

Electric Multipole Moments and (Hyper)Polarizability of $X-C\equiv C-X$, $X = F, Cl, Br$ and I

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Abstract: We have calculated self-consistent field (SCF) and second-order Møller-Plesset perturbation theory (MP2) for the dihaloethynes $X-C\equiv C-X$, $X = F, Cl, Br$ and I . All calculations have been performed with carefully optimized, flexible basis sets of gaussian-type functions. Our best values for the quadrupole moment (Θ/ea_0^2) are -0.6524 (FCCF), 3.6612 (ClCCCl), 5.8143 (BrCCBr) and 8.3774 (ICCI). The dipole polarizability is strongly anisotropic. For the mean ($\bar{\alpha}/e^2a_0^2E_h^{-1}$) and the anisotropy ($\Delta\alpha/e^2a_0^2E_h^{-1}$) we obtain 23.58 and 15.09 (FCCF), 51.75 and 48.30 (ClCCCl), 66.53 and 60.04 (BrCCBr), 93.79 and 78.91 (ICCI). The mean dipole hyperpolarizability ($\bar{\gamma}/e^4a_0^4E_h^{-3}$) increases rapidly as 2932 (FCCF), 9924 (ClCCCl), 17409 (BrCCBr) and 35193 (ICCI). The transversal component of the hyperpolarizability is larger than the longitudinal one for FCCF, $\gamma_{xxxx} > \gamma_{zzzz}$ but this is reversed for the other molecules in the series. Difluoroethyne is less (hyper)polarizable than ethyne.

Keywords: Dihaloeethynes, polarizability, hyperpolarizability, multipole moments.

1. Introduction

The dihaloethynes $X-C\equiv C-X$ ($X = F, Cl, Br$ and I) represent a multiply interesting class of molecules. Difluoroethyne and dichloroethyne [1,2], dibromoethyne [3] and diiodoethyne [4] are of interest to polymer science. Dichloroethyne is a very toxic molecule [5] and its determination in environmental atmospheres containing halogenated hydrocarbons is an important problem [6]. The structure and chemical bonding of dichloroethyne, dibromoethyne and diiodoethyne complexes has attracted some attention [7-9]. Although in the past decade numerous experimental and spectroscopic

studies have focused on the determination of the structure and spectroscopic properties of dihaloethynes [10-20], very little is known about their electric properties. The development of the theory of electric multipole moments and polarizabilities [21,22] has made a decisive contribution to our understanding of fundamental phenomena in many areas of importance to molecular science [23]. Specific directions include the rigorous modeling of intermolecular interactions [24], nonlinear optics [25], collision- and interaction-induced spectroscopy [26] and the simulation of fluids [27]. The systematic use of electric polarizabilities in modeling the pharmacological activity of molecular substances [28] and in quantitative structure-activity relationship (QSAR) studies [29] has also been noted.

In this paper we report a systematic study of the electric properties of the dihalogenated ethynes. The calculation of the properties relies on the finite-field method [30]. Our approach has been presented in some detail in previous work [31-34]. We put emphasis on the design of large, flexible basis sets of gaussian-type functions. The determination of reference, near-Hartree-Fock results or the stability of post-Hartree-Fock values depends strongly on the quality of the basis sets employed in the calculations [35,36].

2. Theory

The energy of uncharged molecule in a weak, static electric field can be written as [37,38]

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

In eq (1), F_α , $F_{\alpha\beta}$, etc are the field, field gradient, etc at the origin. E^0 , μ_α^0 , $\Theta_{\alpha\beta}^0$, $\Omega_{\alpha\beta\gamma}^0$ and $\Phi_{\alpha\beta\gamma\delta}^0$ are the energy and the dipole, quadrupole, octopole and hexadecapole moment of the free molecule. The higher terms are the second, third and fourth-order properties, the dipole polarizability ($\alpha_{\alpha\beta}$), the first ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability, the dipole-quadrupole polarizability ($A_{\alpha,\beta\gamma}$), the quadrupole polarizability ($C_{\alpha\beta,\gamma\delta}$), the dipole-octopole polarizability ($E_{\alpha,\beta\gamma\delta}$) 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. The number of independent components needed to describe the electric multipole moment or polarizability tensors depends on the molecular symmetry [37]. The properties of interest in this work are the multipole moments and the static dipole

