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Density Functional Studies of the bπ.aσ Charge-Transfer Complex Formed between Ethyne and Chlorine Monofluoride

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The bπ.aσ charge-transfer complex formed by ethyne and chlorine monofluoride has been studied with various approximate pure and hybrid density functional methods and the second-order Møller−Plesset (MP2) theory. The calculations demonstrate that one hybrid method, namely, the so-called B3LYP, leads to reasonably good estimates of the experimentally measured rotational constants. Accordingly, the predicted B3LYP intermolecular distance is found to be also close to the experimental value. This enables us to estimate reliably the intermolecular interaction energy, which is found to be 3.43 kcal/mol. The performance of the various approximate density functionals and the MP2 theory is compared and discussed. Finally, we comment on the analysis of the natural bond orbitals, which has been found to be very valuable to shed light on the nature of the weak intermolecular interaction.

Introduction

Charge-transfer complexes between unsaturated olefins and halogen X_2 or interhalogen XY molecules are species of primary importance for the electrophilic addition of halogen/interhalogen molecules to π-bonds.[1] These complexes, labeled bπ.aσ by Mulliken and Pearson,[2] have recently been the subject of substantial rotational spectroscopy research.[3] Indeed, modern microwave spectrometers, fitted with a fast-mixing nozzle,[4] are capable to prevent the otherwise violent chemical reaction that would occur if the components were mixed in the gas phase under normal conditions of temperature and pressure. This novel experimental technique represents a milestone in the accurate experimental characterization of these elusive complexes. Namely, the rotational spectra are capable of giving not only highly accurate structural data but also intermolecular stretching force constants that can be used to assess the strength of the intermolecular binding and nuclear quadrupole coupling constants, from which the electronic charge redistribution of the halogen/interhalogen molecule on complex formation can be determined.[5] On the other hand, all these properties can also be predicted by high-level ab initio calculations. Thus, charge-transfer complexes constitute a convenient common playground for experiment and theory. Indeed, the origin of the forces responsible for intermolecular binding has been the subject of many theoretical studies.[6−8] The analysis of ab initio calculations indicates that the dispersion forces must be handled properly in order to arrive at meaningful results. Thus, inclusion of electron correlation in the calculations is mandatory.[9] Density functional theory (DFT) offers an alternative treatment of electron correlation effects with respect to the more traditional molecular orbital theory,[10] and a substantial interest has recently arisen in the description of weakly bound complexes,[11] in particular hydrogen-bonded systems. However, application of DFT to weaker charge-transfer complexes is nowadays scarce[12−16] and inconclusive. As pointed out by Salahub et al.,[16] charge-transfer complexes clearly represent an important frontier for DFT.

In this paper we present a detailed calculation on the properties of a recently characterized bπ.aσ charge-transfer complex, namely, that consisting of ethyne and chlorine monofluoride.[17]

Computational Method

We have recently shown that a slight modification[18] of the Becke's gradient correction term to the exchange functional yields a noticeably improved performance of the so-called B3LYP hybrid method[19] for the calculated properties of both the G2 set of molecules[20] and some selected charge-transfer and hydrogen-bonded complexes.[21] Also, it has been shown[21] that the 6-311++G(d,p) basis set[22] represents a reasonable compromise between computational cost and accuracy. Consequently, all the calculations presented in this paper have been carried out with the 6-311++G(d,p) basis set, with a locally modified version of the Gaussian94/DFT suite of programs,[23] which incorporates the above-mentioned modification in the Becke's exchange functional. Namely, the modification[18] consists of substituting the standard value of the adjustable parameter β by its best fitting value to the Hartree−Fock exchange energy calculated with the current Gaussian basis set employed in the molecular calculation. This modified gradient correction to the exchange energy is then incorporated into the various approximate DFT methods to calculate the optimum geometrical structure of the complex between ethyne and chlorine monofluoride[17] and its associated molecular properties, which are discussed in the following section. In particular, we have used two sets of approximate functionals,[24] namely, one set of pure functionals, denoted as BX, X = P86, PW91, and LYP, and one set of hybrid functionals, B3X, X = P86, PW91, and LYP. The structure of the bπ.aσ complex between ethyne and chlorine monofluoride has been optimized in the C_{2v} geometry, at every level of theory. Subsequently, frequencies have been calculated on each optimum structure at its corresponding level of theory. This has enabled us to assess the nature of the optimized structures by inspection of the signs of their force constants and also to estimate the zero-point vibrational energy (ZPVE) correction, that was later employed in the calculation of the intermolecular interaction energy. The latter has been calculated as the energy difference between the separated C_2H_2 and ClF fragments and the complex, with corrections for the ZPVE and the basis set superposition error[25] (BSSE) taken account. Finally, we have carried out a natural

