ScienceDirect

Journal of Molecular Graphics and Modelling

Volume 105, June 2021, 107863

Detonation properties and impact sensitivities of trinitromethane derivatives of three-membered heterocyclic ring compounds

Rahana Ameen [a c], Fasila P. M [c], Anakuthil Anoop [b] ✉, Biju A. R [c] ✉

[a] Department of Chemistry, Payyanur College, Edat, Payyanur, Kannur, Kerala, 670327, India

[b] Department of Chemistry, Indian Institute of Technology – Kharagpur, Kharagpur, West Bengal, 721 302, India

[c] Department of Chemistry, Sir Syed College (Affiliated to Kannur University, Kerala),Taliparamba, Karimbam, Kannur, Kerala, 670142, India

Received 23 December 2020, Revised 28 January 2021, Accepted 1 February 2021, Available online 4 February 2021, Version of Record 12 February 2021.

What do these dates mean?

Check for updates

Show less

Share Cite

https://doi.org/10.1016/j.jmgm.2021.107863 ↗

Get rights and content ↗

Highlights

- Quantum mechanical studies of new three-membered heterocyclic compounds as HEDMs.
- Promising trinitromethane derivatives of high energy density materials.

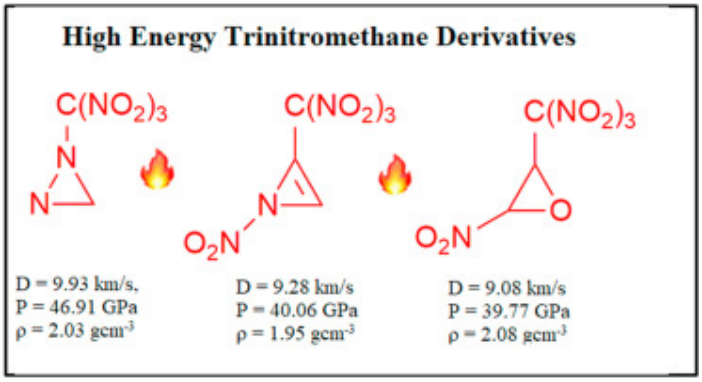
- Calculation of impact sensitivity of high energy density materials.

Abstract

We have carried out the design and theoretical investigation of a series of trinitromethane derivatives of three-membered heterocyclic ring compounds – aziridine, 1H-azirine, diaziridine, 1H-diazirine, triaziridine, 1H-triazirene, oxaziridine, oxadiaziridine, dioxaziridine, oxirane, and dioxirane – in search for new high energy density materials (HEDM). We have estimated the properties relevant to HEDMs of the proposed molecules using Density Functional Theory (B3LYP/aug-cc-pVDZ). The results show that most of the molecules have a high value of solid-phase heat of formation, crystal density, detonation velocity and pressure with satisfying values for impact sensitivities. We have identified some of these molecules, 1-(triinitromethyl)diaziridine, 2-(trinitromethyl)-1-nitro-1*H*-azirine, and (2-(trinitromethyl)-3-nitrooxirane) are potential candidates of energetic molecules among the 60 molecules we investigated. As most of them are having a high positive oxygen balance, they can be recommended for use as oxidisers in solid propellants.

Graphical abstract

Promising high energy density materials(HED's) with trinitromethane derivatives.



Download: Download high-res image (188KB)

Download: Download full-size image

Introduction

The design of new high energy density materials (HEDM) with high detonation performance and insensitivity is often a challenging problem [1,2]. Traditional energetic materials such as 2,4,6-trinitrotoluene(TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) derive most of their energies from the oxidation of the carbon backbone [[3], [4], [5]], whereas nitrogen-rich energetic materials derive energy from their high positive heats of formation [[6], [7], [8], [9]]. Polynitro-substituted cage compounds such as hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC) release energy upon

detonation as a consequence of strain of the cage structure [10]. The design of novel molecules is based on the insights from the traditional materials and by tuning for a high crystal density and chemical energy of detonation.