(hyper)polarizability. For linear non-polar molecules, as the dihalogenated ethynes, $\mu_\alpha^0 = \Omega_{\alpha\beta\gamma}^0 = 0$, while there is only one independent component for either the quadrupole or the hexadecapole moment [37]. With z as the molecular axis we adopt Θ_{zz}^0 and Φ_{zzzz}^0 as the independent components. Simplifying notation we denote them as $\Theta \equiv \Theta_{zz}^0$ and $\Phi \equiv \Phi_{zzzz}^0$. For the (hyper)polarizability there are two independent components for $\alpha_{\alpha\beta}$ and three for $\gamma_{\alpha\beta\gamma\delta}$ [37]. We specify $\alpha_{\alpha\beta}$ by α_{zz} and α_{xx} and $\gamma_{\alpha\beta\gamma\delta}$ by γ_{zzzz} , γ_{xxzz} and γ_{xxxx} . In addition to the Cartesian components we also calculate mean values and anisotropies for the (hyper)polarizability defined as [37]

$$\begin{aligned}\bar{\alpha} &= (\alpha_{zz} + 2\alpha_{xx})/3 \\ \Delta\alpha &= \alpha_{zz} - \alpha_{xx} \\ \bar{\gamma} &= (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15 \\ \Delta_1\gamma &= 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz} \\ \Delta_2\gamma &= \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}\end{aligned}\tag{2}$$

The expansion of eq (1) displays fast convergence for very weak electric fields. We extract the dipole (hyper)polarizability values from the energy of the molecule perturbed by weak, static homogeneous fields [32]. Our approach allows a uniform treatment of Hartree-Fock and post-Hartree-Fock levels of theory. Electron correlation effects are taken into account by second-order Møller-Plesset perturbation theory (MP2). A complete presentation of this method can be found in standard textbooks [39,40] or review papers [41].

All values of the quadrupole and hexadecapole moment are calculated from the induced multipole moments. Thus, the MP2 values of Θ and Φ are obtained through the MP2 density [42].

3. Computational details

All basis sets used in this work were especially designed for the dihaloethynes. This ensures the calculation of reference values for the electric properties. Details on the computational philosophy that underlines the construction of these basis sets may be found in previous work [32].

For FCCF we used a large (12s7p)[7s4p] [43] substrate for both F and C. This substrate was augmented to [8s5p] by the addition of diffuse s- and p-GTF. Further addition of a relatively tight d-GTF (exponent chosen to minimize the energy of the free molecule) and a diffuse d-GTF (exponent chosen to maximize the mean dipole polarizability) gave basis set F0 \equiv [8s5p2d/8s5p2d] (132 CGTF), the first basis set used on FCCF. Larger basis sets are required for the calculation of the hyperpolarizability, so a larger basis set was obtained with the addition of more d-GTF and two f-GTF. This final basis set is F1 \equiv [8s5p4d2f/8s5p4d2f] and consists of 220 CGTF.

For ClCCCl we use a substrate of similar quality, (12s9p)[6s5p] for Cl [44] and (12s7p)[7s4p] for C [43]. Two basis sets were obtained for dichloroethyne, C0 \equiv [7s6p2d/8s5p2d] (136 CGTF) and C1 \equiv [7s6p5d2f/8s5p4d2f] (230 CGTF).

For BrCCBr we relied on a (17s13p6d)[6s5p2d] substrate for Br [45] and (9s5p)[4s2p] for C [46]. Only a diffuse d-GTF was optimized on Br. The two basis sets obtained for dibromoethyne are B0 \equiv [7s6p3d/5s3p2d] (128 CGTF) and B1 \equiv [7s6p5d2f/5s3p3d1f] (198 CGTF).

