**Response to the Reviewers**

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Dear Editor

First of all, we would like to thank you very much for your sincere and kind consideration of our manuscript by providing us a chance to revise it **(**Manuscript ID:  ZNA.2018.0123.R1**)** entitled **"Structural, Electronic and Nonlinear Optical Properties of Novel Derivatives of 9,12-diiodo-1,2-dicarba-closo-dodecaborane: Density Functional Theory Approach"**. We are also thankful to the reviewer’s evaluation with their positive remarks and constructive feedback. All the suggestions of reviewers have been included in revised manuscript and are listed below as well. We have tried our level best to revise the manuscript as per your expectations. Now, we do hope that this revised manuscript would be acceptable for publication in “**Zeitschrift für Naturforschung A**”.

It’s a matter of great honor for us to reply to the editor and reviewer’s valuable suggestions. Please find the following Response (in blue font color) to the Comments (in black font color) of the reviewers:

Sincerely,

Aijaz Rasool Chaudhry, Ph.D.

(Corresponding Author)

**Editor’s comments:**

Thank you again for submitting your revised manuscript  
Manuscript ID: ZNA.2018.0123.R1  
Title: "Structural, Electronic and Nonlinear Optical Properties of Novel Derivatives of 9,12-diiodo-1,2-dicarba-closo-dodecaborane: Density Functional Theory Approach" to Zeitschrift für Naturforschung A (ZNA).

According to the comments of the reviewer, as attached to this message as a separate file, the manuscript still does not meet the requirements for publication in ZNA. The referee has put forward some questions that need to be answered, and some further issues that should be dealt with in a proper manner.    
Therefore, I invite you to respond to the reviewer(s)' comments, and to revise your manuscript accordingly.

**Response:** We have revised the manuscript accordingly. The modifications have been implemented, some new calculations have been done as suggested by the reviewer. The results have been tabulated and discussed accordingly.

**Reviewers' comments:**  
**Reviewer #1:**

Chaudhry et al have revised the manuscript based on the comments of the reviewers. Although the present version of the manuscript is improved slightly from the initial submission, some of the issues are still needed to be addressed. In my opinion, the present form of the manuscript is not suitable for publication in the Zeitschrift für Naturforschung A. Therefore, I recommend the manuscript should be revised again addressing the issues mentioned below. The clarity of the manuscripts also must be improved to make it acceptable for the broad readership of this journal.

The main issues that concerns me are:

**Response:** We have revised the manuscript accordingly. The modifications have been performed, some new calculations have been done as suggested by our respected Reviewer. The results have been tabulated and discussed thoroughly. We have addressed all the issues and tried our level best to clarify/discuss as per suggestions of our respected reviewer. The most important changes include but not limited to following points:

1) NLO calculations have also been carried out at CAM-B3LYP level after optimizing the geometries of all the systems at CAM-B3LYP level. Then these values have been compared with the NLO data calculated from CAM-B3LYP level where B3LYP optimized geometries were used.

2) Optimized coordinates B3LYP and CAM-B3LYP have been provided in supporting information.

3) The background and previous studies on the phenomenon of the direction of charge transfer has been discussed.

4) The importance of intramolecular charge transfer-based molecules for studying of NLO response has been discussed in the introduction part of the manuscript.

5) Several self-citations have been deleted. Some recent literature has been cited on the importance of intramolecular charge transfer-based molecules for studies of NLO response, background and previous studies on this phenomenon of the direction of charge transfer.

1. From the revised manuscript it is not clear to me whether the authors optimized the geometries using CAM-B3LYP functional, followed by NLO response or just used B3LYP optimized geometry for NLO calculations at the CAM-B3LYP level.

In my initial review, I recommended the authors to optimize the geometry using the CAMB3LYP functional, followed by calculation of NLO response. This must be done and clarified in the revised manuscript.

Some recent studies using DFT functionals (not just CAM-B3LYP) suitable for calculation of NLO response properties of charge transfer-based molecules can also be mentioned in the Computational details part of the manuscript.

