

A PBE hybrid functional study of blue-shifting and red-shifting hydrogen bonds in π hydrocarbons

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ABSTRACT: This study examines a selected group of π hydrocarbon complexes, represented by $C_2H_4 \cdots HCF_3$, $C_2H_2 \cdots HCF_3$, $C_2H_4 \cdots HCCl_3$ and $C_2H_2 \cdots HCCl_3$, from a theoretical point of view. From BPBE/6-311++G(d,p) calculations, the geometrical results of these complexes revealed an elongation and shortening of the H–C bond lengths of chloroform ($HCCl_3$) and fluoroform (HCF_3), respectively. In terms of the infrared spectrum, the analysis of stretch frequencies revealed that the variations in the H–C modes are essentially recognized as red and blue-shifting modes. For the purposes of understanding the two vibrational phenomena of the π hydrocarbon complexes studied here, PBE/6-311++G(d,p) calculations were carried out and partitioning of atomic charges derived from the ChelpG algorithm were also used. A theoretical justification of red- and blue-shift effects was drawn up using charge-transfer analysis, which is manifested in the π bonds of acetylene and ethylene to chloroform ($H-CCl_3$) and fluoroform ($H-CF_3$), respectively. Finally, a further debate regarding the distinct polarizability power of chloroform and fluoroform is presented, concluding that, in comparison with fluoroform, chloroform possesses the requisite features for conventional proton donors and a red-shift is therefore observed in the $C_2H_4 \cdots HCCl_3$ and $C_2H_2 \cdots HCCl_3$ complexes.

Keywords: red-shifting, blue-shifting, Hydrogen bonds

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Introduction

For many years, the numerous molecular systems formed by non-covalent interactions have been a focus for research in the chemical, physical and biological sciences [1]. In conceptual terms, although van der Waals's or London's dispersion forces are important, the hydrogen bonds (Y...H) are considered to be one of the most important interactions because there are an enormous number of phenomena inherent in the contact between proton donors (H) and acceptors (Y = F, O, N, S and π centers) [2-4]. In practice, the importance of hydrogen bonding is essential in almost all branches of chemistry, such as, for example, the activation of biomolecules [5], the formation of transition state structures in organic reactions [6] and the development of pharmacological substances [7].

In terms of physical chemistry, hydrogen bonding can be interpreted using the theory of electronic partition, which includes the electrostatic potential term (U), the polarizability effect (P), the exchange spin terms (EX), and charge transfer quantities (Q). The relative contributions of these parameters in quantifying the total energy have been clearly defined, although the electrostatic potential is often the most important [8]. A theoretical study carried out by King and Weinhold [9] revealed the special importance of charge transfer in determining the stabilization energy of HCN linear chains. In traditional hydrogen-bonded complexes, however, the accumulation of charge density on proton donors (HX = Cl, F and CN groups) leads to drastic changes in their structures. One of these changes is the bond length enhancement [10-13], according to which the HX infrared stretch frequencies are shifted downwards and a strong increase in the absorption intensity occurs [14]. In spectroscopy, this phenomenon is known as red-shift, although it should also be remembered that such an effect is commonly observed, not only in van der Waals intermolecular systems, but also in hydrogen-bonded complexes formed by π electron donors [15-16].

However, Hobza *et al.* [17] have recently found a new kind of intermolecular interaction known as antihydrogen bond. Owing to inverse and unusual spectroscopic behavior on the part of the proton donors, a blue- rather than red-shift effect is observed on their bonds [18]. In contrast to the traditional appearance of red-shifts in hydrogen-bonded systems, in antihydrogen-bonded complexes there is a strengthening of the HX bond, which leads to its stretch frequency being shifted to higher wave numbers [19-21]. The anti-hydrogen bonds have thus been designated blue-shifting hydrogen bonds. It is agreed that the blue-shifting hydrogen-bonded systems routinely studied are related to aromatic [22], halogen hydrocarbons [23] and heterocyclic compounds [24], but not to aliphatic hydrocarbons. Although there are still many outstanding questions regarding the

characterization of blue-shifting hydrogen bonds [25], it is of great importance that an investigation and debate be conducted as to whether there are red-shift and blue-shift modes on the C—H bonds in both HCF₃ and HCCl₃ molecules upon the formation of π hydrocarbon complexes formed by acetylene and ethylene, for example. In other words, besides the capacity of acetylene and ethylene to form traditional hydrogen-bonded complexes with monoprotic halogen acids, i.e., hydrochloric acid and hydrofluoric acid [15-16], the formation of blue-shifting hydrogen bonds in C₂H₂⋯HCF₃ and C₂H₄⋯HCF₃ π hydrocarbon complexes requires more thorough examination.

