The static (hyper)polarizabilities of push-pull polyenes：A theoretic study

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Abstract

We have studied the static longitudinal polarizability, and first and second hyperpolarizabilities of push-pull conjugated polyenes (NH_2-$(CH{=}CH)_N$-NO_2) within finite field scheme. Ab initio methods and density functional theory (DFT) are used to evaluate electron correlation effects. B3LYP and CAM-B3LYP are compared with second-order Møller-Plesset perturbation theory (MP2) and highly reliable coupled cluster theory with single and double excitations (CCSD). Our study shows CAM-B3LYP fails to predict correct correlation contributions, and MP2 is also unsatisfactory. CCSD is the only reliable computational tool to this day.

Keywords: polarizability; first and second hyperpolarizabilities; electron correlation effects; MP2, CCSD, CAM-B3LYP

1. Introduction

Organic conjugated systems are intensely investigated both experimentally and theoretically due to its bright future as new materials. Common conjugated structure, which results in delocalized electronic structure, plays a key role in understanding the physical and chemical properties of organic conjugated systems. It is early known electron correlation is essential to describe correctly the electronic structures of organic conjugated systems [1-3].

Ab initio methods, such as many-body perturbation theory and coupled clusters method, are often used to access the electron correlation effects [4, 5]. But the huge computational costs seriously restrict the use of ab initio methods. DFT becomes more and more popular due to its simple picture and competitive efficiency [6, 7]. Unfortunately, researchers found traditional functionals confront difficulties in presenting a correct description for organic conjugated systems [3, 8-9]. Many efforts are devoted to developing new functionals to fix this problem. CAM-B3LYP was shown to perform much better than traditional functionals such as B3LYP in studying conjugated systems [10-14].

Response properties of organic conjugated systems were intensely explored in past decades [15-20]. Many significant developments are reported, but some important issues are still unclear. Yang and coworkers reported their studies on the response properties of push-pull polyenes with newly-developed

OEP and/or OEP-EXX exchange functionals, and they found OEP and/or OEP-EXX exchange functionals perform much better than conventional functionals [15]. Champagne and coworkers studied electron correlation effects on the first hyperpolarizability of push-pull pi-conjugated systems. They found 6-31G(d) basis set is an optimal choice for polyene linkers [16]. Mohammed and coworkers discussed finite field method as an effective tool for calculating the nonlinear optical properties [17-18]. We studied previously electron correlation effect on static response properties of pristine polyenes [2-3, 19-20]. And we report here our recent study on response properties of a typical donor-acceptor derivatives of all-trans polyenes, also known as push-pull polyenes, $NH_2\text{-}(CH{=}CH)_N\text{-}NO_2$.

2. Computational Details

The molecular geometries have an important impact on the properties. We here focus on the performances of different electronic structure methods in the same molecular geometry. The molecular geometries of $NH_2\text{-}(CH{=}CH)_N\text{-}NO_2$ are optimized by Hartree-Fock method (HF) with 6-31G basis set. Basis sets of medium size 6-31G(d) and cc-pVDZ are used to compute molecular energies in this study. The 6-31G(d) basis set were reported to be the optimal choice for study of nonlinear optical properties of push-pull polyenes [16]. Correlated electronic structure methods such as MP2, CCSD, B3LYP and CAM-B3LYP are used to evaluate electron correlation effects.

Finite field scheme is chosen to calculate static response properties of $NH_2\text{-}(CH{=}CH)_N\text{-}NO_2$ [21-25]. First，molecular energies are computed in zero or given electric fields applied along the direction of chains, and the response properties such as longitudinal polarizability (***α***), first hyperpolarizability (***β***) and second hyperpolarizability (***γ***) are obtained with numerical derivatives of energy with respect to electric field as

$$\alpha = -\left(\frac{\partial^2 E}{\partial h^2}\right)\Bigg|_{h=0} = -\frac{E(h)+E(-h)-2E(0)}{h^2} \tag{1}$$

$$\beta = -\left(\frac{\partial^3 E}{\partial h^3}\right)\Bigg|_{h=0} = -\frac{E(2h)-2E(h)+2E(-h)-E(-2h)}{2h^3} \tag{2}$$

$$\gamma = -\left(\frac{\partial^4 E}{\partial h^4}\right)\Bigg|_{h=0} = -\frac{E(2h)-4E(h)+6E(0)-4E(-h)+E(-2h)}{h^4}. \tag{3}$$

The electric field used in this study reads $h = 8\times10^4$ a.u., and $E(h)$ is the molecular energy in electric field ***h***, and so on. Optimized molecular geometries and molecular energies are obtained with Gaussian 09 software package [26]. An extrapolation scheme [3] is used to give the trend as the chain approaches infinite. The properties are obtained with Hartree-Fock method (HF) and correlated electronic structure methods respectively. One can get contributions from electron correlation simply by comparing correlated properties with HF results.

