Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

New tuned range-separated density functional for the accurate calculation of electronic second hyperpolarizabilities (SI2)

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Contents

This document contains the information required for the design and construction of the OT-LC-BLYP functional.

1. Computational details.

All electronic structure calculations were carried out using Gaussian09 Revision E.01 package.[1] Molecular orbitals were constructed using Dunning's correlation-consistent double-ζ basis set including diffuse functions (aug-cc-pVDZ basis set).[2] For all DFT calculations, numerical integrations were performed by using the default grid in Gaussian09, which corresponds to a pruned grid of 75 radial shells and 302 angular points per shell.

The geometries of all systems present in the γ-NLO set but hydrogen chains were optimized at MP2 level of theory, requesting tight convergence criteria on the root-mean square (RMS) and maxima of the forces and displacements as defined in Gaussian09. Molecular set 1 geometries were optimized using CCSD method, which properly reproduces the CASPT2 and experimental singlet-triplet split for these diradical molecules.[3] For hydrogen chains, the alternated separation of 2.0 and 3.0 Bohr between hydrogen atoms was set in order to design a system consisting on moderately interacting molecules of dihydrogen, thus avoiding scenarios where the inclusion of nondynamic correlation is required. All minima in the potential energy surface were characterized by checking that all analytical vibrational frequencies were real.

Before computing the electronic linear polarizabilities and second hyperpolarizabilities, all molecules were reoriented in order to set the Z axis as the principal inertia axis with the highest moment of inertia, allowing us to focus only on the longitudinal component of the static polarizability matrix (*i.e.* α_{zz}) and the second hyperpolarizability tensor (*i.e.* γ_{zzzz}).

To obtain the CCSD(T) benchmark values, the CCSD(T) single point energy calculations necessary for the finite field procedure (see SI1, section 3) were computed with the required convergence criterion to achieve a change in the energy below 10^{-8} atomic units (a.u.). The cutoff to determine the two-electron integrals accuracy was set to 10^{-11} a.u. Then, CCSD(T) electronic static linear polarizability and second hyperpolarizabilities were computed as derivatives of the electronic energy with respect to an external electric field using the finite field (FF) approach.

$$\alpha_{zz} = -\left.\frac{\partial^2 E}{\partial F_z^2}\right|_{F_z=0}$$
$$\gamma_{zzzz} = -\left.\frac{\partial^4 E}{\partial F_z^4}\right|_{F_z=0} \qquad (1)$$

At the DFT level, both α and β can be analytically determined. Hence, to avoid part of the numerical error, γ was calculated numerically as the first derivative of β with respect to the external electric field using the FF approach.

The number of field strengths chosen in the FF procedure varies for each molecule and method (DFAs or CCSD(T)). In particular, the range of field strength used was $F=2^j \cdot 10^{-4}$ a.u. with integer values of *j*=0-7 for all molecules, with the addition of *j*=8-10 when the former field strengths were not enough to obtain converged numerical derivatives. The truncation error affecting the numerical estimation of the derivatives, which come from higher-order terms neglected in the standard central-differentiation formulas, was minimized thanks to application of the Rutishauser-Romberg scheme:[4,5]

$$R^{i,j} = \frac{4^i R^{(i-1),j} - R^{(i-1),(j-1)}}{4^i - 1} \qquad (2)$$

where *R* is the calculated property, *i* is the iteration number, and *j* indicates that the property has been computed using an electric field-strength of $2^j \cdot 10^{-4}$ a.u. in the FF procedure. By using this methodology, we found out that numerical errors on γ CCSD(T) were between <1% and 12% (MAE=2.15%), defining the numerical error as the smallest difference between the converged values generated with RR methodology for two different field strengths.

For the calculation of the ω parameter that enforces the fulfillment of Janak's theorem through the minimization of:

$$J^2(\omega) = \sum_{i=N}^{N+1} [IP^i + \varepsilon_{HOMO}^i(\omega)]^2 \qquad (3)$$

for simplicity, we have computed the IP^i at LC-BLYP level of theory (ω=0.47 $Bohr^{-1}$) at the beginning of the procedure and keep it constant through all the minimization process (i.e. $IP^i \neq IP^i(\omega)$). Nevertheless, we have checked that this approximation only triggers very small changes (if any) on the resulting ω, which is indeed usually far from ω_{CC}.

1. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox Gaussian 09, Revision E.01, Gaussian Inc: **2015**.

2. Jr., T. H. D., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, 90 (2), 1007-1023.

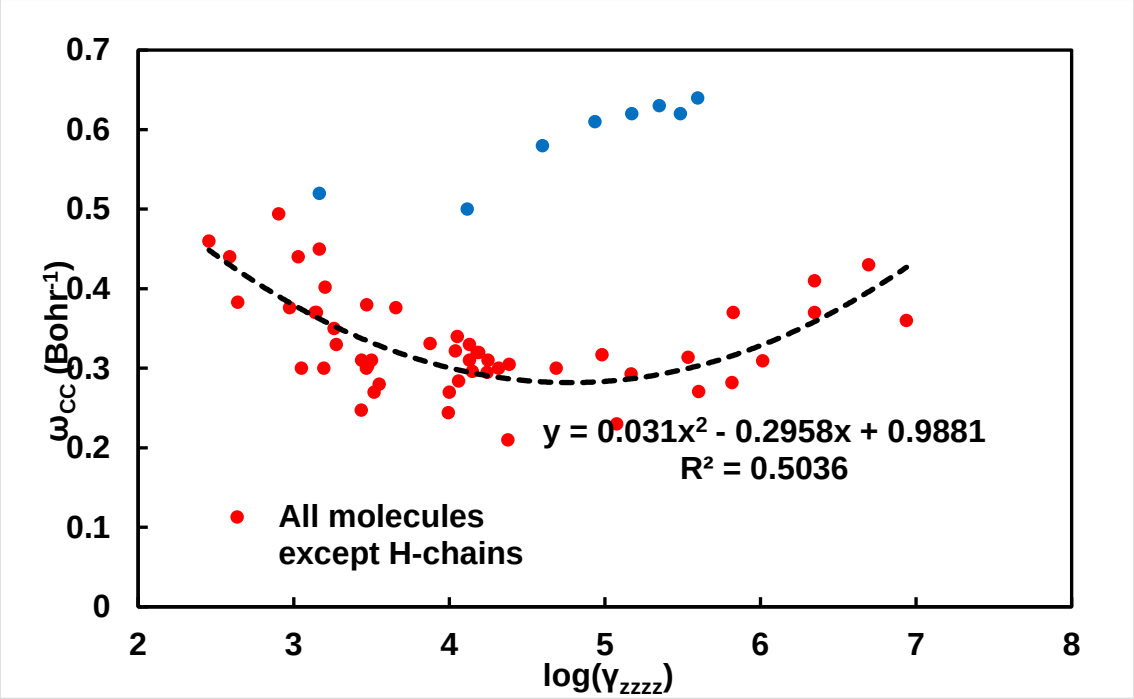
3. Poater, J.; Bickelhaupt, F. M.; Solà, M., Didehydrophenanthrenes: Structure, Singlet−Triplet Splitting, and Aromaticity. *J. Phys. Chem. A* **2007**, 111 (23), 5063-5070.