For the purposes of examining the properties of blue-shifting hydrogen bonds in C₂H₂⋯HCF₃, C₂H₄⋯HCF₃, C₂H₄⋯HCCl₃ and C₂H₂⋯HCCl₃ π -complexes, it is theoretically necessary to use an efficient set of methodologies which efficiently describe the red- and blue-shift effects. The specialized literature reveals a large number of studies of hydrogen-bonded complexes which point to the efficiency of Density Functional Theory (DFT) [26]. Thus, analysis of structural, electronic and, principally vibrational parameters, using DFT hybrid functionals, may produce satisfactory results, not only for red-shift interactions, but also for the blue-shift hydrogen-bond type. Furthermore, the quantification of electronic density is a useful parameter for explaining the formation of intermolecular interactions [27]. In practice, the charge transfer in hydrogen-bonded complexes has been used to characterize the formation of red-shift effects on proton donors [28-29]. This study will thus also include an analysis of the charge transfer on the C₂H₂⋯HCF₃, C₂H₄⋯HCF₃, C₂H₄⋯HCCl₃ and C₂H₂⋯HCCl₃ π systems. This investigation will be performed using the ChelpG algorithm [30], whose efficiency is well-known among the theoreticians [31]. Among many other applications, a number of important studies of the formation of hydrogen-bonded complexes have been published using ChelpG calculations [32-33].

Computational Details

The optimized geometries of the C₂H₂⋯HCF₃, C₂H₄⋯HCF₃, C₂H₄⋯HCCl₃ and C₂H₂⋯HCCl₃ π complexes were obtained using the Perdew-Burke-Ernzerhof (PBE) density functional formulation and combined with the 6-311++G(d,p) basis set, with all calculations carried out using the GAUSSIAN 98W program [34]. The PBE hybrid was chosen due to its competence to describe hydrogen bonds [35] and intermolecular interactions [36]. The intermolecular energies were determined using the supermolecule approach [37], and the energy corrections were obtained by means of Zero Point Energy (ZPE) [38] and Basis Sets Superposition Error (BSSE) [39] calculations. The ChelpG method was used to calculate the atomic charges. All the calculations were performed using the GAUSSIAN 98W program.

Results and Discussion

Geometry and infrared harmonic spectrum

The optimized geometries of the $C_2H_2 \cdots HCF_3$ (**I**), $C_2H_4 \cdots HCF_3$ (**II**), $C_2H_2 \cdots HCCl_3$ (**III**) and $C_2H_4 \cdots HCCl_3$ (**IV**) π complexes are depicted in Figure 1, and their main structural results are listed in Table 1.

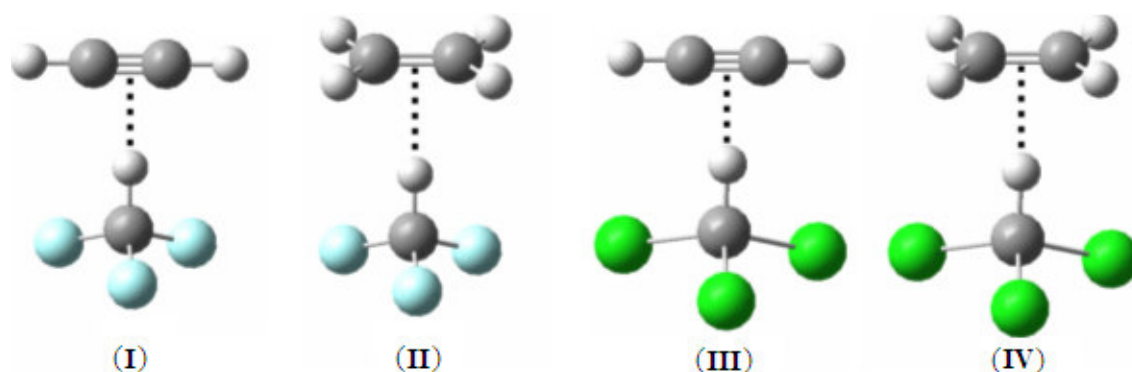


Figure 1. Optimized geometries of the $C_2H_2 \cdots HCF_3$ (**I**), $C_2H_4 \cdots HCF_3$ (**II**), $C_2H_2 \cdots HCCl_3$ (**III**) and $C_2H_4 \cdots HCCl_3$ (**IV**) π complexes using BPBE/6-311++G(d,p) calculations.

