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PAPER

Controlling the action of chlorine radical: from lab to environment†‡

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The strength of Bz—Cl$^•$ complexation has been explored using density functional theory (DFT) calculations, including dispersion-corrected (DFT-D) calculations. Of the methods tested, the ωB97X-D method seems the best performing, along with the previously tested MPW1K method. The effect of substituent (X = NO_2, F, Cl, Br, H, CH_3, OCH_3, OH, NH_2 and $N(CH_3)_2$) on the stabilities of the Ar—Cl$^•$ π-like intermediates show a good correlation with the linear free energy relationships used experimentally, but this is not the case for Ar—Cl$^•$ σ-complexes, suggesting the transition state of abstraction as being π-like in nature. The role of PAH and lignin derivatives in mediating chlorination reactions in nature is explored. Stable π-complexes were identified for lignin derivatives, indicating humic substances may mediate chlorine atom reactivity at the marine boundary layer, in addition to forming chlorolignins.

Introduction

Chlorine atom is being increasingly recognised as a significant contributor to a number of environmental systems, particularly those located at the marine boundary layer,[1] where the conversion of chloride to chlorine radical may occur through a number of mechanisms.[2] At tropospheric levels, concentrations of up to 7×10^5 molecules per cm^3 are expected to be generated.[3] Chlorine radicals are highly reactive towards organic molecules, being more reactive than hydroxyl radicals in hydrogen abstraction reactions,[4] and thus have the potential to direct oxidation events in the environment.

Substrates for oxidation may arise from a number of sources, both natural and manufactured. They may be present as volatile compounds, particulates from dust, pollutants and as the by-products of vegetative decay, implying a reasonable level of many varied types of precursor (both alkyl and aryl) with potential for participation in hydrogen abstraction and halogenation reactions. A significant amount of detailed kinetic work has gone into establishing the rates of chlorinations of simple hydrocarbons, reflecting the importance of these reactions in, especially, the atmosphere and the environment at large.[5] Reactions of chlorine atom with aryl derivatives, which contribute to the production of chlorinated aromatics, are regarded as important models both for $^•$OH-mediated loss of benzene-derivatives in the troposphere and in terms of reactions involving pollutants at the marine boundary layer.[6]

Aromatic derivatives have the potential to alter the outcomes of reactions involving chlorine by changing the selectivity of the atom abstraction step. This was first realised in the context of solvent effects as early as the mid 1950s by Russell,[7–10] and understanding the detailed mechanism by which this is achieved has been an active area for the last 50 years.[6,11,12–17] The selectivity of chlorine-mediated atom abstraction reactions can be controlled through complexation of the radical through either a π- or σ-complex (Fig. 1).[16] The reactivity of the chlorine atom is reduced relative to that of the free species by reducing the electron demand of the reactive intermediate. In the environment this has relevance in identifying different hydrogen abstraction products and pathways and will play a particular role in systems where there is a relatively high local concentration of aromatics, such as areas rich in humic substances and under conditions of pollutant release.

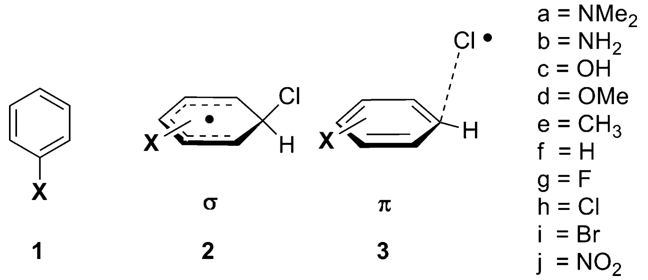

Fig. 1 Structures of the aromatics **1a–j** and complexes **2a–j** and **3a–j** described in this work.

Early experimental studies by Russell,[7–9] and later by Aver'yanov *et al.*,[18,19] indicate a strong electronic basis for the mediation of the selectivity of hydrogen abstraction by aromatics, with

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† Dedicated to the memory of Athel Beckwith.

‡ Electronic supplementary information (ESI) available: Structures of calculated complexes and corresponding starting materials are available as G09 archive entries in the supplementary information along with the correlations of data for compounds **1a–j,2a–j** and **3a–j**. See DOI: 10.1039/c1ob00001b

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Table 1 Stabilisation energies calculated for the η_1-σ (**2f**) and η_1-π (**3f**) complexes of benzene with chlorine, taken as the difference between the calculated energy of the complex and the calculated energies of the components at infinite separation. Counterpoise corrections have not been included

DFT-D method	Stabilisation energy σ complex **2f** (kJ mol^{-1})	Stabilisation energy π complex **3f** (kJ mol^{-1})
BLYP-D/6 31+G(d,p)	37.5	21.1
BLYP-D/aug cc pVTZ	38.3	21.4
CAM-B3LYP/6 31+G(d,p)	25.2	28.6
CAM-B3LYP/aug cc pVTZ	25.8	27.7
M06-2X/6 31+G(d,p)	28.4	31.6
M06-2X/aug cc pVTZ	31.6	31.7
ωB97X-D/6 31+G(d,p)	35.6	35.2
ωB97X-D/aug cc pVTZ	37.5	34.5
ωPBE-D/6 31+G(d,p)	38.4	—
ωPBE-D/aug cc pVTZ	41.1	—
G3X(MP2,ωB97X-D) RAD[a]	37.3	28.7
G3X(MP2,M06-2X) RAD[a]	38.1	30.4
G3X(MP2,ωPBE-D) RAD[a]	37.6	—
G3X(MP2,MPWB1K) RAD[b]	37.0	29.0
G3X(MP2,MPW1K) RAD[b]	36.1	29.0

