1.075
	C ₁ C ₂ C ₃	61.81
	HC ₂ H	114.52
2	C ₁ —C ₃	1.503
	C ₁ —C ₂	1.501
	C ₁ —O ₅	1.415
	C ₃ C ₁ C ₂	59.93
	C ₂ H	1.073
	C ₂ C ₁ C ₄	99.58
	C ₁ C ₂ C ₃	60.13
	C ₁ O ₅ C ₃	64.16
	C ₁ C ₃ O ₅	57.92
	HC ₂ H	116.464
3	C ₁ —C ₃	1.747
	C ₁ —C ₂	1.505
	C ₁ —O ₄	1.400
	C ₂ —H	1.073
	C ₃ C ₁ C ₂	60.68
	C ₁ C ₂ C ₃	58.64
	C ₁ O ₄ C ₃	63.53
	O ₄ C ₁ C ₃	58.24
	O ₄ C ₁ O ₅	94.3
	HC ₂ H	118.03
4	C ₁ —C ₃	1.456
	C ₁ —O ₃	1.393
	C ₃ C ₁ O ₂	58.50
	C ₁ O ₃ C ₃	63.00
	O ₃ C ₁ O ₄	95.18

* The structures, and numbering of atoms, are given in the Figure.

head bond in oxa(1.1.1)propellane drops from 1.543 Å in (1.1.1)propellane to 1.503 Å. In dioxa(1.1.1)propellane and trioxa(1.1.1)propellane it becomes 1.474 Å and 1.456 Å, respectively. This shortening of the C₁—C₃ bond may be understood in terms of the Jackson-Allen (σ bridged π bond) model.¹⁰ These authors explained the unusual bonding in (1.1.1)propellane as follows. The origin of the C₁—C₃ binding is related to the three-centre, two electron molecular orbitals arising from $2p\pi$ AO on C₁ and C₃ and the inward-pointing sp^2 hybrid orbital of the methylene bridge. The C₁—C₃ binding is found to be electron-deficient because the HOMO of (1.1.1)propellane has the non-bonding character.^{10,11} Now when CH₂ group is replaced by an oxygen several things happen. First the removal of hydrogen atoms allows a flow of electrons to the skeleton of a molecule, because hydrogens are ordinarily pulling electrons away from the molecular core. The second thing which happens is that the sp^2 hybrids on oxygen²⁰ overlap to greater extent with $2p\pi$ AO on C₁ and C₃ atoms, than sp^2 hybrids on carbon. Finally, the HOMO in oxapropellanes becomes bonding and this results in shorter C₁—C₃ bond.

In order to see how far this model may be extended we are currently studying thiapropellanes and oxathiapropellanes.

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SAŽETAK

Teorijski studij molekula heteropropelana. Oksapropelani

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Oksa(1.1.1)propelan (2), dioksa(1.1.1)propelan (3) i trioksa(1.1.1)propelan (4) proučavani su s pomoću *ab initio* SCF MO tehnika na razini 6-31G*. Optimizirane su geometrije tih molekula i odgovarajućeg ugljikovodika (1.1.1)propelana. Predskazana je slijedeća središnja veza: 2:1.503 Å, 3:1.474 Å i 4:1.456 Å. Te su veze kraće nego odgovarajuća veza (1.543 Å) u (1.1.1)propelanu.