4. Rutishauser, H., Ausdehnung des Rombergschen Prinzips. *Numer. Math. (Heidelb)* **1963**, 5 (1), 48-54.

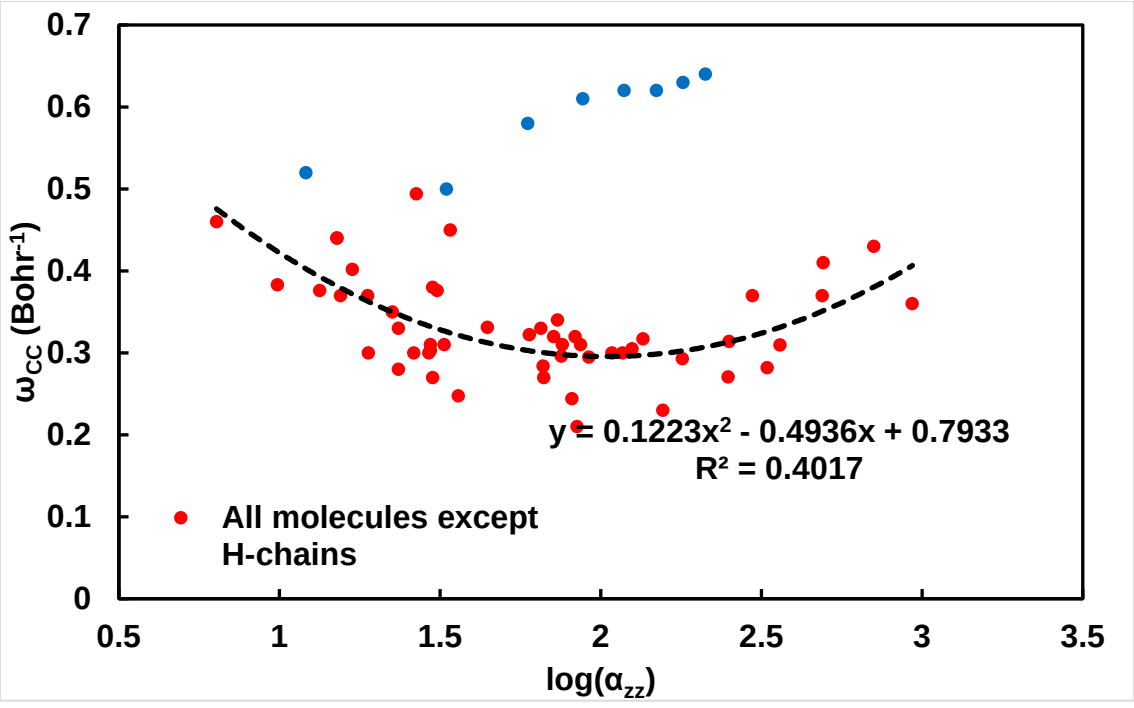
5. Medveď, M.; Stachová, M.; Jacquemin, D.; André, J.-M.; Perpète, E. A., A generalized Romberg differentiation procedure for calculation of hyperpolarizabilities. *J. Mol. Struct.* **2007**, 847 (1), 39-46.

2. Other tested correlations between ω_{cc} and different molecular descriptors

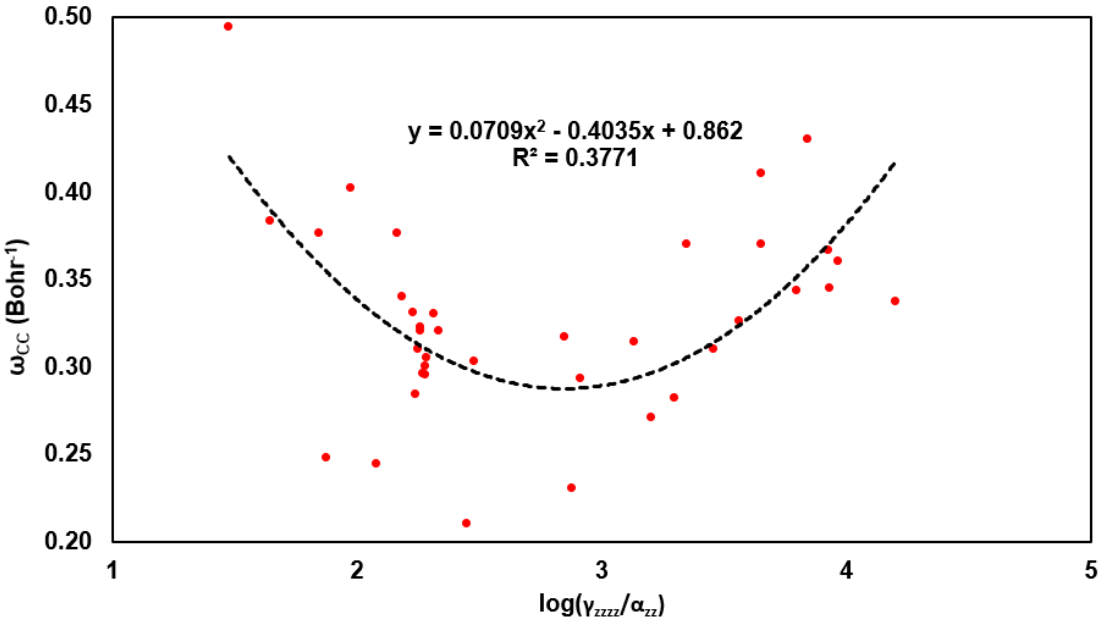
SI2.1 Correlation obtained using log(γ_{zzzz}) as a descriptor. Hydrogen chains displayed in blue and the rest of the molecules in red. The correlation curve is only fitted using red dots.



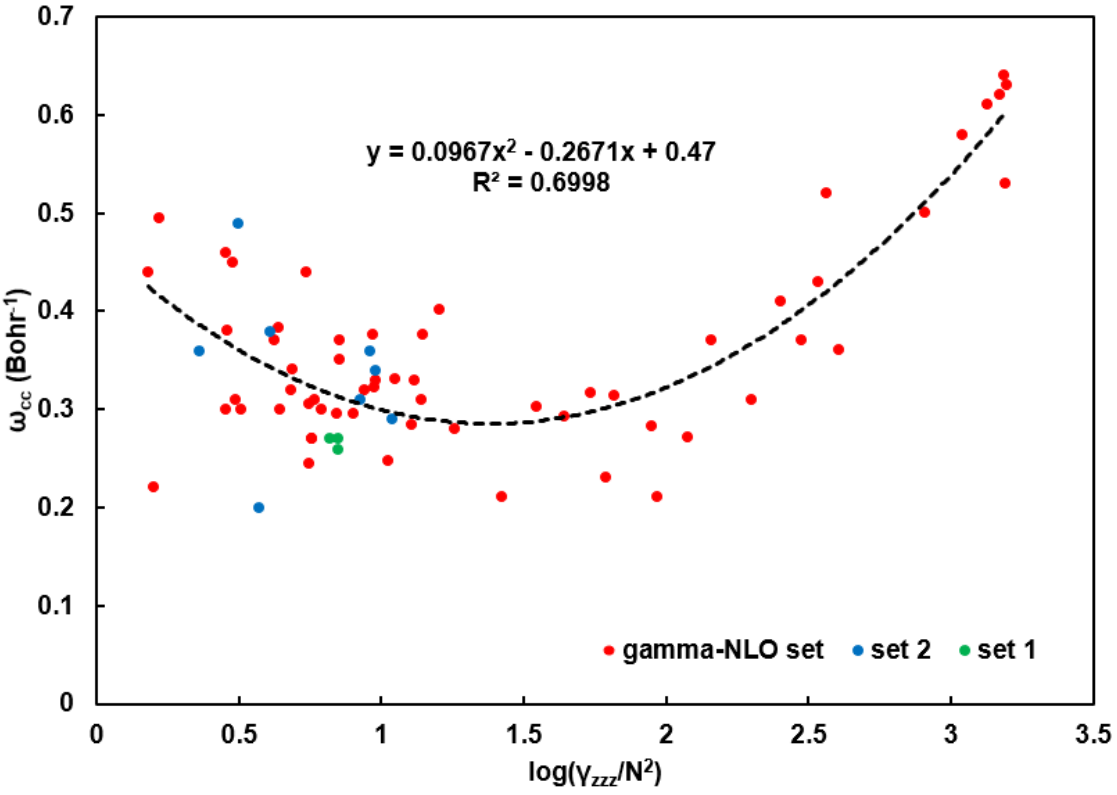
SI2.2 Correlation obtained using log(α_{zz}) as a descriptor. Hydrogen chains displayed in blue and the rest of the molecules in red. The correlation curve is only fitted using red dots.