[a] G3X(MP2)-RAD theory modified in the same style as previous.[26] [b] Modified G3X(MP2)-RAD theory used previously as benchmark values.[26]

electron poor aromatics, such as nitrobenzene, having less impact on selectivity than electron rich aromatics, such as anisole. In the last few years, electronic structure calculations have become feasible for the reliable calculation of the structures and energies of chlorine-aromatic complexes. Whilst early calculations concentrated on *ab initio* methodology,[15,20] work by Radom and co-workers on the general calculation of free radical stabilisation energies indicates that these lower cost, pure *ab initio* methods are not always appropriate.[21,22] Although energetic improvements from DFT can be somewhat unreliable depending on the system examined,[23,24] and should be taken into account, these methods still offer a low computational cost alternative to high level methods and often reasonable geometries,[25] and so should be assessed for systems involving radical complexes. Recently, investigations of the chlorine atom-benzene complex utilising density function theory (DFT) methods have appeared and have been benchmarked against high accuracy methods.[17,26] This opens up the possibility for the detailed theoretical examination of the effect of aromatic substituents on chlorine atom-aromatic complex formation, providing fundamental thermodynamic information. We have examined a range of mono-substituted aromatics with a view to understanding the stereoelectronic factors directing complex formation and the degree to which this might impact on chlorine atom reactivity. The reactions of environmentally-relevant species, such as polycyclic aromatic hydrocarbons (PAHs) and lignin components, are examined and discussed in this context.

Methods

Standard DFT calculations were performed with the Gaussian 03 computational chemistry package[27] and dispersion corrected DFT calculations with Gaussian 09.[28] Geometries were optimised at the specified levels of theory with the int = ultrafine keyword and vibrational frequencies were carried out to verify the nature of the stationary point in each case, with all reported geometries having no imaginary frequencies. All calculations of open shell species were carried out unrestricted unless otherwise specified in the text. URCCSD(T) calculations were carried out with Molpro v2010.1.[29] Where a number of conformers were possible, these were calculated and the lowest energy conformer used.

Those calculations referred to in the text as being calculated at 'infinite separation' have been computed as two separate entities. For the π-complexes, where counterpoise-corrected energies were calculated for DFT structures, the Gaussian counterpoise keyword was used. Zero point energies were scaled using literature scale factors for MPW1K/6-31+G(d,p) (0.949),[30] and M06-2X/6-31+G(d,p) (0.967).[30] All other zero point energies were left unscaled. G3X(MP2,method)-RAD results (Table 1) were generated by the G3X(MP2)-RAD procedure, carried out as described by Radom *et al.*[31] with the exception that the appropriate DFT geometry, using a 6-31+G(d,p) basis set, was substituted for the standard B3LYP/6-31G(2df,p) geometry and scaled ZPE. Scaled ZPEs were used for the MPW methods as above, with all others left unscaled. The standard higher level corrections (HLCs) for G3X(MP2)-RAD were not modified and were used as is.

AIM critical points were located from Gaussian wfn files using AIM2000,[32] and this package was used also to construct the molecular graphs. Density and Laplacian maps were prepared using XAim.[33]

Results and discussion

Assessment of DFT-D and related methods

Chlorine atom-aromatic complexes are known to act as atom abstraction agents that are more selective in their reactions than free chlorine atom.[7] Two potential forms of this complex have been identified, namely a π-complex and a σ-complex, and there is significant literature devoted to the importance of these forms in chlorination reactions.[12–15,17,20,34] From experimental work, no general consensus as to the exact nature of the abstracting complex has been come to, although there is only likely to be a single species acting as an atom-abstracting agent.[13] With the advent of sufficient computational resource, and new methods with the potential for high accuracy, it is possible to examine the thermodynamics of potential complexes at the molecular level. Previous work within our group[26] has established that the MPW1K method

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affords suitable complexation energies for the chlorine-benzene complex, which are consistent with composite high-accuracy calculations, such as those carried out with the G3X(MP2)-RAD[31] and CBS-RAD methods.[21] These latter methods have been especially developed for free radical calculations, as the treatment of open-shell systems can often be complicated by spin contamination. In particular, G3X(MP2)-RAD has recently been confirmed as a suitable method for radical reactions involving chlorine atom, having comparable performance to the much more computationally expensive W1′ method.[35]

Since our last work was published, there have been a number of attempts to develop functionals that account for dispersion interactions, a notable failing of traditional density functional theory methods.[36] These methods are generally known as DFT-D methods and may include empirical corrections to appropriately simulate dispersion effects. Dispersion interactions are especially important for the accurate calculation of complexes. Thus we report here a reassessment of the chlorine-benzene complex using a selection of readily accessible DFT-D methods, and one coulomb-attenuated method, in an attempt to benchmark these for future use with radical complexes. These methods were selected based both on their ready availability in the G09 suite of programmes, and their recent good performance in a benchmarking assessment looking at the accuracy of newer DFT methods in reproducing a range of non-covalent interactions.[37] The results of our calculations for both the η_1-π and η_1-σ benzene-chlorine complexes are presented in Table 1.