Finally, for ICCI we used a (13s10p6d)[5s4p2d] substrate for I [47] and (11s6p)[5s3p] for C [45]. As in the case of bromoethyne, only a diffuse d-GTF was optimized on I. The resulting basis sets are I0 \equiv [6s5p3d/6s4p2d] (128 CGTF) and I1 \equiv [6s5p5d3f/6s4p3d1f] (214 CGTF).

5D and 7F GTF were used for all basis sets.

The following molecular geometries were used in the calculations (bond lengths in Å): for FCCF, $R_{CC}=1.1860$ and $R_{CF}=1.2835$ [16], for ClCCCl, $R_{CC}=1.195$ and $R_{CCl}=1.64$ [48], for BrCCBr, $R_{CC}=1.20$ and $R_{CBr}=1.80$ [48] and for ICCI, $R_{CC}=1.18$ and $R_{CI}=2.03$ [48].

All calculations were performed with GAUSSIAN 92 [49], GAUSSIAN 94 [50] and GAUSSIAN 98 [51].

Unless otherwise indicated, atomic units are used throughout this paper. Conversion factors to SI units are: energy, $1 E_h = 4.3597482 \times 10^{-18}$ J, length, $1 a_0 = 0.529177249 \times 10^{-10}$ m, Θ , $1 ea_0^2 = 4.486554 \times 10^{-40}$ Cm², Φ , $1 ea_0^4 = 1.256363 \times 10^{-60}$ Cm⁴, α , $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41}$ C²m²J⁻¹ and γ , $1 e^4 a_0^4 E_h^{-3} = 6.235378 \times 10^{-65}$ C⁴m⁴J⁻³.

4. Results and discussion

The calculated values for the four dihaloethynes are given in Tables 1(FCCF), 2(ClCCCl), 3(BrCCBr) and 4(ICCI).

Quadrupole and hexadecapole moment. The magnitude of Θ/ea_0^2 and Φ/ea_0^4 increases monotonically from FCCF to ICCI. Both property values are negative for FCCF. Our best SCF values for the quadrupole moment, calculated with basis sets F1, C1, B1 and I1, are $\Theta/ea_0^2 = -0.9085$ (FCCF), 3.9140 (ClCCCl), 6.1017 (BrCCBr) and 8.7027 (ICCI). For the hexadecapole moment we obtain $\Phi/ea_0^4 = -37.87$, 285.21, 495.65 and 893.74, respectively. We expect both sets of values to be reasonably close to the Hartree-Fock limit.

For all calculations performed with the large basis sets, electron correlation reduces the magnitude of the electric moments for all dihaloethynes. This is not the case with the small basis sets where the opposite effect is observed for the hexadecapole moment of BrCCBr and both moments of ICCI. It is rather obvious that one needs basis sets rich enough in d- and f-GTF to obtain very reliable theoretical predictions for the electric moments. Nevertheless, our MP2 values calculated with the F1, C1, B1 and I1 basis sets should be expected to give a fair picture of the change of Θ and Φ in the sequence XCCX, X = F, Cl, Br, I.

Table 1. Electric properties of FCCF^a.

Property	[8s5p2d/8s5p2d]		[8s5p4d2f/8s5p4d2f]	
	SCF	MP2	SCF	MP2
Θ	-0.9421	-0.6827	-0.9085	-0.6524
Φ	-38.03	-22.59	-37.87	-22.33
α_{zz}	31.68	33.62	31.70	33.64
α_{xx}	18.08	18.39	18.25	18.55
α	22.62	23.47	22.73	23.58
$\Delta\alpha$	13.60	15.24	13.45	15.09
γ_{zzzz}	792	1490	502	1200
γ_{xxxx}	2606	2855	3659	3908
γ_{xxzz}	586	700	644	759
γ	2017	2381	2567	2932
$\Delta_1\gamma$	-6292	-4848	-11200	-9756
$\Delta_2\gamma$	-117	144	295	555

^a The four innermost MO were kept frozen in all post-Hartree-Fock calculations.

Table 2. Electric properties of ClCCCl^a.

