JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 253–258 (1992)

STABILIZATION OF MOLECULAR ASSOCIATION: AN AM1/PM3 STUDY OF TETRAHALOMETHANE–ARENE MOLECULAR COMPLEXES

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An AM1/PM3 study of several tetrahalomethane–arene molecular complexes is presented. The results indicate the existence of weak attractive non-dispersion interactions in some of these complexes, which can be rationalized in terms of multipole–multipole and multipole–induced dipole interactions. No evidence was found for the occurrence of charge transfer in the ground states of these complexes.

INTRODUCTION

The binding in electron donor–acceptor (EDA) complexes has been the subject of many experimental and theoretical studies. There has been some disagreement, however, as to the nature of the intermolecular interactions that lead to the formation of these complexes. Earlier this century, interpretation of the stabilities of EDA complexes was based on 'classical' interactions, which may be described in terms of the 'no-overlap' wave function Ψ_0. In the wake of Mulliken's seminal work,[1,2] in which he proposed that the observed properties of EDA complexes could be explained by mixing charge-transfer (CT) excited states Ψ_1 into the ground-state wavefunction Ψ_N of the complex ($\Psi_N = a\Psi_0 + b\Psi_1$), many experimental findings, in particular spectral observations, were (successfully) rationalized in terms of CT interactions. There has been a tendency, however, to overestimate the contribution of CT interactions and, more often than not, models of the binding in EDA complexes were based solely on CT, rather than on a combination of CT and all the other types of interaction, as originally proposed by Mulliken.[1] In a series of papers, Hanna and co-workers[3–5] stressed the importance of the 'no-overlap' wavefunction Ψ_0 in describing the ground-state properties of weak EDA complexes, such as benzene–halogen complexes. They placed special emphasis on the contributions to the heat of formation from multipole–induced dipole and multipole–multipole interactions in these complexes, and concluded that in many cases the contribution from CT interactions had been overestimated in the past.[3]

The nature of the binding in a series of complexes based on tetrahalomethanes and aromatic compounds has been investigated experimentally during the past four decades. Especially the extent to which charge transfer occurs in these complexes has been a moot point (see Ref. 6 for a brief review of several experimental studies of CBr_4–arene complexes). In 1962, Strieter and Templeton[7] reported the crystal structure of a CBr_4–*p*-xylene complex, and in a recent paper[6] the existence in solution of a 1 : 1 CBr_4–toluene molecular complex was demonstrated by means of differential anomalous x-ray scattering (DAS). The DAS results indicate the prevalence of 'centrosymmetric' species with one bromine atom directed at the ring centre and three bromines pointing away from the ring (Figure 1) [6]. This arrangement is very similar to that found in the aforementioned crystal structure of the CBr_4–*p*-xylene complex.[7]

The aim of this work was to investigate with PM3[8,9] and AM1[10] semi-empirical methods the nature of the non-dispersion intermolecular interactions in a series of complexes based on tetrahalomethanes and several aromatic compounds. The merits and drawbacks of these semi-empirical methods are currently being investigated by many groups, and it appears that PM3 gives results of higher accuracy.[11,12] Even so, the calculation of intermolecular potential energy curves may lead to erroneous results, since this type of calculation tends to

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0894–3230/92/050253–06$05.00