The η_1-π complex was identified for each method except ωPBE-D, and was characterised by a C–Cl bond-length between 2.50 and 2.55 Å (Table 2). This is a much more consistent range than was seen previously,[26] where the bond-length values ranged from 2.35–2.57 Å. The lack of a π-solution for the ωPBE-D method is consistent with the failure of PBE to find this minimum in our previous study. The η_1-σ complex was identified for all methods. The C–Cl bond-length for this complex was between 1.83 and 1.93 Å. The structural change between optimisations carried out at the 6-31+G(d,p) and aug-cc-pVTZ basis sets is minimal and is reflected by a minor variation (<0.2 kJmol^{-1}) in aug-cc-pVTZ single point energies taken with each optimised structure. Therefore, the smaller basis set appears perfectly adequate for obtaining consistent geometries for higher-accuracy calculations.

To confirm that the geometries obtained by the tested DFT-D methods were consistent with our previous calculations, the appropriate structures and unscaled zero-point energies were substituted into the G3X(MP2)-RAD procedures in place of those obtained from B3LYP/6-31(2df,p). This process is analogous to the benchmarking process used with the MPW-based calculations from our previous paper.[26] We selected five structures to best represent the range exhibited by our calculations: ωPBE-D σ, M06-2X σ and π, and ωB97X-D σ and π structures. The energies show good agreement with the previous results obtained using the MPW methods, indicating there is little difference in the structures obtained using these methods and that it is likely the potential surface is fairly flat around these minima.

The DFT-D methods all show variability with respect to the benchmark energies using the G3X(MP2)-RAD method, although they are relatively consistent between the small and large basis sets with generally <1 kJ mol^{-1} difference. The M06-2X and CAM-B3LYP both fail to predict the correct relative energetics, with both affording the π-complex as more stable than the σ-complex. This is despite the good agreement of the π-complex energies with the benchmark of <±3 kJ mol^{-1} in each case for both basis sets. The BLYP-D method predicts the σ-complex stabilisation well, but significantly underestimates the stability of the π-complex. Conversely, the ωB97X-D method overestimates the stability of the π-complex, although the absolute difference is less and the match with the experimental value of 30–35 kJ mol^{-1} is reasonable.[14,20,38] This method also has reasonable agreement with the predicted stability of the σ-complex, but the difference in energies between the two complexes is negligible, making it difficult to distinguish between the experimentally-active species by energies alone. The general variability in energies of the DFT methods, relative to the G3(MP2)-RAD benchmark, may be attributed to different levels of DFT exchange. This contribution has been shown to have a significant effect on the calculated energies for differently substituted derivatives of radicals, cations, anions and neutrals.[23] This hypothesis would be consistent with the remarkably poor performance of the pure functional PBE, and the relatively good performance of previously examined MPW1K.

The ωB97X-D method appears to be the best performing of the currently assessed DFT-D methods. Although improved structures might be obtained using other examined methods, as judged by the modified G3X(MP2,DFT-D)-RAD energies, the difference is not substantial and ωB97X-D seems to provide a good compromise. Best performance energetically appears to be with a larger basis set for this method, although the 6-31+G(d,p) basis set is adequate for structure. In comparison, the previously recommended MPW1K/6-31+G(d,p) appears, for this particular $Cl^{\bullet}$-benzene system, to be the best performer in terms of match with the G3X(MP2)-RAD benchmark.

Table 2 Key geometric parameters for the σ and π complexes optimised with the aug-cc-pVTZ basis set

	DFT-D method	Cl–C_1 bond distance	Cl–C_1–C_4 bond angle	H_1–C_1–C_4 bond angle
σ	BLYP-D	1.835	123.4	135.0
	CAM-B3LYP	1.926	118.8	142.7
	M06-2X	1.917	117.4	143.7
	ωB97X-D	1.909	119.0	141.7
	ωPBE-D	1.834	123.4	134.8
π	BLYP-D	2.451	102.2	172.8
	CAM-B3LYP	2.502	103.4	172.7
	M06-2X	2.446	101.2	172.7
	ωB97X-D	2.503	102.0	172.9

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AIM characterisation of Ar-Cl$^•$ complexes

