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Structure, Infrared and Raman Spectra, and Thermochemistry of Trithia[1.1.1]propellane

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Abstract: High-level ab initio calculations of the structure, vibrational spectra, and thermochemical properties of trithia[1.1.1]propellane have been carried out, together with a parallel set of calculations for [1.1.1]propellane, cyclopropane, and thiirane. The excellent agreement between theory and experiment for the latter molecules lends confidence to the predictions for trithia[1.1.1]propellane. Trithia[1.1.1]propellane is predicted to be a tightly-bound molecule which should be experimentally accessible. It is characterized by an interbridgehead C–C bond of length 1.575 Å, a heat of formation ($\Delta H_f{}^{\circ}{}_{298}$) of 542 kJ mol^{-1}, and vibrational spectra with frequencies all lying below 900 cm^{-1}.

Introduction

There has been considerable recent interest in the chemistry of [1.1.1]propellane (**1**).[2-4] Since the pioneering synthesis by Wiberg and Walker[3a] in 1982, this prototypical member of the propellane family[5] has been characterized in detail experimentally[3] and has been the subject of extensive theoretical studies.[3b,4]

Because the "normal" bond angles at sulfur are considerably smaller than those at (tetrahedral) carbon, one might expect that small sulfur-containing rings might be less strained than their hydrocarbon analogues. Indeed, the strain energy of thiirane is about 40 kJ mol^{-1} less than that of cyclopropane.[6] Continuing this argument, one might expect that the sulfur analogue **2** of [1.1.1]propellane (**1**) would be less strained than **1** itself. Accordingly, trithia[1.1.1]propellane (**2**) is an attractive synthetic target, a matter we are currently considering.

As a preliminary to the possible synthesis of trithia[1.1.1]propellane (**2**), we have been carrying out an extensive ab initio study of this molecule. We present in this paper our predictions of the structure, vibrational spectra, and thermochemical properties of trithia[1.1.1]propellane. We also report results of similar calculations for [1.1.1]propellane itself, and for cyclopropane (**3**) and thiirane (**4**), since comparison with experiment is possible in these cases and so provides a measure of the reliability of the predictions for trithia[1.1.1]propellane. A more detailed account will be reported elsewhere.[7]

Computational Details

Standard ab initio molecular orbital calculations[8] were carried out with the GAUSSIAN 86,[9] GAUSSIAN 90,[10] and CADPAC 4[11] programs. Optimized geometries and harmonic vibrational frequencies for **1–4** were obtained at the MP2/6-31G* level, and the geometries were refined at the MP2/6-311G(MC)*[12] level. Total energies, zero-point vibrational energies, and temperature corrections to molecular enthalpies ($H_{298} - H_0$), calculated at these geometries, are presented in Table I. The vibrational frequencies were scaled by a factor of 0.94 in the evaluation of zero-point vibrational corrections and temperature corrections to reaction enthalpies.

Results and Discussion

Structural Comparisons. Geometries for **1–4**, as optimized at the MP2/6-31G* and MP2/6-311G(MC)*[12] levels, are compared with available experimental data[3c,13,14] in Figure 1. The calculated structural parameters, almost without exception,[15] are in very good agreement with the experimental values. The MP2/6-311G(MC)* results are generally closer to experiment, the difference between theoretical and experimental bond lengths exceeding 0.006 Å in only one case, and all angles agreeing to within 1°. We therefore restrict our attention to comparisons at this level of theory. Of particular relevance are the C–C and C–S bond lengths, where there is uniformly good agreement with experiment: 1.507 vs 1.512 Å in cyclopropane (**3**), 1.482 vs 1.483 Å in thiirane (**4**), and 1.521 vs 1.525 Å in [1.1.1]propellane (**1**) for "normal" C–C bonds, 1.602 vs 1.596 for the interbridgehead C–C bond in **1**, and 1.814 vs 1.815 Å for the C–S bond in thiirane (**4**). We note that our MP2/6-311G(MC)* structure for [1.1.1]propellane

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[15] The only case of poor agreement is for the C–H bond lengths in [1.1.1]propellane (**1**) where the theoretical value (1.087 Å) is significantly shorter than the experimental value (1.106 Å). The latter, however, is an r_g estimate from an electron diffraction experiment, and such estimates are often found to be significantly longer than r_e values because of the neglect of vibrational anharmonicity.