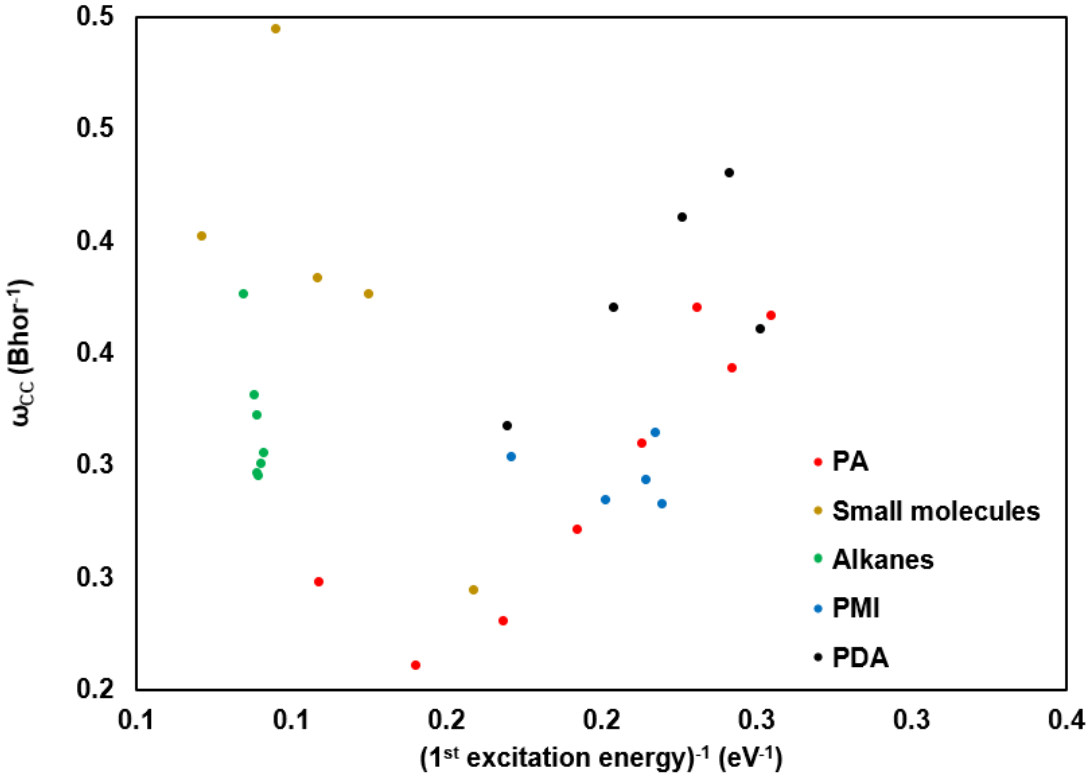
SI2.3 Correlation obtained using log(γ/α) as a molecular descriptor. Hydrogen chains are not included in the model because they are outside off-magnitude.



SI2.4 Correlation obtained using log(γ/N^2) as a molecular descriptor.

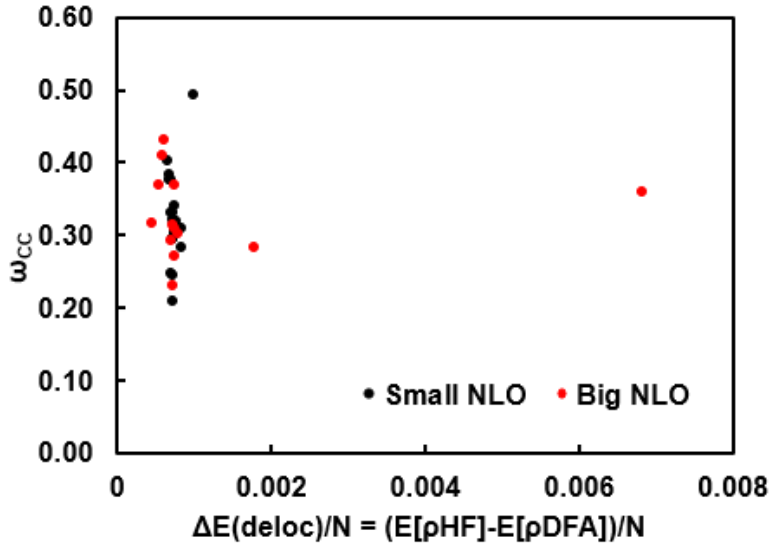


SI2.5 Correlation obtained using first excitation energy (TDDFT) as a molecular descriptor. Small molecules subgroup includes H_2O, NH_3, C_6H_6, CO_2, CH_4. The other subgroups include the first N oligomers.

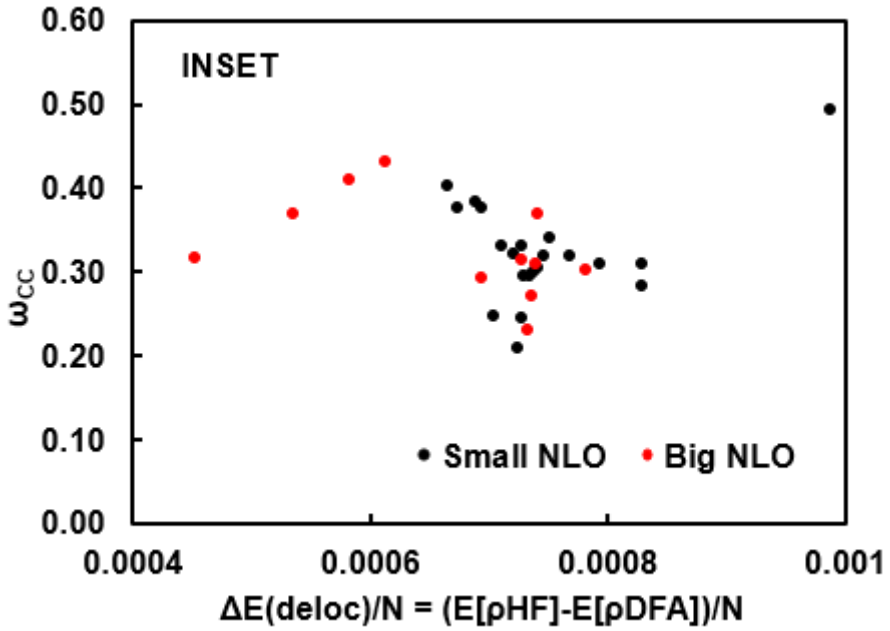


SI2.6 Correlation obtained using several measures of electron delocalization as a molecular descriptors. Small NLOP subgroup include molecules with indicator I_α lower than 1.50 and Large NLOP subgroup includes molecules with indicator I_α greater than 1.50.