Property	[8s5p2d/7s6p2d]		[8s5p4d2f/7s6p5d2f]	
	SCF	MP2	SCF	MP2
Θ	3.8753	3.6056	3.9140	3.6612
Φ	288.07	270.59	285.21	266.25
α_{zz}	80.22	82.60	81.40	83.96
α_{xx}	34.01	34.92	34.55	35.65
α	49.41	50.81	50.17	51.75
$\Delta\alpha$	46.20	47.68	46.84	48.30
γ_{zzzz}	11469	17701	12147	19780
γ_{xxxx}	2848	3562	4415	5690
γ_{xxzz}	1712	2325	2667	3666
γ	5182	7300	6917	9924
$\Delta_1\gamma$	28153	45829	26783	47581
$\Delta_2\gamma$	4042	7312	560	3473

^a The twelve innermost MO were kept frozen in all post-Hartree-Fock calculations.

Table 3. Electric properties of BrCCBr^a.

Property	[5s3p2d/7s6p3d]		[5s3p3d1f/7s6p5d2f]	
	SCF	MP2	SCF	MP2
Θ	6.0970	5.9394	6.1017	5.8143
Φ	491.52	493.04	495.65	460.46
α_{zz}	101.08	105.48	104.33	106.56
α_{xx}	43.81	45.66	45.15	46.52
α	63.14	65.60	64.87	66.53
$\Delta\alpha$	58.00	59.82	59.18	60.04
γ_{zzzz}	18769	30768	23258	37168
γ_{xxxx}	4280	5463	7388	9296
γ_{xxzz}	2936	3962	4787	6272
γ	8385	12237	12422	17409
$\Delta_1\gamma$	47998	82341	54582	93136
$\Delta_2\gamma$	5430	12456	1921	8834

^a The twenty innermost MO were kept frozen in all post-Hartree-Fock calculations.

Table 4. Electric properties of ICCI^a.

Property	[6s4p2d/6s5p3d]		[6s4p3d1f/6s5p5d3f]	
	SCF	MP2	SCF	MP2
Θ	8.8854	8.9994	8.7027	8.3774
Φ	934.39	925.74	893.74	810.79
α_{zz}	140.74	146.25	142.71	146.40
α_{xx}	64.22	67.69	65.74	67.48
$\bar{\alpha}$	89.72	93.88	91.40	93.79
$\Delta\alpha$	76.53	78.56	76.96	78.91
γ_{zzzz}	38697	64303	42413	67362
γ_{xxxx}	10237	13210	19517	23477
γ_{xxzz}	4965	6501	9121	11500
γ	11171	25106	26188	35193
$\Delta_1\gamma$	90039	159573	76534	142678
$\Delta_2\gamma$	19143	38507	7204	21840

^a The thirty-eight innermost MO were kept frozen in all post-Hartree-Fock calculations.

Dipole polarizability. As all basis sets used in this study contain polarization functions optimized for the dipole polarizability, it is reasonable to expect a fair agreement between the SCF values calculated with the small and the large sets. Thus, for the mean polarizability $\bar{\alpha}/e^2a_0^2E_h^{-1}$ we obtain 22.73 (FCCF), 50.17 (CICCCI), 64.87 (BrCCBr) and 91.40 (ICCI) within the large basis sets. The values obtained with the small basis sets are only 0.5, 1.5, 2.7 and 1.8 % lower, respectively. The dihaloethynes are characterized by a largely anisotropic dipole polarizability. The large basis set give $\Delta\alpha/e^2a_0^2E_h^{-1}$ 13.45 (FCCF), 46.84 (CICCCI), 59.18 (BrCCBr) and 76.96 (ICCI). Both the mean and the anisotropy increase monotonically with the atomic number of the halogen.

Electron correlation has a relatively small effect on the components of the dipole polarizability. In case of the diiodoethyne molecule the MP2 values for the large basis are $\bar{\alpha} = 93.79$ and $\Delta\alpha = 78.91$ $e^2a_0^2E_h^{-1}$. These values are just 2.6 and 2.5% above the respective SCF values.