3. Results and Discussion

The 6-31G(d) and cc-pVDZ basis sets are found to make much less difference in this study, and only results obtained by 6-31G(d) are discussed for most cases. The polarizability obtained as second derivatives of the energy with respect to electric field is plotted in Fig. 1. B3LYP is well known to fail to present proper treatment for electron correlation effect. From Table I and Fig. 1, one can see that CCSD and CCSD(T) predict negative electron correlation contributions for polarizability, except for $N = 2$. B3LYP, CAM-B3LYP, and MP2 predict positive electron correlation contributions. CAM-B3LYP performs better than B3LYP, comparing to CCSD. It is worth mentioning MP2 give wrong predictions for correlation contributions too. The trend predicted by MP2 is obviously much better than B3LYP and CAM-B3LYP, comparing to CCSD. CCSD results are very close to CCSD(T) ones for $N = 2,\ 3,\ 4$, and are used as a reference thereafter. The extrapolation result is plotted in Fig. 2, from which damping effect of electron correlation effect on polarizability [3] can be found.

From Table II and Fig. 3, one can see both ab initio methods and DFT predict positive electron correlation contributions for β. CAM-B3LYP performs better than B3LYP, but both B3LYP and CAM-B3LYP give a trend of being steeper than CCSD. MP2 predicts a better trend, but overestimates the electron correlation contributions. As is known, the first hyperpolarizabilities of all-trans polyenes are zero for symmetric structure. The push-pull structure breaks the symmetry and leads to a nonzero $\boldsymbol{\beta}$. The damping effect of electron correlation effect on first hyperpolarizability can be found from Fig. 4.

One can easily see from Table III and Fig. 5 that the second hyperpolarizabilities obtained by MP2 for small systems ($\boldsymbol{N}$ = 2, 3, 4) are close to those obtained by CCSD and CCSD(T), but MP2 predicts a steeper trend. B3LYP and CAM-B3LYP predict a worse trend as the chain length increases. A damping effect of electron correlation for γ can be seen from Fig. 6.

4. Conclusions

Electron correlation effect is essential in studying polarizability and first and second hyperpolarizabilities of organic conjugated systems. Though CAM-B3LYP performs better than B3LYP, it is still far from satisfactory. Searching for proper exchange and correlation functionals describing organic conjugated systems are still much valuable and challenging. MP2 is also questionable, especially for $\boldsymbol{\beta}$ and γ, and is therefore an inappropriate benchmark for developing new functionals for conjugated systems, at least for medium or large conjugated systems. CCSD with appropriate basis set are still the only reliable choice for studying the response properties of conjugated systems.

The damping effect of electron correlation on the second hyperpolarizability of pristine polyenes [3] is also found in push-pull polyenes. And the damping effect of electron correlation on first hyperpolarizability is found for push-pull polyenes.

Acknowledgements

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TABLE I Static longitudinal polarizability per unit cell α_L/N of $NH_2\text{-(CH=CH)}_N\text{-}NO_2$ (in a.u.).

N	2	3	4	5	6
6-31G(d)					
HF	70.32	78.67	87.14	94.61	100.91
MP2	76.16	83.44	90.58	96.56	101.32
CCSD	72.06	76.23	79.99	82.81	84.91
CCSD(T)	72.63	76.98	81.31		
B3LYP	78.64	91.83	107.21	123.07	138.62
CAM-B3LYP	75.74	86.14	97.29	107.68	116.77
cc-pVDZ					
HF	70.42	79.06	87.86	95.66	102.28
MP2	75.75	83.58	91.42	98.18	103.72
CCSD	71.68	76.75	81.50	85.30	88.24
CCSD(T)	72.21	77.50	82.86		
B3LYP	78.48	91.71	107.11	122.98	138.54
CAM-B3LYP	75.59	86.12	97.44	108.00	117.31

TABLE II Static longitudinal first-order hyperpolarizability per unit cell β_L/N of $NH_2\text{-(CH=CH)}_N\text{-}NO_2$ (in 10^2 a.u.).