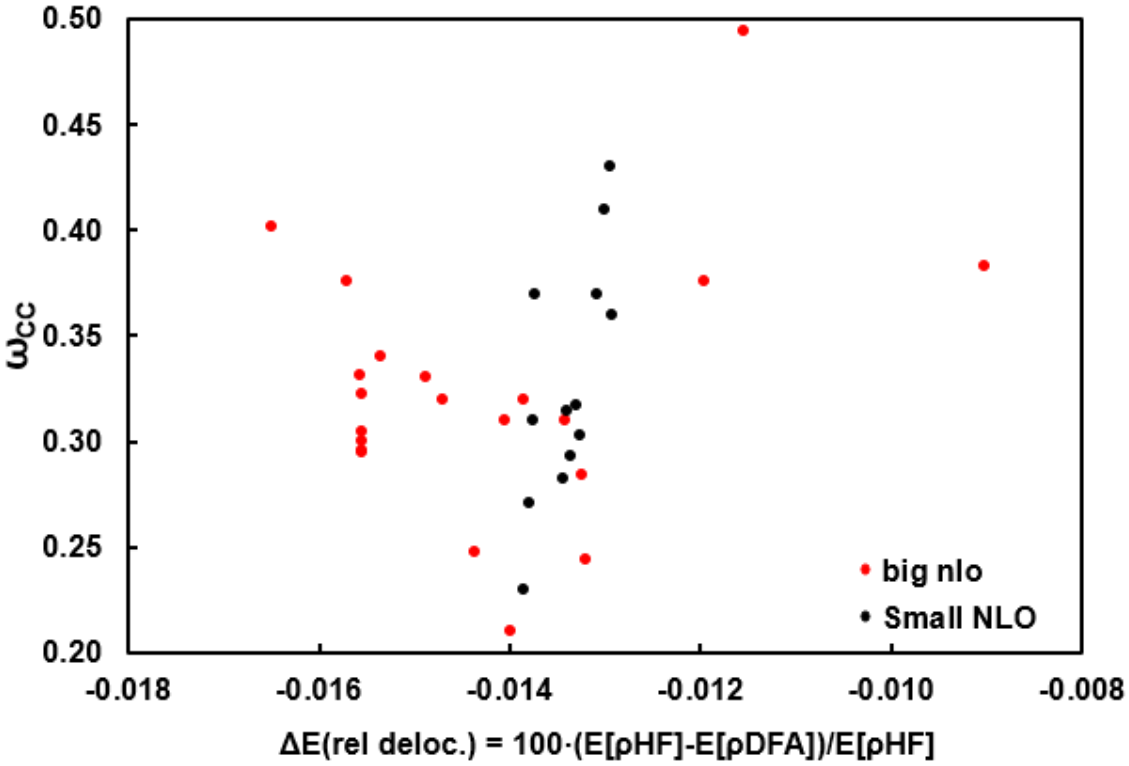
a) Delocalization error computed as the difference on HF energy using the HF and the DFA density divided by the number of electrons.



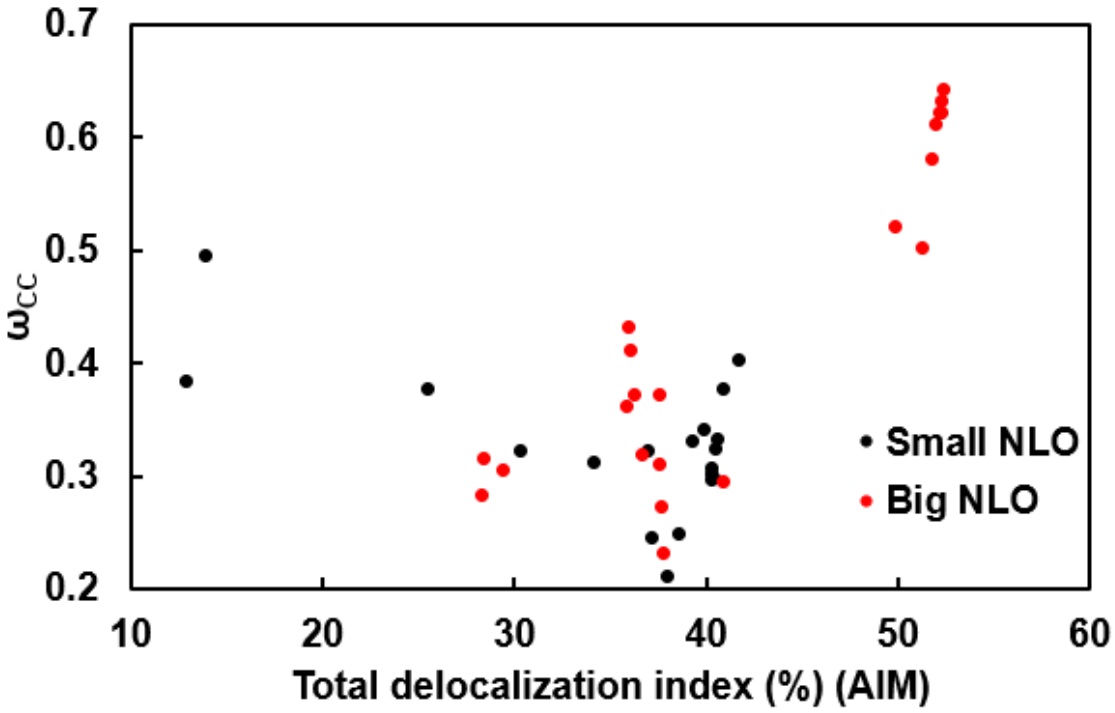
b) Inset of the figure SI2.4 a) in the range 0.0004 to 0.001 in the delocalization error.