**Response:** In the revised manuscript, the NLO response properties have been calculated as suggested “on optimized the geometries using the CAM-B3LYP functional, followed by calculation of NLO response at CAM-B3LYP level and given in Table 5”. (Section 3.4: *Nonlinear optical properties;* page 14)

**Table 5.**

The calculated values of total second-order polarizabilities (βtot, a. u.)a, (βvec, a. u.)a along with their individual components for compounds **1-3** at B3LYP/Genb and CAM-B3LYP/Genb levels of theory, where geometries were also optimized using the same respective methods.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **1** | | **2** | | **3** | |
| β | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP |
| 6-31G\*\* | 6-31+G\*\* | 6-31G\*\* | 6-31+G\*\* | 6-31G\*\* | 6-31+G\*\* |
| βxxx | 5 | 6 | 4 | 15 | 2 | -3 |
| βxxy | 6 | 0 | 1 | 1 | -4 | 4 |
| βxyy | 1 | 0 | -41 | -22 | 0 | 19 |
| βyyy | 7 | 0 | -101 | -28 | 94 | -204 |
| βxxz | 94 | -3 | -31 | -193 | 276 | 80 |
| βxyz | 1 | -2 | -24 | 23 | -72 | 17 |
| βyyz | 238 | 215 | 1587 | 818 | 2760 | 1256 |
| βxzz | 1 | -1 | -129 | -72 | -5 | 41 |
| βyzz | 8 | 0 | -20 | -7 | -19 | -19 |
| βzzz | 495 | 340 | 4832 | 2403 | 4305 | 2887 |
| βX | 7 | 5 | -166 | -79 | 3 | 57 |
| βY | 21 | 0 | -120 | -34 | -71 | -219 |
| βZ | 827 | 552 | 6388 | 3028 | 6789 | 4063 |
| βtot | 827 | 552 | 6391 | 3029 | 6789 | 4069 |
| βvec | 496 | 331 | 4808 | 1818 | 4074 | 2442 |
| *η*c | 0.480 | 0.63 | 0.328 | 0.34 | 0.641 | 0.44 |
| βvec */* βtot | 0.60 | 0.60 | 0.75 | 0.60 | 0.60 | 0.60 |

a Conversion factors for *β*tot from a.u. to SI and esu units: 1 a. u. =8.639418x10-33 esu

bGen. is a split basis set consisting of LAN2DZ for Iodine atom

c *η* is the ratio between off-diagonal (βyyz) and diagonal (βzzz) components

Additionally, some recent studies using DFT functionals which were suitable for calculations of NLO response properties of charge transfer-based molecules have been also highlighted in the computational details part of the manuscript. (Section 2: *Computational details;* page 6)

We optimized compounds **1-3** in ground state at CAM-B3LYP/6-31+G\*\* (LANL2DZ) and B3LYP/6-31+G\*\* (LANL2DZ) levels of theory. The static second-order polarizabilities along with their individual components have been computed at CAM-B3LYP/6-31+G\*\* (LANL2DZ) and given in Table 5 for comparison. In present investigation, we have calculated static total second-order polarizabilities (*β*tot)according to equations 2 to 5 as given in computational details (Section 2). From Table 5, it can be seen that second-order polarizability values are dominated by their diagonal (*β*zzz) components among all other components. Comparatively higher amplitudes of characteristic components of the second-order polarizability illustrate a significant delocalization/transfer of charges along these directions. For example, in present case, the *z*-axis is the main axis of charge transfer (see Figure 1) and it has the highest *z*-components of βtot values in almost all the systems as given in Table 5.