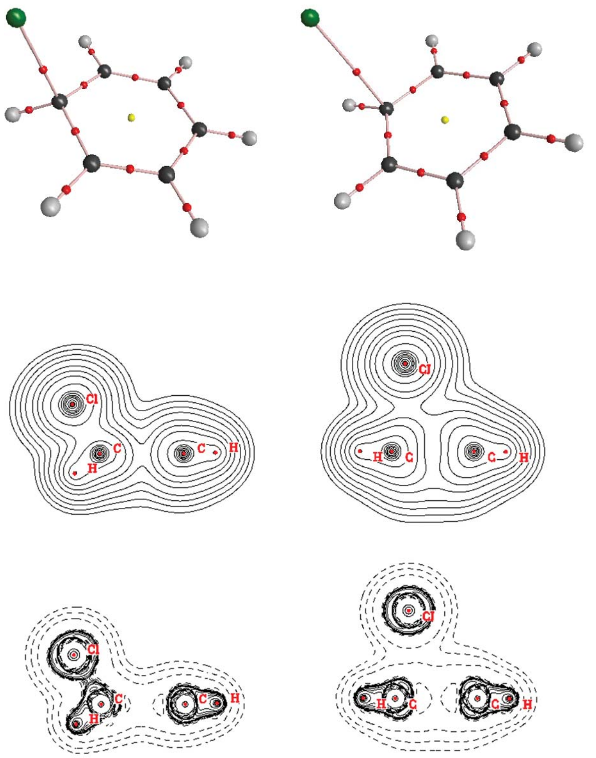
Atoms-in-molecules analysis of the wavefunctions of molecules can give very detailed information on the bonding patterns and classification of bonds within a structure.[39] As such, the wavefunctions for each method using the aug-cc-pVTZ basis set were analysed. For both the η_1-π and η_1-σ complexes, a bond, as defined by a (-3,-1) critical point linking two nuclei, was identified. Examples of the molecular graphs, contour maps and Laplacians for each complex are shown in Fig. 2, and they were qualitatively the same for all DFT-D methods examined.

The contour plots of the density and Laplacian (Fig. 1) are clearly distinct between σ and π complexes and these differences are reflected in the calculated ρ-values for the density at the critical point. The σ complexes afforded values of 0.164 e bohr^{-3} for the ωPBE and BLYP-D functionals and 0.133–0.138 e bohr^{-3} for the other methods. The π complexes were characterised by ρ values of 0.042 e bohr^{-3} and 0.043 e bohr^{-3} for the BLYP-D and M06-2X methods, respectively and 0.038 e bohr^{-3} for both ωB97X-D and CAM-B3LYP. These variations in ρ-values correspond with the overall C–Cl bond distances for the optimised structures.

Substituted aromatics and reactivity

Substitution of aromatics can influence the strength of the aromatic-chlorine complex, as has been inferred from chlorination profiles in radical chlorination reactions.[8,19] More electron-rich aromatics lead to greater selectivity for tertiary abstraction over primary,[8,19] indicating either a greater role of the reactive chlorine-aromatic complex in these reactions, a stronger complex, or both. To probe the role of both the σ and π complexes further, structures and stabilisation energies were obtained for complexes **2a–j** and **3a–j** with a range of substituents spanning the electronic spectrum, and are listed in Table 3.

At standard temperature and pressure, the free energy of the complexes indicates spontaneous formation of a σ-complex, including the *para* σ-complex for all electron-deficient aromatics **1g–j**, although it is noted that the free energy of stabilisation is small (2.4–7.0 kJmol^{-1}) (Table 4). The formation of a complex is consistent with experimental data, where all aromatics are seen to stabilise chlorine radical above non-complexing solvents to some extent. For electron-rich aromatics (**1a–e**), π-complexes were generally either more stable (**1a**) or had comparable stablility, relative to the corresponding σ-complexes, and both should contribute to the reactive species pool in these cases.



2f **3f**

Fig. 2 AIM analysis of the benzene-Cl complexes σ **2f** (left) and π **3f** (right). In each case a bond is confirmed by the bond critical point between the chlorine and the carbon of the ring, confirming a η_1-complex (top). The electron density ρ shows density between the chlorine and the ring (centre). The Laplacian of the electron density indicates the type of bond in each case (bottom).

Table 3 Stabilisation energies calculated at MPW1K/6-31+G(d,p) for the η_1-π and η_1-σ complexes of substituted benzenes **1a–1j** with chlorine, taken as the difference between the calculated energy of the complex and the calculated energies of the components at infinite separation. These values are presented in graphical form for **1a,1b** and **1d–j** in Fig. S1 (ESI‡)

	Stabilisation energy MPW1K/6-31+G(d,p) (kJ mol^{-1})					
	ortho		*meta*		*para*	
Arene	σ-complex **2**	π-complex† **3**	σ-complex **2**	π-complex† **3**	σ-complex **2**	π-complex† **3**
1a	—	60.6	59.0	—	—	55.0
1b	58.0	54.3	33.9	—	—	50.7
1c	46.6	42.0	30.9	—	40.2	37.7
1d	44.5	37.1	28.6	—	41.1	39.5
1e	42.6	34.9	36.6	27.7	39.8	32.3
1f^a	35.6	26.5	35.6	26.5	35.6	26.5
1g	32.0	22.8	31.5	20.5	33.4	27.5
1h	34.2	22.0	31.3	20.2	36.6	25.7
1i	36.9	21.5	32.9	20.2	38.1	25.4
1j	30.5	11.8	25.6	15.4	35.6	13.7

†Counterpoise correction included.^{a} For reference. A hyphen indicates this structure was not identified in this study.