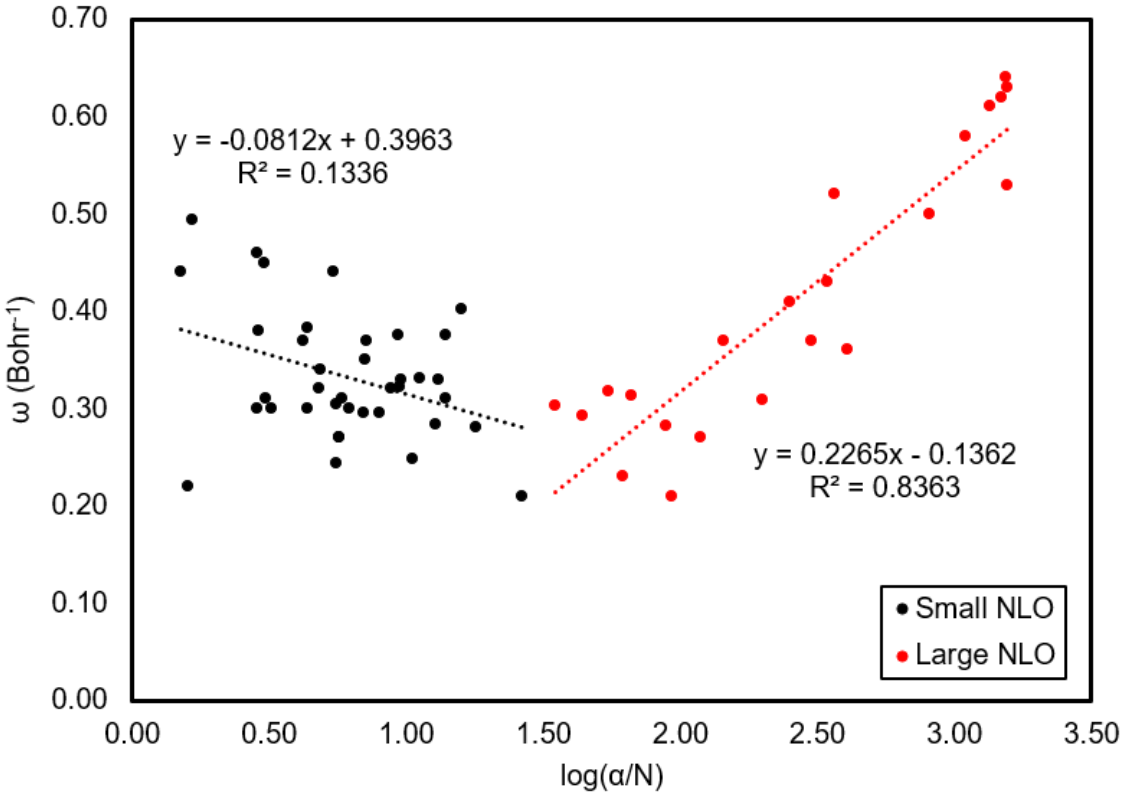
c) Delocalization error computed as the percentage error of the HF energy using the DFA density respect to the HF energy using the HF density.



d) Percentile total delocalization index (TDI) computed using AIMall software as *100 - the percentage of localized electrons*. "Atoms in Molecules - A Quantum Theory" R.F.W. Bader, Oxford University Press, Oxford, 1990.



SI2.7 Correlation obtained using log(α/N) as a molecular descriptor. Two straight lines model. Small NLOP subgroup include molecules with indicator I_α lower than 1.50 and Large NLOP subgroup includes molecules with indicator I_α greater than 1.50.



3. γ_{zzzz} values for the molecular sets 1 and 2 at following levels of theory: CCSD(T), B3LYP, BH&HLYP, PBE0, M06-2X, MN15, ωB97XD, CAM-B3LYP, LC-BLYP, OT-LC-BLYP and Tα-LC-BLYP

SI2.8 Values of the second hyperpolarizabilities (γ_{zzzz}) for molecular sets 1 and 2 obtained using LC-BLYP, T_{α}-LC-BLYP, CAM-B3LYP, OT-LC-BLYP, B3LYP, BH&HLYP, PBE0, M06-2X, MN15, ωB97XD density functionals as well as CCSD(T) method. aug-cc-pVDZ basis set used in all cases.

	Electronic second hyperpolarizabilities (a.u.)										
Set 1	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**Tα-LC-BLYP**	**CCSD(T)**
orto-benzyne	1.770E+04	1.604E+04	1.820E+04	1.504E+04	1.482E+04	1.437E+04	1.683E+04	1.446E+04	1.507E+04	1.507E+04	1.529E+04
meta-benzyne	1.183E+04	2.810E+04	1.204E+04	1.691E+04	1.801E+04	1.923E+04	2.059E+04	2.401E+04	2.234E+04	2.384E+04	2.713E+04
para-benzyne	1.574E+04	1.228E+04	1.408E+04	1.308E+04	1.352E+04	1.257E+04	1.285E+04	1.070E+04	1.226E+04	1.314E+04	1.317E+04

	Electronic second hyperpolarizabilities (a.u.)										
Set 2	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**Tα-LC-BLYP**	**CCSD(T)**
FCN···HCN	8.304E+03	5.511E+03	7.583E+03	6.182E+03	6.535E+03	2.702E+03	6.550E+03	5.239E+03	5.311E+03	6.412E+03	6.093E+03
FCN··HF	3.655E+03	2.306E+03	3.307E+03	2.404E+03	2.705E+03	2.717E+03	2.895E+03	2.346E+03	2.281E+03	2.796E+03	2.877E+03
HCN···HCCH	1.271E+04	8.529E+03	1.117E+04	8.846E+03	9.591E+03	8.603E+03	9.331E+03	7.168E+03	7.828E+03	9.128E+03	8.381E+03
HCN···HNC	1.268E+04	8.354E+03	1.141E+04	9.804E+03	9.662E+03	1.002E+04	9.751E+03	7.476E+03	8.409E+03	1.003E+04	9.613E+03
HNC···HCN	1.119E+04	7.621E+03	1.026E+04	8.934E+03	8.475E+03	3.982E+03	8.781E+03	6.597E+03	6.477E+03	8.724E+03	9.012E+03
HNC···HNC	1.555E+04	9.827E+03	1.396E+04	1.164E+04	1.120E+04	1.164E+04	1.149E+04	8.534E+03	9.633E+03	1.198E+04	1.258E+04
N_2···HF	2.753E+03	1.751E+03	2.479E+03	1.983E+03	2.042E+03	2.201E+03	2.218E+03	1.804E+03	1.767E+03	2.225E+03	1.741E+03
OC···HF	3.413E+03	2.156E+03	3.077E+03	2.335E+03	2.474E+03	2.263E+03	2.689E+03	2.135E+03	2.052E+03	2.750E+03	2.453E+03

SI2.9 Absolute errors of the second hyperpolarizabilities (γ_{zzzz}) respect to CCSD(T) benchmark values for molecular sets 1 and 2 obtained using LC-BLYP, T_{α}-LC-BLYP, CAM-B3LYP, OT-LC-BLYP, B3LYP, BH&HLYP, PBE0, M06-2X, MN15, ωB97XD density functionals. aug-cc-pVDZ basis set used in all cases.

