

Reviewer Comments:

The manuscript by Mossri et al. presents a compelling computational investigation into the reactions of green stabilizers, specifically curcumin in nitrocellulose-based propellants, using density functional theory (DFT). The study explores the interactions between curcumin and nitrogen dioxide (NO₂) to examine potential stabilizing mechanisms. However, several key points need to be addressed, both major and minor, before the manuscript can be considered for publication:

Answer: We appreciate the referee's detailed and thorough review of our manuscript and the valuable comments. All changes and additions to the original manuscript and the Supplementary Material are marked in the highlighted versions of both documents.

1. The abstract would benefit from rephrasing to improve clarity and concisely summarize the main outcomes.

Answer: We thank the referee for the comment. Therefore, we have rewritten the abstract to improve its clarity and concisely summarize the main findings.

2. In Figure 2, the color range between -0.931e₀ and +0.931e₀ should be adjusted to eliminate red and blue overlap, ensuring more distinct visualization.

Answer: We thank the referee for the comment. In this regard, we have included a new Figure 2 with a more adequate color scale.

3. In the Methods section, where DFT with B3LYP/6-311+G(d) is used, it would be useful to include a comparison without the diffuse function, given the absence of experimental activation energy values. Additionally, using different DFT methods with various basis sets for validation would enhance the robustness of the results.

Answer: Thank you for the suggestion. Therefore, we have carried out additional calculations for the R1 and R2 reactions with diffuse functions and different exchange-correlation functionals. Following recommendations from the literature, we have selected the ωB97M-V functional for its accuracy in predicting energy barriers and included the widely used M06-2X functional, as well as the original B3LYP, for comparisons. For each functional, we computed the energy barriers for the transition state, reactant, and product structures using the 6-311+G(d) and 6-311G(d) basis sets to assess the effect of diffuse functions.

4. The FMO orbital data should be further refined to improve the clarity of the interpretation.

Answer: We agree with the suggestion. Thus, an analysis of the electron density surfaces of the frontier molecular orbitals has been included as an additional tool for the interpretation of the structures involved in the reactions.

5. NBO charge data should be included for comparative analysis to deepen the understanding of charge distributions.

Answer: Thank you for the interesting suggestion. Accordingly, we have included in Table 2 NBO charges for the atoms involved in the reaction. For Reaction 1, we found a significant decrease in the charge of the hydrogen atom (H) from 0.260e in the reactant state (R1) to nearly neutral (0.00 e) in the product state (P1), suggesting a possible charge transfer associated with bond breaking involving hydrogen. The carbon atom (C) also shows a notable charge shift, which may indicate a redistribution of electron density during the reaction. In contrast, the nitrogen atom (N) maintains a relatively constant charge, suggesting a stable role without significant electronic changes. The oxygen atoms (O1 and O2) display slight variations in charge, indicating a subtle redistribution of electron density likely due to bonding interactions.

Similarly, in Reaction 2, the hydrogen atom increases its charge, while the carbon atom exhibits a substantial charge shift associated with breaking the C-H bond. The nitrogen atom shows a charge reduction in the transition state, confirming its role in the charge transfer. Oxygen atoms O1 and O2 again change charge values, indicating redistribution related to O-H bond formation. The charges for the remaining atoms are provided in Supplementary Figures 2S to 7S.

6. Thermodynamic data should be incorporated to strengthen the support for the computational findings.

Answer: Thank you for the suggestion. In response, we have incorporated the ΔG_R and ΔH_R thermodynamic data for the reactions in the supplementary material to further support the computational findings (Table S2).

7. A 3D structure of the transition states (TS), along with optimized data, should be provided to present a more comprehensive view of the reaction mechanism.

Answer: Thank you for the suggestion. In this regard, we have included the 3D structures of the transition states (TS) in the revised Figure 6, along with updated thermodynamic data. These additions indeed provide a more comprehensive view of the reaction mechanism. Additionally, Figure 1S has been revised, and 3D structures of the transition states have been added.

8. The absence of experimental data makes it difficult to fully validate the computational results based solely on DFT. To enhance the accuracy of the predictions, higher-level Gaussian methods (such as G3MP2, G3MP2B3, or CBS-QB3) should be considered.

Answer: We appreciate the reviewer's valuable suggestion to include calculations using higher-level methods, such as G3MP2, G3MP2B3, or CBS-QB3, to improve the accuracy of the predictions. However, the high computational cost of these methods made it impossible to perform the suggested calculations. We have made attempts to employ computational nodes with 32 processors and 3 TB of memory, but unfortunately, these simulations could not be completed in time for this resubmission. Nevertheless, we believe that the comparisons presented in the text with thermodynamic data from other systems can provide a satisfactory basis to justify the methodological choices adopted in this study.

If these revisions are made, the manuscript has strong potential for publication in the *Journal of Molecular Structure*.

Additional comments. All the figures and tables in the main text and the supplementary material have been revised and improved to ensure greater clarity in the presentation of the results. Additionally, the input and output files related to calculations of the two reactions have been removed from the supplementary material because all files have been made available in our Github repository, as indicated in the main text. This repository also includes a detailed spreadsheet with all the results.