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Table 4 Free energies for gas-phase complex formation calculated at MPW1K/6-31+G(d,p) for the η_1-π and η_1-σ complexes of substituted benzenes **1a–1j** with chlorine. Consistent with Tables 1 and 3, positive values indicate that the complex is favoured at 298 K, whereas negative values indicate complex formation is disfavoured

	Gibbs Free Energy MPW1K/6-31+G(d,p)[§] (kJ mol^{-1})					
	ortho		*meta*		*para*	
Arene	σ-complex **2**	π-complex **3**	σ-complex **2**	π-complex **3**	σ-complex **2**	π-complex **3**
1a	—	32.3	3.9	—	—	28.6
1b	25.5	26.4	3.6	—	—	23.3
1c	15.2	14.8	0.8	—	9.3	10.3
1d	12.8	9.8	—1.0	—	10.4	12.1
1e	8.0	5.1	3.6	0.7	8.6	5.2
1f[a]			4.5	0.0		
1g	0.5	–4.0	0.8	–4.1	2.4	0.7
1h	2.5	–4.9	0.7	–5.2	5.5	–0.9
1i	5.4	–2.3	2.3	–3.9	7.0	–0.1
1j	–2.1	–12.0	–4.8	–10.5	4.3	–11.7

[§]Calculated at STP.[a] For reference. A hyphen indicates this structure was not identified in this study.

Table 5 Stabilisation energies calculated at ωB97X-D/6-31+G(d,p) for the η_1-π and η_1-σ complexes of substituted benzenes **1a–1j** with chlorine

	Stabilisation energy ωB97X-D/6-31+G(d,p) (kJ mol^{-1})					
Arene	*ortho* σ-complex **2**	*meta* π-complex† **3**	*para* σ-complex **2**	π-complex† **3**	σ-complex **2**	π-complex† **3**
1a	—	76.6	37.7	—	—	64.9
1b	—	66.1	35.7	—	—	60.4
1c	—	52.0	32.1	—	—	47.2
1d	47.7	48.3	30.5	—	—	49.6
1e	44.3	44.5	37.9	37.6	40.8	41.1
1f[a]	35.6	35.2	35.6	35.2	35.6	35.2
1g	32.9	32.3	32.0	—	34.8	36.6
1h	34.8	31.4	31.8	—	37.1	34.2
1i	37.9	34.8	33.5	31.4	38.7	35.0
1j	32.0	—	26.1	25.1	35.1	22.6

[a] For reference. A hyphen indicates this structure was not identified in this study.

Comparison of the stabilisation data obtained with MPW1K with the best performing method tested in this study, ωB97X-D, using both the affordable 6-31+G(d,p) (Table 5) and the larger 6-311+G(3df,2p) (Table S1) basis sets, shows that general trends are preserved. Both basis sets afford larger stabilisation energies than MPW1K/6-31+G(d,p) for both σ and π species, with this difference being most apparent for electron-rich complexes. The larger basis set emphasises the difference between the energies of similarly localised complexes, consistent with the results seen between basis sets for the benzene complex. Some complexes were not identified, and this is attributed to relatively more shallow minima for these structures.

Although many of these solvents can be regarded as "non-innocent", *i.e.* they undergo reaction themselves with chlorine atom to afford chloro-benzene products,[6,15,40] they clearly are able to mediate the outcome of chlorination of aliphatic systems prior to their consumption. Aver'yanov and co-workers[19] have demonstrated a correlation of the experimental abstraction rates with Swain-Lupton R constants,[41] in addition to correlation with the HOMO energies of the corresponding aryl **1**. Calculated values for the HOMO energies using both the MPW1K and ωB97X-D methods are presented in Table 6. Comparison with experimentally-derived ionisation energy (IE) values shows a much better absolute correspondence with the ωB97X-D calculated values, however both methods appear internally consistent.

The difference in complexation energy between the substituted complexes (denoted E_1) and that of either **2f** in the σ-series or **3f** in the π-series (E_0) can be used to interpret the nature of the transition state, because of the relationship of the energies of the reactive intermediates to those of the corresponding transition states through Hammond's postulate. The reactive geometry leading to the transition state could be conceived in a number of ways; either as related to the most stable complex, a weighted average of the complexes around the ring, or in terms of a single complex, such as the *para*-complex. Regardless of which of these variations was selected (see ESI‡), the relative difference in energy between the substituted and unsubstituted complexes *i.e.* E_1-E_0 showed a significantly better correlation with the Swain-Lupton R constants (R^2 = 0.94-0.96) and both experimental (R^2 = 0.94–0.96) or calculated (R^2 = 0.94–0.96) HOMO energies, than the sigma complex (R^2 = 0.79–0.83, 0.85–0.87, and 0.81–0.83, respectively). This suggests that a loose, π-like complex better describes the nature of the transition state, based on the experimental data, than the σ-complex. This is consistent with the Swain-Lupton *R* constant accounting for 'resonance' effects, rather than through-bond field effects. The implication therefore is that the active

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Table 6 HOMO energies calculated with both MPW1K and ωB97X-D for substituted benzenes **1a–1j**, compared to experimental ionisation energy values

Arene	MPW1K Calculated HOMO (eV)	ωB97X-D Calculated HOMO (eV)	Experimental IE (eV)[a]
1a	−6.24	−7.21	7.12
1b	−6.66	−7.64	7.72
1c	−7.29	−8.28	8.49
1d	−7.15	−8.12	8.20
1e	−7.63	−8.66	8.83
1f	−7.99	−8.94	9.24
1g	−7.99	−8.98	9.20
1h	−7.92	−8.93	9.07
1i	−7.82	−8.81	9.00
1j	−8.89	−9.91	9.94

[a] Evaluated NIST database value (http://webbook.nist.gov/chemistry, S. G. Lias).

abstracting species in chlorination reactions is also the π-complex, although this may be reached from the σ-complex in a two stage process, due to the low barrier of interconversion. Further calculations in this area are ongoing within our group to clarify this.