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Table I. Calculated Total Energies, Zero-Point Vibrational Energies (ZPVE), and Temperature Corrections to Molecular Enthalpies ($H_{298} - H_0$)

molecule		energy, hartrees MP2/6-31G*	energy, hartrees MP2/6-311G(MC)*	ZPVE,[a] kJ mol^{-1} MP2/6-31G*	$H_{298} - H_0$,[b] kJ mol^{-1} MP2/6-31G*
cyclopropane	**3**	−117.462 83	−117.547 26	220.4	11.4
thiirane	**4**	−475.949 62	−476.145 95	149.5	11.4
[1.1.1]propellane	**1**	−193.374 71	−193.511 49	251.5	13.0
trithia[1.1.1]propellane	**2**	−1268.772 81	−1269.248 91	33.7	14.5

[a] Values tabulated are unscaled, but scaling by 0.94 was carried out before evaluation of zero-point vibrational corrections to reaction enthalpies. [b] The MP2/6-31G* vibrational frequencies were scaled by 0.94 in calculating $H_{298} - H_0$ values.

Table II. Calculated[a] and Experimental Vibrational Frequencies (cm^{-1})

cyclopropane (**3**)			thiirane (**4**)			[1.1.1]propellane (**1**)			trithia[1.1.1]propellane (**2**)	
sym	calcd	exptl[b]	sym	calcd	exptl[c]	sym	calcd	exptl[d]	sym	calcd
a_2''	3118	3102	b_1	3109	3088	e'	3085	3080	a_1'	872
e''	3102	3082	a_2	3098		a_2'	3082		e'	789
a_1'	3028	3038	a_1	3015	3014	a_1'	3000	3029	e''	605
e'	3020	3024	b_2	3013	3013	e'	2997	3020	a_1'	483
a_1'	1492	1479	a_1	1470	1457	a_1'	1494	1502	a_2''	448
e'	1441	1438	b_1	1442	1436	e'	1449	1459	e'	361
a_1'	1192	1188	a_2	1160		e'	1183	1186		
e''	1180	1188	a_1	1125	1110	e''	1113	1146		
a_1''	1129	1126	b_1	1060	1051	a_1'	1106	1124		
a_2'	1053	1070	a_1	1035	1024	a_2''	1092	1096		
e'	1045	1028	b_1	948	945	e'	1071	1083		
e'	880	869	a_2	896		e''	1041	1064		
a_2''	837	854	b_1	817	824	a_2'	938			
e''	724	739	b_1	672		a_1''	884			
			a_1	641	627	a_1'	875	908		
						e''	739	714		
						a_2''	651	612		
						e'	521	529		

[a] MP2/6-31G* values, scaled by 0.94. [b] From ref 16. [c] From ref 17. [d] From ref 3b.

(**1**) is the highest-level structure yet reported for this molecule.

The excellent results for the reference systems lend confidence to our predictions for the structure of the yet-to-be-synthesized trithia[1.1.1]propellane (**2**) molecule, also displayed in Figure 1. The C–C interbridgehead bond length is predicted to decrease from 1.602 Å in [1.1.1]propellane (**1**) to 1.575 Å in trithia[1.1.1]propellane (**2**), making it closer to the range of lengths of normal carbon–carbon single bonds. The C–S bonds are somewhat shorter in **2** than in thiirane (**4**): 1.801 vs 1.814 Å. Thus, trithia[1.1.1]propellane (**2**) appears to be more tightly bound than [1.1.1]propellane (**1**).

Vibrational Spectra. Calculated and experimental[3b,16,17] vibrational frequencies for **1**, **3**, and **4** are compared in Table II. The MP2/6-31G* values have been scaled by 0.94, a factor suggested by our more detailed study,[7] to take into account the overestimation of vibrational frequencies at this level of theory. There is very good agreement between theory and experiment. The mean absolute error (40 comparisons) is just 13 cm^{-1} with a maximum error of 39 cm^{-1}. This lends confidence to our predictions of the vibrational frequencies for trithia[1.1.1]propellane (**2**), also included in Table II. A striking feature is that the vibrational frequencies for **2** are all predicted to lie below 900 cm^{-1}.