Table 1. Structural parameters and infrared modes of HCF_3 and $HCCl_3$ monomers, as well as of $C_2H_2 \cdots HCF_3$ (**I**), $C_2H_4 \cdots HCF_3$ (**II**), $C_2H_2 \cdots HCCl_3$ (**III**) and $C_2H_4 \cdots HCCl_3$ (**IV**) π complexes using the PBE/6-311++G(d,p) calculations.

Parameters	Molecular systems					
	HCF_3	$HCCl_3$	(I)	(II)	(III)	(IV)
$R(H \cdots \pi)$	—	—	2.9304	2.9898	2.8298	2.8338
$r(C-H)$	1.0987	1.0913	1.0983	1.0984	1.0925	1.0928
$\Delta r(C-H)$	—	—	-0.0004	-0.0003	0.0012	0.0015
$\nu(H \cdots \pi)$	—	—	35.9	37.3	41.10	40.00
$I(H \cdots \pi)$	—	—	0.2	0.15	0.30	0.25
$\nu(C-H)$	3057.1	3104.2	3059.8	3058.4	3088.4	3084.6
$I(C-H)$	36.6	0.04	7.3	6.3	32.0	36.8
$\Delta \nu(C-H)$	—	—	2.8	1.3	-15.8	-19.6
$I(C-H)_c / I(C-H)_m$	—	—	0.2	0.17	800.0	920.0

* Values of R and r are given in Å;

* Values of ν and I are given in cm^{-1} and $km\ mol^{-1}$, respectively.

Initially, one important structural observation in (**I**) and (**II**) is the contraction of -0.0004 Å and -0.0003 Å for the $r(C-H)$ bond of the fluoromethane, as well as the changes on its $\nu(C-H)$ frequencies which are shifted upward to values of $2.8\ cm^{-1}$ and $1.3\ cm^{-1}$ followed by a substantial diminution in absorption intensities, e.g., ratios of 0.2 and 0.17.

As it is widely known that these infrared changes are blue-shifting, it can be presumed that **(I)** and **(II)** are blue-shifting hydrogen complexes. On the other hand, the $r(\text{C—H})$ bond length of chloroform increases by 0.0012 Å and 0.0015 Å on the formation of the **(III)** and **(IV)** systems, respectively. The $\Delta\nu(\text{C—H})$ results of -15.8 cm^{-1} and -19.6 cm^{-1} as well as absorption ratios $I(\text{C—H})_c/I(\text{C—H})_m$ of 800 and 920 indicate behavior opposite to that observed for **(I)** and **(II)**. In fact, π systems formed by chloroform present typical red-shifts on their C—H bonds. Therefore, both **(III)** and **(IV)** can be called conventional hydrogen-bonded complexes. In terms of interaction strength, the **(III)** and **(IV)** complexes present shorter $R(\text{H}\cdots\pi)$ distance values, which, in comparison with the C=C bond of ethylene, shows that the higher electronic density on C≡C bond of acetylene is not responsible for stronger hydrogen-bonded complexes. The π systems formed by chloroform, specifically **(III)** and **(IV)**, are thus the most strongly bonded systems. In fact, regardless of whether vibrational or structural parameters are considered, it can be observed that more strongly ($I(\text{C—H})_c/I(\text{C—H})_m \geq 1$) and more weakly ($I(\text{C—H})_c/I(\text{C—H})_m < 1$) bonded systems are connected with red- (**I-II**) and blue-shift (**III-IV**) π hydrocarbons, respectively. According to Barnes [40], analysis of infrared intensity provides an argument for interpreting the formation of red- and blue-shift hydrogen bonds, which are identified by a drastic increase or decrease, respectively, in their absorption intensities.