It is worth noting that one of the outliers for the π-complexes is that of phenol **3c**, which appears more stable than the correlations would suggest. Here, and in the σ-complex **2c**, the *ortho* complex appears to be stabilised by a specific hydrogen-bonding interaction between the phenolic OH and the Cl atom, as indicated by the upward tilt of the H, away from the plane of the aromatic ring (26° for the σ-complex **2c** and 25° for the π-complex **3c**). The lack of a bonding interaction was confirmed by AIM analysis, which fails to show a ring critical point for the aromatic-OH-Cl-aromatic cycle or a bond critical point between the phenolic hydrogen and chlorine atom (Fig. 3).

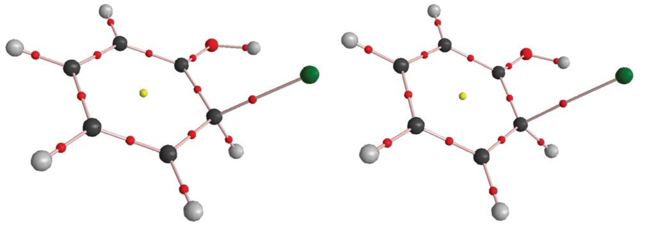

Fig. 3 AIM molecular graph for the chlorine σ-complex **2c** (left) and π-complex **3c** (right) at the position *ortho* to the phenolic OH, calculated with the ωB97X-D/aug-cc-pVTZ//MPW1K/6-31+G(d,p) method. The lack of ring critical point and bond critical point confirm that the deviation of the OH bond from planarity with the ring is a not due to a bonding interaction.

This lack of bond critical points suggests that the deviation from planarity, whilst not due to hydrogen bonding, may be due to electrostatic attraction, since this deviation is not seen in the corresponding *para* complexes, where alignment of the lone pair would also be expected to be important. Electrostatic surface potential (ESP) maps confirm that an electrostatic interaction is likely (see Fig. S2 in the ESI‡).

Complexes of potential environmental significance

Nature is an important source of organochlorines.[42] There are a number of aromatic species produced both naturally and anthropogenically that may interact with naturally produced chlorine atom.

Polycyclic aromatic hydrocarbons (PAHs) constitute a major source of atmospheric pollution and the chlorinated products can be toxic. Reaction with chlorine is a known pathway,[43] and these molecules could potentially interact with chlorine atoms to form π-complexes that may mediate the outcome of other atmospheric reactions. Some examples of PAHs include naphthalene **4**, anthracene **5**, acenaphthylene **6**, phenanthrene **7**, fluoranthene **8**, benz[a]anthracene **9**, pyrene **10** and chrysene **11** (Fig. 4).

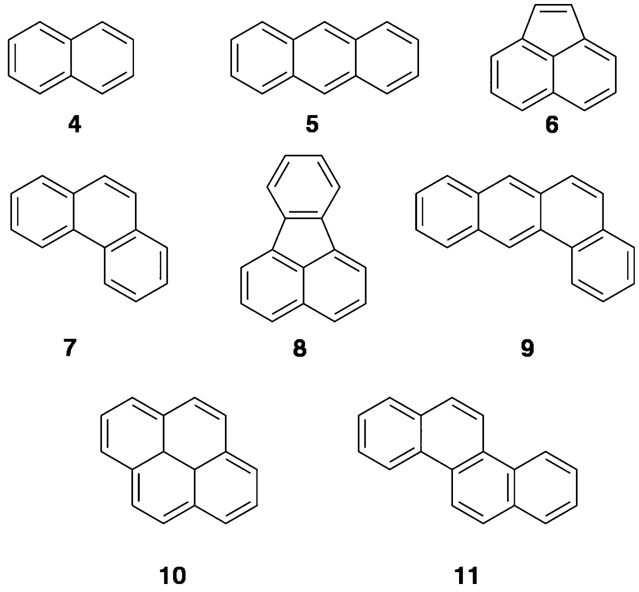

Fig. 4 PAHs **4–11** examined in this work.

The range of calculated HOMO energies exhibited by a selection of common PAH molecules **4–11**, obtained at both MPW1K/6-31+G(d,p) and ωB97X-D/6-31+G(d,p), is within the range of the corresponding HOMO energies obtained for the substituted aromatics **1a–1d**, calculated with the same method (Table 7). As for the substituted aromatics, the ωB97X-D method gives values much closer to the experimental ionisation energies, although both methods are internally consistent and show the same trends. On this basis, it may be anticipated that π-complexes would be favoured at low IP values, as seen for the amino derivative **1a**.