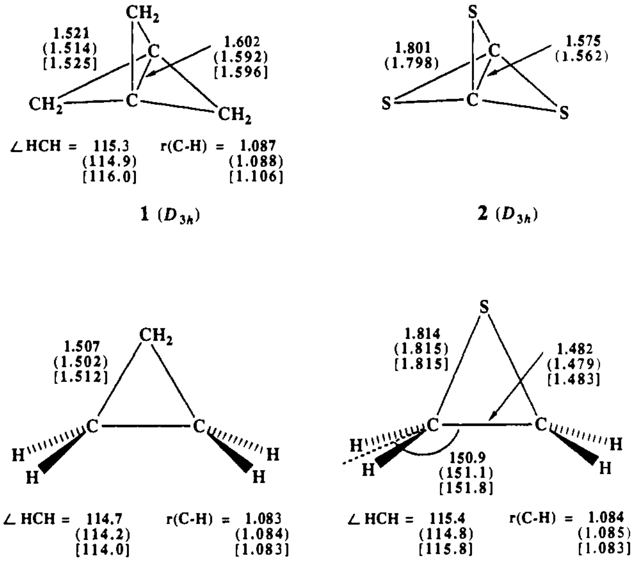

Figure 1. Comparison of calculated and experimental structural parameters for cyclopropane (**3**), thiirane (**4**), and [1.1.1]propellane (**1**) and predicted structure for trithia[1.1.1]propellane (**2**). The calculated values are at the MP2/6-311G(MC)* and MP2/6-31G* (in parentheses) levels, and the experimental values[3c,13,14] are presented in square brackets.

We have also calculated the infrared and Raman intensities for [1.1.1]propellane (**1**) and trithia[1.1.1]propellane (**2**), and so produced the infrared and Raman spectra shown in Figures 2 and 3.[18] The infrared spectrum for **1** has been calculated previously at the HF/6-31G* level and gave good agreement with experiment.[3b] The MP2/6-31G* level yields even better results, and the experimental and new theoretical infrared spectra for [1.1.1]propellane (**1**) match up very nicely indeed. Again, the good results for [1.1.1]propellane (**1**) add weight to the reliability of our predicted infrared spectrum of trithia[1.1.1]propellane (**2**), shown in Figure 3.

There is somewhat poorer agreement between the calculated and experimental Raman spectra for [1.1.1]propellane (**1**) (Figure 2). This can be attributed in part to the variation in bandwidths in the experimental spectrum and perhaps also to the fact that the Raman intensities do not correspond fully to MP2 calculations.[11] The good agreement between calculated and experimental frequencies, however, holds equally for the infrared and Raman spectra. We note in this regard that the Raman spectrum is likely to provide several more vibrational frequencies than will the infrared spectrum for the identification of trithia[1.1.1]propellane.

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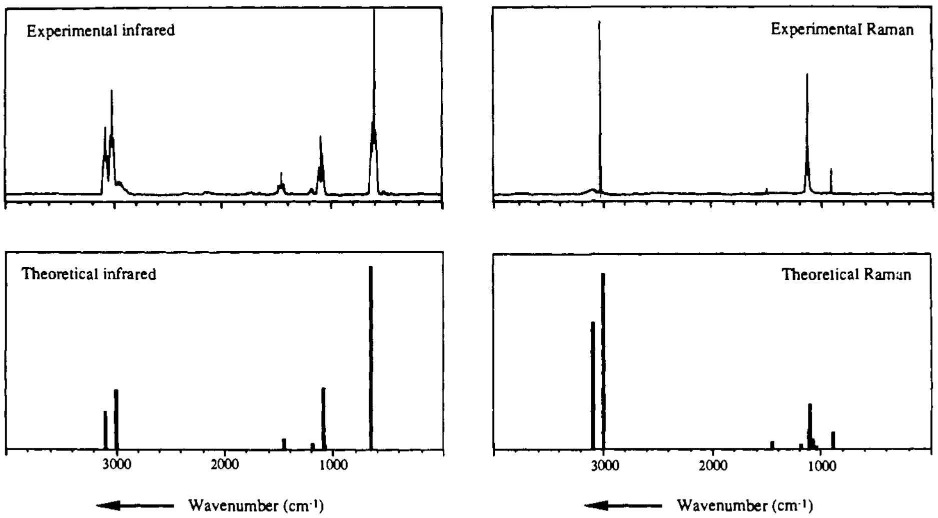

Figure 2. Calculated (MP2/6-31G*, see text) and experimental (redrawn from ref 3b) infrared and Raman spectra of [1.1.1]propellane (**1**). Nonfundamental bands deleted from the experimental Raman spectrum.