Received 24 September 1991
Revised 22 January 1992

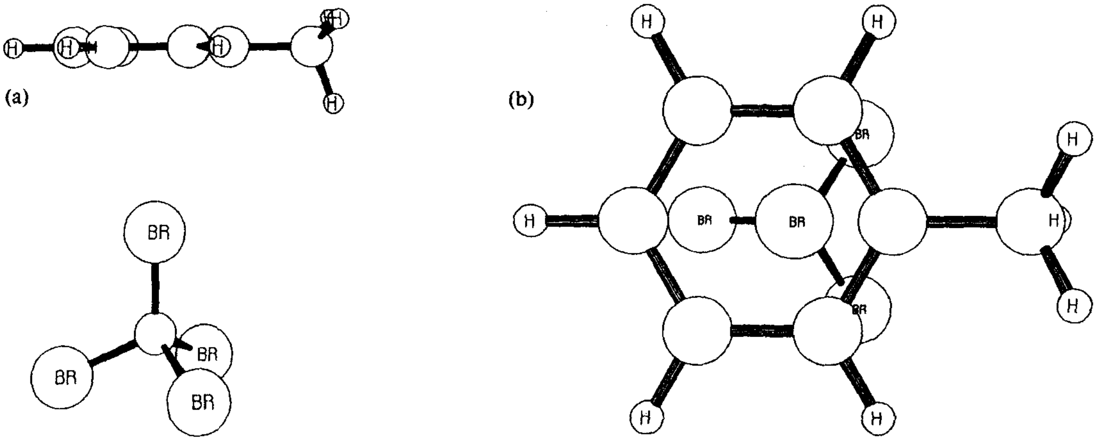

Figure 1. ORTEP diagram[22] of the 'centrosymmetric' intermolecular geometry chosen for the AM1 and PM3 calculations. (a) Side view; (b) top view

underestimate the dispersion interaction between the constituent molecules in an EDA complex.[12,13] Neglect of the dispersion part of the 'classical' wavefunction has two effects:[14] (1) since van der Waals (vdW) dispersion forces are invariably attractive, the complexes may appear to be less stable than they actually are, and (2) the equilibrium distances obtained from the calculations are too large. There are, however, several reasons why neglect of dispersion interactions does not affect the conclusions drawn in this paper. First, the trend of increasing stability in the series of benzene–tetrahalomethane complexes discussed below is merely enhanced by addition of attractive dispersion forces, because the one major factor that varies in the series, i.e. polarizability, affects dispersion forces and multipole–induced dipole interactions in a similar fashion (Table 1). Second, since all aromatic systems investigated in this work have very similar polarizabilities (cf. Table 2), the trend observed in the series of CBr_4–arene complexes is not affected by the inclusion of vdW forces: the potential energy curves are merely shifted to lower energies by an equal amount. Third, the question of whether or not a particular EDA complex will be formed in solution (as is the case with the system investigated previously[6]) does not really depend on the strength of the vdW dispersion forces, since arene–arene and CBr_4–CBr_4 dispersion interactions should be of comparable strength. Hence, only the study of the non-dispersion interactions in these complexes will help explain the preferred formation of particular complexes and their relative stabilities. This work was undertaken to elucidate qualitatively the relative stabilities of a series of complexes involving aromatic systems and tetrahalomethanes in terms of the non-dispersion intermolecular interactions.

METHOD OF CALCULATION

The calculations were performed using the AM1 and PM3 methods as implemented in the MOPAC 6.0 package.[15,16] The final results were obtained using the PRECISE option and taking account of the relevant symmetry constraints, i.e. the molecular point group (e.g. C_2 in the case of chlorobenzene). All calculations were carried out on a SUN SPARCstation 2.

Calculations of the gas-phase heats of formation, the point charges on the constituent atoms and the atomic orbital electron populations were performed for the following molecules and molecular complexes: CF_4, CCl_4, CBr_4, $PhNH_2$ ($Ph = C_6H_5$), $PhCH_3$, PhH, PhCl, $PhNO_2$, CF_4–PhH, CCl_4–PhH, CBr_4–PhH, CBr_4–$PhNH_2$, CBr_4–$PhCH_3$, CBr_4–PhCl and CBr_4–$PhNO_2$. The molecular complexes were examined at a fixed relative orientation (Figure 1) at various intermolecular distances with the reaction path option. The intramolecular geometry (all parameters) are optimized, taking account of the aforementioned symmetry constraints.

RESULTS AND DISCUSSION

The potential energy curves in Figures 2 and 3 were obtained by the following procedure: The heats of formation ΔH_f of the molecular complexes were obtained by the methods described in the preceding section. At distances C_{CHal_4} – ring centre larger than *ca* 20 Å no significant change in the heats of formation was detectable. These values were taken as the heats of formation at infinite separation ΔH_f^∞ and subtracted from the heats of formation obtained at shorter distances, thus yielding the interaction energy of the system

