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An **ab initio** study of CX₃- substitution (X = H, F, Cl, Br, I) effects on the static electric polarizability and hyperpolarizability of diacetylene

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ABSTRACT

We report a systematic ab initio and density functional theory study of the electric properties of the $X_3C-C\equiv C-C\equiv C-H$ ($X = H, F, Cl, Br$ and I) sequence of substituted diacetylenes. We rely on finite-field Møller-Plesset perturbation theory and coupled-cluster calculations with large, flexible basis sets. Our best values at the second-order Møller-Plesset perturbation theory level for the mean dipole polarizability and second hyperpolarizability are $\bar{\alpha} / e^2 a_0^2 E_h^{-1} = 64.46$ ($-CH_3$), 65.59 ($-CF_3$), 110.11 ($-CCl_3$), 138.90 ($-CBr_3$), 184.98 ($-CI_3$) and $\bar{\gamma} / e^4 a_0^4 E_h^{-3} = 21020$ ($-CH_3$), 13469 ($-CF_3$), 32708 ($-CCl_3$), 57599 ($-CBr_3$), 105251 ($-CI_3$). For comparison, the analogous MP2 values for diacetylene [P.Karamanis and G.Maroulis, Chem.Phys.Lett. 376, 403 (2003)] are $\bar{\alpha} / e^2 a_0^2 E_h^{-1} = 49.17$ and $\bar{\gamma} / e^4 a_0^4 E_h^{-3} = 16227$. For the mean first hyperpolarizability we report $\bar{\beta} / e^3 a_0^3 E_h^{-2} = -205.8$ ($-CH_3$), -55.7 ($-CF_3$), 120.8 ($-CCl_3$), 443.8 ($-CBr_3$) and 725.4 ($-CI_3$).

INTRODUCTION

The nonlinear optics (NLO) of organic molecules have attracted particular attention in recent years¹. This is understandably motivated by the need for development of new materials for potential applications in advanced technologies^{2,3}. The synthesis of new molecules, the conception of novel molecular architectures and the experimental and theoretical determination of their NLO properties is of central importance to this research current⁴. The theory of electric polarizability is a key element for the rational approach to the interpretation of the NLO behavior of atoms and molecules⁵. The various computational aspects of the theoretical prediction of electric polarizabilities and the convergence of theory and experiment have been the object of many comprehensive reviews^{6,7,8,9}. It should also be emphasized that electric polarizability is a universal characteristic of atoms and molecules and finds use in a wide range of fields such as electron scattering^{10,11}, the simulation of fluids¹², the accurate analysis of spectroscopic observations^{13,14,15,16} and even the understanding of pharmacological activity^{17,18}.

In this paper we focus on the evolution of the dipole moment and the electric (hyper)polarizability of $X_3C-C\equiv C-C\equiv C-H$ ($X = H, F, Cl, Br$ and I). We are interesting in observing patterns of evolution for the molecular properties in CX_3 -substituted diacetylene. Such systematic studies provide valuable insight on the effects of substitution¹⁹. Diacetylene is currently of interest due to the increasing importance of acetylenic chemistry²⁰. Its electric properties have been studied at various levels of theory^{21,22,23,24}. Several experimental studies of the hyperpolarizability of diacetylene derivatives have been reported recently^{25,26,27}. Very little is known about the molecular properties of the $X_3C-C\equiv C-C\equiv C-H$ sequence. Both $H-C\equiv C-C\equiv C-H$ and $H_3C-C\equiv C-C\equiv C-H$ have been detected in space^{28,29}. The dipole moment of methyldiacetylene has been deduced by Bester *et al.* from measurements of the millimeter wave spectrum³⁰.

Our method for the calculation of electric properties relies on the finite-field method³¹. An presentation of the computational philosophy underlining our approach may be found in recent work^{32,33,34}. The values of the properties are extracted from perturbed molecular energies^{35,36,37} or the induced multipole moments^{38,39,40} in the presence of a static electric field. We rely on both **ab initio** and density functional theory (DFT) methods for our calculations. DFT offers an attractive alternative to

1
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3 demanding high-level **ab initio** methods. Thus, it is both instructive and useful to
4 accumulate experience on the performance of DFT methods on various classes of
5 molecular properties^{41,42,43,44,45,46}. We have given particular attention to the choice of
6 suitable basis sets as this is a problem of capital importance in electric
7 (hyper)polarizability predictions^{47,48,49,50,51}.
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THEORY

The energy of an uncharged molecule in a weak, static electric field can be expanded as^{52,53}

$$\begin{aligned}
 E^P &\equiv E^P(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, \dots) \\
 &= E^0 - \mu_\alpha F_\alpha - (1/3)\Theta_{\alpha\beta} F_{\alpha\beta} - (1/15)\Omega_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - (1/105)\Phi_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} + \dots \\
 &\quad - (1/2)\alpha_{\alpha\beta} F_\alpha F_\beta - (1/3)A_{\alpha,\beta\gamma} F_\alpha F_{\beta\gamma} - (1/6)C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} \\
 &\quad - (1/15)E_{\alpha,\beta\gamma\delta} F_\alpha F_{\beta\gamma\delta} + \dots \\
 &\quad - (1/6)\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/6)B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} + \dots \\
 &\quad - (1/24)\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots
 \end{aligned} \tag{1}$$

where F_α , $F_{\alpha\beta}$, $F_{\alpha\beta\gamma}$, etc., are the field, field gradient, etc. at the origin. E^0 , μ_α , $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ are the energy and the permanent dipole, quadrupole, octopole and hexadecapole moment of the free molecule. The second, third and fourth-order properties (**in bold**) are the dipole polarizability ($\alpha_{\alpha\beta}$), the first ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability, the dipole-quadrupole ($A_{\alpha,\beta\gamma}$) and dipole-octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability, the quadrupole polarizability ($C_{\alpha\beta,\gamma\delta}$) and the dipole-dipole-quadrupole hyperpolarizability ($B_{\alpha\beta,\gamma\delta}$). The subscripts denote Cartesian components and a repeated subscript implies summation over x, y and z. In the case of a homogeneous field the expansion of eq. 1 reduces significantly to

$$E^P = E^0 - \mu_\alpha F_\alpha - (1/2)\alpha_{\alpha\beta} F_\alpha F_\beta - (1/6)\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/24)\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \tag{2}$$

The number of independent components needed to specify the dipole tensors is dictated by symmetry. For molecules of C_{3v} symmetry, as $X_3C-C\equiv C-C\equiv C-H$, μ_α has one independent component, $\alpha_{\alpha\beta}$ two, $\beta_{\alpha\beta\gamma}$ three and $\gamma_{\alpha\beta\gamma\delta}$ four. The choice made here is merely a convenient one, reflecting the adopted molecular orientation shown in Fig. 1, along the lines of previous work on ammonia⁵⁴. In addition to the Cartesian components we compute also the following invariants:

$$\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$$

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx}$$

$$\begin{aligned}\bar{\beta} &= (3/5)(\beta_{zzz} + 2\beta_{zxx}) \\ \bar{\gamma} &= (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15\end{aligned}\quad (3)$$

For sufficiently weak electric fields the expansion of eq. 2 converges rapidly and the electric properties can be safely extracted from the perturbed molecular energies. We will not give details here, see Refs. 32 and 33 (and references therein).

We have taken into account electron correlation effects via Møller-Plesset perturbation theory and coupled cluster techniques. Illuminating accounts for both classes of methods are easily found in high-level textbooks^{55,56} and comprehensive reviews^{57,58}. Thus, the **ab initio** methods employed in this work are:

SCF, self-consistent-field

MP2, second-order Møller-Plesset perturbation theory

MP4, second-order Møller-Plesset perturbation theory

CCSD, singles and doubles coupled cluster, and

CCSD(T), which includes an estimate of connected triples via a perturbational treatment.

The CCSD(T) method is, presumably, the one with the highest predictive capability of all the above but its applicability is limited to rather small molecules. Here, it is applied only to $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$. For the remaining molecules we rely on the MP2 method.

We have also recourse to the widely used B3LYP and B3PW91 DFT-based methods (as implemented in the GAUSSIAN 98 program). Their presentation and a discussion of their potential in electric polarizability calculations may be found in previous work^{59,60}.

COMPUTATIONAL STRATEGY

The calculation of electric (hyper)polarizabilities requires flexible, adequately polarized basis sets. In practice, this means the construction of purpose-oriented basis sets. The preparation of such basis sets is straightforward for atoms^{61,62}, diatomic^{63,64} and triatomic^{65,66,67} molecules and small clusters^{68,69,70} or polyatomics^{71,72,73}. A different strategy is usually adopted for systematic sequences of molecules, as clusters of A_n or $(AB)_n$ type, where one relies on basis sets optimized on the A or AB subunits^{74,75,76,77}.

As very little is known on the electric properties of the $X_3C-C\equiv C-C\equiv C-H$ molecules we have chosen to obtain purpose-oriented basis sets for all molecules, despite their large size. Thus, we ensure the maximum possible flexibility in all cases. We give here in brief the composition of the basis sets. The basis sets for each center are given in C/H/X order. The exponents of the Gaussian-type functions (GTF) are given in parentheses, in units of a_0^{-2} . As in previous work, the initial substrate is augmented with diffuse functions, tight polarization functions with exponents chosen to minimize the energy of the free molecule and diffuse polarization functions with exponents chosen to maximize the mean dipole polarizability (optimized exponents in **bold**).

