A Group Additivity Algorithm for Polychlorinated Dibenzofurans Derived from Selected DFT Analyses

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The difficulty in measuring the heats of combustion of polychlorinated dibenzofurans (PCDFs) has resulted in a shortage of data on their heats of formation, required for the purpose of developing an understanding of the role of thermodynamics and kinetics in their production via industrial processes. B3LYP density functional theory calculations have been carried out on a number of PCDFs using 6-31G(d) and 6-311+G(3df,p) basis sets to estimate their heats of formation based on the known experimental values for dibenzofuran, benzene and chlorobenzene. By examining the interactions among chlorine substituents, it is shown that energy contributions arising from successive chlorination can be interpreted in a predictable way, based on a small number of key energy parameters associated with ring position and chlorine atom repulsions. These parameters have been presented as the basis for a simplified prediction algorithm, which can be used to reproduce the predicted DFT heat of formation to within a few kJ/mol, avoiding the need to carry out extensive DFT calculations on the possible 135 isomers of the dibenzofuran group.

Introduction

Dioxin emission limits for industrial processes, such as iron ore sintering, continue to fall,[1,2] and the underlying formation process becomes more difficult to identify as the formation pathway becomes an increasingly minor part of the complex range of reactions linked to the combustion process. In attempting to determine the manner in which the polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) are formed, it is useful to determine to what extent the thermodynamic equilibrium concentration distribution is approached. This requires the generation of thermodynamic data, which at the same time can be used to construct kinetic data for reversible chemical reactions associated with the formation process. Determination of the heats of formation of chlorinated dioxins and dibenzofurans requires the use of combustion calorimetry using a rotating bomb calorimeter, and there are only a limited number of evaluations available for PCDDs[3−6] and none for PCDFs. Consequently there have been several attempts to derive thermodynamic data for some of the 210 isomers using predictive methods. Unsworth and Dorans[7] and Saito and Fuwa[8] used MOPAC,[9] while other workers have used group additivity methods.[10−13] In view of the approximations involved in the use of MOPAC, and the lack of facility for tracing program-related errors in predictions, the group additivity method, when used with care, is regarded as more reliable. The changes in heat of formation with chlorination and values for parameters used in making adjustments for interaction between chlorine atoms have been estimated for PCDD/Fs by various authors. The basis of the original estimate by Shaub[11] differs from later authors, whose estimates are summarized by Dorofeeva et al.[13] Thermodynamic predictions of the isomer distributions, with degrees of chlorination of dioxins and dibenzofurans, have been carried out using the various sets of thermodynamic data from MOPAC and group additivity in the past,[7,12,14] but they are inconclusive, other than confirming that the amounts formed and predicted do not suggest any particular isomer preference on the grounds of exceptional stability, and the depth to which meaningful comparison of experiment and predictions can be carried out is limited by uncertainties in the thermodynamic data.

It might be expected, in view of the concerns over dioxin formation, that a program of calorimetric measurements of the heats of formation would have been carried out or be in progress. In principle, the difficulties of incomplete combustion can now be minimized by use of modern analytical techniques for product analysis and the use of thermodynamic predictive packages to account for incomplete combustion, but this advance is offset by the cost of safety requirements which would apply to any such procedure. The range of chlorinated compounds which have been examined is small, and when those experiments suspected of inaccuracy are excluded from consideration, the range is still smaller. Such limited data therefore restrict the judgments which can be made to account for energy differences between isomers, in particular, interactions between chlorine substituents and the influence of different substituent positions relative to the oxygen bridge.

It is therefore of considerable interest to note that Lee et al.[15] carried out ab initio calculations for PCDDs which, when converted to group additivity parameters, imply a less stable substitution of chlorine adjacent to the oxygen bridge than at positions remote from the bridge. Application of these data to the hepta-CDDs show relative stabilities which are in agreement with typical published experimental observations. However, the predicted distributions using these group additivity terms do not agree with those for PCDFs,[16] where the 1,2,3,4,6,7,8-isomer