Intermolecular energies and charge transfer

Recent studies of hydrogen-bonded complexes have established intermolecular energy as a parameter widely used to explain the interaction strength [29] and, in some cases, the hydrogen bond stretch frequencies also corroborate this. Therefore, in strong agreement with findings reported by van der Veken *et al.* [41], the results of this study also indicated that blue- and red-shifts are related to weak ($\text{C}_2\text{H}_2\cdots\text{HCF}_3$ and $\text{C}_2\text{H}_4\cdots\text{HCF}_3$) and strong ($\text{C}_2\text{H}_2\cdots\text{HCCl}_3$ and $\text{C}_2\text{H}_4\cdots\text{HCCl}_3$) bonded systems, respectively. According to Table 2, note that, the interaction energy values ΔE^C for **(I)** and **(II)** lie in the range of $2.30\text{--}2.35\text{ kJ mol}^{-1}$, whereas the **(III)** and **(IV)** complexes are bonded by energy values varying from 2.56 kJ mol^{-1} to 2.65 kJ mol^{-1} . Even though the energy difference between the complexes formed by fluoroform and chloroform are in the range of 0.3 kJ mol^{-1} , it should be noted that these interaction energy levels are lower than those documented for model blue-shifting complexes formed by halogen hydrocarbons and water [42], for instance. Taking into account important studies of π hydrogen-bonded complexes [11, 15], which report that the quantification of charge transfer can help to interpret the variation in the stretch frequencies of proton donors, in particular their red-shifts, for the intermolecular systems under study here the Figure 2 illustrates the relationship between the values of infrared changes on C—H bonds and ΔQ^{ChelpG} intermolecular charge transfer

values.

Table 2. Electronic parameters of the $C_2H_2 \cdots HCF_3$ (**I**), $C_2H_4 \cdots HCF_3$ (**II**), $C_2H_2 \cdots HCl_3$ (**III**) and $C_2H_4 \cdots HCl_3$ (**V**) complexes using PBE/6-311++G(d,p) calculations.

Parameters	Complexes			
	(I)	(II)	(III)	(IV)
ΔE	2.9	3.0	4.1	4.3
BSSE	0.54	0.69	1.45	1.74
ΔE^C	2.35	2.30	2.65	2.56
ΔQ^{ChelpG}	-0.031	-0.030	-0.025	-0.023
$\Delta\mu$	0.31	0.36	0.40	0.45

* Values of ΔE , BSSE and ΔE^C are given in kJ mol^{-1} ;

* Values of ΔQ^{ChelpG} are given in electronic units (e.u.);

* Values of μ for HCF_3 and HCl_3 monomers are 1.68 D and 1.15 D, respectively.

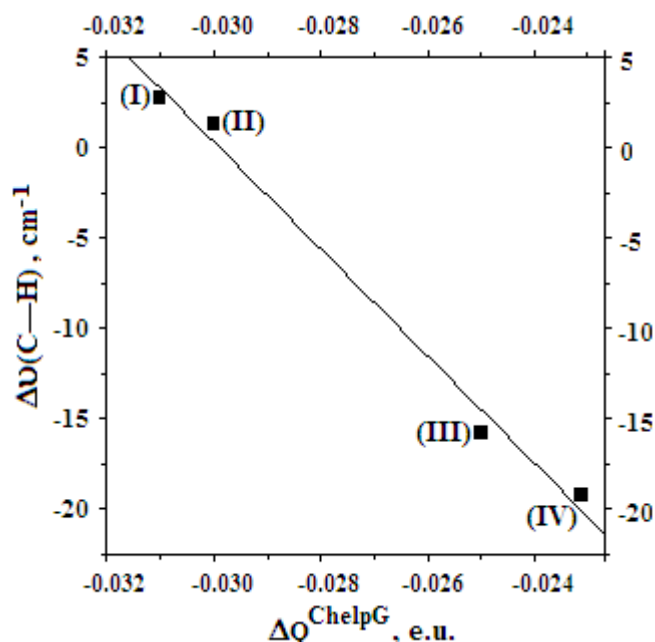


Figure 2. Relationship between the infrared changes in C—H bonds and ΔQ^{ChelpG} intermolecular charge transfer in $C_2H_2 \cdots HCF_3$ (**I**), $C_2H_4 \cdots HCF_3$ (**II**), $C_2H_2 \cdots HCl_3$ (**III**) and $C_2H_4 \cdots HCl_3$ (**IV**) π complexes using BPBE/6-311++G(d,p) calculations.

