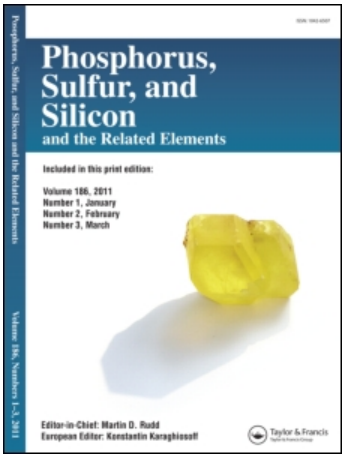

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Trithia[1.1.1]Propellane

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TRITHIA[1.1.1]PROPELLANE

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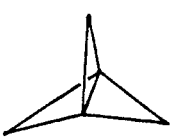
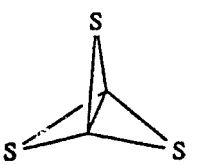
Abstract Trithia[1.1.1]propellane **2** is predicted to be a tightly-bound molecule which should be experimentally accessible. It is characterized by an intrabridgehead C-C bond of length 1.575Å, a heat of formation (ΔH°_{298}) of 542 kJ mol^{-1}, and vibrational spectra with frequencies all lying below 900 cm^{-1}. The synthesis of a key precursor to **2** is currently underway.

INTRODUCTION

Both theoretical and experimental studies on the structure, energies, strain energies, bonding, and charge distribution in small-ring propellanes have been important in the development of modern organic chemistry.[1] The smallest conceivable member of this series of hydrocarbons is [1.1.1]propellane **1** which was synthesized some years ago and found to be remarkably stable.[2]. Since the "normal" bond angles at sulfur are considerably smaller than those at the corresponding (tetrahedral) carbon, one might expect that small sulfur-containing rings might be less strained than the hydrocarbon analogue (e.g. $S.E._4 < S.E._3$)[3]. Accordingly, the sulfur analogue (**2**) of **1** should be less strained than **1** itself, and, therefore, an attractive synthetic target.



1



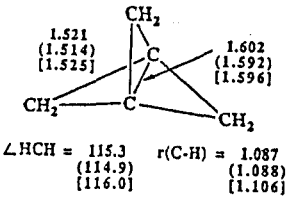
2

High-level ab initio molecular orbital calculations of the structure and vibrational frequencies for the trithia[1.1.1]propellane **2** have been carried out at the Mp2/6-31G* level, together with a parallel set of calculations for [1.1.1]propellane **1**, cyclopropane and thiirane (**3** & **4** respectively). This was done as a preliminary to the possible synthesis of **2**.

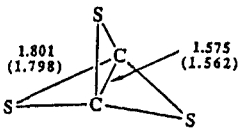
RESULTS AND DISCUSSION[4]

Geometries for **1** and **2** as optimized at the MP2/6-31G* (in parentheses) and

MP2/6-311G(MC)* levels are compared below with available experimental data.[5]



1 (D_{3h})



2 (D_{3h})

The calculated heats of formation for **1-4** from the MP2/6-311G(MC)* energies of bond separation reactions together with experimental heats of reference molecules[6] are given in Table I.

TABLE I Calculated and Experimental Heats of Formation (ΔH°_{f298}, kJ mol^{-1})

Molecule		calc	exptl
[1.1.1]propellane	**1**	352	351
trithia[1.1.1]propellane	**2**	542	-
cyclopropane	**3**	58	53.3
thiirane	**4**	71	82.1

The vibrational frequencies and the infrared and raman intensities for **1-4** have been also calculated at the MP2/6-31G* level and compared with available experimental data.

The excellent agreement between our theoretical calculations and experiment for the known molecules lends confidence to our predictions for trithia[1.1.1]propellane **2**: The C-C intrabridgehead bond lenth is predicted to decrease from 1.602Å in **1** to 1.575 Å in **2**, making it closer to the range of lenths of normal C-C single bonds and the value of only 11 kJ mol^{-1} (at 298K) obtained for the difference in strain energy (S.E.) between **2** and **1**, should make the former experimentally accessible. The synthesis of a possible key precursor (2,4-dichloro, 1,3,5-trithia-bicyclopentane) to **2** is currently underway.

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