HC≡C-C≡C-CH₃

BH1 ≡ [5s3p2d/3s2p] 156 contracted GTF from a D95≡ [4s2p/2s]⁷⁸ C/H substrate

+C: s(0.0474), p(0.0365), d(0.75, **0.1193**)

+H: S(0.0483), p(1.0, **0.2387**)

BH2≡ [5s3p3d/3s3p] CGTF from D0

+C: D(0.1193)

+H: P(0.1166)

BT1 ≡ (13s9p2d/7s2p) 302 GTF from a (12s8p/6s)⁷⁹ C/H substrate

+C s(0.04266049), p(0.03053568), d(**0.7786**, **0.1089**)

+H s(0.03130155), p(**1.1371**, **0.2415**)

BT2 ≡ (13s9p4d/7s4p) 376 GTF from T1

+C d(0.2911, 0.0407)

+H p(0.5240, 0.1113)

HC≡C-C≡C-CF₃

BF1 ≡ [5s3p2d/3s2p/5s3p2d] 201 CGTF from a D95≡ [4s2p/2s/4s2p] substrate

+C: s(0.0474), p(0.0365), d(0.75, **0.1213**)

+F: s(0.1093), p(0.0796), d(0.9, **0.2279**)

+H: s(0.0483), p(1.0, **0.2754**)

BF2 ≡ [5s3p3d/3s3p/5s3p3d] 244 CGTF from DF1

+C: d(0.3016)

+F: d(0.5248)
+H: p(0.4528)

HC≡C-C≡C-CCl₃**BCl1** ≡ [5s3p2d/3s2p/7s5p2d] 225 CGTF from a D95 C/H and [6s4p]⁸⁰ Cl substrate

+C: s(0.0474), p(0.0365), d(0.75, **0.1191**)
+Cl s(0.0673), p(0.0527), d(0.6, **0.1392**)
+H: s(0.0483), p(1.0, 0.2729)

BCl2 ≡ [5s3p3d/3s3p/7s5p3d] 268 CGTF from DCl1

+C: d(0.2989)
+Cl d(0.5223)
+H: p(0.2890)

HC≡C-C≡C-CBr₃**DBr0** ≡ [5s3p2d/3s2p/5s4p2d] 210 CGTF from [4s2p/2s] and (13s10p4d)/[4s3p1d]⁸¹

+C: s(0.0474), p(0.0365), d(0.75, **0.1206**)
+Br s(0.05461048), p(0.03339403), d(**0.1368**)
+H: s(0.0483), p(1.0, **0.2630**)

DBr1 ≡ [5s3p3d/3s3p/5s4p4d] 268 CGTF from DBr1

+C: d(0.3007)
+Br: d(0.4877, 0.0383)
+H: p(0.5128)

HC≡C-C≡C-CI₃**DI0** ≡ [5s3p2d/3s2p/6s5p3d] 237 CGTF from [4s2p/2s] and (16s13p7d)[5s4p2d]⁷⁴

+C: s(0.0474), p(0.0365), d(0.75, **0.1143**)
+I: s(0.04268666), p(0.02749172), d(**0.0998**)
+H: s(0.0483), p(1.0, **0.2790**)

DI1 ≡ [5s3p3d/3s3p/6s5p5d] 295 CGTF from DI1

+C: d(0.0446)
+I: d(0.2842, 0.0350)
+H: p(0.2790)

It is worth noting that for the D95 basis for H, C, F, and Cl instead of optimizing the tight p- or d-GTF we have used the estimates proposed by Dunning and Hay (Ref. 73): H(1.0), C(0.75), F(0.9) and Cl(0.6). 5D and 7F GTF were used on all basis sets.

All optimizations and subsequent calculations were performed at the theoretical geometries obtained in this work. The basis sets used in the geometry calculations were the standard D95** (as implemented in the Gaussian 98 program) for the C, F, Cl and H atomic centers. On the heavier atoms we used [4s3p1d] and [5s4p2d] for Br and I, respectively (see ref. 74). All geometry optimizations were performed at the MP2(FULL) level of theory.

Weak, homogeneous electric fields of $0.005 \text{ e}^{-1} \text{ a}_0^{-1} \text{ E}_h$ were found suitable for the finite-field calculations of the electric properties.

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3 The Gaussian 98⁸² program was used in all calculations.
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5 Unless otherwise specified, atomic units are used throughout this paper.
6
7 Conversion factors to SI units are, Energy, $1 E_h = 4.3597482 \times 10^{-18} \text{ J}$, Length, $1 a_0 =$
8 $0.529177249 \times 10^{-10} \text{ m}$, μ , $1 e a_0 = 8.478358 \times 10^{-30} \text{ Cm}$, α , $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times$
9 $10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$, β , $1 e^3 a_0^3 E_h^{-2} = 3.206361 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$ and γ , $1 e^4 a_0^4 E_h^{-3} =$
10 6.235378×10^{-65} . Property values are given as pure numbers, that is $\mu/e a_0$, $\alpha/e^2 a_0^2 E_h^{-1}$,
11 $\beta/e^3 a_0^3 E_h^{-2}$ and $\gamma/e^4 a_0^4 E_h^{-3}$.
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RESULTS AND DISCUSSION

Geometry and other important molecular characteristics. In Fig. 2 we show the details of the theoretical MP2(FULL) geometries calculated in this work. We also show atomic charges obtained via a NBO analysis at the MP2(FULL) level of theory with the optimized DH1, DF1, DC11, DBr1 and DI1 basis sets. In Fig. 3 we show the evolution of the bond lengths in the C-CX₃ subunit of X₃C-C≡C-C≡C-H. We observe a rapid increase of the C-X bond length as H→F→Cl→Br→I while the C-C bond length shows a slow decrease. Turning our attention to the atomic charges (Fig. 2) we observe little change on the C≡C-C≡CH subunit. Significant changes are visible on the charges on the atoms of the -CX₃ group. With the notable exception of the -CH₃ case, the charge on the halogen increases as F(-0.37) < Cl(+0.03) < Br(+0.16) < I(+0.27). The opposite is observed for the adjacent C atom where from the strongly positive character in the -CF₃ group (+1.14) we pass to a strongly negative in -Cl₃ (-0.76). In Fig. 4 we show the displacement of charge in the molecular frame, following the application of a static homogeneous field of $\pm 0.02 e^{-1}a_0^{-1}E_h$ along the dipole moment axis (C₃ axis). The changes become increasingly more important and are clearly reflected in the enhancement of dipole moment $\mu \equiv \mu_z$.

Last, in Fig. 5 we show a HOMO and LUMO representation of all HC≡C-C≡C-CX₃ molecules.

Electric properties. SCF values for all properties calculated with all basis sets are shown in Table 1. Correlated values for the dipole moment and polarizability are given in Table 2. The respective values for the first and second hyperpolarizability are in Tables 3 and 4, respectively. Last, SCF, MP2, B3LYP and B3PW91 values calculated with basis sets BH1 (H₃C-C≡C-C≡C-H), BF1 (F₃C-C≡C-C≡C-H), BC11 (Cl₃C-C≡C-C≡C-H), BBr1 (Br₃C-C≡C-C≡C-H) and BI1 (I₃C-C≡C-C≡C-H) are collected in Table 5.

Table 1 offers an eloquent picture of the SCF values of the studied molecules. The dipole moment of H₃C-C≡C-C≡C-H is negative but that of the other molecules is positive and increases monotonically in the direction F→Cl→Br→I. The axial components of the (hyper)polarizability are the most important in magnitude. Within the X₃C-C≡C-C≡C-H, X = F, Cl, Br, I sequence we observe a monotonic increase of the mean values $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$. It is worth noticing that the invariants $\bar{\alpha}$, $\Delta\alpha$, $\bar{\gamma}$ for

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3 $F_3C-C\equiv C-C\equiv C-H$ are lower than those calculated for $H_3C-C\equiv C-C\equiv C-H$. Similar
4 effects have been reported previously by other authors⁸³ and us^{84,85}.
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6

7 Electron correlation reduces the size of the dipole moment of $H_3C-C\equiv C-C\equiv C-$
8 H , for all basis sets used in this work. Our CCSD(T)/BH1 value is $\mu = -0.4601$ that is
9 11.4% lower in magnitude than the SCF result of -0.5191 . Electron correlation
10 reduces the magnitude of both components of the dipole polarizability. We obtain
11 CCSD(T)/BH1 values (SCF results in parentheses) $\alpha_{xx} = 40.17$ (40.34) and $\alpha_{zz} =$
12 111.33 (113.34). Consequently the mean and the anisotropy at the CCSD(T) level of
13 theory are $\bar{\alpha} = 63.89$ and $\Delta\alpha = 71.16$, 1.2 and 2.5% lower than the respective SCF
14 values $\bar{\alpha} = 64.68$ and $\Delta\alpha = 73.00$. We observe that the MP2 method yields values in
15 close agreement with the presumably most accurate CCSD(T). For the other two
16 methods, the dipole polarizability values obey the relationship $MP4 > CCSD(T) >$
17 $CCSD$.
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20 The dipole moment of $F_3C-C\equiv C-C\equiv C-H$ is positive. Electron correlation at the
21 MP2 level reduces the dipole moment by $\approx 11.0\%$ for both basis sets BF1 and BF2.
22 MP2 yields polarizability values slightly higher than the respective SCF ones. The
23 MP2/BF2 values for the invariants are $\bar{\alpha} = 65.59$ and $\Delta\alpha = 68.88$, or 1.7 higher and
24 0.1% lower than the respective SCF values of $\bar{\alpha} = 64.52$ and $\Delta\alpha = 68.98$.
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27 Turning our attention to the higher members of the sequence $X_3C-C\equiv C-C\equiv C-$
28 H , $X = Cl, Br$ and I , we observe that MP2/BCl2 predicts a dipole moment lower than
29 SCF/BCl2. However for the two remaining molecules MP2/BBr2 and MP2/BI2
30 predict dipole moments higher than the SCF/BBr2 and SCF/BI2. For the mean dipole
31 polarizability the MP2/BCl2, MP2/BBr2 and MP2/BI2 values are $\bar{\alpha} = 110.11$, 138.90
32 and 184.98, respectively. They represent increases of 2.0, 1.8 and 1.2% over the
33 respective SCF values of 107.93 (BCl2), 136.51 (BBr2) and 182.77 (BI2). Thus the
34 correlation effect is rather small for the mean dipole polarizability. For the anisotropy
35 we obtain MP2 values (SCF in parentheses) $\Delta\alpha = 79.38$ (79.09), 82.20 (79.97) and
36 76.53 (71.86) for BCl2, BBr2 and BI2, respectively. This corresponds to an increase
37 of 0.4, 2.8 and 6.5%. For both the mean and the anisotropy, the MP2 electron
38 correlation effect is only a few percent of the SCF value.
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59 The magnitude of the components of the first hyperpolarizability of $H_3C-C\equiv C-$
60 $C\equiv C-H$ increases as $|\beta_{xxx}| < |\beta_{zxx}| < |\beta_{zzz}|$. The latter component is by far the largest of