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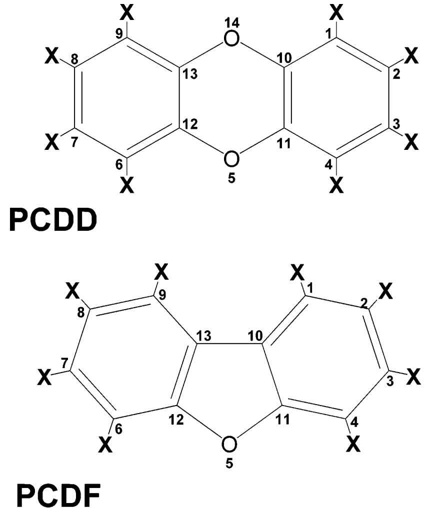


Figure 1. Atom numbering for PCDD and PCDF, where X = chlorine. For X = hydrogen, the species are dibenzo-p-dioxin and dibenzofuran.

is much more abundant than the others. In view of the difficulties in measuring heats of combustion of PCDFs, and the large number of DFT simulations involved in assessing the 135 possible isomers, we have carried out DFT calculations on a number of representative isomers to determine the feasibility of applying a group additivity approach to the whole of the PCDF population. Establishing these thermodynamic parameters is the first step in determining the role of equilibrium or kinetic control in the distribution of these during formation from industrial processes.

Computation Details

The method used in estimating the standard heats of formation of the PCDF molecules described, begins with the calculation of a heat of reaction involving each of the target molecules, and combines this reaction enthalpy with known values for the heats of formation of the other species involved. The heats of reaction are calculated from the vacuum energies of the individual molecules involved in each reaction. Molecular energies are calculated at the ab initio level, using the *Gaussian* code.[17] In each case, the model chemistry used a density functional approach based on the B3LYP functional method.[18,19]

The procedure follows that used by León et al.[20] in the study of PCDDs and employs an isodesmic reaction scheme to minimize systematic errors from the use of code. This requires knowledge of the experimental heats of formation of all of the participating species apart from the PCDF required, and the uncertainties in the values for the more highly chlorinated benzenes precludes their use as reactants and requires a careful choice of reaction scheme.

The experimental measurement of the heat of formation of benzene is unusually well characterized: the error limit given by Pedley[21] of ±0.7 kJ/mol is small. The somewhat larger error limit of the heat of formation of chlorobenzene, ±1.3 kJ/mol is also, nonetheless, small in calorimetric terms and implies reliability.

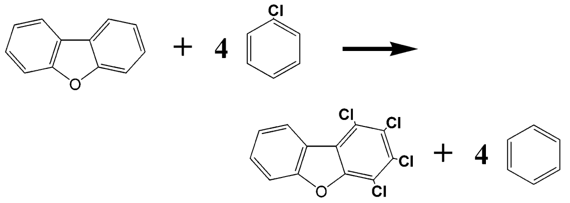
Chirico et al.[22] obtain a standard heat of formation of 55.2 kJ/mol for dibenzofuran. This replaces an earlier value provided by Cass et al.,[23] and in view of the large discrepancy between the earlier value, obtained for comparative purposes, and the more recent evaluation aimed at obtaining an absolute value, the more recent result is preferred. These three species are therefore used as the basis of a reaction scheme in each case.

Conventional atom numbering is used as shown in Figure 1.

The following is an example of the generating reaction used for each of the target molecules considered:

target molecule 1,2,3,4-teCDF

Generating reaction from dibenzofuran (DF), benzene and chlorobenzene:



(1)

By equating the calculated heat of reaction with the known standard heats of formation of reactants and products, i.e.

$$\Delta H_{\mathrm{r}} = \sum_{\text{products}} \Delta H_{\mathrm{f}}^{\mathrm{o}} - \sum_{\text{reactants}} \Delta H_{\mathrm{f}}^{\mathrm{o}}$$

the unknown heat of formation of the target molecule may be deduced. For all of the CDFs considered, predicted heats of formation are based on the published values for dibenzofuran, benzene, and chlorobenzene of 55.2,[22] 82.6,[21] and 52.0[21] kJ/mol respectively.

Each molecule involved in the reaction was subject to calculations at two levels of accuracy. An optimized geometry was first established using a medium basis set (6-31G(d)), which uses energy minimization as the optimization criterion within an SCF framework, and which is recognized as providing a good geometry representation. Single-point energy calculations were then carried out at a higher level of accuracy on the optimized geometry using a larger basis set (6-311+G(3df,p)), and these were used to represent the molecular vacuum energy at 0 K.

The vibrational frequencies available within the software enable the calculation of zero-point energies(ZPE), and the vibrational, rotational, and translational contributions to the overall molar enthalpy at 298 K. ZPE values were scaled by a factor of 0.9804, corresponding to the 6-31G(d)[24] basis set used for frequency calculations.