	Error (abs) vs CCSD(T)									
Set 1	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**Tα-LC-BLYP**
orto-benzyne	2.404E+03	7.501E+02	2.908E+03	2.555E+02	4.715E+02	9.260E+02	1.539E+03	8.319E+02	2.217E+02	2.217E+02
meta-benzyne	1.531E+04	9.696E+02	1.509E+04	1.022E+04	9.118E+03	7.897E+03	6.543E+03	3.124E+03	4.793E+03	3.296E+03
para-benzyne	2.570E+03	8.872E+02	9.081E+02	8.464E+01	3.498E+02	5.999E+02	3.166E+02	2.463E+03	9.065E+02	3.135E+01
[a]MAE (a.u.)	6.760E+03	8.689E+02	6.302E+03	3.521E+03	3.313E+03	3.141E+03	2.800E+03	2.140E+03	1.974E+03	1.183E+03
[b]RMSD (a.u)	9.067E+03	8.736E+02	8.888E+03	5.905E+03	5.275E+03	4.604E+03	3.885E+03	2.347E+03	2.819E+03	1.908E+03
[c]MAX (a.u.)	1.531E+04	9.696E+02	1.509E+04	1.022E+04	9.118E+03	7.897E+03	6.543E+03	3.124E+03	4.793E+03	3.296E+03

	Error (abs) vs CCSD(T)									
Set 2	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**Tα-LC-BLYP**
FCN···HCN	2.210E+03	5.827E+02	1.490E+03	8.895E+01	4.413E+02	3.392E+03	4.562E+02	8.542E+02	7.827E+02	7.244E+02
FCN··HF	7.777E+02	5.710E+02	4.295E+02	4.733E+02	1.720E+02	1.602E+02	1.814E+01	5.312E+02	5.962E+02	2.441E+01
HCN···HCCH	4.326E+03	1.484E+02	2.794E+03	4.657E+02	1.210E+03	2.220E+02	9.503E+02	1.213E+03	5.525E+02	1.161E+03
HCN···HNC	3.063E+03	1.259E+03	1.796E+03	1.914E+02	4.927E+01	4.050E+02	1.376E+02	2.137E+03	1.204E+03	9.327E+02
HNC···HCN	2.174E+03	1.391E+03	1.244E+03	7.777E+01	5.370E+02	5.030E+03	2.313E+02	2.416E+03	2.535E+03	1.479E+02
HNC···HNC	2.975E+03	2.748E+03	1.386E+03	9.382E+02	1.378E+03	9.318E+02	1.084E+03	4.041E+03	2.942E+03	5.955E+02
N_2···HF	1.011E+03	9.382E+00	7.383E+02	2.423E+02	3.009E+02	4.595E+02	4.773E+02	6.325E+01	2.581E+01	3.901E+02
OC···HF	9.608E+02	2.969E+02	6.245E+02	1.174E+02	2.165E+01	1.892E+02	2.365E+02	3.171E+02	4.008E+02	7.261E+01
MAE[a] (a.u.)	2.187E+03	8.759E+02	1.313E+03	3.244E+02	5.138E+02	1.349E+03	4.489E+02	1.447E+03	1.130E+03	5.061E+02
RMSD[b] (a.u.)	2.477E+03	1.217E+03	1.493E+03	4.249E+02	7.044E+02	2.184E+03	5.746E+02	1.914E+03	1.499E+03	6.400E+02
MAX[c] (a.u.)	4.326E+03	2.748E+03	2.794E+03	9.382E+02	1.378E+03	5.030E+03	1.084E+03	4.041E+03	2.942E+03	1.161E+03

[a] MAE: Mean Absolute Error.

[b] RMSD: Root-Mean-Square Deviation.

[c] MAX: Maximum absolute error.

SI2.10 Absolute values for the relative errors of the second hyperpolarizabilities (γ_{zzzz}) respect to CCSD(T) benchmark values for molecular sets 1 and 2 obtained using LC-BLYP, T_α-LC-BLYP, CAM-B3LYP, OT-LC-BLYP, B3LYP, BH&HLYP, PBE0, M06-2X, MN15, ωB97XD density functionals. aug-cc-pVDZ basis set used in all cases.

	Error (abs) vs CCSD(T) in %									
Set 1	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**T_α-LC-BLYP**
orto-benzyne	15.72	4.90	19.02	1.67	3.08	6.06	10.07	5.44	1.45	1.45
meta-benzyne	56.41	3.57	55.62	37.68	33.61	29.11	24.12	11.52	17.67	12.15
para-benzyne	19.52	6.74	6.90	0.64	2.66	4.56	2.40	18.71	6.88	0.24
MAPE (%)	30.55	5.07	27.18	13.33	13.12	13.24	12.20	11.89	8.67	4.61
RSME (%)	35.64	5.24	34.17	21.78	19.54	17.36	15.15	13.07	10.98	7.07
MAX (%)	56.41	6.74	55.62	37.68	33.61	29.11	24.12	18.71	17.67	12.15

	Error (abs) vs CCSD(T) in %									
Set 2	**B3LYP**	**BH&HLYP**	**PBE0**	**M06-2X**	**MN15**	**wB97XD**	**CAM-B3LYP**	**LC-BLYP**	**OT-LC-BLYP**	**Tα-LC-BLYP**
FCN···HCN	36.28	9.56	24.45	1.46	7.24	55.66	7.49	14.02	12.84	11.89
FCN··HF	27.03	19.85	14.93	16.45	5.98	5.57	0.63	18.46	20.72	0.85
HCN···HCCH	51.61	1.77	33.34	5.56	14.44	2.65	11.34	14.48	6.59	13.85
HCN···HNC	31.86	13.10	18.68	1.99	0.51	4.21	1.43	22.23	12.52	9.70
HNC···HCN	24.12	15.44	13.81	0.86	5.96	55.81	2.57	26.80	28.13	1.64
HNC···HNC	23.65	21.85	11.02	7.46	10.96	7.41	8.62	32.13	23.40	4.74
N_2···HF	58.09	0.54	42.41	13.91	17.28	26.39	27.41	3.63	1.48	22.40
OC···HF	39.17	12.11	25.47	4.79	0.88	7.71	9.64	12.93	16.34	2.96
MAPE (%)	36.48	11.78	23.01	6.56	7.91	20.68	8.64	18.09	15.25	8.50
RSME (%)	38.37	13.80	25.10	8.52	9.69	29.75	11.79	19.91	17.33	10.98
MAX (%)	58.09	21.85	42.41	16.45	17.28	55.81	27.41	32.13	28.13	22.40

[a] MAPE: Mean Absolute Percentage Error.
[b] RMSD: Root-Mean-Square Deviation.
[c] MAX: Maximum absolute percentage error.

4. Cartesian coordinates of sets 1 and 2 (Å).

The geometries from set 2 are taken from Zaleśny, R. et al., *Phys. Chem. Chem. Phys.* 2018, 20 (30), 19841-19849.