It is important to note down here that many critical studies indicated that B3LYP is not appropriate for the calculation of NLO polarizabilities as reported by Champagn et al.[1, 2]. Recently, Misra et al., [3] reported that the CAM-B3LYP and MP2 are suitable to calculate the NLO response, whereas the CAM-B3LYP is considered as more appropriate for NLO response without compromising the computing cost and accuracy [3]. Previously, the hybrid functional CAM-B3LYP has been reported as useful for evaluating the NLO response of several charge transfer base molecules [4-6]. To overcome such discrepancies, we have also optimized the compounds **1-3** at CAM-B3LYP method along with relatively larger basis set 6-31+G\*\* (LANL2DZ) for ground state. The static second-order polarizabilities at CAM-B3LYP/6-31+G\*\* (LANL2DZ) have been evaluated for compounds **1-3** initially optimized atB3LYP/6-31G\*\* (LANL2DZ) level of theory and are tabulated in Table 5 and S2 of supporting information. Furthermore, we also compute the static second-order polarizabilities at CAM-B3LYP/6-31+G\*\* (LANL2DZ) for compounds **1-3** optimized at CAM-B3LYP/6-31+G\*\* (LANL2DZ) level of theory and presented in Table 5.

2. The optimized geometries of the molecules (Cartesian coordinates) at all the level of theory (B3LYP & CAM-B3LYP) should be provided in the supporting information.

**Response:** The optimized geometries of all molecules (Cartesian coordinates) at B3LYsP/6-31G\*\* and CAM-B3LYP/6-31+G\*\* levels of theory have been given in Tables S3, S4 and S5 of supporting information and given below

**Table S3:** Optimized geometries of the molecules (Cartesian coordinates) of ground state for compounds **1** at the B3LYP/Genb and CAM-B3LYP/Genc methods levels of theory

|  |  |
| --- | --- |
| B3LYP/6-31G\*\* | CAM-B3LYP/6-31+G\*\* |
| I -2.12915800 -1.35435900 -0.00000700  I 2.13043100 -1.35239300 -0.00000100  C -0.81435800 3.19851900 0.00013800  H -1.29611500 4.16787800 0.00021200  C 0.81138100 3.19926800 0.00001600  H 1.29223000 4.16907900 -0.00005800  B -0.00120100 2.77842900 1.45473800  H -0.00153100 3.56271100 2.33600300  B -1.44063300 1.89944400 0.89461900  H -2.45465800 2.05217400 1.48000800  B -1.44064600 1.89951300 -0.89441900  H -2.45471100 2.05238800 -1.47971500  B -0.00140500 2.77861200 -1.45458000  H -0.00181500 3.56294800 -2.33579600  B 1.43892600 1.90073600 0.89441300  H 2.45289900 2.05435000 1.47966600  B -0.00036900 1.01368400 1.45836400  H -0.00004200 0.41318200 2.47608800  B -0.89414200 0.46384500 -0.00001400  B -0.00059000 1.01389600 -1.45841700  H -0.00035000 0.41356800 -2.47625300  B 1.43879800 1.90085500 -0.89461600  H 2.45264300 2.05468000 -1.48003800  B 0.89363400 0.46461900 -0.00021000 | I -2.10703800 -1.34544300 -0.00000200  I 2.10717100 -1.34523600 0.00000000  C -0.80729800 3.18012900 0.00006800  H -1.28890400 4.14889600 0.00011000  C 0.80700600 3.18019700 0.00001800  H 1.28852800 4.14900500 0.00000600  B -0.00007700 2.76312900 1.44671400  H -0.00009000 3.54725700 2.32723900  B -1.43258000 1.88890400 0.88947800  H -2.44671700 2.04110100 1.47364600  B -1.43261500 1.88894500 -0.88937000  H -2.44678700 2.04121400 -1.47346400  B -0.00018200 2.76322900 -1.44664700  H -0.00023700 3.54739000 -2.32714200  B 1.43244000 1.88901600 0.88937000  H 2.44661100 2.04128000 1.47346300  B -0.00000100 1.00672400 1.45068300  H 0.00005200 0.40471800 2.46712800  B -0.88863400 0.45973500 -0.00001400  B -0.00011200 1.00682100 -1.45073300  H -0.00011600 0.40491000 -2.46723600  B 1.43238100 1.88906900 -0.88947600  H 2.44649400 2.04142500 -1.47364700  B 0.88855600 0.45979500 -0.00010300 | |