all. We expect our largest basis sets BT2 to yield $\beta_{\alpha\beta\gamma}$ values sufficiently close the respective Hartree-Fock limit. Our CCSD(T)/BH1 calculations yield a mean hyperpolarizability $\bar{\beta} = -187.0$, or 26.1 larger in magnitude than the respective SCF result $\bar{\beta} = -148.3$. The MP2 electron correlation correction, defined as $D2 = MP2 - SCF$, varies with basis set size as $D2 = -53.3$ (BH1), -52.5 (BH2), -52.2 (BT1) and -52.0 (BT2). Thus the effect is nearly basis-set insensitive. Our MP2 values for $HC\equiv C-C\equiv C-CF_3$ show a very strong effect on the β_{zzz} component. Although the D2 correction is rather small for the β_{xxx} and β_{zxx} components, the MP2/BT2 value of the axial component is $\beta_{zzz} = -9.0$, an impressive reduction of the magnitude of the SCF value $\beta_{zzz} = -61.8$. Consequently, the MP2/BT2 value (SCF value in parenthesis) is $\beta_{zzz} = -55.7$ (-85.2), which represents a reduction by 53.0%.

The mean first hyperpolarizability is positive for the higher members of the sequence $X_3C-C\equiv C-C\equiv C-H$, $X = Cl, Br$ and I . Although the pattern $|\beta_{xxx}| < |\beta_{zxx}| < |\beta_{zzz}|$ is still present, we observe significant changes in the electron correlation effects on the components of the first hyperpolarizability. For $Cl_3C-C\equiv C-C\equiv C-H$ electron correlation affects strongly the β_{xxx} and β_{zxx} components but even more strongly the axial one β_{zzz} . The SCF/BCl2 value $\beta_{zzz} = 29.0$ and the MP2/BCl2 one $\beta_{zzz} = 120.8$ or 317% higher. For $Br_3C-C\equiv C-C\equiv C-H$ the MP2/BBR2 values of the hyperpolarizability components are (SCF values in parentheses) $\beta_{xxx} = 13.7$ (16.2), $\beta_{zxx} = 77.2$ (52.2) and $\beta_{zzz} = 585.4$ (312.9). Consequently, the mean is $\bar{\beta} = 443.8$ (250.4), which corresponds to an increase of the SCF value by an impressive 77.2%. The SCF/BI2 values for $I_3C-C\equiv C-C\equiv C-H$ are $\beta_{xxx} = 103.8$, $\beta_{zxx} = 203.9$ and $\beta_{zzz} = 471.6$. Although electron correlation reduces the magnitude of the β_{xxx} component, it increases significantly the magnitude of the axial component. The MP2/BI2 value of the mean is $\bar{\beta} = 725.4$ that is 37.5% above the SCF/BI2 one of $\bar{\beta} = 527.7$.

Our best SCF values for the components of the second hyperpolarizability of $H_3C-C\equiv C-C\equiv C-H$ were obtained with the BT2 basis set and are $\gamma_{xxxx} = 7934$, $\gamma_{zzzz} = 35476$, $\gamma_{xxzz} = 5119$ and $\gamma_{xxxz} = 107$. The axial component is the most important in magnitude. Electron correlation correction has a large effect on the components of $\gamma_{\alpha\beta\gamma\delta}$. At the CCSD(T)/BH1 level we obtain (SCF values in parentheses) $\gamma_{xxxx} = 6091$ (5502), $\gamma_{zzzz} = 50338$ (35571), $\gamma_{xxzz} = 4822$ (4031) and $\gamma_{xxxz} = 111$ (103). The effect

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3 represents an increase by 10.7, 41.5, 19.6 and 7.8% of the respective SCF values. The
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5 CCSD(T)/BH1 value for the mean is $\bar{\gamma} = 17174$, 29.4% above the SCF/BH1 one of
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7 13273. Compared to the CCSD(T)/values, MP2/BH1 overestimates and MP4/BH1
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9 underestimate the electron correlation correction for $\bar{\gamma}$. The SCF values of the second
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11 hyperpolarizability of $F_3C-C\equiv C-C\equiv C-H$ display the same relative magnitude as in
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13 $H_3C-C\equiv C-C\equiv C-H$ but their size is significantly reduced. The MP2 values show a
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15 positive electron correlation effect. Our best MP2/BF2 value is $\bar{\gamma} = 13469$, 40.9
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17 above the SCF/BF2 one of 9557.

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19 The $\gamma_{\alpha\beta\gamma\delta}$ values for the higher members in the sequence $X_3C-C\equiv C-C\equiv C-H$, X
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21 = Cl, Br, I, show significant enhanced with the substitution Cl→Br→I. Our best
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23 values for the SCF level of theory are $\bar{\gamma} = 20971$ (BC12), 35685 (BBr2) and 65165
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25 (BI2). The respective MP2 values are 32708, 57959 and 105251. The effect is
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27 impressive: 56.0, 61.4 and 61.5% for $Cl_3C-C\equiv C-C\equiv C-H$, $Br_3C-C\equiv C-C\equiv C-H$ and I_3C-
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29 $C\equiv C-C\equiv C-H$. Moreover, the effect is uniform for all components of $\gamma_{\alpha\beta\gamma\delta}$.

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31 In Table 5 we have collected SCF, MP2, B3LYP and B3PW91 values for all
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33 properties. We expect this collection of data to be of some value to workers relying on
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35 DFT methods. The overall agreement between conventional **ab initio** and DFT values
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37 is fair. In some cases, as is the case of higher members $Br_3C-C\equiv C-C\equiv C-H$ and I_3C-
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39 $C\equiv C-C\equiv C-H$, we observe significant divergence in some cases. Such is the case of the
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41 dipole moment of $I_3C-C\equiv C-C\equiv C-H$ where the SCF/BI1 and MP2/BI1 values are
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43 0.5720 and 0.4991, respectively. The B3LYP and B3PW91 are significantly higher at
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45 0.6838 and 0.7061, respectively. More expected is the divergence between **ab initio**
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47 and DFT methods for high-order properties as the second hyperpolarizability. For
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49 $X_3C-C\equiv C-C\equiv C-H$, X = Cl, Br and I, we obtain MP2 values (SCF in parentheses)
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51 32612 (20736), 53973 (33024) and 92082 (54665). The respective B3LYP and
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53 B3PW91 values are 39551 and 37245 (BC11), 61761 and 56985 (BBr1), 102777 and
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55 95346 (BI2). An eloquent picture of the relative performance of the **ab initio** and
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57 DFT methods is shown in Figs, 6 (μ), 7 ($\bar{\alpha}$), 8 ($\Delta\alpha$), 9 ($\bar{\beta}$) and 10 ($\bar{\gamma}$). For most
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59 properties, the case of $F_3C-C\equiv C-C\equiv C-H$ is almost an anomaly. Overall, the most
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important divergence is observed in the case of the dipole polarizability anisotropy.
The magnitude of $\Delta\alpha$ is somewhat exaggerated by DFT methods.

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With the notable exception of a recent paper by Vijayakumar and Kolandaivel⁸⁶ that includes theoretical work on H₃C-C≡C-C≡C-H, we are not aware of previous work on the electric properties of the molecules studied here. Their B3LYP/6-311++G** values for the dipole moment and mean dipole polarizability are $\mu = 0.537$ and $\bar{\alpha} = 60.566$. Our B3LYP/BH1 and B3PW91/BH1 values for the dipole moment are close to theirs. Our mean dipole polarizability values for H₃C-C≡C-C≡C-H, either **ab initio** or DFT, are systematically higher than theirs. The experimentally determined dipole moment, see Bester et al., is $|\mu| = 0.475$. Our CCSD(T)/BH1 value is $\mu = -0.4601$, very close to the measured value.

It is worth noticing that we have not included the estimation of relativistic effects on the electric properties, as this is rather beyond the scope of the present work. In their paper on the electric properties of cyanogen halides Kellöe and Sadlej⁸⁷ found that the relativistic correction for the longitudinal effect is negligible for BrCN and only ~ 1% for ICN.

CONCLUSIONS

We have obtained electric polarizabilities and hyperpolarizabilities for the substituted diacetylenes $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I . Our values have been extracted from finite-field Møller-Plesset perturbation theory and coupled cluster calculations with large, carefully designed gaussian-type basis sets. In addition, we have also calculated the electric properties with the widely used DFT methods, B3LYP and B3PW91. Our best MP2 values for the mean dipole polarizability and second hyperpolarizability are $\bar{\alpha} / e^2 a_0^2 E_h^{-1} = 64.46$ ($-CH_3$), 65.59 ($-CF_3$), 110.11 ($-CCl_3$), 138.90 ($-CBr_3$), 184.98 ($-CI_3$) and $\bar{\gamma} / e^4 a_0^4 E_h^{-3} = 21020$ ($-CH_3$), 13469 ($-CF_3$), 32708 ($-CCl_3$), 57599 ($-CBr_3$), 105251 ($-CI_3$). For comparison the analogous MP2 values for diacetylene (see Ref. 23) are $\bar{\alpha} / e^2 a_0^2 E_h^{-1} = 49.17$ and $\bar{\gamma} / e^4 a_0^4 E_h^{-3} = 16227$.