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TABLE 1: Rotational Constants (MHz), Intramolecular Stretching Force Constant, k_σ (N m^{-1}), Intermolecular Distances, d(*···Cl) (Å), and Dissociation Energies, E_0 (kcal/mol) of C_2H_2···ClF, for Various Approximate DFT Methods[a]

	rotational constants					
	A	B	C	k_σ	d(*···Cl)	E_0
BP86	34709 (34606)	2326.1535 (2370.9470)	2180.0498 (2218.9186)	12.96 (14.23)	2.566 (2.533)	−6.88 (−7.18)
BPW91	34806 (34694)	2306.2958 (2353.6134)	2162.9728 (2204.0880)	11.37 (12.55)	2.585 (2.548)	−5.58 (−5.90)
BLYP	34883 (34781)	2197.1414 (2239.6271)	2066.9508 2104.1386)	10.31 (11.32)	2.668 (2.634)	−5.70 (−5.84)
B3P86	35428 (35353)	2256.5615 (2290.0856)	2121.4379 (2150.7638)	9.05 (9.78)	2.673 (2.646)	−4.27 (−4.50)
B3PW91	35393 (35317)	2200.6538 (2236.6124)	2071.8313 (2103.4058)	7.28 (7.93)	2.723 (2.693)	−3.07 (−3.25)
B3LYP	35472 (35398)	2129.3176 (2158.9142)	2008.7366 (2034.8129)	7.18 (7.60)	2.780 (2.754)	−3.43 (−3.54)
MP2	34718	1971.5913	1865.6453	4.70	2.957	−2.39
exp[b]	35650 (4)	2099.7094 (4)	1977.9630 (4)	10.01 (3)	2.873 (8)	

[a] In parentheses are values obtained with the standard Becke's gradient corrected exchange functional. [b] Taken from ref 17.

bond orbital (NBO) analysis[26] for all the methods used in the present paper. Thus, atomic charges, estimated by means of the natural population analysis and second-order interactions energies, among the calculated natural bond orbitals, will be used to characterized the electronic charge redistribution that takes place on complex formation. NBO calculations have been performed with the NBO code[27] included in GAUSSIAN94/DFT.

Results and Discussion

The computed molecular properties at the selected approximate DFT methods with the 6-311++G(d,p) basis set are shown in Table 1. For comparison we have included in Table 1 results from the second order Møller−Plesset (MP2)[28] calculation, with the same basis set, and the experimental values.[17]

Due to the delicate balance between the dispersion and polarization contributions along with the charge-transfer term, existing in these complexes,[29] their adequate description represents a harsh and tight test for density functionals.[16] Indeed, inspection of Table 1 reveals that all three pure approximate functionals, BP86, BPW91, and BLYP are far from satisfactory. Thus, rotational constants are poorly described, and, as expected, the intermolecular distance is found appreciably shorter than the experimental value. These suggest that the calculated intermolecular interaction energies should be appreciably overestimated by our three selected approximate pure functionals. Indeed, as observed from Table 1, the intermolecular distances calculated with the three BX, X = P86, PW91, and LYP, approximate pure functionals are 0.31, 0.28, and 0.20 Å, respectively, shorter than the experimental value. Concomitantly, intermolecular interaction between energies are seen to decrease with the increase of the intermolecular distances. Nevertheless, it is worth mentioning that using our recommended modified Becke's gradient-corrected exchange functional, improves all of the calculated properties in the right direction and that the overall performance of the functionals decreases as follows: BLYP, BPW91, BP86. The latter is suggestive of the quality ordering for the LYP, PW91, and P86 electron correlation approximate functionals. Given the well-known importance of the electron correlation effects for these complexes[9] and that the three pure approximate functionals mentioned above have the same piece for the exchange part, improving in the functional's performance should be attributed to the quality of the electron correlation piece. Finally we would like to point out that all the three functionals predict a small negative force constant for the wagging mode of the C_2H_2 moiety with respect to the C_{2v} axis.