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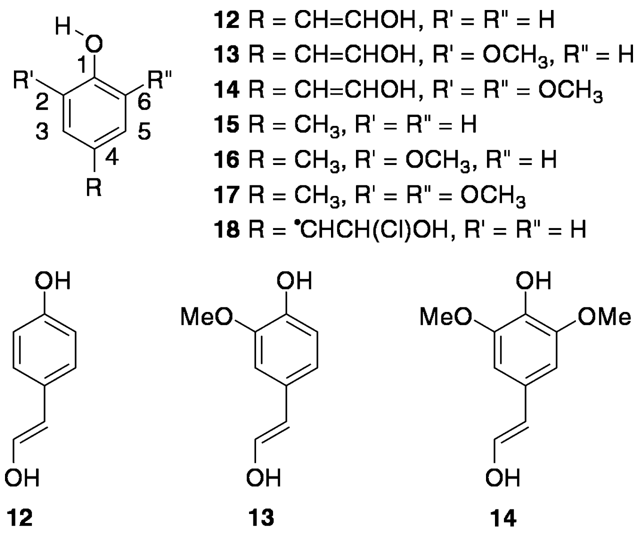
Table 7 HOMO energies for selected PAH molecules **4–11** calculated with both MPW1K and ωB97X-D. The values lie within the ranges calculated for the electron-rich substituted benzenes **1a–1d**

Arene	MPW1K Calculated HOMO (eV)	ωB97X-D Calculated HOMO (eV)	Experimental IE (eV))[a]
4	−6.95	−7.96	8.14
5	−6.30	−7.29	7.44
6	−7.07	−8.12	8.12
7	−6.88	−7.87	7.89
8	−6.89	−7.88	7.9
9	−6.40	−7.39	7.45
10	−6.38	−7.34	7.43
11	−6.63	−7.61	7.60

[a] Evaluated NIST database value (http://webbook.nist.gov/chemistry, S. G. Lias).

Chlorine π-complexes were constructed for naphthalene **4**, anthracene **5** and pyrene **10**, the latter two having the overall lowest calculated HOMO energies, and thus most likely to display a π-complex. The complexes were created at positions on each arene that showed high HOMO density (illustrated in the SI). In all cases, only the σ-complex was identified after optimisation without counterpoise correction, and using both MPW1K and ωB97X-D methods (see SI for details). This suggests that the examined PAHs do not form π-complexes that are relevant in environmental systems and, further, that they are likely to solely react to form chlorine derivatives, as has already been reported in the literature.[43]

Dissolved organic matter (DOM) is found in aqueous systems and consists of solubilised organic compounds derived from decomposing plant matter. These materials are particularly significant at the marine-boundary layer, accounting for over 6.85×10^{17} g C in the ocean.[44] A large component of this matter is humic substances, which are primarily derived from lignins.[45] The structure of lignin is based on polymerisation of a mixture of coumaryl alcohol **12**, coniferyl alcohol **13** and sinapyl alcohol **14** (Fig. 5), with ratios depending on the origin. As such, there are a number of aromatic groups that could potentially mediate the reactivity of chlorine atom formed at the marine-boundary layer.



12 R = CH=CHOH, R' = R" = H
13 R = CH=CHOH, R' = OCH_3, R" = H
14 R = CH=CHOH, R' = R" = OCH_3
15 R = CH_3, R' = R" = H
16 R = CH_3, R' = OCH_3, R" = H
17 R = CH_3, R' = R" = OCH_3
18 R = $^{\bullet}$CHCH(Cl)OH, R' = R" = H

Fig. 5 Structures of model lignin derivatives **12–18**.

Lignin precursors **12–14** and simple models **15–17** afforded both σ– and π-complexes, analogous to those identified for the substituted benzenes. The stability of the complexes at positions C2 (*ortho* (*a*)) and C3 (*meta* (*a*)), where the phenolic hydrogen atom points towards the substituents on this side (as illustrated in Fig. 5), differed from the stability at C6 (*ortho* (*b*)) and C5 (*meta* (*b*)), respectively, indicating an influence of the phenolic OH orientation and, for compounds **12–14**, the orientation of the alkene substituent (Table 8). Under normal circumstances this is expected to average out due to free rotation, however, where there is specific hydrogen bonding that restricts rotation (such as in **13**, or that may be present with external interactions), this is likely to result in preferential complex formation on one side of the molecule.

Reaction with the double bond is predicted for molecules **12–14** and is calculated as exothermic by 123 kJmol^{-1} (at MPW1K/6-31+G(d,p)) to afford the coumaryl product **18**. This is around twice the exothermicity of complex formation, but reaction might be minimised in many circumstances in DOM by steric hinderance. For humic substances where this double bond has already reacted, complex formation becomes a more significant pathway.

The largest difference between σ– and π-complex stability is seen for the coumaryl derivatives **12** and **15**, the least substituted of the lignin models examined. Conversely, π-complexes were identified for the sinapyl models **14** and **17**, and then only the *ipso* and *meta* complexes for both, with the *para* for **17**. The increased stability of *ipso* **14** *vs ipso* **17** can be accounted for in terms of the extra stability afforded by the exocyclic double bond.