Molecular set 1

Optimized at CCSD/aug-cc-pVDZ level.

ortho-benzyne

6 0.000000000 1.114900116 0.711596051
6 0.000000000 -0.079613971 1.473701106
6 0.000000000 1.114900116 -0.711596051
1 0.000000000 -0.082595971 2.565708187
1 0.000000000 2.076036186 -1.237137090
6 0.000000000 -1.202706054 0.633452044
6 0.000000000 -0.079613971 -1.473701106
1 0.000000000 -0.082595971 -2.565708187
6 0.000000000 -1.202706054 -0.633452044
1 0.000000000 2.076036186 1.237137090

meta-benzyne

6 0.000000000 0.000000000 -1.476190114
6 0.000000000 1.174764084 -0.689868056
6 0.000000000 -1.174764084 -0.689868056
1 0.000000000 2.182862158 -1.110977087
1 0.000000000 -2.182862158 -1.110977087
6 0.000000000 0.956388069 0.682536042
6 0.000000000 -0.956388069 0.682536042
6 0.000000000 0.000000000 1.662479114
1 0.000000000 0.000000000 2.752244192
1 0.000000000 0.000000000 -2.573799192

para-benzyne

6 0.000000000 0.709134053 1.245279090
6 0.000000000 -0.709134053 1.245279090
6 0.000000000 1.337531095 0.000000000
1 0.000000000 -1.275906091 2.181388156
6 0.000000000 -1.337531095 0.000000000
6 0.000000000 0.709134053 -1.245279090
1 0.000000000 1.275906091 -2.181388156
6 0.000000000 -0.709134053 -1.245279090
1 0.000000000 -1.275906091 -2.181388156
1 0.000000000 1.275906091 2.181388156

Molecular set 2

FCN···HCN, CCSD(T)/aug-cc-pVTZ
F 0.00000 0.00000 3.03565
C 0.00000 0.00000 1.76942
N 0.00000 0.00000 0.60800
H 0.00000 0.00000 -1.60266
C 0.00000 0.00000 -2.67483
N 0.00000 0.00000 -3.83534

FCN···HF, CCSD(T)/aug-cc-pVTZ
F 0.00000 0.00000 2.34725
C 0.00000 0.00000 1.08289
N 0.00000 0.00000 -0.07625
H 0.00000 0.00000 -1.94118
F 0.00000 0.00000 -2.87206

HCN···HCCH, CCSD(T)/aug-cc-pVTZ
H 0.00000 0.00000 4.01981
C 0.00000 0.00000 2.95541
C 0.00000 0.00000 1.74413
H 0.00000 0.00000 0.67636
N 0.00000 0.00000 -1.66503
C 0.00000 0.00000 -2.82410
H 0.00000 0.00000 -3.89214

HCN···HNC, MP2/aug-cc-pVTZ
C 0.00000 0.00000 2.72042
N 0.00000 0.00000 1.54408
H 0.00000 0.00000 0.53221
N 0.00000 0.00000 -1.39929
C 0.00000 0.00000 -2.56330
H 0.00000 0.00000 -3.62943

HNC···HCN, MP2/aug-cc-pVTZ
N 0.00000 0.00000 2.94546
C 0.00000 0.00000 1.77786
H 0.00000 0.00000 0.70576
C 0.00000 0.00000 -1.62416
N 0.00000 0.00000 -2.79790
H 0.00000 0.00000 -3.79650

HNC···HNC, MP2/aug-cc-pVTZ
C 0.00000 0.00000 2.77993
N 0.00000 0.00000 1.60356
H 0.00000 0.00000 0.58887
C 0.00000 0.00000 -1.45710
N 0.00000 0.00000 -2.62862
H 0.00000 0.00000 -3.62759

N_2···HF, MP2/aug-cc-pVTZ
N 0.00000 0.00000 -1.99169
N 0.00000 0.00000 -0.87848
H 0.00000 0.00000 1.17613
F 0.00000 0.00000 2.10146

OC···HF, MP2/aug-cc-pVTZ
O 0.00000 0.00000 -1.96277
C 0.00000 0.00000 -0.82700
H 0.00000 0.00000 1.22995
F 0.00000 0.00000 2.15908

5. Field-dependent CCSD(T) electronic energies for sets 1 and 2

Electronic energies computed at CCSD(T)/aug-cc-pVDZ level of theory, with the required convergence criterion to achieve a change in the energy below 10^{-8} atomic units (a.u.)

Molecular set 1

***ortho*-benzyne**, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.30295842511193E+02
0.0001	-2.30295842935854E+02
0.0002	-2.30295844187859E+02
0.0004	-2.30295849195961E+02
0.0008	-2.30295869233704E+02
0.0016	-2.30295949382066E+02
0.0032	-2.30296270024317E+02
0.0064	-2.30297553382858E+02
0.0128	-2.30302699853190E+02
0.0256	-2.30323524290133E+02
0.0512	-2.30454392451460E+02
0.1024	-2.31688345945506E+02
-0.0001	-2.30295842935831E+02
-0.0002	-2.30295844187884E+02
-0.0004	-2.30295849195653E+02
-0.0008	-2.30295869233852E+02
-0.0016	-2.30295949382066E+02
-0.0032	-2.30296270024460E+02
-0.0064	-2.30297553382954E+02
-0.0128	-2.30302699853253E+02
-0.0256	-2.30323524289941E+02
-0.0512	-2.30454392464007E+02
-0.1024	-2.31688345945493E+02

***meta*-benzyne**, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.30273445640855E+02
0.0001	-2.30273467412344E+02
0.0002	-2.30273490020142E+02
0.0004	-2.30273537750927E+02
0.0008	-2.30273643263788E+02
0.0016	-2.30273894493063E+02
0.0032	-2.30274557785700E+02
0.0064	-2.30276528374019E+02
0.0128	-2.30283060497046E+02
0.0256	-2.30306898950323E+02
0.0512	-2.31256212296352E+02
0.1024	-2.31769443116159E+02
-0.0001	-2.30273424707842E+02
-0.0002	-2.30273404612729E+02
-0.0004	-2.30273366935610E+02
-0.0008	-2.30273301638035E+02
-0.0016	-2.30273211275853E+02
-0.0032	-2.30273191624607E+02
-0.0064	-2.30273798382407E+02
-0.0128	-2.30277623915267E+02
-0.0256	-2.30296775785948E+02
-0.0512	-2.30538393677612E+02
-0.1024	-2.31852674992430E+02

***para*-benzyne**, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.30254862610311E+02
0.0001	-2.30254863021847E+02
0.0002	-2.30254864236775E+02
0.0004	-2.30254869082262E+02
0.0008	-2.30254888466987E+02
0.0016	-2.30254966005215E+02
0.0032	-2.30255276205273E+02
0.0064	-2.30256517675550E+02
0.0128	-2.30261494010122E+02
0.0256	-2.30281583560734E+02
0.0512	-2.30535327500624E+02
0.1024	-2.31656935603121E+02
-0.0001	-2.30254863021735E+02
-0.0002	-2.30254864237265E+02
-0.0004	-2.30254869081928E+02
-0.0008	-2.30254888468032E+02
-0.0016	-2.30254966006865E+02
-0.0032	-2.30255276202791E+02
-0.0064	-2.30256517678277E+02
-0.0128	-2.30261494005068E+02
-0.0256	-2.30281583560824E+02
-0.0512	-2.30535329621354E+02
-0.1024	-2.31656935600387E+02

Molecular set 2

FCN···HCN, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.85446961964280E+02
0.0001	-2.85446728613934E+02
0.0002	-2.85446495797630E+02
0.0004	-2.85446031767657E+02
0.0008	-2.85445110115246E+02
0.0016	-2.85443292419490E+02
0.0032	-2.85439759331422E+02
0.0064	-2.85433101216437E+02
0.0128	-2.85421411050181E+02
0.0256	-2.85404523980061E+02
0.0512	-2.85632438691460E+02
0.1024	-2.86816537994068E+02
-0.0001	-2.85447195848727E+02
-0.0002	-2.85447430267746E+02
-0.0004	-2.85447900710138E+02
-0.0008	-2.85448848011867E+02
-0.0016	-2.85450768308548E+02
-0.0032	-2.85454711853966E+02
-0.0064	-2.85463012371747E+02
-0.0128	-2.85481281315987E+02
-0.0256	-2.85524664698607E+02
-0.0512	-2.85643040175919E+02
-0.1024	-2.87056145120446E+02