Each molecular enthalpy is then represented by

$$H(298) = E_{\mathrm{elec}} + E_{\mathrm{zpe}} + E_{\mathrm{vib}}(298) + E_{\mathrm{rot}}(298) + E_{\mathrm{trans}}(298) + RT\ (T = 298)$$

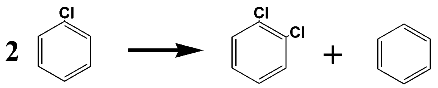
The reaction enthalpy change ΔH_{r} is then calculated from

$$\Delta H_{\mathrm{r}} = \sum_{\text{products}} H_i(298) - \sum_{\text{reactants}} H_j(298)$$

Results and Discussion

Published values for the heat of formation of chlorinated benzenes[20] and PCDDs[15] derived from ab initio calculations show some differences from the results obtained experimentally for chlorination of benzene[25] and those inferred from group additivity considerations for dibenzo-p-dioxins.

In order to show reproducibility with other published work, we have carried out DFT calculations for the heats of chlorination of chlorobenzene to 1,2-, 1,3-, and 1,4-dichlorobenzene based on the reaction scheme shown:



(2)

These results are compared in Table 1 with the values obtained by León et al.[20] and available experimental values.

TABLE 1: Comparison of Calculated Heats of Formation of Dichlorobenzenes (kJ/mol) and Published Results

	experimental		calculated	
compound	Platonov−Simulin	Pedley[21]	this work	León et al[20]
chlorobenzene	54.4[26]	52.0		
1,2-dichlorobenzene	33.0[27]	30.2	34.2	34.0
1,3-dichlorobenzene	28.1[27]	25.7	25.0	24.6
1,4-dichlorobenzene	24.6[27]	22.5	25.4	24.8

TABLE 2: Calculated Heats of Formation and Chlorination Energies for Mono- and DiCDFs

CDF isomer	heat of formation (kJ/mol)	heat of full chlorination (kJ/mol)	heat of 2nd chlorination (kJ/mol)
1-monoCDF	28.4	−26.8	
2-monoCDF	29.1	−26.1	
3-monoCDF	28.7	−26.5	
4-monoCDF	34.4	−20.8	
1,2-diCDF	13.8	−41.4	−14.6
1,3-diCDF	4.1	−51.1	−24.3
1,4-diCDF	11.4	−43.8	−23.0

TABLE 3: Examination of the Interring Interactions on Multiple Chlorine Substitutions

CDF isomer	heat of formation (kJ/mol)	heat of full chlorination (kJ/mol)	heat of 2nd chlorination (kJ/mol)
1,7-diCDF	1.3	−53.9	−27.1
2,8-diCDF	3.5	−51.7	−25.6
1,9-diCDF	28.7	−26.5	0.3

TABLE 4: Bond Lengths (Å) and Angles (deg) in Unchlorinated and Chlorinated Dibenzofuran

	DF	1,2,3,4-teC DF	1,2,3,4,6,7-hexaCDF	1-monoCDF	1,9-diCDF
$C_{10}-C_1$	1.400	1.398	1.389	1.390	1.393
$C_{13}-C_{10}$	1.450	1.450	1.450	1.450	1.470
$C_{12}-C_{13}$	1.400	1.400	1.400	1.400	1.410
$C_{12}-O_5$	1.370	1.370	1.370	1.370	1.360
$C_{11}-O_5$	1.370	1.360	1.360	1.370	1.360
$C_{13}-C_{10}-C_1$	135.7	136.1	135.9	136.9	140.0
$C_{10}-C_1-Cl_1$		119.4	119.4	120.3	123.8
$C_{10}-C_1-H_1$	120.7				

The experimental data for the heat of chlorination of benzene provided by Pedley[21] is −30.6 kJ/mol for the first chlorination, and 21.8, 26.3, and 29.5 kJ/mol for further chlorination in the 2-, 3-, and 4-positions respectively.