To our knowledge this is the first systematic theoretical study of the $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I substituted diacetylenes.

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Table 1. SCF values for the electric dipole moment, polarizability and hyperpolarizability of $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I .

Molecule	Basis	μ	α_{xx}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	β_{xxx}	β_{zxx}	β_{zzz}	$\bar{\beta}$	γ_{xxxx}	γ_{zzzz}	γ_{xxzz}	γ_{xxxz}	$\bar{\gamma}$
$H_3C-C\equiv C-C\equiv C-H$	BH1	-0.5191	40.34	113.34	64.68	73.00	4.9	-28.3	-190.7	-148.3	5502	35571	4031	103	13273
	BH2	-0.5203	40.74	113.33	64.94	72.58	4.5	-34.7	-183.9	-151.9	7129	35632	5086	105	14997
	BT1	-0.5161	40.55	113.17	64.75	72.63	5.1	-29.7	-183.6	-145.9	5979	35120	4247	105	13610
	BT2	-0.5182	40.78	113.43	64.99	72.66	4.4	-35.3	-185.7	-153.8	7934	35476	5119	107	15422
$F_3C-C\equiv C-C\equiv C-H$	BF1	1.2926	41.43	110.30	64.39	68.87	-6.0	-39.0	-60.9	-83.3	4314	23629	2861	3	9315
	BF2	1.2955	41.53	110.51	64.52	68.98	-6.3	-40.1	-61.8	-85.2	4439	23796	3038	60	9557
$Cl_3C-C\equiv C-C\equiv C-H$	BC11	0.8252	81.21	160.20	107.54	78.99	-8.2	-22.8	93.8	28.9	9322	56212	5652	302	20736
	BC12	0.8159	81.57	160.66	107.93	79.09	-10.5	-23.0	94.2	29.0	9482	56241	5832	261	20971
$Br_3C-C\equiv C-C\equiv C-H$	BBr1	0.8179	109.13	188.58	135.61	79.45	27.5	51.3	286.8	233.6	16575	84066	9214	802	33024
	BBr2	0.7854	109.85	189.82	136.51	79.97	16.2	52.2	312.9	250.4	19158	85839	10374	579	35685
$I_3C-C\equiv C-C\equiv C-H$	BI1	0.5720	157.37	228.37	181.04	71.00	114.2	207.1	401.9	489.7	32202	119680	16943	2362	54665
	BI2	0.5268	158.82	230.68	182.77	71.86	103.8	203.9	471.6	527.7	43653	125142	21069	1920	65165

Table 2. Electron correlation effects on the SCF values of the dipole moment and polarizability of $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I .

Molecule	Basis	Method	μ	α_{xx}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
H₃C-C≡C-C≡C-H	BH1	SCF	-0.5191	40.34	113.34	64.68	73.00
		MP2	-0.4657	40.16	111.59	63.97	71.43
		MP4	-0.4718	40.30	114.11	64.90	73.81
		CCSD	-0.4502	39.77	108.55	62.70	68.78
		CCSD(T)	-0.4601	40.17	111.33	63.89	71.16
	BH2	SCF	-0.5203	40.74	113.33	64.94	72.58
		MP2	-0.4667	40.59	111.59	64.26	70.99
	BT1	SCF	-0.5161	40.55	113.17	64.75	72.63
		MP2	-0.4599	40.31	110.98	63.87	70.67
	BT2	SCF	-0.5182	40.78	113.43	64.99	72.66
MP2		-0.4679	40.81	111.77	64.46	70.96	
F₃C-C≡C-C≡C-H	BF1	SCF	1.2926	41.43	110.30	64.39	68.87
		MP2	1.1503	42.67	111.21	65.52	68.53
	BF2	SCF	1.2955	41.53	110.51	64.52	68.98
		MP2	1.1526	42.63	111.51	65.59	68.88
Cl₃C-C≡C-C≡C-H	BC11	SCF	0.8252	81.21	160.20	107.54	78.99
		MP2	0.8253	83.41	162.43	109.75	79.02
	BC12	SCF	0.8159	81.57	160.66	107.93	79.09
		MP2	0.8031	83.65	163.03	110.11	79.38
Br₃C-C≡C-C≡C-H	BBr1	SCF	0.8179	109.13	188.58	135.61	79.45
		MP2	0.7302	112.33	193.46	139.38	81.13
	BBr2	SCF	0.7854	109.85	189.82	136.51	79.97
		MP2	0.7924	111.50	193.69	138.90	82.20
I₃C-C≡C-C≡C-H	BI1	SCF	0.5720	157.37	228.37	181.04	71.00
		MP2	0.4991	159.20	234.84	184.41	75.64
	BI2	SCF	0.5268	158.82	230.68	182.77	71.86
		MP2	0.5825	159.47	236.00	184.98	76.53

Table 3. Electron correlation effects on the SCF values of the first hyperpolarizability of $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I .

Molecule	Basis	Method	β_{xxx}	β_{zxx}	β_{zzz}	$\bar{\beta}$
$H_3C-C\equiv C-C\equiv C-H$	BH1	SCF	4.9	-28.3	-190.7	-148.3
		MP2	4.6	-32.5	-270.9	-201.6
		MP4	4.7	-26.6	-237.7	-174.6
		CCSD	4.6	-26.6	-240.3	-176.2
		CCSD(T)	4.5	-29.6	-252.4	-187.0
	BH2	SCF	4.5	-34.7	-183.9	-151.9
		MP2	4.1	-39.2	-262.3	-204.4
	BT1	SCF	5.1	-29.7	-183.6	-145.9
		MP2	5.0	-33.0	-264.2	-198.1
	BT2	SCF	4.4	-35.3	-185.7	-153.8
MP2		3.3	-40.0	-263.1	-205.8	
$F_3C-C\equiv C-C\equiv C-H$	BF1	SCF	-6.0	-39.0	-60.9	-83.3
		MP2	-5.9	-41.3	-9.8	-55.4
	BF2	SCF	-6.3	-40.1	-61.8	-85.2
		MP2	-6.5	-41.9	-9.0	-55.7
$Cl_3C-C\equiv C-C\equiv C-H$	BCI1	SCF	-8.2	-22.8	93.8	28.9
		MP2	-5.0	-15.4	231.7	120.5
	BCI2	SCF	-10.5	-23.0	94.2	29.0
		MP2	-7.7	-14.3	229.8	120.8
$Br_3C-C\equiv C-C\equiv C-H$	BBr1	SCF	27.5	51.3	286.8	233.6
		MP2	43.0	87.5	527.1	421.2
	BBr2	SCF	16.2	52.2	312.9	250.4
		MP2	13.7	77.2	585.4	443.8
$I_3C-C\equiv C-C\equiv C-H$	BI1	SCF	114.2	207.1	401.9	489.7
		MP2	85.3	232.3	654.1	671.3
	BI2	SCF	103.8	203.9	471.6	527.7
		MP2	42.6	211.8	785.4	725.4

Table 4. Electron correlation effects on the SCF values of the second hyperpolarizability of $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I .

Molecule	Basis	Method	γ_{xxxx}	γ_{zzzz}	γ_{xxzz}	γ_{zzxz}	$\bar{\gamma}$
$H_3C-C\equiv C-C\equiv C-H$	BH1	SCF	5502	35571	4031	103	13273
		MP2	6232	54161	5170	121	18292
		MP4	5607	44872	4341	115	15438
		CCSD	5689	46054	4405	113	15769
		CCSD(T)	6091	50338	4822	111	17174
	BH2	SCF	7129	35632	5086	105	14997
		MP2	8141	54273	6511	132	20405
	BT1	SCF	5979	35120	4247	105	13610
		MP2	6742	53838	5407	129	18689
	BT2	SCF	7934	35476	5119	107	15422
		MP2	9172	54199	6610	131	21020
	$F_3C-C\equiv C-C\equiv C-H$	BF1	SCF	4314	23629	2861	3
MP2			4919	38767	3702	33	13338
BF2		SCF	4439	23796	3038	60	9557
		MP2	5019	38616	3836	113	13469
$Cl_3C-C\equiv C-C\equiv C-H$	BC11	SCF	9322	56212	5652	302	20736
		MP2	13296	94623	8245	654	32612
	BC12	SCF	9482	56241	5832	261	20971
		MP2	13430	94079	8412	567	32708
$Br_3C-C\equiv C-C\equiv C-H$	BBr1	SCF	16575	84066	9214	802	33024
		MP2	26522	142040	14275	2124	53973
	BBr2	SCF	19158	85839	10374	579	35685
		MP2	30099	144162	15892	1560	57599
$I_3C-C\equiv C-C\equiv C-H$	BI1	SCF	32202	119680	16943	2362	54665
		MP2	56542	201580	27013	5569	92082
	BI2	SCF	43653	125142	21069	1920	65165
		MP2	69638	211056	32375	5144	105251

Table 5. SCF, MP2, B3LYP and B3PW91 values for the electric dipole moment, polarizability and hyperpolarizability of $X_3C-C\equiv C-C\equiv C-H$, $X = H, F, Cl, Br$ and I .