N	2	3	4	5	6
6-31G(d)					
HF	6.80	11.88	17.64	23.10	27.55
MP2	15.15	26.56	39.24	51.10	60.70
CCSD	14.60	23.82	31.84	37.37	40.25
CCSD(T)	15.49	24.83	33.08		
B3LYP	8.35	16.54	29.38	47.89	72.78
CAM-B3LYP	9.14	17.29	28.28	41.12	54.41
cc-pVDZ					
HF	6.35	11.22	16.83	22.18	26.70
MP2	13.92	24.67	36.92	48.75	58.68
CCSD	12.94	21.61	29.77	35.90	39.68
CCSD(T)	13.61	22.42	30.95		
B3LYP	7.91	15.86	28.28	46.15	70.13
CAM-B3LYP	8.60	16.39	26.93	39.28	52.13

TABLE III Longitudinal second-order hyperpolarizability per cell γ_L/N of NH2-(CH=CH)$_N$-NO2 (in 10^4 a.u.)

N	2	3	4	5	6
6-31G(d)					
HF	3.1518	9.4760	21.5609	39.3065	60.9501
MP2	7.1885	23.5264	54.7753	100.3947	155.4416
CCSD	9.4954	27.3940	54.6792	86.3269	116.1628
CCSD(T)	11.2739	31.2911	61.1759		
B3LYP	1.4093	6.6420	22.4183	60.6237	140.0925
CAM-B3LYP	2.8426	11.2753	31.9916	71.1198	131.6961
cc-pVDZ					
HF	3.0089	9.0068	20.5871	36.8609	59.1967
MP2	6.6044	21.6309	51.0172	95.0994	149.8380
CCSD	8.2236	23.9669	51.1046	82.0634	114.8293
CCSD(T)	9.6284	27.1768	57.9478		
B3LYP	1.5666	6.9540	22.8413	60.8804	139.2329
CAM-B3LYP	2.8670	11.0342	31.0094	68.6723	127.0823

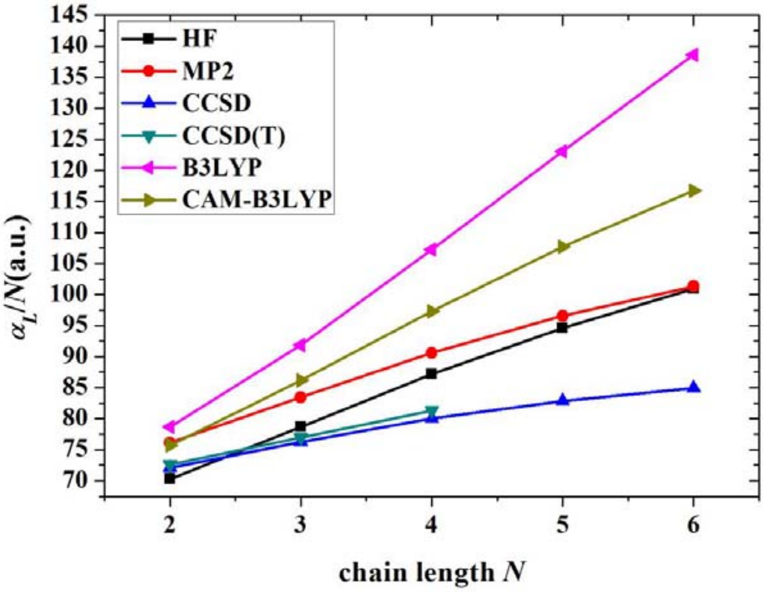

Fig. 1. Static longitudinal polarizability α_L/N of NH_2-$(CH{=}CH)_N$-NO_2 (in a.u.) obtained by different methods with 6-31G(d) basis set.