FCN···HF, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.92509590443015E+02
0.0001	-2.92509396436240E+02
0.0002	-2.92509202779956E+02
0.0004	-2.92508816518086E+02
0.0008	-2.92508048196981E+02
0.0016	-2.92506528349724E+02
0.0032	-2.92503555739364E+02
0.0064	-2.92497878150957E+02
0.0128	-2.92487588831869E+02
0.0256	-2.92471253158220E+02
0.0512	-2.92455847862228E+02
0.1024	-2.93052628808702E+02
-0.0001	-2.92509784800029E+02
-0.0002	-2.92509979507175E+02
-0.0004	-2.92510369973843E+02
-0.0008	-2.92511155115691E+02
-0.0016	-2.92512742246169E+02
-0.0032	-2.92515984003223E+02
-0.0064	-2.92522738472612E+02
-0.0128	-2.92537339842601E+02
-0.0256	-2.92570998953750E+02
-0.0512	-2.92657238671577E+02
-0.1024	-2.93277643626327E+02

HCN···HCCH, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-1.70329942900536E+02
0.0001	-1.70330084207875E+02
0.0002	-1.70330226101186E+02
0.0004	-1.70330511651604E+02
0.0008	-1.70331089802105E+02
0.0016	-1.70332274308400E+02
0.0032	-1.70334756208838E+02
0.0064	-1.70340172273400E+02
0.0128	-1.70352822099803E+02
0.0256	-1.70385513969237E+02
0.0512	-1.71132806262456E+02
-0.0001	-1.70329802180926E+02
-0.0002	-1.70329662049197E+02
-0.0004	-1.70329383546539E+02
-0.0008	-1.70328833589789E+02
-0.0016	-1.70327761857219E+02
-0.0032	-1.70325731105382E+02
-0.0064	-1.70322120468089E+02
-0.0128	-1.70316705927742E+02
-0.0256	-1.70313193314532E+02
-0.0512	-1.70718894314361E+02

HCN···HNC, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-1.86397568110029E+02
0.0001	-1.86397854767332E+02
0.0002	-1.86398141951774E+02
0.0004	-1.86398717900465E+02
0.0008	-1.86399876122235E+02
0.0016	-1.86402217880886E+02
0.0032	-1.86407002818395E+02
0.0064	-1.86416979887053E+02
0.0128	-1.86438578631880E+02
0.0256	-1.86488556040644E+02
0.0512	-1.86755846224638E+02
0.1024	-1.88007502624599E+02
-0.0001	-1.86397281979364E+02
-0.0002	-1.86396996374608E+02

-0.0004	-1.86396426745087E+02
-0.0008	-1.86395293802425E+02
-0.0016	-1.86393053161958E+02
-0.0032	-1.86388672757637E+02
-0.0064	-1.86380314766509E+02
-0.0128	-1.86365207858898E+02
-0.0256	-1.86341501108994E+02
-0.0512	-1.86586447432836E+02
-0.1024	-1.88180860669025E+02

HNC···HCN, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-1.86393255422179E+02
0.0001	-1.86393526958166E+02
0.0002	-1.86393799012458E+02
0.0004	-1.86394344678380E+02
0.0008	-1.86395442237758E+02
0.0016	-1.86397662280469E+02
0.0032	-1.86402202197489E+02
0.0064	-1.86411682596067E+02
0.0128	-1.86432258739730E+02
0.0256	-1.86480032719903E+02
0.0512	-1.89301573383440E+02
0.1024	-1.87872535409059E+02
-0.0001	-1.86392984404621E+02
-0.0002	-1.86392713905970E+02
-0.0004	-1.86392174464322E+02
-0.0008	-1.86391101801362E+02
-0.0016	-1.86388981347515E+02
-0.0032	-1.86384839844224E+02
-0.0064	-1.86376953984212E+02
-0.0128	-1.86362770554220E+02
-0.0256	-1.86340827801156E+02
-0.0512	-1.86898908604410E+02
-0.1024	-1.88142376474110E+02

HNC···HNC, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-1.86374422202003E+02
0.0001	-1.86374713645198E+02
0.0002	-1.86375005634615E+02
0.0004	-1.86375591251771E+02
0.0008	-1.86376769041403E+02
0.0016	-1.86379150868540E+02
0.0032	-1.86384019732729E+02
0.0064	-1.86394180339323E+02
0.0128	-1.86416213812268E+02
0.0256	-1.86467385060416E+02
0.0512	-1.87095993050458E+02
0.1024	-1.88005720645285E+02
-0.0001	-1.86374131304176E+02
-0.0002	-1.86373840951897E+02
-0.0004	-1.86373261884603E+02
-0.0008	-1.86372110293005E+02
-0.0016	-1.86369832778213E+02
-0.0032	-1.86365383663405E+02
-0.0064	-1.86356901311024E+02
-0.0128	-1.86341600582374E+02
-0.0256	-1.86317670955624E+02
-0.0512	-1.86609670389028E+02
-0.1024	-1.88227656308240E+02

N_2···HF, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.09562297940455E+02
0.0001	-2.09562389390377E+02
0.0002	-2.09562481074826E+02
0.0004	-2.09562665147302E+02
0.0008	-2.09563036726453E+02
0.0016	-2.09563789897002E+02
0.0032	-2.09565341287646E+02
0.0064	-2.09568624403603E+02
0.0128	-2.09575913782414E+02
0.0256	-2.09593411115113E+02
0.0512	-2.09640534046208E+02
0.1024	-2.10099691621813E+02
-0.0001	-2.09562207352236E+02
-0.0002	-2.09562116371558E+02
-0.0004	-2.09561935115476E+02
-0.0008	-2.09561575416758E+02
-0.0016	-2.09560867274025E+02
-0.0032	-2.09559496008972E+02
-0.0064	-2.09556933584396E+02
-0.0128	-2.09552529988611E+02
-0.0256	-2.09546627519415E+02
-0.0512	-2.09546865769372E+02
-0.1024	-2.09979708694644E+02

OC···HF, CCSD(T)/aug-cc-pVDZ

Field (a.u.)	Electronic energy (a.u.)
0	-2.13343528168790E+02
0.0001	-2.13343628628028E+02
0.0002	-2.13343729335106E+02
0.0004	-2.13343931491103E+02
0.0008	-2.13344338773588E+02
0.0016	-2.13345165228839E+02
0.0032	-2.13346865777202E+02
0.0064	-2.13350458089026E+02
0.0128	-2.13358413796558E+02
0.0256	-2.13377474726106E+02
0.0512	-2.13429111342328E+02
0.1024	-2.13830777843215E+02
-0.0001	-2.13343427956652E+02
-0.0002	-2.13343327991400E+02
-0.0004	-2.13343128803461E+02
-0.0008	-2.13342733393354E+02
-0.0016	-2.13341954299621E+02
-0.0032	-2.13340443724632E+02
-0.0064	-2.13337611686388E+02
-0.0128	-2.13332700416892E+02
-0.0256	-2.13325881480086E+02
-0.0512	-2.13324499124345E+02
-0.1024	-2.14076783270023E+02