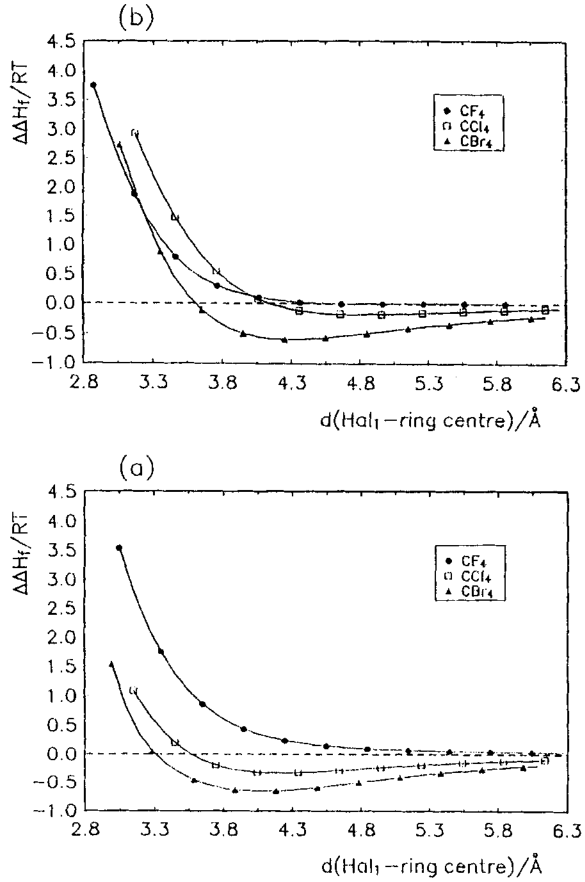

Figure 2. Binding energy $\Delta\Delta H_f$ (in multiples of $RT = 0{\cdot}5921$ kcal mol^{-1} at $T = 298$ K) of various benzene–tetrahalomethane EDA complexes as a function of the intermolecular distance d. (a) AM1 results; (b) PM3 results. •, CF_4; □, CCl_4; ▲, CBr_4

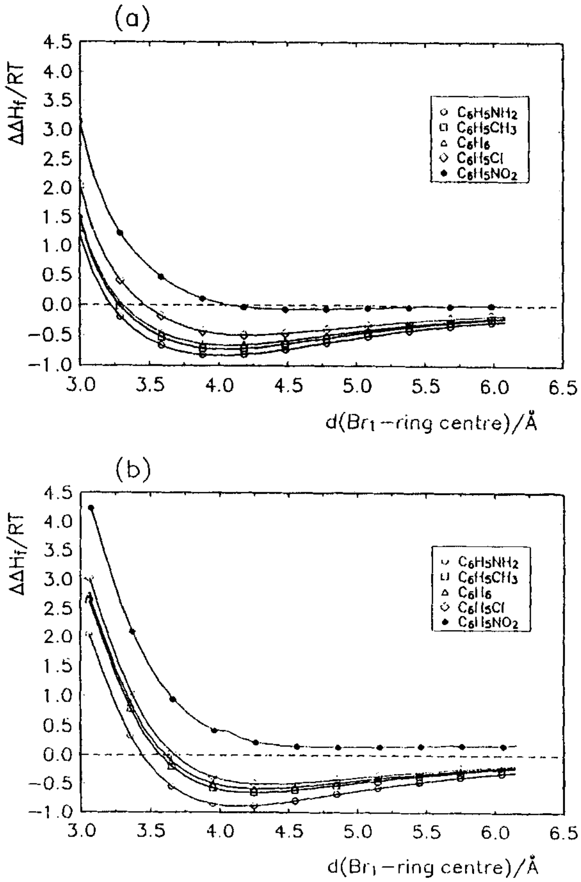

Figure 3. Binding energy $\Delta\Delta H_f$ (in multiples of $RT = 0{\cdot}5921$ kcal mol^{-1} at $T = 298$ K) of various arene–tetrabromomethane EDA complexes as a function of the intermolecular distance d. (a) AM1 results; (b) PM3 results. ○, $C_6H_5NH_2$; □, $C_6H_5CH_3$; △, C_6H_6; ◇, C_6H_5Cl; •, $C_6H_5NO_2$

$\Delta\Delta H_f = \Delta H_f - \Delta H_f^{\infty}$. The results in Figures 2 and 3 are given in multiples of RT (at 298 K: $RT = 0{\cdot}5921$ kcal mol^{-1}), R being the gas constant and T the temperature. The electron populations n_e^{π} of the π systems of the aromatic rings were obtained by adding up the populations of the p_z atomic orbitals of the phenyl carbon atoms. The results of these calculations are given in Tables 1 and 2 (the subscript eq refers to values at equilibrium separation, i.e. the minima in the potential energy curves).