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

cGen = 6-31+G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

**Table S4:** Optimized geometries of the molecules (Cartesian coordinates) of ground state for compound **2** at the B3LYP/Genb at B3LYP and CAM-B3LYP/Genc methods levels of theory, respectively.

|  |  |
| --- | --- |
| B3LYP/6-31G\*\* | CAM-B3LYP/6-31+G\*\* |
| I -5.20437100 2.12696000 0.01819400  I -5.20428200 -2.12700500 -0.01822700  C -0.62860500 0.87365100 0.00800300  C -0.62856300 -0.87350600 -0.00813700  B -1.06607800 -0.01193500 1.43812800  H -0.29582200 -0.01993100 2.32952500  B -1.95994900 1.43799000 0.90840500  H -1.81449800 2.43699900 1.51949800  B -1.95887400 1.45312000 -0.88303700  H -1.81363200 2.46257800 -1.47683900  B -1.06610600 0.01206900 -1.43822300  H -0.29589400 0.02008300 -2.32966000  B -1.95876800 -1.45301000 0.88295500  H -1.81349700 -2.46244700 1.47678700  B -2.83127400 -0.01260100 1.45324900  H -3.42225400 -0.02185000 2.47654300  B -3.39045400 0.89247200 0.00757700  B -2.83131200 0.01265700 -1.45330600  H -3.42231000 0.02187900 -2.47659000  B -1.95991800 -1.43792100 -0.90848500  H -1.81446000 -2.43694700 -1.51954500  B -3.39041300 -0.89245000 -0.00762600  C 0.63493500 1.53504900 0.01376500  C 0.63500800 -1.53484400 -0.01385900  C 1.70236800 2.11004800 0.01951000  C 1.70243600 -2.10985200 -0.01959100  C 2.95401900 2.79305900 0.02432100  C 3.66931100 2.95486600 1.22831500  C 3.48294500 3.31104800 -1.17542600  C 4.88995900 3.61850000 1.23432300  H 3.25907100 2.55845500 2.15051100  C 4.70254000 3.97656400 -1.17393300  H 2.92954200 3.18783000 -2.09980500  C 5.38693600 4.11840200 0.03195300  H 5.45974000 3.75650600 2.14453800  H 5.13069100 4.38476600 -2.08070600  C 2.95405700 -2.79292700 -0.02432800  C 3.67025100 -2.95322900 -1.22799400  C 3.48204300 -3.31251300 1.17513900  C 4.89083900 -3.61696500 -1.23394700  H 3.26073500 -2.55559100 -2.14998400  C 4.70159400 -3.97811600 1.17370000  H 2.92795800 -3.19046200 2.09926400  C 5.38687900 -4.11846400 -0.03185200  H 5.46127100 -3.75387600 -2.14392000  H 5.12903900 -4.38749300 2.08027700  N 6.68242900 4.82226000 0.03579400  