SHORT PAPER

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Investigation of structural properties of heteropropellane compounds by *ab initio* methods[†]

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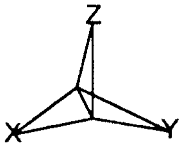
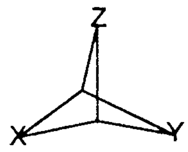
Molecular structure and relative stability of the ground state of [1.1.1] propellane, various [1.1.1] heteropropellane compounds and also their respective hydrogenated bicyclo compounds along with inversion barrier energy of nitrogen and its corresponding transition state in some of these compounds have been determined using *ab initio* molecular orbital and hybrid HF-density functional methods.

It is well known that more drastic distortions from ideal geometry are found when several small rings are assembled into bicyclic, tricyclic, and more complex molecules. The synthesis of such highly strained molecules is not only a challenge to the imagination and skill of chemists, but also provides the opportunity to test bonding theories by probing the effects of unusual bonding on the properties of molecules. For that reason, the formation of tricyclic compounds joined by a carbon–carbon single bond, such as propellane and heteropropellane compounds has been of great interest[1–2]. Even though [1.1.1] propellane (**a1**) is a highly strained propellane compound, it is stable at room temperature. This compound and many other propellane and heteropropellane compounds have successfully been synthesized (see refs 1, 3, 4 and references therein). Although bond angles of both bridgehead C-1 and C-3 atoms are not tetrahedral and possess an inverted configuration, X-ray analysis revealed that the central C1–C3 bond in [1.1.1] propellane has the normal length (154 pm) as the unstrained ethane [4,5].



(a)



(b)

a1, b1; X=Y=Z=CH_2
a2, b2; X=Y=Z=NH
a3, b3; X=Y=Z=O
a4, b4; X=Y=CH_2 , Z=NH
a5, b5; X=Y=CH_2 , Z=O
a6, b6; X=Y=CH_2 , Z=S
a7, b7; X=Y=NH , Z=CH_2
a8, b8; X=Y=O , Z=CH_2
a9, b9; X=Y=O , Z=NH

Generally, geometry and energy of various molecular systems can be estimated reasonably well with semiemprical and *ab initio* methods, however, for small polar molecular systems with a basis set of modest size, neither semiemprical nor *ab initio* methods can generate accurate results [6–8]. Nevertheless, successful applications of density functional theory (DFT) have broadened the applicability of the computational methods.

Jursic has demonstrated that some density functional theory based methods represent an interesting approach for determination of geometry, activation barrier and energies of molecules (see ref. 9 and references therein). In this work, *ab initio* molecular orbital and hybrid HF-density functional methods[10,11] have been used for determination of ground state molecular structure and relative stability of the propellane and heteropropellane compounds (**a1**–**a9**) and their respective hydrogenated bicyclo compounds (**b1**–**b9**), as well as energy barrier of nitrogen inversion and its corresponding transition

Table 1 Calculated geometric parameters of a1-a9 propellane and heteropropellane compounds and transition state structure of N-inversion in a4 and a9 compounds. Bond lengths are in angstrom units and angles in degrees.

		a1	a2	a3	a4	a5	a6	a7	a8	a9	a4(TS)	a9(TS)
HF	C-C	1.54	1.48	1.46	1.52	1.50	1.55	1.50	1.47	1.46	1.53	1.47
	C-X	1.50	1.45	1.39	1.50	1.50	1.50	1.45	1.40	1.40	1.51	1.41
	C-Z	1.50	1.45	1.39	1.46	1.42	1.79	1.50	1.51	1.45	1.42	1.41
	X-C-Y	96.01	96.18	95.17	97.52	99.55	97.40	95.07	94.30	94.58	96.78	93.34
	X-C-Z	96.01	96.18	95.17	93.66	94.59	98.55	94.97	96.80	94.92	95.07	95.88
	C-X-C	61.77	61.50	63.01	60.67	60.07	62.00	61.63	63.49	62.98	60.86	63.23
	C-Z-C	61.77	61.05	63.01	62.78	64.11	51.36	59.83	58.60	60.78	65.28	63.18
B3LYP	C-C	1.58	1.52	1.49	1.55	1.54	1.58	1.53	1.51	1.49	1.57	1.50
	C-X	1.52	1.48	1.43	1.56	1.52	1.52	1.49	1.44	1.44	1.53	1.45
	C-Z	1.52	1.48	1.43	1.49	1.45	1.82	1.52	1.52	1.47	1.44	1.42
	X-C-Y	95.46	95.33	95.47	96.98	98.99	97.14	94.93	94.61	94.89	96.13	93.39
	X-C-Z	95.46	95.33	95.47	97.30	94.34	97.98	98.66	96.56	94.73	94.78	96.01
	C-X-C	62.60	61.67	62.59	61.53	60.94	62.99	62.06	63.19	62.48	61.48	62.65
	C-Z-C	62.60	61.67	62.59	62.97	63.97	51.51	60.67	59.44	60.89	65.95	63.89

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Calculated geometric parameters of b1-b9 bicyclo compounds and transition state structure of N-inversion in b4 and b9 compounds. Bond lengths are in angstrom units and angles in degrees.