The obtained heats of formation agree very well with the experimental values (Table 1); the only significant discrepancy shows up in the heats of formation of CBr_4. PM3 yields a value twice as large as that obtained by AM1. Comparison with the experimental values provides no criterion for assessing the quality of the calculations, because there is a startling discrepancy of 19 kcal mol^{-1} between the two experimental values. It should be noted, however, that the second value of 35 kcal mol^{-1} is an estimated value[17] and does not appear to be reliable (even the authors doubted its correctness[17]). This discrepancy, however, does not seem to have an influence on the interaction energies obtained. In fact, the relative stabilities calculated with AM1 [Figures 2(a) and 3(a)] and PM3 [Figures 2(b) and 3(b)] are almost identical. In the following subsections we shall examine these results in more detail.

CHal$_4$–benzene EDA complexes

Figure 2 shows the potential energy curves for the interaction of benzene with CF_4, CCl_4 and CBr_4. The trends

Table 1. Experimental and calculated heats of formation and calculated point charges on the Hal$_l$ atoms of various tetrahalomethanes

Compound	Method	$\bar{\alpha}$[a]	ΔH_f^{exp} [e]	ΔH_f^{calc} [g]	q_0^{Hal} [h]	$q_{Hal_l}^{complex,eq}$ [i]	$\Delta q_{Hal_l}^{complex,eq}$ [j]
CF_4	AM1	38·38[b]	−221	−225·7	−0·144	−0·140	+0·004
	PM3			−211·9	−0·111	−0·113	−0·002
CCl_4	AM1	105[c]	−24·6	−28·1	−0·008	+0·003	+0·011
	PM3			−26·0	+0·055	+0·062	+0·007
CBr_4	AM1	144[d]	16	15·9	+0·101	+0·113	+0·012
	PM3		35[f]	32·9	+0·072	+0·106	+0·034

[a] Mean polarizability, in 10^{-25} cm^3.
[b] From Ref. 23.
[c] From Ref. 24.
[d] Value estimated from the mean polarizability of a C—Br bond ($36{\cdot}0\times10^{-25}$ cm^3).[24]
[e] In kcal mol^{-1}; from Ref. 23.
[f] From Ref. 17.
[g] In kcal mol^{-1}.
[h] Point charge on the halogen atoms of a free $CHal_4$ molecule (in atomic units: −1·000 is the charge of an electron).
[i] Point charge on the Hal$_l$ atom of a $CHal_4$ molecule in a $CHal_4$–benzene complex (in atomic units: −1.000 is the charge of an electron).
[j] Deviation of the point charge on the Hal$_l$ atom of a $CHal_4$ molecule in a $CHal_4$–benzene complex from its value in a free $CHal_4$ molecule: $\Delta q_{Hal_l}^{complex,eq} = q_{Hal_l}^{complex,eq} - q_0^{Hal}$ (in atomic units: −1·000 is the charge of an electron).

Table 2. Point charges and numbers of phenyl π electrons in various tetrahalomethane–arene (C_6H_5X) complexes

X	Method	$\bar{\alpha}$[a]	Δn_e^{π} [b]	$q_{Br_l}^{complex,eq}$ [c]	$\Delta q_{Br_l}^{complex,eq}$ [d]	d_{eq}(Br_l–ring centre)[e]
NO_2	AM1	129·2	−0·03	+0·097	−0·004	4·58
	PM3		−0·03	+0·042	−0·030	4·86
Cl	AM1	122·5	+0·04	+0·109	+0·008	4·18
	PM3		+0·04	+0·102	+0·030	4·35
H	AM1	103·2	0·00	+0·113	+0·012	4·08
	PM3		0·00	+0·106	+0·034	4·25
CH_3	AM1	122·6	+0·02	+0·114	+0·013	4·08
	PM3		+0·02	+0·108	+0·036	4·25
NH_2	AM1	—	+0·16	+0·119	+0·018	3·98
	PM3		+0·17	+0·114	+0·042	4·15

[a] Mean polarizability of C_6H_5X, in 10^{-25} cm^3; from Ref. 24.
[b] Deviation of the number of π electrons of the C_6H_5 moiety from the value of benzene (6·00 π electrons).
[c] Calculated point charge on the Br_l atom directed at the ring centre (cf. Table 1, footnote i).
[d] Deviation of $q_{Br_l}^{complex,eq}$ from the value found for a free CBr_4 molecule (cf. Table 1, footnote j).
[e] Equilibrium distance (in Å) between Br_l and the ring centre.