However, inclusion of part of the Hartree−Fock exchange, through the hybrid methods B3X (X = P86, PW91, LYP), greatly improves the agreement between experiment and theory, as shown by inspection of the bottom half of Table 1. In particular, the agreement with respect to the experimental values of the calculated rotational constants is remarkable. Thus, inspection of Table 1 reveals that the averaged error for the rotational constants is less than 1% for the B3LYP method, with our modified Becke's exchange gradient correction term. Notice that using the standard Becke's exchange gradient correction term, this average error grows up to 2.1%. A parallel behavior is also found for the BLYP pure functional. Thus, when the modified Becke's term is used, the averaged error in the predicted values of the rotational constants is 3.6%; however, using the standard Becke's exchange gradient correction term, the error raises to 4.9%. The latter figure compares well with the error associated with the MP2 calculated rotational constants, namely, 4.8%, a fact that comes along with the reported close behavior of the BLYP and MP2 methods for both, strongly bound molecules[30] and weakly bound ion−molecule complexes.[31] However, BLYP and MP2 behave oppositely with respect to experiment. Thus, while the BLYP rotational constants B and C are overestimated, the MP2 underestimates them. This is reflected in the calculated intermolecular distance, d(*···Cl), i.e., the BLYP value, 2.668 Å, is too short and the MP2 value, 2.975 Å, too large with respect to the value of 2.873(8) Å deduced from the experimental rotational constants.[17] This is remedied, in part, by the B3LYP method, which leads to an intermolecular distance of 2.780 Å, only 0.08 Å shorter than the experimental result. This reasonable agreement, between the B3LYP and experiment, should, however, be expected from the above-mentioned excellent prediction of the rotational constants. Accordingly, the MP2/6-311++G(d,p) calculated interaction energy is smaller than the obtained at the B3LYP/6-311++G(d,p) level of theory. Since the latter is known to yield interaction energies of charge-transfer complexes[16,21] around the lower bound of the experimental uncertainty range, our calculations indicate that the MP2/6-311++G(d,p) should underestimate the intermolecular interaction energy of the C_2H_2···ClF complex by more than 1 kcal/mol. This result is consistent with previous calculations on related systems[16,21] and with the trend observed for the calculated intramolecular stretching harmonic force constant, k_σ. Thus, inspection of Table 1 reveals that the MP2 level of theory underestimates k_σ severely with respect to the experimental estimate of 10.01(3) M m^{-1}. Notice that this property is slightly overestimated by the three pure functionals considered in the present paper, while their corresponding hybrids slightly underestimate it. This trend agrees fully with the calculated intramolecular interaction energies. Nevertheless, one must not expect our calculated harmonic force constants to describe properly the highly anharmonic intramolecular stretching mode, and hence close matching between theoretical and experimental values of k_σ should be attributed to a fortuitous cancellation of errors rather than to a proper handling of the physical phenomena governing the intramolecular stretching vibration mode.

TABLE 2: Natural Population Analysis Excess Charges (*e*) with the 6-311++G(d,p) Basis Set[a]

	MP2	B3LYP	BLYP
$\Delta Q_{C_2H_2}$	0.022	0.074 (0.078)	0.134 (0.138)
ΔQ_F	−0.019	−0.040 (−0.042)	−0.057 (−0.060)
ΔQ_{Cl}	0.003	−0.034 (−0.036)	−0.077 (−0.078)

[a] In parentheses values obtained with the standard Becke's gradient corrected exchange functional.

TABLE 3: NBO Second-Order Interaction Energy Analysis ($\Delta E_{ij}^{(2)}$) for the $\pi_{CC} \rightarrow \sigma^*_{ClF}$ Donor−Acceptor Interaction with the 6-311++G(d,p) Basis Set

	MP2	B3LYP	BLYP
$\Delta E_{ij}^{(2)}$ (kcal/mol)	5.94	9.22 (9.83)	17.12 (13.17)
F_{ij} (au)	0.052	0.043 (0.045)	0.040 (0.042)
$E_i - E_j$ (au)	0.58	0.25 (0.25)	0.17 (0.17)

[a] In parentheses values obtained with standard Becke′s gradient corrected exchange functional. See text for the definitions of the symbols used.

As shown earlier[3,12,31] the charge redistribution on complex formation can be derived from analysis of the nuclear quadrupole coupling constants. Thus, as a result of the careful inspection of the nuclear quadrupole coupling constants associated with the inner and outer halogen nuclei for several complexes, a simple proportional rule between the increment of the electronic charge of the outer halogen and the observed intermolecular stretching force constant has been observed.[3] Using this rule, the increment of electronic charge of the F atom is estimated to be 0.04 electron.[17] This figure is consistent with the natural bonding analysis excess charges, shown in Table 2, which correspond to the difference between the electronic charge in the complex with respect to the free molecule. Thus, the B3LYP predicted amount of electronic charge transferred over the outer halogen atom (F), $\Delta Q_F = -0.0040e$, matches the experimental estimate,[17] while the MP2 and BLYP predictions are smaller and larger, respectively, than the experimental value. Nevertheless, our analysis is suggestive of a net, though weak, transfer of electronic charge from the C_2H_2 moiety to the halogen dimer; very small at the MP2/6-311++G(d,p) level of theory, $\Delta Q_{C_2H_2} = 0.022e$ and a bit large at the B3LYP and BLYP methods, $\Delta Q_{C_2H_2} = 0.074e$ and $\Delta Q_{C_2H_2} = 0.134e$, respectively. Recall that these figures correlate with the intermolecular bond distance; the more electronic charge transferred, the shorter the intermolecular distance.