Second dipole hyperpolarizability. Basis set effects are predictably much more important for $\gamma_{\alpha\beta\gamma\delta}$. Although the F0→I0 sequence of basis set gives a fair description of the trends in the hyperpolarizability of the dihaloethynes, only the F1→I1 basis sets are large enough for the accurate prediction of the this property, either at the Hartree-Fock or the post-Hartree-Fock level of theory. The SCF values of the mean hyperpolarizability calculated with the small basis sets are $\bar{\gamma}/e^4a_0^4E_h^{-3} = 2017$ (FCCF), 5182 (CICCCI), 8385 (BrCCBr) and 11171 (ICCI). The respective values for the large basis sets are 2567, 6917, 12422 and 26188, respectively. Basis set completeness becomes a major problem as the size of the molecule increases. An examination of the Cartesian components of $\gamma_{\alpha\beta\gamma\delta}$ for FCCF shows that the transversal component is significantly larger than the longitudinal one, $\gamma_{xxxx} > \gamma_{zzzz}$. Consequently, the anisotropy $\Delta_1\gamma$ is large and negative. This effect is reversed for the higher dihaloethynes, as now γ_{zzzz} is much larger than γ_{xxxx} and the anisotropy $\Delta_1\gamma$ is positive and increases considerably as Cl→I. Moreover, $\Delta_1\gamma > \Delta_2\gamma$ in all cases.

Electron correlation has a very strong effect on the hyperpolarizability. The effect on the Cartesian components is not uniform. The MP2 values of the mean hyperpolarizability, calculated with the large basis sets, are $\bar{\gamma}/e^4 a_0^4 E_h^{-3} = 2932$ (FCCF), 9924 (CICCCI), 17409 (BrCCBr) and 35193 (ICCI). These values represent an increase of 14.2, 43.5, 40.1 and 34.4 % over the respective SCF results. The change of the anisotropy is even more interesting. Let us consider the $\Delta_1\gamma$ anisotropy. The electron correlation correction MP2 – SCF varies as $\Delta_1\gamma/e^4 a_0^4 E_h^{-3} = 1444$ (FCCF), 20798 (CICCCI), 38554 (BrCCBr) and 66144 (ICCI).

Comparison with previous results. The experimental determination of the electric properties of the dihaloethynes does not seem to have attracted attention. We are aware of only one theoretical determination of the electric polarizability of these molecules. An early paper of Lippincott et al. [52] relied on the δ -function model of chemical binding [53,54] to deduce dipole polarizability values of $\bar{\alpha}/e^2 a_0^2 E_h^{-1} = 43.87$ (CICCCI), 55.98 (BrCCBr) and 76.55 (ICCI). These values offer a rather reasonable estimate of the evolution of the dipole polarizability of the dihaloethynes.

Concluding remarks

We have calculated electric moments and dipole (hyper)polarizabilities for the dihaloethynes. Our findings bring forth many interesting trends in the evolution of the electric properties for the sequence FCCF, CICCCI, BrCCBr and ICCI. It is worth noticing that for the first member of this sequence, difluoroethyne, the SCF values of the mean (hyper)polarizability are $\bar{\alpha}/e^2 a_0^2 E_h^{-1} = 22.73$ and $\bar{\gamma}/e^4 a_0^4 E_h^{-3} = 2567$. The respective values for ethyne are 23.41 and 5510 [55,56]. Thus, FCCF is less (hyper)polarizable than ethyne. The mean of $\alpha_{\alpha\beta}$ and $\gamma_{\alpha\beta\gamma\delta}$ increases rapidly with molecular size. Both properties are characterized by very large anisotropies. Our best values for Θ/ea_0^2 , Φ/ea_0^4 , $\bar{\alpha}/e^2 a_0^2 E_h^{-1}$ and $\bar{\gamma}/e^4 a_0^4 E_h^{-3}$ are obtained at the MP2 level of theory and are -0.6524, -22.33, 23.58 and 2932 (FCCF), 3.6612, 226.25, 51.75 and 9924 (CICCCI), 5.8143, 460.46, 66.53 and 17409 (BrCCBr) and 8.3774, 810.79, 93.79 and 35.193 (ICCI).

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