in the relative stabilities are very similar: in the case of CF_4 there is no minimum in the potential energy, suggesting a highly repulsive interaction between the Hal$_l$ atom (i.e. the one closest to the ring centre) and the π electrons of the ring. In contrast, a shallow minimum shows up in the potential energy curve for the CCl_4–benzene complex [d_{eq} = 4·14 (AM1), 4·75 Å (PM3); $\Delta\Delta H_f^{eq}$ = −0·196 (AM1), −0·104 kcal mol^{-1} (PM3)]. The CBr_4–benzene complex is more stable, with even closer agreement of the results from PM3 and AM1 [d_{eq} = 4·08 (AM1), 4·25 Å (PM3); $\Delta\Delta H_f^{eq}$ = −0·392 (AM1), −0·348 kcal mol^{-1} (PM3)]. Closer inspection of Figure 2 reveals that the intermolecular potentials obtained by PM3 are more repulsive at shorter distances than those from AM1, a fact which was pointed out by Messinger and Buss[12] in a study of TCNE–arene complexes.

The results of the calculations tie in very well with Hanna's analysis of the 'no-overlap' interactions in weak EDA complexes.[3] The absence of dispersion interaction greatly facilitates the interpretation of the data, since the rationalization of the attractive interactions in terms of electrostatic multipole–induced dipole and multipole–multipole interactions will be much more straightforward. Analysis of the charge distribution in the complexes (carried out for all intermolecular distances; cf. Figure 2) shows that no charge transfer occurs in their ground states (a dipole moment normal to the phenyl ring indicates the existence of a CT interaction[18]). The multipole–multipole interaction depends on the (permanent) charge distribution in the constituent molecules, and can be attractive or repulsive. In the present case this type of interaction would occur between the π electrons of the ring and the Hal_1 atom next to it. Table 1 shows that the point charge on the F atoms in CF_4 is highly negative – a fact which would explain the distinctly repulsive potential in Figure 2. On the other hand, the multipole–induced dipole interaction is always attractive and should help to reduce the repulsiveness of the potential. However, the data in Table 1 show that, in spite of the attractive induction interactions, there is still a negative charge on the F_1 atom, and, what is more, that this charge is hardly influenced by the benzene ring – a fact which is attributable to the very low polarizability of CF_4. By contrast, in CCl_4 there is only a small negative (AM1, $-0{\cdot}008$), or even a slightly positive (PM3, $+0{\cdot}055$), charge on the Cl atoms, leading to an only slightly repulsive, or even an attractive, interaction between the benzene π electrons and the Cl_1 atom in the complex. The attractive effect is further enhanced by the induction interaction: in the complex the charge on the Cl_1 atom is more positive than in a free CCl_4 molecule and, as the variation $\Delta q_{Hal_1}^{complex,eq}$ of the charge on the Hal_1 atom in the complex at the equilibrium distance d_{eq} shows, the effect is much more pronounced than in CF_4, owing to the significantly higher polarizability of CCl_4. This effect is even more marked in the case of the CBr_4–benzene complex. The attractive interaction between the π electrons and the positively charged [$+0{\cdot}101$ (AM1), $+0{\cdot}072$ (PM3)] Br_1 atom is further strengthened by the induction interaction [$q_{Br_1}^{complex,eq} = +0{\cdot}113$ (AM1), $+0{\cdot}106$ (PM3)], which is stronger than in CCl_4 or CF_4, because CBr_4 has the highest polarizability of the three tetrahalomethanes.

As mentioned above, inclusion of dispersion interaction would render this trend even more marked, since also the vdW forces are governed by the polarizability of the constituent molecules.

CBr_4–arene EDA complexes

In a second series of calculations, we investigated the dependence of the intermolecular potential in CBr_4–arene EDA complexes on the type of aromatic donor, in particular on the π electron density of the phenyl group. To that end, we studied the electron-releasing, or -withdrawing, character of a number of substituents, and the resulting variation of the positive point charge on the Br_1 atom next to the ring centre.

The term 'electron-releasing or -withdrawing group' is a useful concept in organic chemistry and serves as a qualitative measure of the reactivity of a given aromatic compound in electrophilic and nucleophilic aromatic substitution reactions. The reaction mechanism of the electrophilic aromatic substitution is generally believed to involve the initial formation of a 'π complex', i.e. a loose association of the electrophile (e.g. Br_2) and the phenyl ring. Several types of complexes are discussed in the literature,[18,19] and x-ray studies established the 'axial' or 'centrosymmetric' form to be extant in the crystals of the benzene complexes with Cl_2 and Br_2.[20,21] This 'axial' form is identical with the intermolecular orientation discussed in this paper.

