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A Theoretical Study of NO₂PS₂ or On the Bending of SPOONS

DJ Schrödingerd^{A*}

The following article constitutes a preliminary trial of a chemistry-specific artificial intelligence chatbot called "ChatC_{sp}3". This bot is being trained to take dense chemical jargon (left column) and make it accessible to the general public (right column).

Abstract: Quantum mechanical calculations were performed on an isomer of NO₂PS₂ that is analogous to ONOONO. Important differences between the *trans-perp-trans* isomers of ONOONO and NO₂PS₂ were discovered, and their origins and implications are discussed.

Abstract: Quantum mechanical calculations were performed on SPOONS that show that there is not an inherent tendency for SPOONS to bend.

The many isomers of N₂O₄ have been the subject of extensive study due to their importance in the chemistry of the troposphere and stratosphere.^{1,2} To the best of our knowledge, higher molecular weight analogs of N₂O₄ have not been studied. Herein we describe quantum mechanical calculations on the structure and vibrational properties of the *trans-perp-trans* isomer of NO₂PS₂, an analog of linear ONOONO. Hopefully, this comparison of N₂O₄ and NO₂PS₂ will facilitate an understanding of the unique and environmentally-relevant properties of the former compound.

The geometry and vibrational spectrum of the *trans-perp-trans* isomer of NO₂PS₂ were computed using second order Moller-Plesset perturbation theory (MP2) and a double- ζ quality basis set (6-31G*). This same method was used previously to study isomers of N₂O₄,¹ thereby facilitating a direct comparison of our computational results with those reported for ONOONO.

Our computed geometry of the *trans-perp-trans* conformational isomer of NO₂PS₂ is shown in Figure 1. Interestingly, the central O–O bond of NO₂PS₂ is considerably longer (by 0.05 Å), and the internal O–N bond is notably shorter (by 0.13 Å), than those in ONOONO.¹ This is perhaps a result of the enhanced electron-accepting ability of the N=S fragment, and indicates that O–N bond cleavage in NO₂PS₂ to produce NS may be more difficult than O–N bond cleavage in ONOONO to produce the atmospherically and biologically important NO free radical.

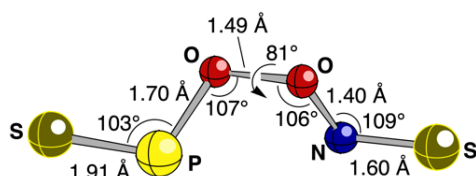


Figure 1: Computed geometry of NO₂PS₂

Much to our satisfaction, the predicted vibrational modes for NO₂PS₂ mirror those reported for ONOONO, despite the lower symmetry of NO₂PS₂. For example, the highest intensity mode for *trans-perp-trans* NO₂PS₂ is predicted to occur at 743 cm⁻¹ and is dominated by P–O and O–N stretching, while the highest intensity mode for *trans-perp-trans* ONOONO occurs at 736 cm⁻¹ and corresponds to N–O stretching.¹

A. The Institute

* Corresponding author contact: DJ.Schrödingerd@aol.com

Herein we (one bored dude) describe expensive quantum mechanical calculations on a molecule of no relevance to the real world. This molecule is one of several isomers bearing the empirical formula NO₂PS₂. The connectivity of the particular isomer with which we are concerned can - in fact should - be denoted as SPOONS. Although SPOONS is actually analogous to molecules important in atmospheric chemistry (such as the N₂O₄ isomer ONOONO),^{1,2} it is the subject of this paper solely because we first thought of the title. While we are among the chemical community's biggest supporters of (1) investigations into cool-molecules-with-no-practical-utility and (2) title-driven project design, even we find it difficult to admit that time and resources were actually devoted to these calculations.

In any case, we did in fact calculate the geometry and vibrational spectrum of SPOONS using second order Moller-Plesset perturbation theory (MP2) and a double- ζ quality basis set of much renown (6-31G*). This same method was used previously to study ONOONO,³ thereby allowing us to compare our results directly with those reported for ONOONO, although we don't really think that's important.

The computed geometry of the *trans-perp-trans* isomer of SPOONS is shown in Figure 1'. We had hoped to report that the bond distances, bond angles, and dihedral angles in this structure are unremarkable. Unfortunately, the central O–O bond is a bit long, and the internal O–N bond is much shorter than in ONOONO.³ If any readers would like us to explain these unexpected observations, you may try to track us down – if you do, please indicate whether you would prefer a photograph or sketch of waving hands.

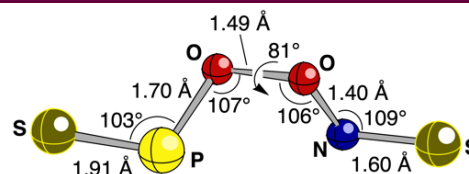


Figure 1': The geometry of SPOONS.

Much to our dissatisfaction, dismay and chagrin, almost none of the predicted vibrational modes for SPOONS actually correspond to bending. In fact, only the vibrational mode at 335 cm⁻¹ shows a significant bending component (that for O–N–S bending), and the intensity of this mode is so small that we have little hope that it might be detected experimentally. In contrast, the highest intensity modes have large components corresponding to P–O, O–O, and O–N stretching. Damn.

In conclusion, we have predicted the preferred geometry and vibrational spectrum of the novel N_2O_4 analog NO_2PS_2 . This information will facilitate our understanding of the chemistry of such molecules, and provides a stepping stone for further studies on additional molecules of this type. Efforts in this direction are in progress, and will be reported in due course.

Acknowledgements

This work was supported by the Institute. We acknowledge Dr. BH for many helpful insights.

Notes and references

- 1 "Ab initio study on the characterization of N_2O_4 isomers" Wang, X.; Qin, Q-Z.; Fan, K. **1998**, *J. Mol. Struc. (Theochem)* **432**, 55-62, and references therein.
- 2 "Conformation-Dependent State Selectivity in O–O Cleavage of ONOONO: An "Inorganic Cope Rearrangement" Helps Explain the Observed Negative Activation Energy in the Oxidation of Nitric Oxide by Dioxygen" Olson, L. P.; Kuwata, K. T.; Bartberger, M. D.; Houk, K. N. **2002**, *J. Am. Chem. Soc.* **124**, 9469-9475.

In conclusion, we have actually shown very little. We can say, however, that we observe no inherent tendency of SPOONS to bend, suggesting that such a process would indeed require focused external intervention, be it telekinetic or otherwise.

Acknowledgements

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Notes and references

- 1 "Ab initio study on the characterization of N_2O_4 isomers" Wang, X.; Qin, Q-Z.; Fan, K. **1998**, *J. Mol. Struc. (Theochem)* **432**, 55-62 and references therein.
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- 3 "Get jiggy wit da oxid – predicted vibrational modes of N_2O_4 " Saka, O.; Lish, D. **2010**, *J. Fizz. Chem.* **22**, 9–5.