Molecule	Basis	Method	μ	α_{xx}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	β_{xxx}	β_{zxx}	β_{zzz}	$\bar{\beta}$	γ_{xxxx}	γ_{zzzz}	γ_{xxzz}	γ_{xxxz}	$\bar{\gamma}$
$H_3C-C\equiv C-C\equiv C-H$	BH1	SCF	-0.5191	40.34	113.34	64.68	73.00	4.9	-28.3	-190.7	-148.3	5502	35571	4031	103	13273
		MP2	-0.4657	40.16	111.59	63.97	71.43	4.6	-32.5	-270.9	-201.6	6232	54161	5170	121	18292
		B3LYP	-0.5602	40.78	124.03	68.53	83.24	27.8	-36.6	-267.7	-204.5	6990	59633	6514	559	20864
		B3PW91	-0.5651	40.27	123.14	67.90	82.87	22.8	-33.7	-261.0	-197.1	6580	55499	5982	511	19396
$F_3C-C\equiv C-C\equiv C-H$	BF1	SCF	1.2926	41.43	110.30	64.39	68.87	-6.0	-39.0	-60.9	-83.3	4314	23629	2861	3	9315
		MP2	1.1503	42.67	111.21	65.52	68.53	-5.9	-41.3	-9.8	-55.4	4919	38767	3702	33	13338
		B3LYP	1.2012	43.30	123.22	69.94	79.93	-16.7	-50.7	-96.5	-118.7	5732	40412	4724	173	14924
		B3PW91	1.1802	42.80	122.42	69.34	79.62	-16.4	-51.1	-93.6	-117.5	5458	38165	4335	37	14012
$Cl_3C-C\equiv C-C\equiv C-H$	BCl1	SCF	0.8252	81.21	160.20	107.54	78.99	-8.2	-22.8	93.8	28.9	9322	56212	5652	302	20736
		MP2	0.8253	83.41	162.43	109.75	79.02	-5.0	-15.4	231.7	120.5	13296	94623	8245	654	32612
		B3LYP	0.8155	85.52	181.51	117.52	95.99	14.1	-28.7	203.2	87.5	16004	111896	11295	1406	39951
		B3PW91	0.8303	84.57	180.40	116.51	95.83	-25.8	-31.4	198.7	81.5	14776	105471	10337	1209	37245
$Br_3C-C\equiv C-C\equiv C-H$	BBr1	SCF	0.8179	109.13	188.58	135.61	79.45	27.5	51.3	286.8	233.6	16575	84066	9214	802	33024
		MP2	0.7302	112.33	193.46	139.38	81.13	43.0	87.5	527.1	421.2	26522	142040	14275	2124	53973
		B3LYP	0.8644	113.49	214.71	147.23	101.22	41.9	59.9	512.9	379.5	31564	148827	18952	3631	61761
		B3PW91	0.8768	112.20	213.21	145.87	101.01	47.4	50.0	489.0	353.4	28492	139440	17376	3012	56985
$I_3C-C\equiv C-C\equiv C-H$	BI1	SCF	0.5720	157.37	228.37	181.04	71.00	114.2	207.1	401.9	489.7	32202	119680	16943	2362	54665
		MP2	0.4991	159.20	234.84	184.41	75.64	85.3	232.3	654.1	671.3	56542	201580	27013	5569	92082
		B3LYP	0.6838	161.39	258.71	193.83	97.32	171.3	218.4	696.2	679.8	66526	198120	34590	8563	102777
		B3PW91	0.7061	159.81	256.73	192.12	96.92	209.0	205.7	689.7	660.7	60912	186239	32015	6029	95346

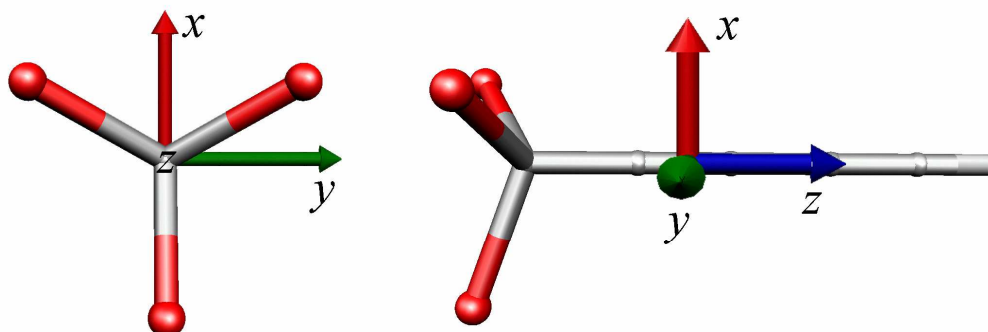


Figure 1. Orientation of the $X_3C-C\equiv C-C\equiv C-H$ molecules adopted in the definition of the electric property tensor components

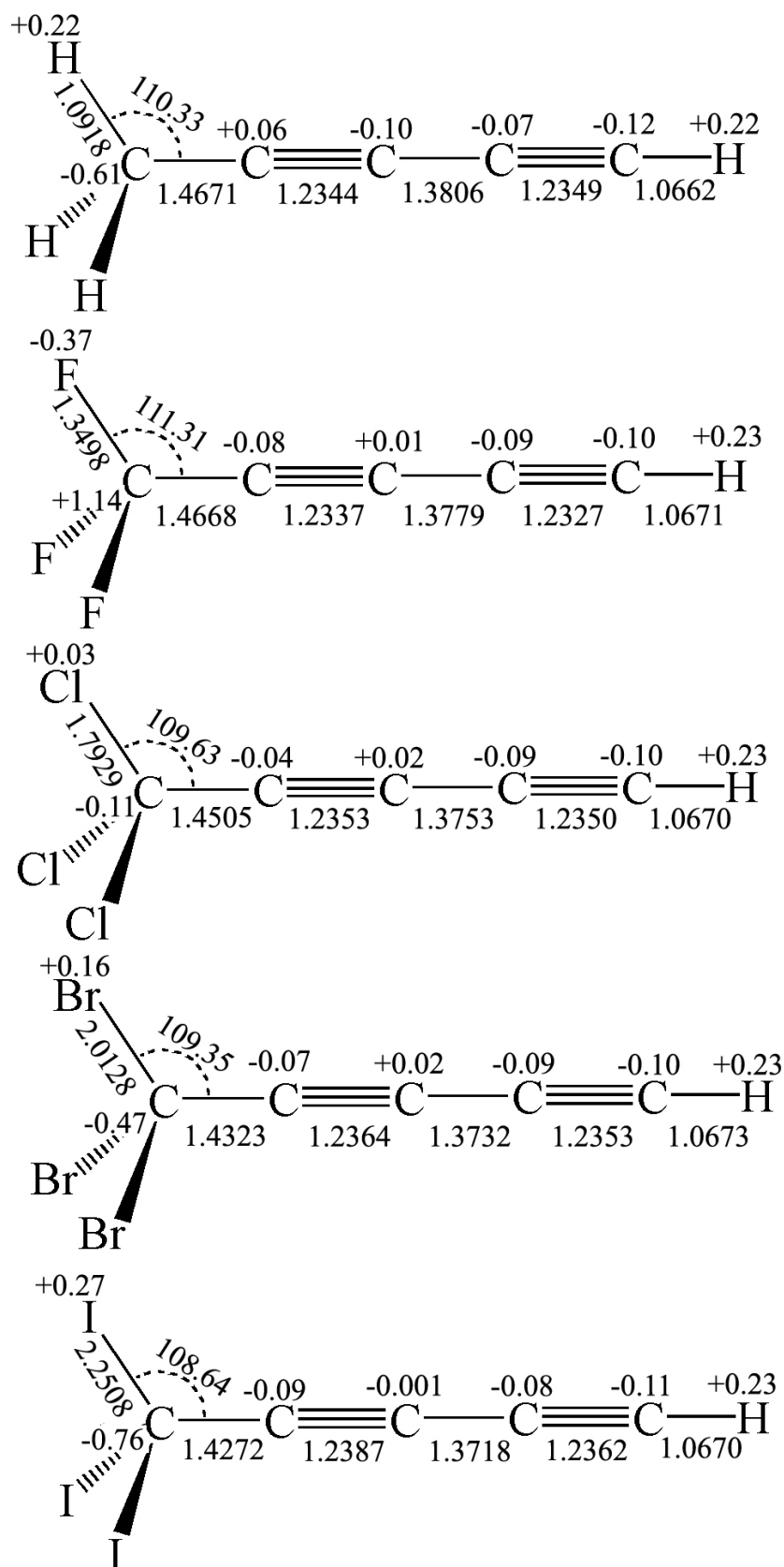


Figure 2. Full specification of the molecular geometry of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I . All quantities in (Å, deg). NBO atomic charges are also shown. See text for details.