O 7.09700400 5.25183000 -1.03900200  O 7.26387900 4.93298100 1.11341400  N 6.68230800 -4.82242800 -0.03563900  O 7.09621900 -5.25311200 1.03896800  O 7.26436800 -4.93213900 -1.11303500 | I -5.18288300 -2.10585300 -0.01981100  I -5.18287500 2.10585800 0.01977100  C -0.63311900 -0.84296800 -0.00841600  C -0.63311600 0.84295400 0.00849400  B -1.07393000 0.01338200 -1.44137400  H -0.29617000 0.02210400 -2.32489500  B -1.95460800 -1.42701300 -0.90356200  H -1.80154800 -2.42952200 -1.50531900  B -1.95378500 -1.44367600 0.87577900  H -1.80094000 -2.45751600 1.45838500  B -1.07396700 -0.01339400 1.44144100  H -0.29623000 -0.02212000 2.32498100  B -1.95375600 1.44366700 -0.87573600  H -1.80089100 2.45750700 -1.45833800  B -2.82764500 0.01383900 -1.44577900  H -3.42198300 0.02393400 -2.46658600  B -3.38040200 -0.88850500 -0.00840300  B -2.82768300 -0.01384300 1.44579900  H -3.42204800 -0.02393700 2.46659100  B -1.95462500 1.42700400 0.90360600  H -1.80157700 2.42951300 1.50536600  B -3.38039800 0.88850300 0.00840900  C 0.63325100 -1.51281300 -0.01449400  C 0.63325700 1.51279400 0.01460500  C 1.69246400 -2.08769400 -0.01943000  C 1.69247000 2.08767300 0.01955700  C 2.94817700 -2.77464200 -0.02373200  C 3.65759500 -2.93469400 -1.22223100  C 3.47012500 -3.29063600 1.17069500  C 4.87456900 -3.59917600 -1.22953900  H 3.24888500 -2.53729600 -2.14417600  C 4.68588800 -3.95733200 1.17072300  H 2.91675900 -3.16763600 2.09462400  C 5.36614800 -4.09805900 -0.03108600  H 5.44175600 -3.73606400 -2.14139300  H 5.10978000 -4.36593600 2.07917200  C 2.94817700 2.77463200 0.02380800  C 3.65760500 2.93475600 1.22229300  C 3.47011000 3.29056500 -1.17065200  C 4.87457400 3.59924800 1.22955200  H 3.24890700 2.53740600 2.14426400  C 4.68586800 3.95727000 -1.17072800  H 2.91673700 3.16750900 -2.09456900  C 5.36613800 4.09806800 0.03106700  H 5.44176900 3.73619100 2.14139300  H 5.10974900 4.36582700 -2.07920300  N 6.65771000 -4.80355100 -0.03481800  O 7.07091800 -5.23345500 1.03199900  O 7.23829900 -4.91583800 -1.10437900  N 6.65769400 4.80357100 0.03474800  O 7.07089500 5.23340300 -1.03210100  O 7.23829900 4.91590400 1.10429500 | |