Table 1 shows that the calculated heats of formation in this work are close to those from León et al.[20] and within 2 kJ/mol of the experimental values, which provides an expected lower limit of error for predicted values for the PCDFs considered. The experimental chlorination energy for benzene is also close to the value for substitution in dibenzo-p-dioxin in the 2-position (−26.2 kJ/mol) predicted by Lee et al.[15]

Group Interactions in PCDFs. In order to identify the main contribution to energy differences between the PCDF isomers, the monoCDFs and a number of the diCDFs are first examined, and this set is later supplemented by representative examples of more highly chlorinated isomers. Results for key members of this initial group are summarized in Table 2 and are based on the experimental heat of formation of dibenzofuran using an equation equivalent to eq 1 above.

In Table 2, heats of second chlorination are the difference in formation energies between the di- and corresponding monoCDF.

The results for the monoCDFs predict small variations in the stability of single atom substitutions in the 1, 2, and 3 positions, with that of the 4-monoCDF showing the 4-position substitution as markedly less stable than the other three.

While the heats of chlorination at the 1-, 2-, and 3-positions, (−26.8, −26.1, and −26.5 kJ/mol) are closely similar, the predicted heat of chlorination for conversion of monoCDF to a diCDF varies considerably with the location of the two chlorine atoms on the benzene rings. Considering only the formation of 1,2-, 1,3-, and 1,4-diCDF, the first two starting with either position substituted, the third with the 4-position substituted, to obtain a measure of second chlorination without the influence of the oxygen bridge, the second chlorination has a heat of −14.6 kJ/mol (1,2- from 1-), −24.3 kJ/mol (1,3- from 1-), and −23.0 kJ/mol (1,4- from 4-). For comparison, further chlorination of chlorobenzene to the 1,2-, 1,3-, and 1,4-dichlorobenzene is predicted to involve heats of chlorination of −17.8, −27.0, and −26.6 kJ/mol respectively. The corresponding experimental heats reported by Pedley[21] of 1,2- from 1-, 1,3- from 1-, and 1,4- from 1- are −21.8, −26.3, and −29.5 kJ/mol, respectively. The comparable PCDD result for the chlorination of a second carbon adjacent to the first, i.e., conversion of 2-monoCDD to 2,3-diCDD, is −12.9 kJ/mol according to Lee et al.:[15] direct comparison for chlorination in the 1,3- and 1,4-positions is to be viewed with caution as it involves chlorination of one carbon adjacent to the oxygen bridge of dibenzo-p-dioxin in the 1,3-case and two such chlorine atoms substituted adjacent to the bridges in the 1,4-case. The heat of chlorination of 1-monoCDD to 1,3-diCDD from Lee et al.[15] is −22.7 kJ/mol.

These results collectively indicate that the predicted heat of chlorination without further chlorine interaction is in the range 23−27 kJ/mol and there is a destabilizing interaction for adjacent chlorine atoms of 12−13 kJ/mol.

The prediction of a smaller heat of chlorination in the 4-position (−20.8 kJ/mol) is comparable to a reduced calculated heat of chlorination in the 1-position in dibenzo-p-dioxin reported by Lee et al.[15] (−18.6 kJ/mol) and by León et al.[20] (−19.5 kJ/mol). A examination of a range of 1-substituted PCDFs indicates that the destabilizing interaction for a chlorine atom close to the oxygen bridge in these is consistently found to be of the order of 6 kJ/mol.

The effect of multiple chlorination on different benzene rings can be demonstrated using the diCDFs, and these features have also been found to be applicable to more highly substituted isomers. Table 3 shows heats of formation and chlorination for three examples. The 1,7- and 2,8-isomers have been chosen to avoid the specific interaction energies associated with the 4 and 6 positions, and it can be seen that the heats of second chlorination are closely similar. This suggests that inter-ring substitution effects may be small and that additive heats of chlorination on different rings may be applicable within an overall methodology to estimate a heat of formation.

The 1,9-substitution demonstrates a significant deviation from this rule and can be accounted for with reference to Figure 1. For 1,9-substitutions in PCDF, the Cl_1-Cl_9 distance is around 3.25 Å and is a source of significant repulsive interaction. This contrasts with the PCDD geometry where the corresponding chlorine−chlorine distance is around 4.7 Å.

Table 4 presents some bond lengths and angles for DF and four CDFs, including the 1,9-isomer.

This confirms the view that these parameters are almost unaffected by chlorine substituents, with the exception of the 1,9-case where chlorine repulsion causes a $C_{13}-C_{10}$ bridge length increase of 0.02 Å and an opening of the $C_{13}-C_{10}-C_1$ and $C_{10}-C_1-Cl_1$ angles associated with this position by more than 3°.