In order to be able to assess the (π) electron-'releasing or -withdrawing' character of the substituents in more quantitative terms, we calculated the number of electrons contained in the π system of a given aromatic donor by adding up the atomic orbital electron populations of the carbon p_z orbitals. The deviation Δn_c^{π} from the value for benzene ($6{\cdot}00$ π electrons) of the number of π electrons of the C_6H_5 moiety is shown in Table 2. The results tie in well with chemical intuition: the NO_2 group is found to be electron withdrawing, the NH_2 group is established to be strongly π electron releasing. The complex stabilities follow a similar trend (Figure 3); electron-rich arenes form relatively stable complexes, while the π-electron-depleted C_6H_5 moiety in nitrobenzene does not interact attractively with CBr_4. Again, this may be rationalized in terms of electrostatic interactions. In EDA complexes involving electron-rich donors, such as aniline, and CBr_4 both the multipole–multipole and multipole–induced dipole interactions are attractive. In addition, the more electron-rich the donor, the stronger is its inductive effect on the Br_1 atom, as is revealed by the variation of the point charge on the Br_1 atom in each complex (Table 2). The very shallow minimum observed in the case of C_6H_5Cl does seem to run counter to this conjecture; there is, however, a second aspect to be considered: the presence of a substituent with a strongly negative inductive effect may reduce the electron density in the σ skeleton of the phenyl ring so as to counterpoise the effect of a (slightly) enhanced π electron density. Indeed, analysis of the atomic orbital electron populations of those orbitals that form the σ bonds in the C_6H_5 moiety shows that in the case of chlorobenzene and nitrobenzene the σ electron density, in particular on the $(CH)_2$–$(CH)_6$ atomic groups, is drastically reduced {C_6H_5Cl: $\Delta n_c^{\sigma}[(CH)_{2-6}] = -0{\cdot}071$ (AM1), $-0{\cdot}054$ (PM3); $C_6H_5NO_2$: $\Delta n_c^{\sigma}[(CH)_{2-6}] = -0{\cdot}116$ (AM1), $-0{\cdot}108$ (PM3)}; in other words, these molecules are 'σ dipoles,' with the positive charge centred in a region close to the C_{2-6} atoms. In the case of C_6H_5Cl this effect is not strong enough to offset completely the enhanced π electron density (it should be noted that the interaction between an aromatic donor and a bromine atom is mainly of the $d\pi$–$a\sigma$ type); with nitrobenzene the inductive effect of the NO_2 group is so pronounced that the charge on the ring is indeed a positive one [the point charge on the Br_1 atom is, in fact, diminished by the presence of the nitrobenzene molecule, $\Delta q_{Br_1}^{complex,eq} = -0{\cdot}004$ (AM1), $-0{\cdot}030$ (PM3), indicating the existence of a positive charge on the phenyl ring].

As already mentioned in the Introduction, inclusion of dispersion interaction would lead to a shift of all the potential energy curves in Figure 3 to lower energies by an equal amount, since the polarizabilities of all aromatic systems investigated in this work are of the same order of magnitude (cf. Table 2). They would not help explain the preferred formation of certain EDA complexes based on tetrahalomethanes and aromatic compounds. For instance, the *p*-xylene–CBr_4 complex is a solid at room temperature, whereas a 1:1 mixture of CBr_4 and toluene is a liquid at 305 K (of course, packing effects may contribute to this observation). Neglect of dispersion terms may explain the discrepancy in the equilibrium distances obtained by AM1 and PM3 (*ca* 4·0–4·1 Å) and the experimental values for the *p*-xylene–CBr_4 complex (crystal structure, 3·35 Å[7]) and the liquid-phase toluene–CBr_4 complex (3·54 Å[6]).

Analysis of the charge distribution normal to the phenyl ring (carried out for all intermolecular distances; cf. Figure 3) indicates that no charge transfer occurs in the ground state of any of the complexes investigated.

CONCLUSIONS

This study provides evidence for the existence of weak attractive non-dispersion interactions in some tetrahalomethane–arene complexes. The observed trends can be rationalized in terms of multipole–multipole and multipole–induced dipole interactions, as originally suggested by Hanna.[3] The results indicate the absence of charge transfer in the ground states of these complexes.

ACKNOWLEDGEMENTS

The authors thank the Stipendienfonds des Verbandes der chemischen Industrie for generous support of this work.

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