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

cGen = 6-31+G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

**Table S5:** Optimized geometries of the molecules (Cartesian coordinates) of ground state for compound **3** at the B3LYP/Genb at B3LYP and CAM-B3LYP/Genc methods levels of theory, respectively.

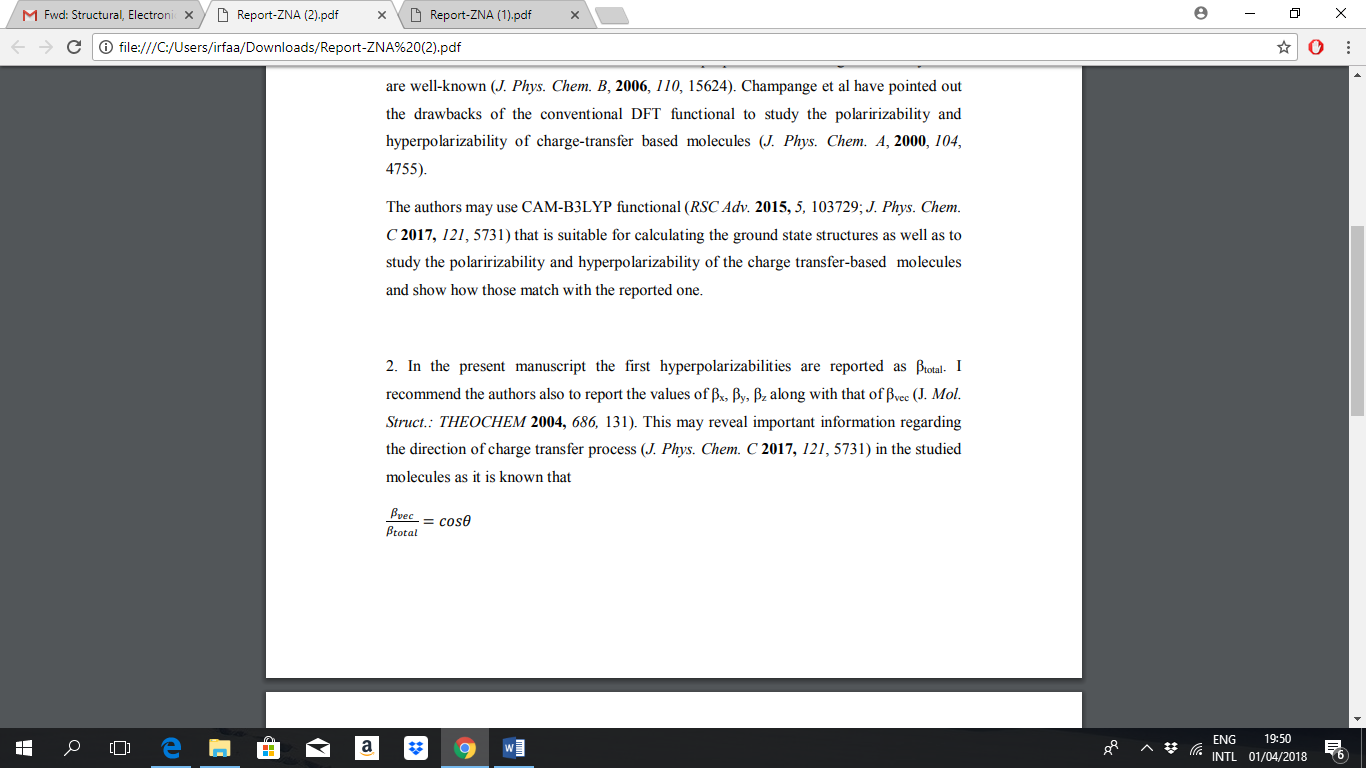
|  |  |
| --- | --- |
| B3LYP/6-31G\*\* | CAM-B3LYP/6-31+G\*\* |
| I -4.54624000 2.12307800 0.01222400  I -4.54623800 -2.12307200 -0.01228800  C 0.03465700 0.91877700 0.00646700  C 0.03466200 -0.91875300 -0.00645800  B -0.38394400 -0.00759900 1.41176900  H 0.37279300 -0.01381600 2.31540600  B -1.29682600 1.44518700 0.90445700  H -1.16978000 2.43916800 1.52873600  B -1.29516500 1.45549300 -0.88613300  H -1.16828300 2.45662100 -1.49896000  B -0.38394400 0.00761500 -1.41177300  H 0.37280900 0.01383900 -2.31539700  B -1.29516800 -1.45549300 0.88614700  H -1.16826100 -2.45662200 1.49896600  B -2.15704400 -0.00877500 1.45124300  H -2.74756100 -0.01578200 2.47558800  B -2.72375700 0.88908000 0.00525200  B -2.15704400 0.00878100 -1.45123200  H -2.74758400 0.01578300 -2.47556500  B -1.29680800 -1.44516600 -0.90444700  H -1.16976200 -2.43914400 -1.52873100  B -2.72375200 -0.88907800 -0.00524700  C 1.29514900 1.56788600 0.00922200  C 1.29515700 -1.56786400 -0.00921000  C 2.37954700 2.11746100 0.01039900  C 2.37954900 -2.11744800 -0.01037200  C 3.63796100 2.77471200 0.01028800  C 4.31865600 3.03734400 1.21759100  C 4.23972600 3.18608100 -1.19744400  C 5.54463900 3.68266300 1.21849300  H 3.86939800 2.72989300 2.15639700  C 5.46512100 3.83253300 -1.19920900  H 3.72882500 2.99448300 -2.13554200  C 6.14179900 4.09392900 0.00953400  H 6.05495800 3.87378600 2.15887100  H 5.91320200 4.14055400 -2.14025700  C 3.63795700 -2.77470200 -0.01024600  C 4.31933000 -3.03607300 -1.21744100  C 4.23902900 -3.18735100 1.19739300  C 5.54530600 -3.68140500 -1.21832400  H 3.87060600 -2.72762800 -2.15617600  C 5.46440700 -3.83383500 1.19917100  H 3.72760200 -2.99672900 2.13540300  C 6.14176700 -4.09396800 -0.00946200  H 6.05616200 -3.87153600 -2.15861200  H 5.91194600 -4.14285800 2.14014900  N 7.38724100 