TABLE 5: Demonstration of the 8,9 Chlorine Interaction in the Presence of C_1 and C_9 Chlorine Substitution

CDF isomer	heat of formation (kJ/mol)
1,6,8,9-teCDF	3.3
1,6,7,9-teCDF	−2.3
1,2,3,4,6,7,9-heptaCDF	−24.8
1,2,3,4,6,8,9-heptaCDF	−19.5

Examination of the energies in Table 3 and those of other isomers studied, confirms that a 1,9-repulsion interaction energy of close to 27 kJ/mol consistently applies.

It has been found that a further consequence arises from this repulsive interaction when there are also chlorine substituents at the 2 or 8 position, due to the bending of the C−Cl group away from the C−C bridge. This has been found to increase the destabilizing interaction for adjacent chlorine atoms. This was indicated above to be approximately 12 kJ/mol, independent of the position of adjacent chlorines within the isomer. Table 5 shows the calculated heats of formation for two pairs of isomers which have identical contributions to the formation energy in terms of the parameters already identified. Both have 1,9-chlorine substitution, and in each case, one member of the pair has the chlorine at C_7 transferred to C_8.

This gives rise to an additional repulsion term as described above and is reflected in the higher heat of formation for 8-substituted isomer in the cases shown.

Examination of a number of isomers meeting this 1,9-substitution condition has shown that an additional repulsion interaction of around 5 kJ/mol for each substitution of the 2- or 8-positions applies.

PCDF Prediction Algorithm. The discussion above suggests that there are six principal parameters which can be used to determine the heat of formation of the PCDF family based on dibenzofuran, and examination of a number of isomers allows average values to be assigned to these as follows:

	kJ/mol	symbol
heat of formation of DF	55.2	E_1
chlorination energy for each chlorine	−26.1	E_2
repulsion energy for each pair of adjacent chlorines	13.0	E_3
repulsion energy for C_4 or C_6 chlorine substitution	7.5	E_4
repulsion energy for simultaneous C_1 and C_9 chlorine substitution	27.1	E_5
repulsion correction for C_1 and C_9 chlorine substitutions when either C_2 or C_8 are substituted	5.5	E_6

Calculation of a predicted heat of formation can thus be given by an algorithm based on the following, using 1,2,3,4,7,8,9-heptaCDF as an example:

$$\text{heat of formation} = E_1 + 7E_2 + 5E_3 + E_4 + E_5 + 2E_6 = -16.9 \text{ kJ/mol}$$

Table 6 provides a comparison of predicted heats of formation based on the DFT calculation and those obtained by using the algorithm, for 33 isomers of PCDF.

The two sets of values show an rms error of 1.7 kJ/mol, which is considered to be an adequate representation of the DFT predicted results when compared with the likely systematic errors of these in predicting experimental values, and the existing uncertainties of measured values when these are available.

The algorithm shows a number of similarities with the energy contributions presented by Lee et al.[15] in their analysis of the PCDD family. These authors examine a number of chlorine−chlorine repulsion energy contributions to the overall formation energy. For example, the Cl−Cl repulsion energy for a single

TABLE 6: Comparison of DFT Predicted PCDF Heats of Formation with Those Predicted by the Algorithm

PCDF isomer	heat of formation using DFT (kJ/mol)	heat of formation using algorithm kJ/mol	differences (algorithm − DFT) (kJ/mol)
1-monoCDF	28.4	29.1	0.7
2-monoCDF	29.1	29.1	0
3-monoCDF	28.7	29.1	0.4
4-monoCDF	34.4	36.6	2.2
1,2-diCDF	13.8	16.0	2.2
1,3-diCDF	4.1	3.0	−1.1
1,4-diCDF	11.4	10.5	−0.9
1,6-diCDF	8.3	10.5	2.2
1,9-diCDF	28.7	30.1	1.4
2,3-diCDF	14.8	16.0	1.2
2,4-diCDF	12.4	10.5	−1.9
3,4-diCDF	19.0	23.5	4.5
1,7-diCDF	1.3	3.0	1.7
2,7-diCDF	3.1	3.0	−0.1
2,8-diCDF	3.5	3.0	−0.5
1,2,3-triCDF	2.7	2.9	0.2
1,2,4-triCDF	−2.0	−2.6	−0.6
1,3,4-triCDF	−3.7	−2.6	1.1
2,3,4-triCDF	7.5	10.4	2.9
1,2,3,4-teCDF	−4.6	−2.7	1.9
2,3,7,8-teCDF	−23.7	−23.2	0.5
1,2,6,9-teCDF	1.7	3.9	2.2
1,6,8,9-teCDF	3.3	3.9	0.6
1,6,7,9-teCDF	−2.3	−1.6	0.7
2,3,4,6,7,8-hexaCD F	−35.2	−34.4	0.8
1,2,3,4,6,7-hexaCD F	−36.0	−34.4	1.6
1,3,4,6,7,8-hexaCD F	−45.6	−47.4	−1.8
1,2,3,7,8,9-hexaCD F	−13.2	−11.3	1.9
1,2,3,4,6,78-heptaC DF	−45.9	−47.5	−1.6
1,2,3,4,6,7,9-hepta CDF	−24.8	−27.9	−3.1
1,2,3,4,6,8,9-hepta CDF	−19.5	−22.4	−2.9
1,2,3,4,7,8,9-hepta CDF	−16.1	−16.9	−0.8
octaCDF	−23.0	−22.5	0.5