		b1	b2	b3	b4	b5	b6	b7	b8	b9	b4(TS)	b9(TS)
	C-X	1.55	1.48	1.42	1.54	1.54	1.54	1.49	1.43	1.43	1.55	1.43
	C-Z	1.55	1.48	1.42	1.50	1.45	1.86	1.54	1.54	1.47	1.47	1.44
HF	X-C-Y	87.21	90.33	91.18	88.40	89.65	87.38	89.50	91.07	91.09	87.65	89.48
	X-C-Z	87.21	90.33	91.18	86.80	88.67	89.83	91.07	89.90	89.80	87.81	90.67
	C-X-C	74.42	70.05	68.86	71.74	70.31	76.83	71.86	71.93	69.57	72.04	70.28
	C-Z-C	74.42	70.05	68.86	74.38	75.22	62.00	69.55	66.30	67.40	76.89	69.89
	C-X	1.56	1.51	1.45	1.55	1.55	1.55	1.52	1.47	1.47	1.57	1.47
	C-Z	1.56	1.51	1.45	1.55	1.49	1.90	1.46	1.54	1.50	1.48	1.45
B3LYP	X-C-Y	87.25	90.67	91.78	90.35	89.95	87.85	89.59	91.47	91.65	87.70	89.71
	X-C-Z	87.25	90.67	91.78	88.60	88.79	89.91	91.53	90.38	90.12	88.03	91.25
	C-X-C	74.36	69.59	67.99	71.94	70.61	76.81	71.16	70.79	68.49	71.85	69.05
	C-Z-C	74.36	69.59	67.99	73.49	73.85	61.05	69.74	66.73	67.04	76.65	70.32

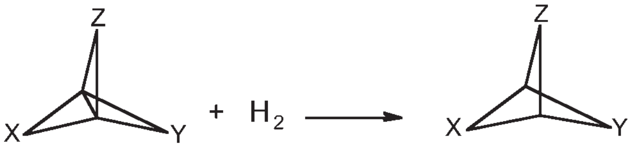
Table 3 *Ab initio* calculated Gibbs free energy and enthalpy changes for central bond homolytic cleavage reactions (*ai→bi*). The reported values of enthalpy and Gibbs free energy changes are in kJ/mol units.

	HF		B3LYP	
$a_i \to b_i$	ΔG_r	ΔH_r	ΔG_r	ΔH_r
1	−157.8	−196.4	−134.3	−172.8
2	−203.3	−242.7	−160.1	−199.1
3	−330.4	−369.1	−243.5	−289.4
4	−164.7	−203.4	−136.5	−175.1
5	−185.3	−224.1	−149.5	−188.1
6	−170.9	−209.4	−145.2	−183.6
7	−179.9	−218.8	−144.9	−183.7
8	−244.2	−283.9	−188.9	−228.2
9	−279.7	−320.9	−213.1	−253.2

state structure in some of these compounds (**a4**, **a9**, **b4** and **b9**). *Ab initio* calculations with geometry optimization were performed for the propellane compounds using GAUSSIAN-98 package programs [12] and the 6-31G(d,p) basis set. The results of the *ab initio* calculations were obtained the application of HF method and the Becke, Lee, Yang and Parr density functional method (B3LYP). The B3LYP functional method combines Becke's three-parameter exchange function[10] with the correlation function of Lee, *et al.*[11]. The molecular symmetry conditions option of the package has been used, whenever possible, especially for the calculation of the transition states. The nature of the stationary points for all propellane compounds has been fixed by virtue of the number of imaginary frequencies. For minimum state structures, only real frequency values and in the transition state only one imaginary frequency value was accepted.

The calculated geometric parameters of propellane compounds (**a1**–**a9**) are reported in Table 1. The results show that as the C atoms in the bridges are substituted by N or O, the length of the central C1–C3 bond is comparatively more decreased in the series. However, when these C bridge atoms are substituted by S, the length of the C1–C3 bond is only slightly modified but X–C—Z angle changes more in comparison with the other propellane compounds. Except for **a6** compound, where the C–Z–C angle is significantly decreased (by about 10 degrees), the variation of angles (X–C–Y, X–C–Z and C–Z–C) in the **ai** series propellane compounds is generally very low.

Similar calculated results concerning the corresponding hydrogenated bicyclo compounds (**b1**–**b9**) are presented in Table 2. Almost the same characteristics as before are found for the **b1**–**b9** bicyclo compounds. The stability of these propellane and heteropropellane compounds can be compared according to the strength of the central bond toward homolytic cleavage. The energy of homolytic cleavage is strongly influenced by the difference in the energy of the reactant and the resulting product. For the most reactive molecule, the most strain is released by the bond rupture. Accordingly, the stability of **a1**–**a9** compounds and particularly, the effect of the presence of N, O and S atoms in these propellane compounds, could reasonably be estimated using their respective free energy changes produced in the following reaction:



The value of ΔG_r and ΔH_r calculated for this reaction are presented in Table 3. The results show that, the **ai** series compounds have lower energy than the **bi** series compounds and as the bridge head carbon atoms are substituted by N, O or S, the molecule becomes more reactive. There is, however, not a trend toward decreasing stability with increasing strain. It is interesting to note that the *ab initio* calculated results allow N-inversion for some of the **a1**—**b9** compounds. The molecular transition state structures (TS) and the calculated ΔH^* and ΔG^* for nitrogen inversion in **a4**, **a9** heteropropellanes and their respective hydrogenated bicyclo compounds **b4**, **b9** are given in Tables 1, 2, and 4. As it should be expected, these energy values (*ca* 100 kJ/mol) are higher than the corresponding N-inversion energy barrier for NH_3 (*ca* 24 kJ/mol) [13].

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Table 4 *Ab initio* ΔH^* and ΔG^* calculated for nitrogen inversion in a4, a9 heteropropellanes and corresponding hydrogenated bicyclo compounds b4 and b9. The reported values of enthalpy and Gibbs free energy changes are in kJ/mol units.

	HF				B3LYP			
	a4	**b4**	**a9**	**b9**	**a4**	**b4**	**a9**	**b9**
ΔG^*	100.1	93.3	98.0	93.0	97.5	93.3	92.2	87.5
ΔH^*	100.3	93.3	98.9	92.9	97.7	93.3	91.5	87.0

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