4.69605400 0.00605600  N 7.38720300 -4.69610800 -0.00591600  H 7.63590100 5.22697700 -0.81556600  H 7.69107900 5.12208000 0.86916300  H 7.69151700 -5.12123500 -0.86929800  H 7.63539400 -5.22789700 0.81528700 | I 4.51834100 2.10467100 -0.02031100  I 4.51848400 -2.10457900 0.02027800  C -0.03771300 0.85513600 -0.00961600  C -0.03765400 -0.85535300 0.00968500  B 0.39941300 -0.01325900 -1.43138200  H -0.37048000 -0.02314900 -2.32182900  B 1.28691400 1.42722900 -0.90328600  H 1.14259600 2.42823700 -1.51011800  B 1.28482100 1.44442900 0.87354000  H 1.14071400 2.45713300 1.46077900  B 0.39944400 0.01307200 1.43144200  H -0.37043000 0.02290900 2.32190600  B 1.28490000 -1.44455600 -0.87350000  H 1.14084900 -2.45727000 -1.46073600  B 2.15626800 -0.01456100 -1.44464300  H 2.75153300 -0.02576500 -2.46556700  B 2.71053700 0.88672200 -0.00877600  B 2.15629900 0.01449300 1.44466300  H 2.75158600 0.02573800 2.46557400  B 1.28703100 -1.42735500 0.90332600  H 1.14279500 -2.42837300 1.51016100  B 2.71059800 -0.88675200 0.00878300  C -1.30192800 1.52115000 -0.01452500  C -1.30182300 -1.52145700 0.01462300  C -2.36772000 2.08846800 -0.01686600  C -2.36763500 -2.08873700 0.01698100  C -3.62366400 2.76528900 -0.01889100  C -4.33452700 2.95661600 -1.21252000  C -4.17552000 3.25766100 1.17262900  C -5.55100400 3.61550700 -1.21645400  H -3.92131300 2.58232800 -2.14314200  C -5.39113600 3.91824600 1.17244700  H -3.63770700 3.11906800 2.10457400  C -6.09945600 4.10976300 -0.02340300  H -6.08933500 3.75016600 -2.15013400  H -5.80406400 4.28999100 2.10570500  C -3.62367500 -2.76537900 0.01894200  C -4.33458000 -2.95668800 1.21254900  C -4.17555500 -3.25764900 -1.17260900  C -5.55111500 -3.61547300 1.21643300  H -3.92134100 -2.58249300 2.14319700  C -5.39122900 -3.91812700 -1.17247800  H -3.63770200 -3.11908200 -2.10453600  C -6.09959000 -4.10962800 0.02335000  H -6.08947100 -3.75013200 2.15009800  H -5.80416800 -4.28980500 -2.10575800  N -7.33365600 4.73333000 -0.01994100  N -7.33384400 -4.73308700 0.01984000  H -7.56661600 5.30312300 0.77854500  H -7.67877400 5.08998400 -0.89755200  H -7.67900900 -5.08974700 0.89743000  H -7.56683900 -5.30282700 -0.77867400 |