Heterocyclic compounds are of considerable interest as HEDM due to their high density, high positive heat of formation (HOF), better oxygen balance, good thermal stability, and low sensitivity [[11], [12], [13], [14]]. The strained ring compounds such as ethylene oxide, oxadiaziridine, triazirine, and triaziridine exhibit high performance as they release a large amount of strain energy during ring opening [[15], [16], [17], [18]]. The introduction of explosophoric groups such as O–NO_2, N–NO_2, C–NO_2, –$NHNO_2$, –N_3, and –$C(NO_2)_3$ make the compound exhibit superior detonation performances [[19], [20], [21], [22]]. Among these groups, the trinitromethyl functionality possesses both the benefits of high nitrogen and oxygen content, thus found to be an important energetic group [[23], [24], [25], [26]]. Tartakovskii et al. had reported the synthesis of trans-1,2,3-tris(nitramino)cyclopropane (NACP) [18]. The detonation performance studies of a series of nitro-triaziridines showed that the oxygen balance must be considered for designing high-energy compounds [27]. DFT study of a series of ethylene oxide derivatives showed that they have good thermal stabilities [15,28]. Works on the energetic properties of oxadiaziridines showed that they are potential energetic candidates [17,29].

Theoretically examining the molecular structure and properties of a compound allows the selection of powerful and productive HEDM reducing expensive and risky experiments [[30], [31], [32]]. Here we have designed 60 novel derivatives of three-membered ring compounds aziridine, 1H-azirine, diaziridine, 1H-diazirine, triaziridine, 1H-triazirene, oxaziridine, oxadiaziridine, dioxaziridine, oxirane, and dioxirane by introducing trinitromethyl (TNM) and nitro groups, to increase their detonation properties (Scheme 1). To predict the performance of these proposed molecules, we have computed several properties using density functional theory (DFT) — B3LYP functional and aug-cc-pVDZ basis set with Gaussian 09 set of programs [33]. The detonation velocity and pressure are high if the molecule has a high chemical energy of detonation and density [34,35]. We calculated the detonation velocity and pressure of these designed compounds using the Kamlet-Jacobs equation [36]. We assessed the impact sensitivity of the optimised structures using electrostatic potential [37]. The results show that, in general, the compounds have a high oxygen balance, and maybe introduced as high-performance oxidisers for use in solid propellants. We have ranked some of these molecules as the most promising candidate as HEDMs among the 60 molecules analysed.

Access through your organization

Check access to the full text by signing in through your organization.

Access through **your institution**

Section snippets

Theory and computational details

We used the density functional theory (DFT) for predicting the energetic properties of HEDMs. The geometry optimisation of the compounds and their related properties were done by Gaussian 09 set of programs using B3LYP functional with aug-cc-pVDZ as the basis set.

Based on the Monte-Carlo method and electrostatic potential analysis, the corrected crystal density (ρ) of energetic materials could be predicted using the following expression [38]. $\rho = \alpha(\mathrm{M}/\mathrm{Vm}) + \beta(\upsilon\sigma_{\mathrm{tot}}^{2}) + \gamma$where M is the molecular…

Results and discussions

We have designed several molecules by introducing two high energy containing groups, –$C(NO_2)_3$ and –NO_2, into the framework of three-membered heterocyclic compounds – aziridine, 1H-azirine, diaziridine, 1H-diazirine, triaziridine, 1H-triazirene, oxaziridine, oxadiaziridine, dioxaziridine, oxirane, and dioxirane – resulting in the formation of 60 molecules.

Aziridine derivatives (AZ1-AZ15): The molecules AZ1-AZ6 has one trinitromethyl (TNM) functional group on one of the C atoms (**AZ**). AZ1 has one…

Conclusion

In this work, we have theoretically studied a large number of three-membered heterocyclic compounds to guide the design of new three-membered heterocyclic energetic compounds as HEDMs. The theoretical studies were done in the Gaussian 09 set of programs using DFT - B3LYP method. We studied the heat of formation, energetic properties, stability, impact sensitivity and vibrational frequency calculations of these compounds. The substituent group, trinitromethane, is found to be very beneficial in…