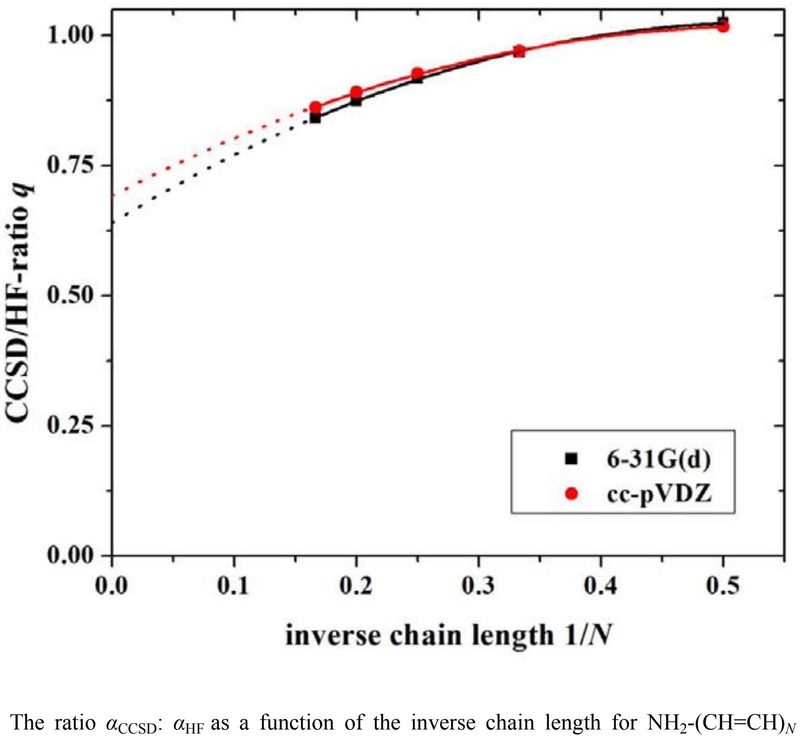

Fig. 2. The ratio α_{CCSD}: α_{HF} as a function of the inverse chain length for NH_2-$(CH{=}CH)_N$-NO_2. Values at $N\to\infty$ were obtained by a quadratic extrapolation.

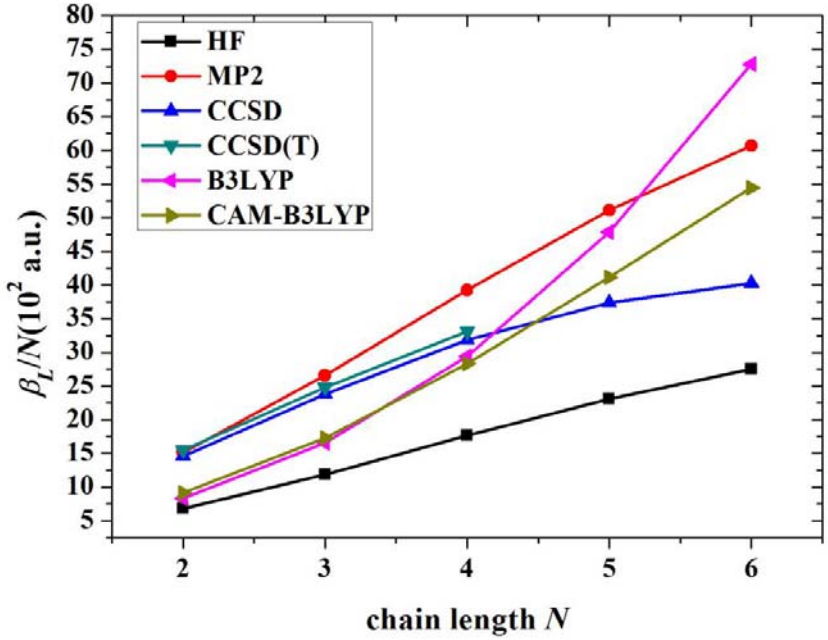

Fig. 3. Static longitudinal first-order hyperpolarizability β_L/N of NH_2-(CH=CH)$_N$-NO_2 (in 10^2 a.u.) obtained by different methods with 6-31G(d) basis set.

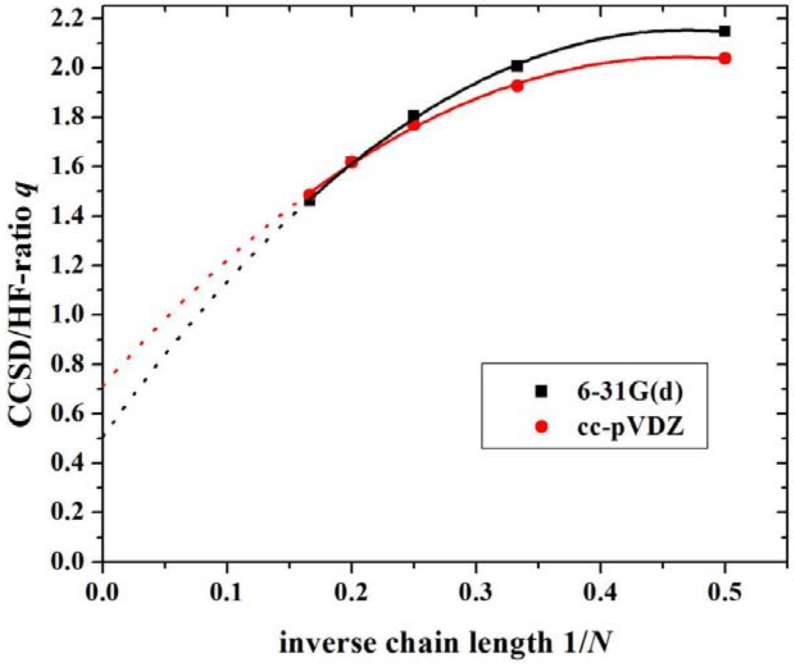

Fig. 4. The ratio β_{CCSD}: β_{HF} as a function of the inverse chain length for NH_2-(CH=CH)$_N$-NO_2. Values at $N\to\infty$ were obtained by a quadratic extrapolation.