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

cGen = 6-31+G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

3. The authors reported the first hyperpolarizabilities as βvec as I recommended. However, my point regarding the direction of charge transfer is not addressed properly. I suggest the authors to mention the background and any previous studies on this phenomenon.

it is known that



where, θ is the angle between the vector formed by βvec components and the dipole moment vector.

A brief description on this will help the readers to understand the direction of charge transfer process better.

**Response:** A brief description of direction of charge transfer has been added to the introduction section of revised manuscript as: (Section 2: *Introduction;* page 4)

We have calculated the static total second-order polarizabilities **(***β*tot**)** of compounds **1-3** to check their possible NLO response. Furthermore, a comparison of *β*tot and *β*vec has been done and presented in Table 5 of section 3.4 of results and discussion. It is also important to mention that the amplitude of *β*tot is always positive irrespective of the sign of individual tensorial component which cannot be measured experimentally. Whereas, the amplitude of *β*vec may be positive or negative depending on the direction of dipole moment and charge transfer process for typical molecular system [3, 7]. The relation between *βvec* and *βtot* presents essential evidence about the direction of charge transfer in the molecules [3, 8] and specified by equation:

In above equation, θ is the angle among vector formed by βvec components and the dipole moment vector. Usually, this ratio near to 1 indicates a unidirectional charge transfer within the molecular systems where *β*tot and *β*vec carry the similar amplitudes.

4. In addition to comment 3, the authors may mention the importance of intramolecular charge transfer-based molecules for studies of NLO response in the Introduction part of the manuscript.

From the two-state model proposed by Ouder, one can predict high NLO response of ICT molecules. Although this theory is not entirely valid, the difference in dipole moment between ground and excited state has been useful to understand the NLO response of many ICT molecules.

Mentioning the details and citing some recent review articles/books on NLO response properties of ICT molecules will help the interested readers to understand the background of the present study.

**Response:** The importance of intramolecular charge transfer-based molecules for studies of NLO response has been added in the introduction part of the manuscript and recent review articles/books on NLO response properties have been cited in the text. (Section 2: Introduction; page 3)

Previously, it has been shown that due tobetter phase matching and increased stability two-dimensional (2D) chromophores having large off-diagonal *β*-tensor components have advantage over 1D chromophores [9, 10].Nowadays, compounds with great off-diagonal *β* tensor components are being recommended as they can offer large macroscopic NLO responses. Hitherto, NLO properties of numerous 2D compounds were studied by substituting donor and/or acceptor (D/A) in V-shaped molecules [10, 11]. It was shown that angle between the intramolecular charge transfer (ICT) axis is important parameter to check the relative magnitude of off-diagonal and diagonal components. In current study of derivatives, the charge transfer comprises both sides of dicarba-closo-dodecaborane. Additionally, Coe *et al.* work showed that large off-diagonal *β* tensor components are intensely interconnected to oscillator strength, low-lying energy excited states with the electron transition dipole moment between two states that are perpendicular to the dipolar axis [11].

Earlier, ICT has been studied through bridging effect on first hyperpolarizability [12]. In some other studies NLO response properties of various ICT compounds were explored [3, 13, 14].There is great demand to improve new organic–inorganic hybrid compounds that can associate benefits of organic materials (high NLO efficiency) as well as inorganic materials (good stability, wide transparency range). Owing to good thermal stability of dicarba-closo-dodecaborane and its versatile nature, they are being used in various functional materials [15]. It is anticipated that due to V-shaped structures of dicarba-closo-dodecaborane derivatives might lead to better NLO properties. In current study, we have designed organic-inorganic hybrid proficient NLO-phores. The present investigations aim to explore the structure-property relationship of V-shaped derivatives and their potential as NLO-phores.

5. Excessive self-citation: it seems that more than one third of the references are selfcitation. I am not against authors citing their own papers, if necessary. However, this ratio seems to be high.

**Response:**

A number of Self-citations have been deleted. Some recent literature has been cited about the importance of intramolecular charge transfer-based molecules for studies of NLO response and background as well as previous studies on this phenomenon of the direction of charge transfer.

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