The improved relative stability of the σ-complex *vs.* the π-complex for the less substituted derivatives **12** and **15** correlates well with the observation of more chlorinated by-products in the related model systems, relative to more highly-substituted derivatives, and the virtual absence of chlorination for the more highly-substituted compounds.[42]

The ωB97X-D method affords stabilisation energies that are larger than those obtained by MPW1K (Table 9). Concurrently, optimised structures for some of the less stable species identified by MPW1K were not identified when using ωB97X-D. However, the general trends remain broadly similar, in that more electron rich lignin derivatives exhibit larger stabilisation energies; and that *meta* π-complexes are identified for almost all species.

Solvation by water of complexes **12–17** is anticipated to further stabilise π-complexes relative to the corresponding σ-complexes. This is because π-complexes have a larger relative dipole, and thus can interact more favourably with polar solvents. As such,

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Table 8 Stabilisation energies calculated for the η_1-π and η_1-σ complexes of lignin precursors **12–14** and models **15–17** with chlorine. The substitution is designated as follows: *ipso* C1, *ortho* (*a*) C2, *ortho* (*b*) C6, *meta* (*a*) C3, *meta* (*b*) C5 and *para* C4. Calculations were carried out at MPW1K/6-31+G(d,p)

	Stabilisation energy MPW1K/6-31+G(d,p) (kJ mol^{-1})											
	ipso		*ortho* (*a*)		*ortho* (*b*)		*meta* (*a*)		*meta* (*b*)		*para*	
Derivative	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π
12	54.4	45.9	49.4	48.8	43.1	38.5	60.6	—	49.3	42.2	—	39.1
13	—	56.6	—	—	—	—	56.5	55.7	56.7	52.8	—	—
14	—	68.5	—	—	—	—	—	69.6	—	56.9	—	—
15	35.7	—	50.4	48.3	43.4	38.5	44.5	37.1	40.3	34.4	40.8	40.5
16	45.0	—	—	51.0	39.8	38.4	—	46.2	48.1	48.5	47.1	—
17	—	61.8	—	—	—	—	—	60.0	—	56.6	—	49.7

Table 9 Stabilisation energies calculated at ωB97X-D/6-31+G(d,p) for the η_1-π and η_1-σ complexes of lignin precursors **12–14** and models **15–17** with chlorine. The substitution is designated per Table 9

	Stabilisation energy ωB97X-D/6-31+G(d,p) (kJ mol^{-1})											
	ipso		*ortho* (*a*)		*ortho* (*b*)		*meta* (*a*)		*meta* (*b*)		*para*	
Derivative	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π
12	60.3	—	—	65.1	51.0	54.4	68.7	63.7	55.8	56.9	—	58.4
13	—	—	—	72.4	—	—	—	68.7	60.4	62.8	—	—
14	76.2	83.4	—	—	—	—	—	85.4	—	70.9	—	—
15	37.1	—	—	58.9	47.2	49.7	47.1	—	41.9	—	—	53.8
16	—	—	—	67.4	44.8	—	—	59.8	—	59.7	54.0	—
17	—	78.2	—	—	—	—	—	74.9	—	71.5	—	64.3

it can be expected that π-complexation may be favoured at the marine-boundary layer, potentially resulting in an attenuation of the anticipated reactivity of the chlorine radical in this environment.

Conclusions

We have evaluated the performance of five DFT-D methods against the G3X(MP2)-RAD method for the benzene-chlorine atom complex. Of these methods, all appear to provide reasonable geometries, with the exception of the ωPBE-D method, with which we were unable to identify the π-complex. The best reproduction of energies was achieved with ωB97X-D/aug-cc-pVTZ, although this was not as good as the previously identified MPW1K/6-31+G(d,p) for the benzene-chlorine complex. Problems with using DFT functionals to describe systems of this type may originate in the degree of DFT-exchange, so care must be taken when using these methods.[23] It is likely however, that, due to the good performance of the ωB97X-D functional for other species, this method might be practical for more complex systems.

The complex stabilities have been calculated for a range of different substituted aromatics **1a–j**, spanning the range of electronic effects. More electron rich aromatics had π-complexes closer in energy to the corresponding σ-complex and the complex stabilisation for the π-complex correlates well with the HOMO energy and Swain-Lupton R constants. The correspondence of the energetic trends for the π-complexes **3a–j** with the reactive outcomes reported from experimental studies, suggests that these intermediates may reflect the nature of the transition-state species in these reactions.

By extension, simple PAHs **4–11**, with HOMO energies in the same range as the aryl complexes **1a–d**, were expected to afford analogous π-complexes of reasonable stability. In our hands, only σ-complexes were obtained for the examined complexes **4**,**5** and **10**, relating well to the established chlorination products identified in the environment.[43]

In contrast, lignin precursors **12–14** and models **15–17** demonstrated chlorine-atom complex formation, with the π-complex more pronounced in the more electron rich derivatives, to the point where no σ-complex was identified for either **14** or **17**. The stability of the π-complexes may improve in water and other polar solvents due to their increased dipole moment, relative to the corresponding σ-complexes. Such complexes may exist in lignin-rich areas where chlorine radicals are present and these π-complexes have potential to be an important source of mediation of chlorine atom reactivity, for example at the marine boundary layer or in paper-bleaching facilities.

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