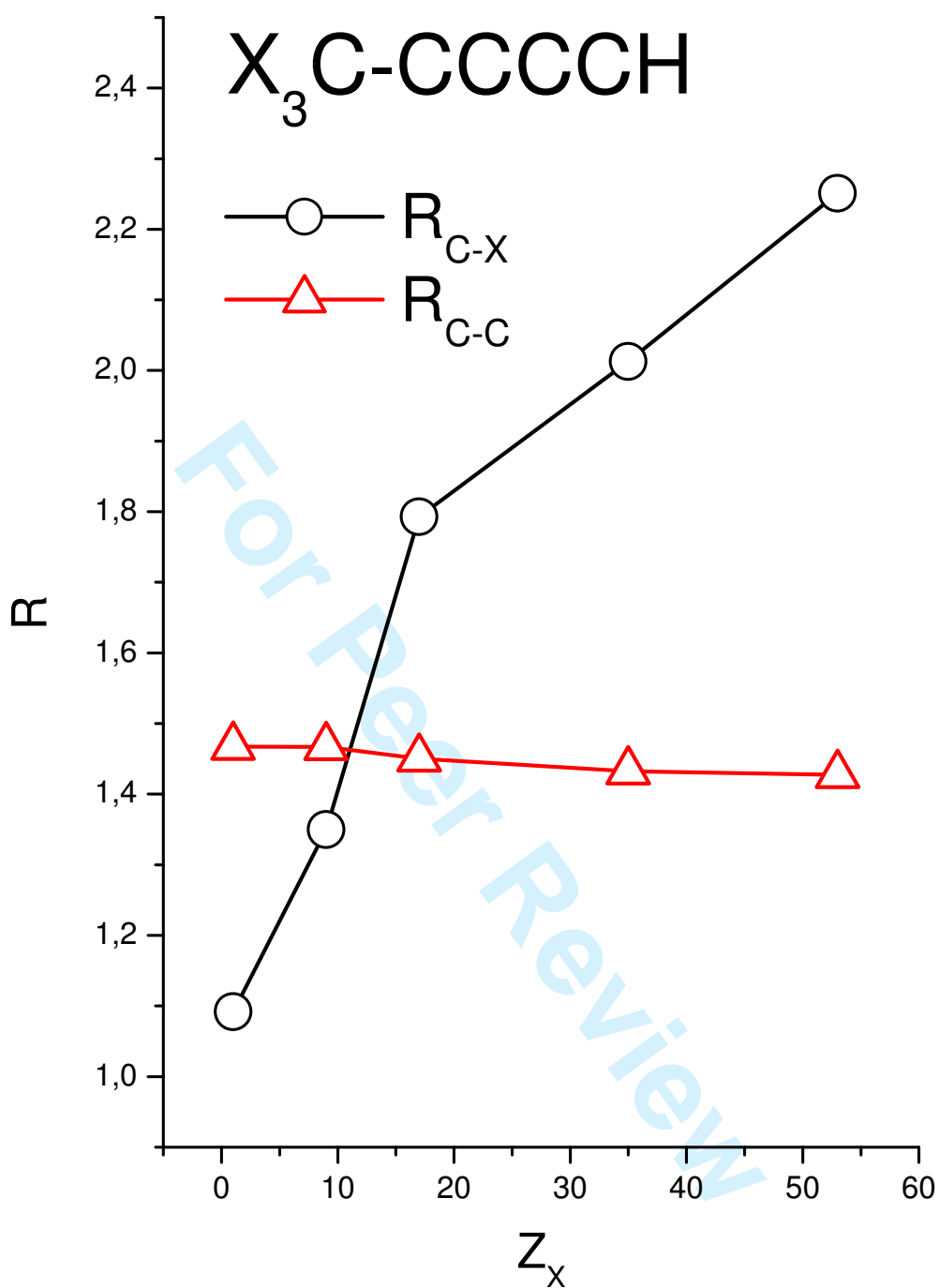


Figure 3. Evolution of the bond lengths (in Å) with the nuclear charge Z_X in the X_3C-C subunit of $X_3C-C\equiv C-C\equiv C-H$.

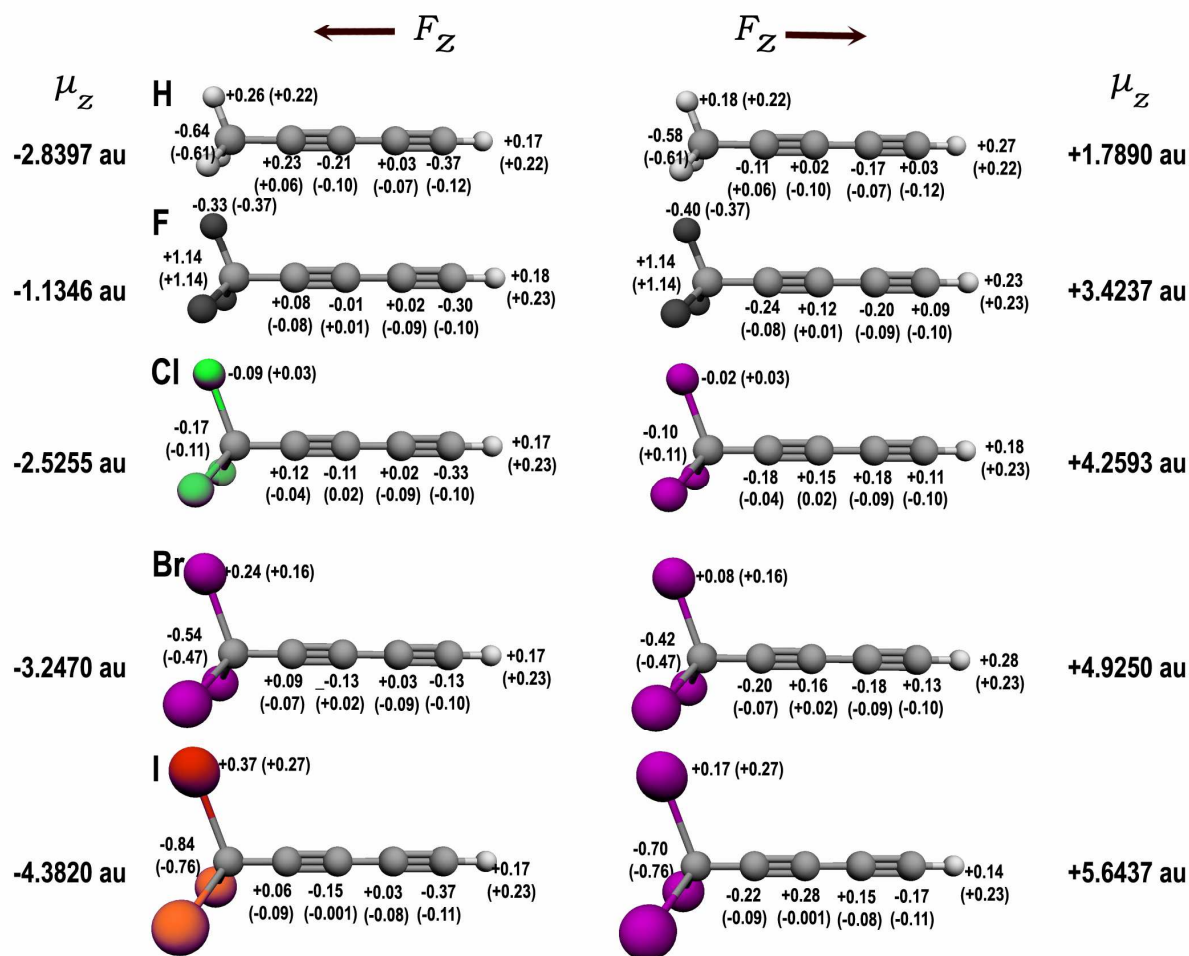


Figure 4. Field-induced polarization in $X_3C-C\equiv C-C\equiv C-H$. NBO atomic charges and dipole moments in the presence of a static homogeneous electric field of $0.02 e^{-1}a_0^{-1}E_h$ along the dipole moment axis (C_3). Atomic charges of the free molecules at the same level of theory in parentheses.

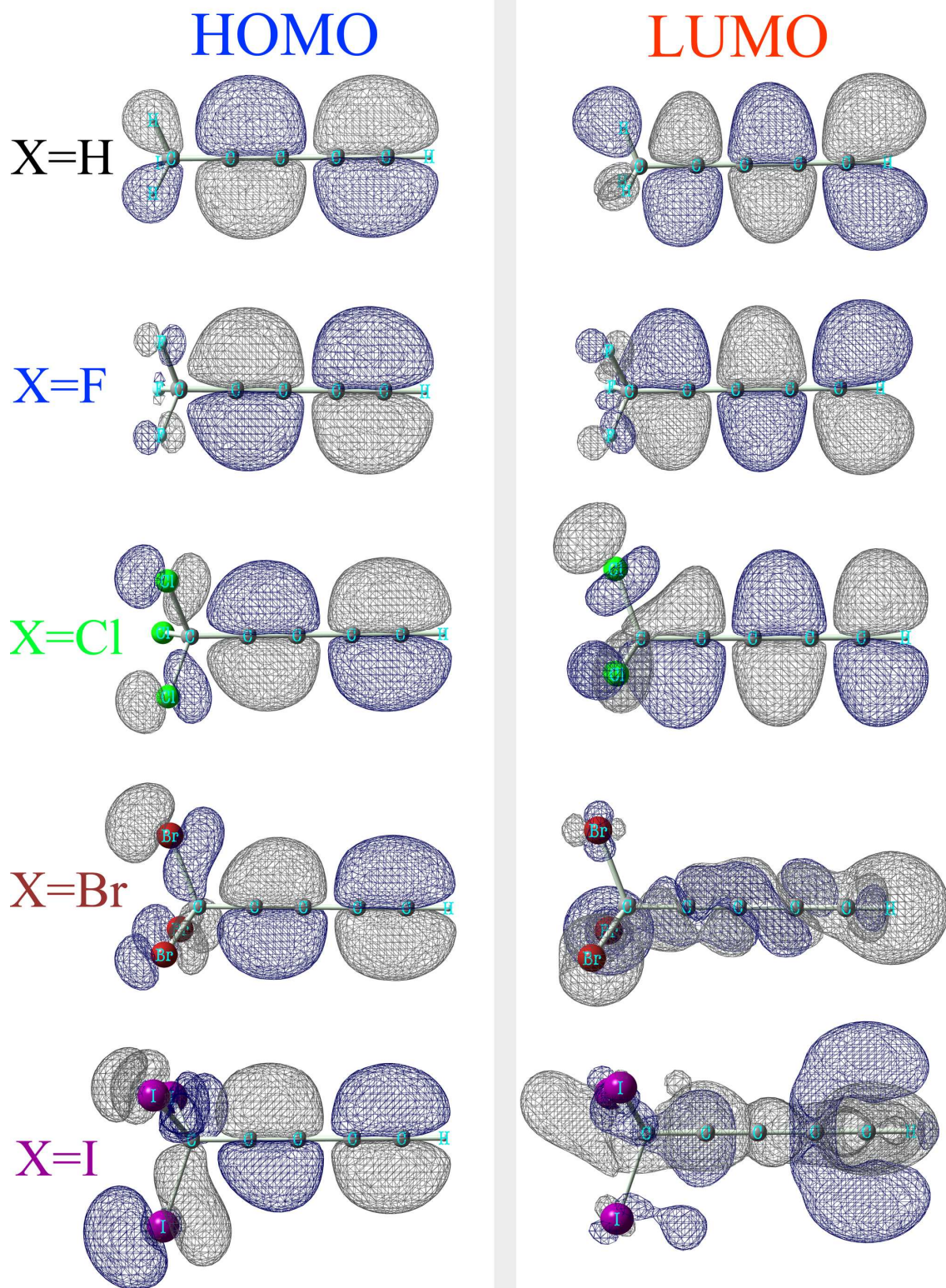


Figure 5. HOMO and LUMO representation of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .

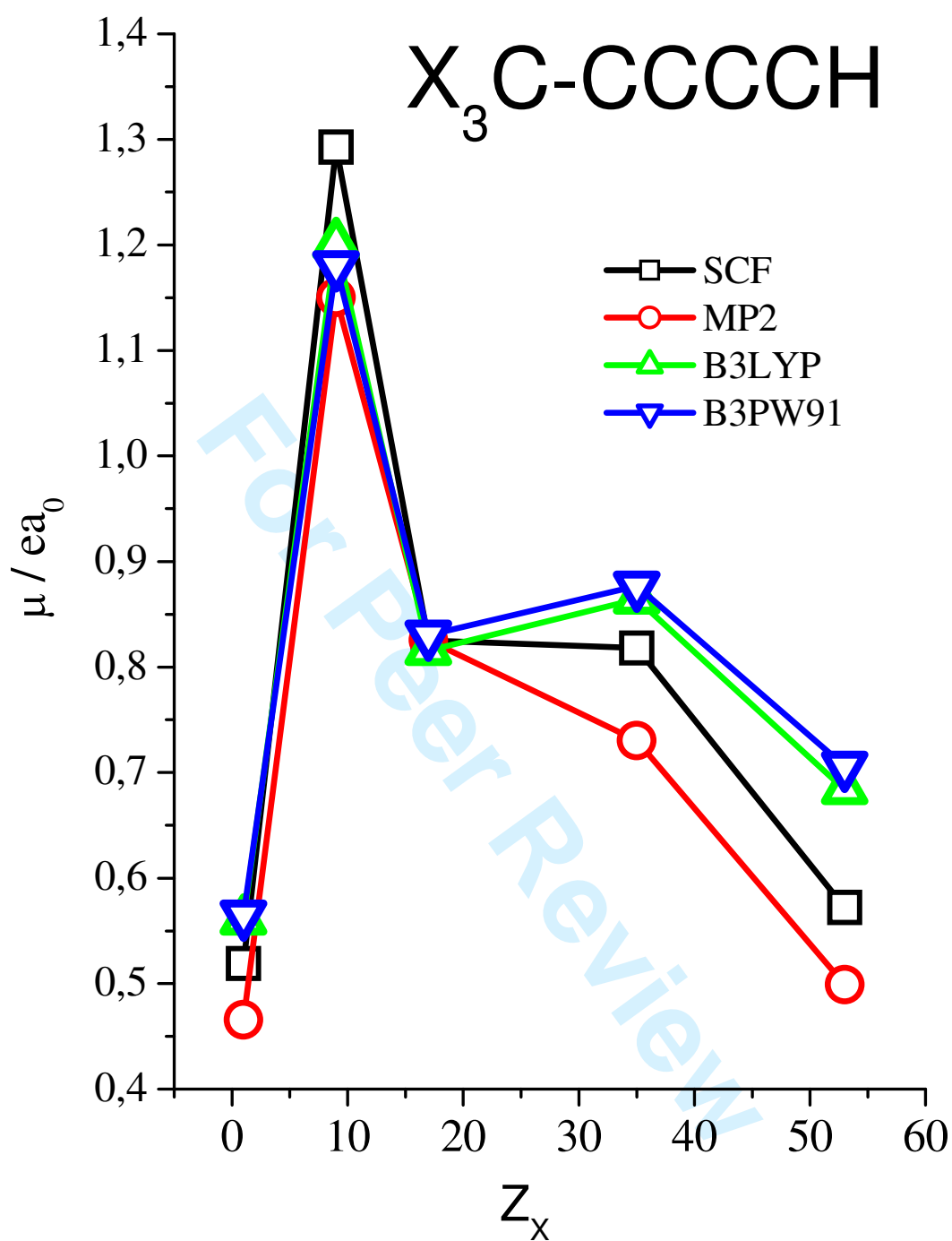


Figure 6. Method dependence of the dipole moment (μ) of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .

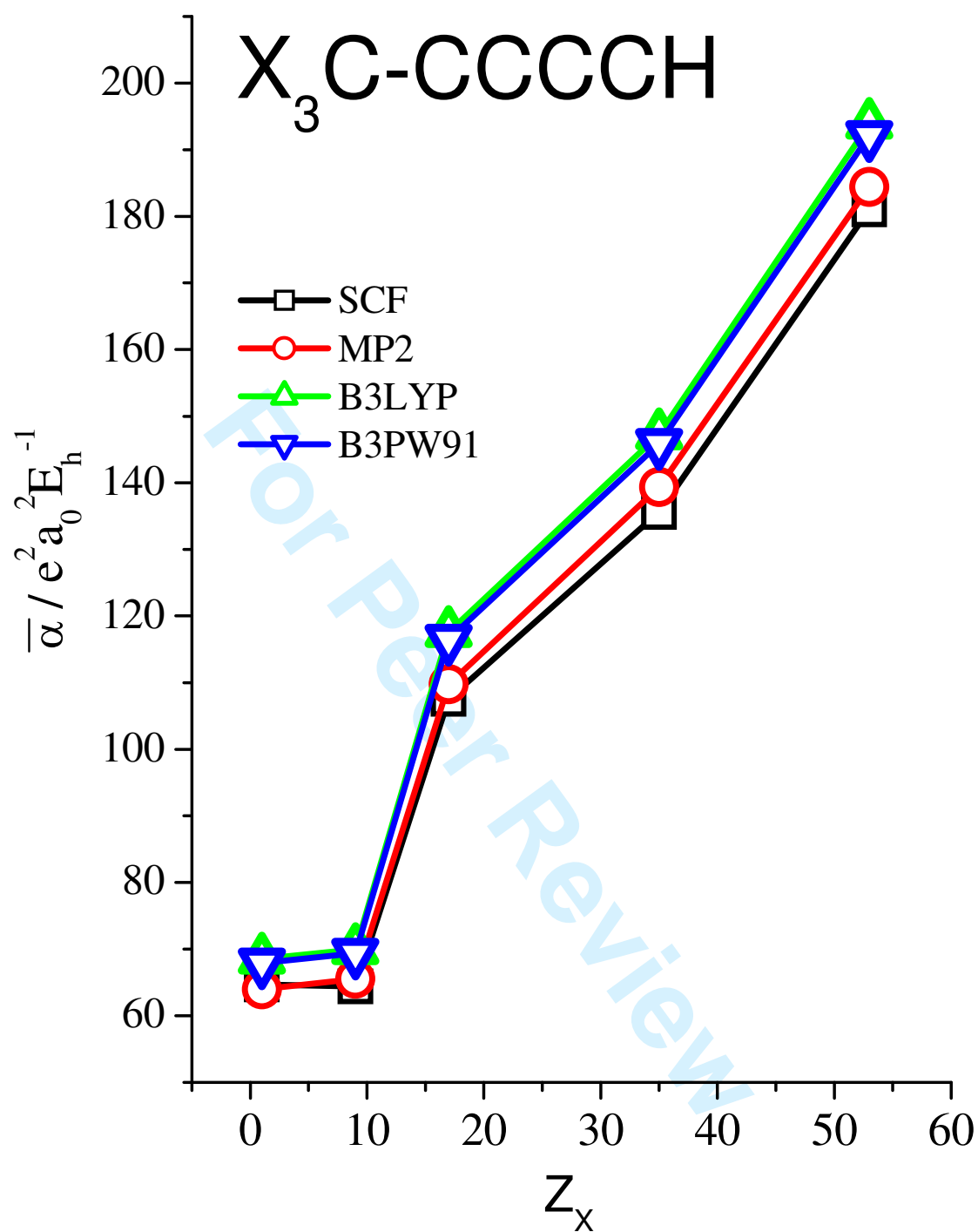


Figure 7. Method dependence of the mean dipole polarizability ($\bar{\alpha}$) of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .

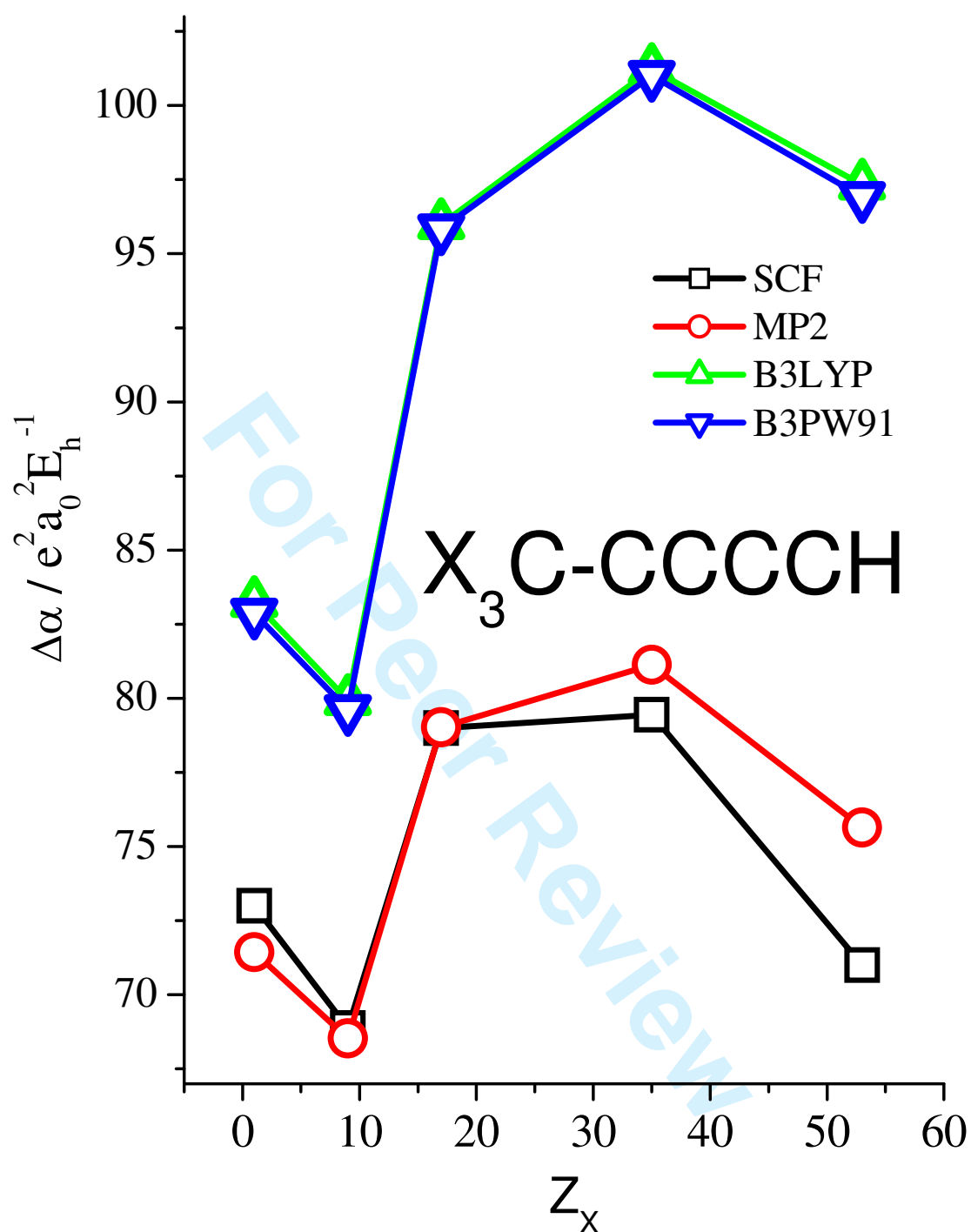


Figure 8. Method dependence of the dipole polarizability anisotropy ($\Delta\alpha$) of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .

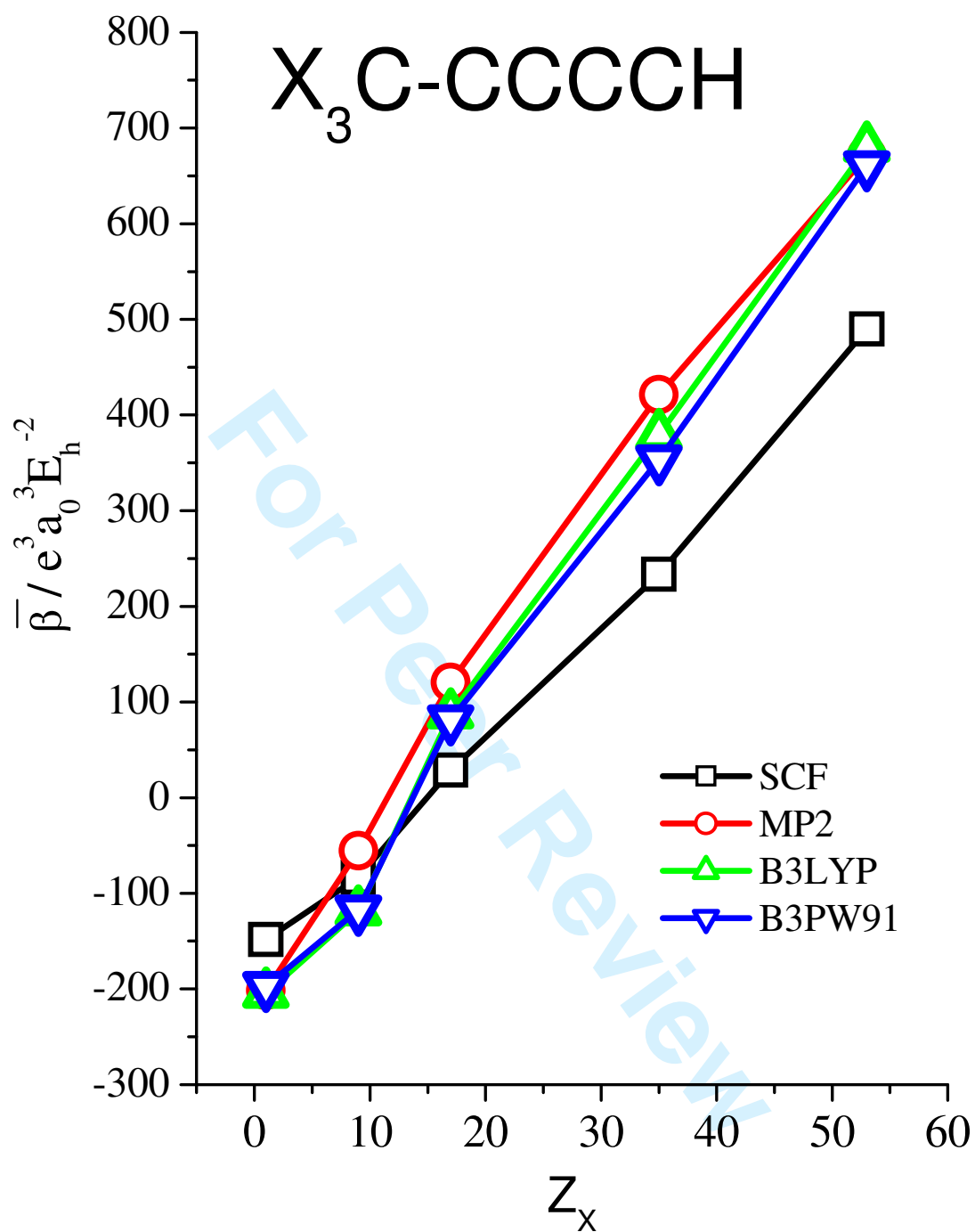


Figure 9. Method dependence of the mean first hyperpolarizability ($\bar{\beta}$) of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .

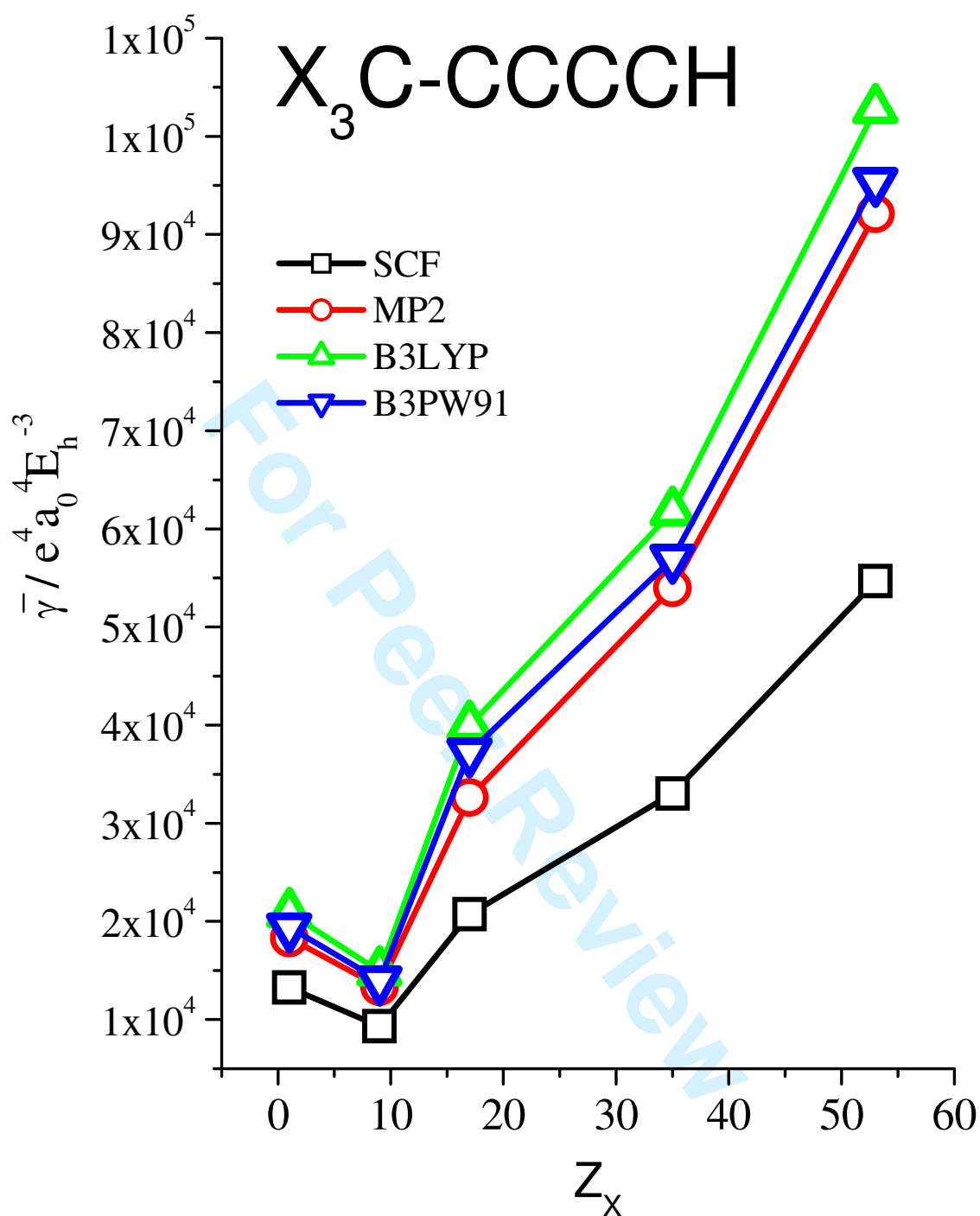


Figure 10. Method dependence of the mean second hyperpolarizability ($\bar{\gamma}$) of $X_3C-C\equiv C-C\equiv C-H$, $X=H, F, Cl, Br$ and I .