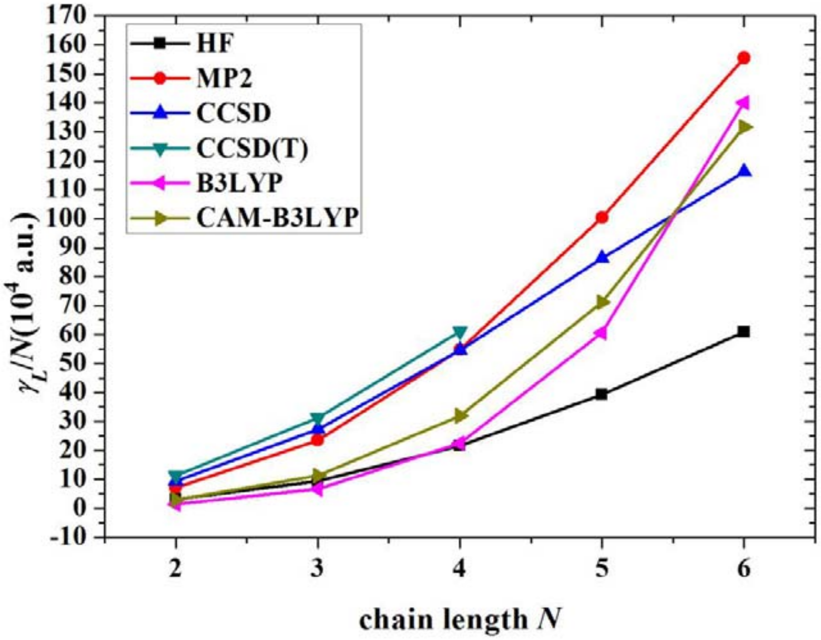

Fig. 5 Static longitudinal second-order hyperpolarizability γ_L/N of NH_2-(CH=CH)$_N$-NO_2 (in 10^4 a.u.) obtained by different methods with 6-31G(d) basis set.

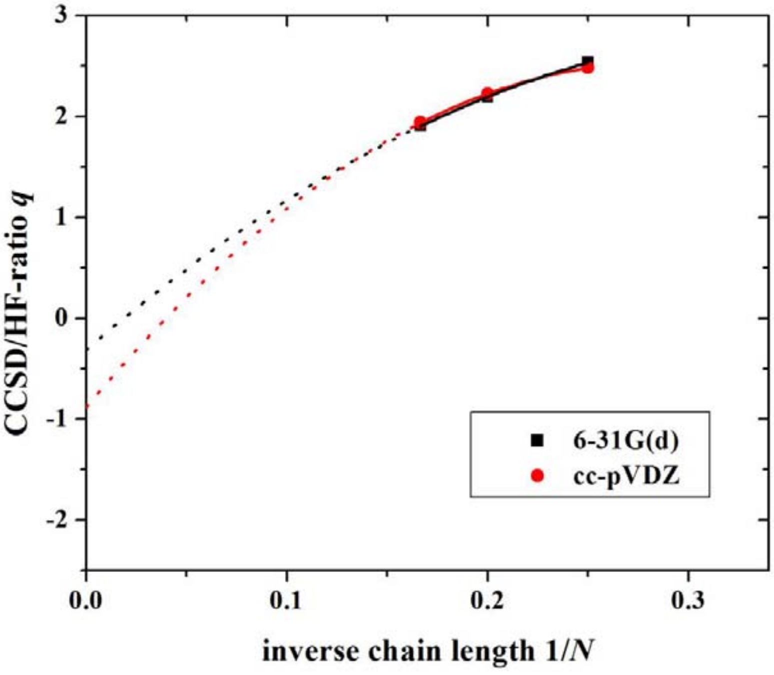

Fig. 6. The ratio γ_{CCSD}:γ_{HF} as a function of the inverse chain length for NH_2-(CH=CH)$_N$-NO_2. Values at $N\rightarrow\infty$ were obtained by a quadratic extrapolation.