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TRITHIA[1.1.1]PROPELLANE

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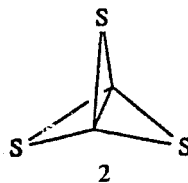
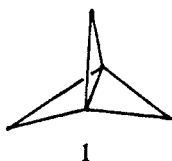
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Abstract Trithia[1.1.1]propellane **2** is predicted to be a tightly-bound molecule which should be experimentally accessible. It is characterized by an intrabridgehead C-C bond of length 1.575 Å, a heat of formation (ΔH_{298}°) of 542 kJ mol⁻¹, and 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.

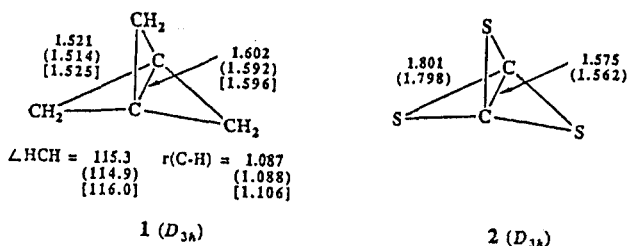


High-level ab initio molecular orbital calculations of the structure and vibrational frequencies for the trithia[1.1.1]propellane **2** have been carried out at the Mp2/6-31G* level, together with a parallel set of calculations for [1.1.1]propellane **1**, cyclopropane and thiirane (**3** & **4** respectively).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

RESULTS AND DISCUSSION⁴

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



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 molecules⁶ are given in Table I.

TABLE I Calculated and Experimental Heats of Formation (ΔH_{298}° , 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 length is predicted to decrease from 1.602 Å in 1 to 1.575 Å in 2, making it closer to the range of lengths 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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