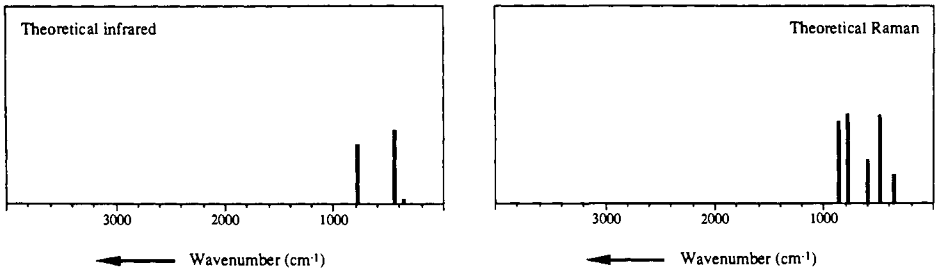

Figure 3. Predicted (MP2/6-31G*, see text) infrared and Raman spectra of trithia[1.1.1]propellane (**2**).

Table III. Calculated and Experimental Heats of Formation

molecule		$\Delta H_f{}^\circ{}_{298}$, kJ mol^{-1} calcd[a]	exptl[b]
cyclopropane	**3**	58	53.3
thiirane	**4**	71	82.1
[1.1.1]propellane	**1**	352	351
trithia[1.1.1]propellane	**2**	542	

[a] Calculated using MP2/6-311G(MC)* bond separation energies and $\Delta H_f{}^\circ{}_{298}$ values for reference molecules (see refs 20 and 21). [b] From ref 20.

Thermochemical Properties. We have calculated heats of formation for **1**–**4** from the MP2/6-311G(MC)* energies of bond separation reactions,[19] e.g.,

$$\mathbf{2} + 6CH_4 + 3H_2S \rightarrow CH_3CH_3 + 6CH_3SH \qquad (1)$$

together with experimental heats of formation for reference molecules.[20,21] The results are shown in Table III. There is good agreement in the cases (**1**, **3**, and **4**) where the heats of formation are experimentally known, but we would still estimate an uncertainty of 10–20 kJ mol^{-1} in our predicted heats of formation for trithia[1.1.1]propellane (**2**): $\Delta H_f{}^\circ{}_0$ = 543 kJ mol^{-1}, $\Delta H_f{}^\circ{}_{298}$ = 542 kJ mol^{-1}.

The theoretical heats of formation for **1** and **2** may be used together with experimental heats of formation for propane and dimethyl sulfide[20,21] to estimate the difference in strain energy of trithia[1.1.1]propellane (**2**) and [1.1.1]propellane (**1**) as the energy change for the reaction:

$$\mathbf{2} + 3CH_3CH_2CH_3 \rightarrow \mathbf{1} + 3CH_3SCH_3 \qquad (2)$$

The value obtained is just 11 kJ mol^{-1} (at 298 K), indicating that, within the estimated uncertainties of our predictions, trithia[1.1.1]propellane (**2**) is comparably strained to the parent [1.1.1]propellane (**1**).

We note that fragmentation of trithia[1.1.1]propellane (**2**) to carbon monosulfide + carbon disulfide, i.e.,

$$\mathbf{2} \rightarrow C{\equiv}S + S{=}C{=}S \qquad (3)$$

is calculated (using experimental[20,21] $\Delta H_f{}^\circ{}_{298}$ values for CS and CS_2) to be exothermic by 158 kJ mol^{-1} (at 298 K), in contrast to the endothermicity (calculated using experimental[20,21] $\Delta H_f{}^\circ{}_{298}$ values for HCCH and CH_2CCH_2) of 67 kJ mol^{-1} for the corresponding fragmentation of [1.1.1]propellane itself:

$$\mathbf{1} \rightarrow HC{\equiv}CH + CH_2{=}C{=}CH_2 \qquad (4)$$

However, reaction 3 involves the breakage of three C–S bonds and one C–C bond and hence may be inhibited by a significant barrier.

Concluding Remarks

Our ab initio calculations predict that trithia[1.1.1]propellane (**2**) is a tightly-bound molecule. It should be experimentally accessible. We would hope that the detailed characterization of its structure, vibrational spectra, and heat of formation presented here will assist in its experimental identification.

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