Further inspection of the NBO second-order interaction energies unveils the $\pi_{C-C} \rightarrow \sigma^*_{ClF}$ donor−acceptor interaction as the source of such intermolecular charge transfer. For the sake of brevity, Table 3 collects only the MP2, B3LYP, and BLYP second-order interaction energies, which are calculated as[26]

$$\Delta E_{ij}^{(2)} = \frac{2F_{ij}^2}{E_i - E_j} \qquad (1)$$

with $F_{ij} = \langle \phi_i | \mathbf{F} | \phi_j \rangle$, where **F** is the Fock operator and E_i and E_j are the orbital energies of the donor ϕ_i and acceptor ϕ_j natural bond orbitals. Thus, from Table 2 it is observed that the energy term F_{ij} is rather independent of the method, contrary to the energy resonance term ($E_i - E_j$) which does markedly depend on the method. Namely, the best method, B3LYP, yields an energy difference of 0.25 au, intermediate between the MP2 and BLYP values. However, it is not only this donor−acceptor NBO orbital energy resonance term that determines the intermolecular interaction. A correct description of the σ^*_{ClF} orbital is also compulsory to describe properly the sharing within the halogen molecule of the electronic charge donated by the ethyne. Notice that for the B3LYP method of the 0.074*e* withdrawn from the C_2H_2 moiety, 54% (0.040*e*) goes to the fluorine and 46% (0.034*e*) to the chlorine. However, for the BLYP method, 42% (0.057) of the withdrawn electronic charge goes to the fluorine atom, and 58% goes to the chlorine atom of the interhalogen acceptor moiety. This erratic behavior for the sharing of the withdrawn electronic charge should be associated with the difficult correct description of the σ^*_{ClF} natural bond orbital. A task apparently only achieved by the B3LYP method. Salahub et al.[16b] has noticed similar behavior in both ethylene and ammonia complexes with halogen molecules.

Conclusions

The recently experimentally characterized[17] bπ.aσ charge transfer complex between ethyne and chlorine monofluoride ($C_2H_2 \cdots ClF$) has been studied with various density functional methods including gradient corrections for both the exchange and electron correlation functionals and the second-order Møller−Plesset (MP2) theory, with the 6-311++G(d,p) basis set. In particular, two sets of approximate functionals have been used, namely, approximate pure functionals (BP86, BPW91, BLYP) and hybrid methods (B3P86, B3PW91, B3LYP). The B stands for the Becke's correction[19] to the exchange density functional and P86, PW91 and LYP stand for three popular approximations to the electron correlation functional.[24] Then, all the density functional calculations have been carried out with a slightly modified Becke's correction term,[18] which has been found to yield improved results for both strongly bound molecules[20] and weakly bound complexes.[21] The latter has been found to be the case also for the $C_2H_2 \cdots ClF$ charge-transfer complex.

In general it is observed that the approximate pure functionals, BX, X = P86, PW91, and LYP, describe poorly the rotational constant and hence do not reproduce the experimental intermolecular distance satisfactorily. Indeed all three functionals underestimate severely the intermolecular distance. Therefore, it is expected that they will lead to a erroneous underestimation of the intermolecular energies. The hybrid methods, however, perform markedly better than their corresponding approximate pure functionals. In particular, the B3LYP method predicts reasonably well the rotational constants, and hence it yields a very good estimate, only 0.08 Å shorter, of the experimental intermolecular distance. Accordingly, the calculated intermolecular energy of 3.4 kcal/mol is expected to represent a reasonable guess of the experimental value, not determined yet. The MP2 predicted rotational constants have an error of 4.8% with respect to the experimental values. Consequently the predicted intermolecular distance and interaction energy are expected to be far from satisfactory.

Finally, the analysis of the natural bonds orbitals sheds light on the nature of the weak intermolecular interactions. Namely, it is found that on average, the C_2H_2 moiety transfers electronic charge to the ClF, and then this charge is redistributed among the two halogen atoms. This conclusion is reached by analyzing the $\pi_{CC} \rightarrow \sigma^*_{ClF}$ donor−acceptor interaction between the π_{CC} and σ^*_{ClF} natural bond orbitals of the complex. The proper description of the delicate balance between the amount of electronic charge transferred and its subsequent redistribution among the two halogen atoms has been proven to be a very difficult task, apparently achieved only by the B3LYP method with a sufficiently flexible basis set.

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Supporting Information Available: Cartesian coordinates and harmonic vibrational frequencies (4 pages). Ordering information is given on any current masthead page.

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