Not surprisingly, the R^2 linear coefficient yielded by equation (1) is a strong indicator of the formation of blue-shifting and red-shifting hydrogen bonds on the (**I**), (**II**), (**III**) and (**IV**) π systems, respectively.

$$\Delta\nu(C-H) = -88.7 - 2970 \Delta Q^{ChelpG} ; R^2 = -0.99. \quad (1)$$

In terms of notation, although several methods are routinely used to calculate atomic charges [43], the ChelpG calculations have provided excellent results for charge transfer [29, 32]. In fact, this is a decisive point because the electronic transfer between

the HOMO and LUMO orbital of proton acceptor and donor need to be accurately evaluated. Thus, according to the ΔQ^{ChelpG} values for -0.031 e.u. and -0.030 e.u. of the **(I)** and **(II)** complexes, their blue-shifting effects are directly correlated with larger charge transfers, while the **(III)** and **(IV)** have smaller results for -0.025 e.u. and -0.023 e.u., respectively.

Influence of the polarizability of the proton donors

It should also be mentioned that the polarizabilities of HCF_3 and HCCl_3 proton donors must affect their interactions with π molecules, such as acetylene and ethylene. However, the nature of blue-shift hydrogen bonds has been debated by Hobza and Havlas [44], who have demonstrated that the C—H bond length of fluoroform is drastically affected by variation in its dipole moment. It has been pointed out that, in case of HCF_3 , the shortening its bond length leads to larger dipole moments [45], as demonstrated in Figure 3. Similar conclusions have also been reported by Barnes [40], who also discusses whether negative dipole moment derivatives ($\delta\mu^0/\delta\mu\text{HX}$) also reveal the propensity of proton donors to bind with high density centers of red and blue-shift systems. In other words, as also demonstrated by Hobza and Havlas [44], as presented above, this study confirms the trend towards reduction and increase in the dipole moment of fluoroform and chloroform, respectively. In fact, the shortening of the C—H bonds of **(I)** and **(II)** reinforces the idea that these π systems are blue-shifting hydrogen-bonded complexes.

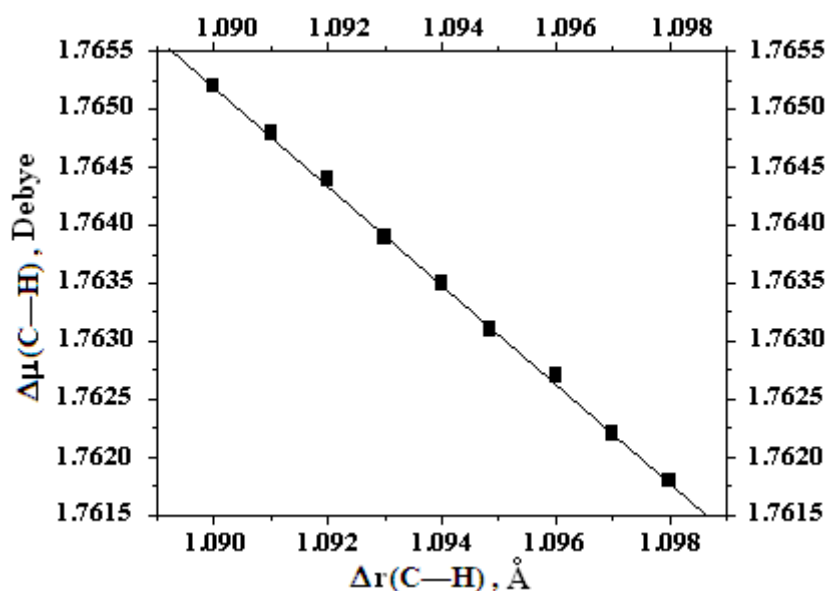


Figure 3. Variation of dipole moment ($\bar{\mu}$) and changes of C—H bond length of the HCF_3 molecule using PBE/6-311++G(d,p) calculations.