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgments

ARB thank Ajit Balakrishnan and Ajit Balakrishnan foundation for establishing computational lab at Sir Syed College. ARB also thank DST-FIST fund for Sir Syed College (C.Dy.No.2292/IFD/2014-2015 dated 24.07.12014) by Department of Science & Technology, Government of India.…

Recommended articles

References (60)

P. Politzer *et al.*
Computational investigation of the structures and relative stabilities of amino/nitro derivatives of ethylene
J Mol Struct THEOCHEM (1998)

P. Yin *et al.*
Chapter four-nitrogen-rich azoles as high density energy materials: reviewing the energetic footprints of heterocycles
Adv. Heterocycl. Chem. (2017)

A.J. Tricamo *et al.*
G2, G3, and complete basis set calculations of the thermodynamic properties of two isomers of diazadiboretidine, cyclo-B2N2H4
J Mol Struct THEOCHEM (2007)

M. Malow *et al.*
On the explosive properties of 1H-benzotriazole and 1H-1, 2, 3-triazole
Tetrahedron Lett. (2007)

H.S. Jadhav *et al.*
Synthesis, characterization and thermolysis studies on new derivatives of 2,4,5-trinitroimidazoles: potential insensitive high energy materials
J. Hazard Mater. (2007)

A. Karahodza *et al.*
Cyclic triamines as potential high energy materials. Thermochemical properties of triaziridine and triazirine
J Mol Struct THEOCHEM (2005)

D.M. Badgujar *et al.*
Advances in science and technology of modern energetic materials: an overview
J. Hazard Mater. (2008)

O.V. Golovina *et al.*
Synthesis and structure elucidation of novel 5-dinitromethyl-7-alkylamino-1, 2, 4-triazolo [4, 3-a]-1, 3, 5-triazines
Tetrahedron Lett. (2013)

S. Ghanta

Theoretically predicted Fox-7 based new high energy density molecules
J. Mol. Struct. (2016)

M. Jaidann *et al.*
ADFT theoretical study of heats of formation and detonation properties of nitrogen-rich explosives
(2010)

View more references

Cited by (5)

Theoretical investigation of high energy density materials based on trinitromethyl substituted 1,3-diazete

2024, Computational and Theoretical Chemistry

Show abstract

Theoretical investigation of energetic performance and impact sensitivities of nitro and trinitromethyl substituted ozonides of ethylene and cyclopentene

2021, Computational and Theoretical Chemistry

> *Citation Excerpt :*
>
> …Fused heterocyclic compounds are also known due to their energetic performances [10–13]. Extensive studies have been going on the energetic nature of derivatives of nitrogen heterocyclic compounds such as pyridine [14], azete [15] and aziridene based compounds [16]. Nitrogen rich heterocyclic compounds, such as, azole and tetrazine [17,18] based energetic materials are often used as explosives due to the reduced sensitivity and good thermal stabilities of the resulting compounds[19,20].…

Show abstract

Theoretical studies of azete based high energy density materials with trinitromethane functional group

2021, Computational and Theoretical Chemistry

> *Citation Excerpt :*
>
> …Among these trinitromethyl (TNM) functional group, due to its high nitrogen and oxygen content, positive oxygen balance and high energy has attracted considerable attention[14–17]. The TNM derivatives of three membered heterocyclic ring compounds are found to be highly energetic [18]. Another tactic for the design of HEDMs includes, utilizing ring or cage compounds, which can take advantage of the extra strain energy released during the ring opening when the decomposition takes place [2,19].…

Show abstract

Theoretical study of a series of 1,2-diazete based trinitromethyl derivatives as potential energetic compounds ↗

2024, Journal of Molecular Modeling

New trends in diaziridine formation and transformation (A review) ↗

2021, Molecules

View full text

© 2021 Elsevier Inc. All rights reserved.

ELSEVIER

All content on this site: Copyright © 2024 Elsevier B.V., its licensors, and contributors. All rights are reserved, including those for text and data mining, AI training, and similar technologies. For all open access content, the Creative Commons licensing terms apply.

RELX™