However, analysis of Figure 4 shows that HCCl_3 behaves in a similar fashion with polar molecules, such as water, where the elongation of C—H leads to an increase in the

dipole moment value. Therefore, this study casts no doubt on the efficiency of the PBE functional to detect the dispersion energy and attractions forces and the results presented here are in satisfactory agreement with the explanations put forward by Hobza and Havlas [44]. With regard to this, even though many works have demonstrated that HCCl_3 has the property of forming blue-shifting hydrogen bond complexes [46], our results revealed an intriguing feature of HCF_3 and HCCl_3 , which provide the formation of blue-shifting hydrogen bonds in **(I)** and **(II)**, as well as red-shifting hydrogen bonds in **(III)** and **(IV)** π complexes, respectively. Nevertheless, some studies have demonstrated that chloroform has the property of forming conventional hydrogen-bonded complexes [41] or those whose stretch frequency of C—H bond is set to red wave numbers [47]. Finally, the red-shift behavior of chloroform is not surprising because such a phenomenon has already been detected experimentally in solution [48, 49] or in gaseous phase [50].

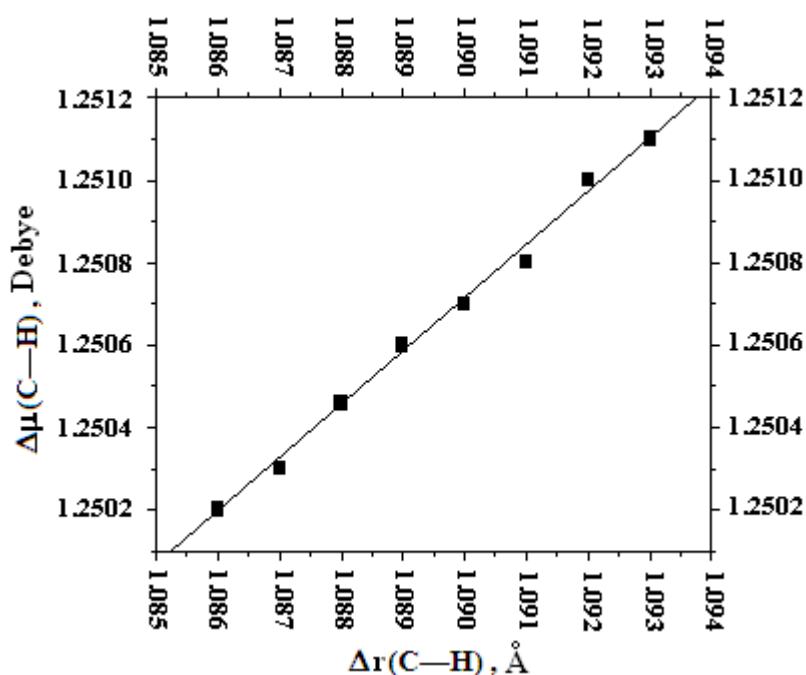


Figure 4. Variation of dipole moment ($\bar{\mu}$) and changes of C—H bond length of the HCCl_3 molecule using BPBE/6-311++G(d,p) calculations.

Conclusions

A theoretical study of the molecular properties and infrared spectrum of the $\text{C}_2\text{H}_2 \cdots \text{HCF}_3$, $\text{C}_2\text{H}_4 \cdots \text{HCF}_3$, $\text{C}_2\text{H}_2 \cdots \text{HCCl}_3$ and $\text{C}_2\text{H}_4 \cdots \text{HCCl}_3$ π complexes has been presented in this paper. According to PBE/6-311++G(d,p) calculations, structural evidence has been adduced to show that the blue-shifting hydrogen bonds and red-shifting hydrogen bonds

result from the shortening and lengthening of the C—H of fluoroform and chloroform, respectively. Using spectroscopy, the deformations in C—H bonds can be shown to lead to changes in their stretch frequencies, which are shifted to blue and red regions of the infrared spectrum when the respective $C_2H_2 \cdots HCF_3$, $C_2H_4 \cdots HCF_3$, $C_2H_2 \cdots HCCl_3$ and $C_2H_4 \cdots HCCl_3$ π complexes are formed. In terms of electronic parameters, the intermolecular energy corroborates the blue- and red-shift effects, with the quantification of higher and lower ΔQ^{ChelpG} charge transfers fully explaining these vibrational phenomena. Finally, analysis of the dipole moment leads to the conclusion that chloroform has a similar behavior to polar molecules; namely, an increase in C—H bond lengths as well as dipole moment. On the other hand, fluoroform causes contraction of the C—H bond lengths and hence, diminishes its dipole moment.

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