pair of adjacent chlorines is 13.0 kJ for 1,2-diCDD, which is identical with the E_3 value derived in the present work for the algorithm. The destabilization energy for a chlorine adjacent to the oxygen bridge, e.g., 1-monoCDD is 7.36 kJ compared with the present E_4 value of 7.5 kJ.

Some significant differences also exist, however. The authors identify additional Cl−Cl repulsion terms of 3.7 kJ for 1,3-substitutions and 2.4 kJ for 1,4-substitutions, as well as inter-ring chlorine−chlorine repulsions of around 1.2 kJ per chlorine pair in CDDs. The present work with PCDFs also shows additional repulsion terms originating from such interactions, but of a lower magnitude, being below 2 kJ, and not showing a consistent pattern of behavior.

For example, DFT calculated chlorination energies for the formation of 1-monoCDF and 2-monoCDF are −26.8 and −26.1 kJ, respectively, whereas the energies of second chlorination to form 1,7-, 2,7-, and 2,8-diCDF are −27.2, −25.9, and −25.6 kJ respectively, indicating the inter-ring interaction to be a fraction of a kJ.

The algorithm therefore does not consider these additional interactions and relies on those dominant terms which show a consistent pattern of behavior within the congeners considered. This compromise provides a somewhat simpler algorithm for practical purposes and results in a level of error with DFT results which is considered tolerable when compared with present experimental uncertainties.

Concluding Remarks

Dibenzofurans and dibenzo-p-dioxins provide a good isomer set for the application of the group additivity method, providing the method is based on sound experimental values or a good level of ab initio calculation such as DFT. The stability of the ring system results in very little distortion with successive chlorine substitution, and energy changes can mainly be accounted for through chlorine-ring and chlorine−chlorine interactions, providing a basis for a simple additive model.

The enthalpies of formation generated in this way have been shown to be close to the DFT predicted values and should provide accessibility to realistic thermodynamic parameters for those who are engaged in the understanding of formation mechanisms of PCDFs with a view to reduction of these through modified process design.

It has been shown that, provided isodesmic reactions are modeled, DFT calculations for the initial chlorination of dibenzofuran provide results which are consistent with those presented in the literature for initial chlorination of benzene and dibenzo-p-dioxin. A small loss of stability when chlorination occurs adjacent to the oxygen bridge is consistent with prediction of this interaction for dibenzo-p-dioxin reported by others. Calculations for further chlorination at the neighboring carbon atom of a carbon already chlorinated predict somewhat higher loss of stability than is observed for monochlorobenzene or predicted for monochlorobenzene and monochlorodibenzo-p-dioxin second chlorination. Substitution on both carbon atoms adjacent to the carbon−carbon bridge of DF results in repulsive interaction which is of similar magnitude to the heat of chlorination predicted for the substitution of the first of the two chlorine atoms. Except when both carbon atoms adjacent to the carbon−carbon bridge are chlorinated, substitutions in the two benzene rings of the dibenzofuran are essentially non-interactive, and further interaction when the 1,9-positions are substituted only applies to 2- and 8-substitution.

Within the limits of accuracy of experimental or computational determination, the results for the heats of formation of the PCDFs examined can be represented by an algorithm with six parameters, which can be used to model the whole 135 PCDF isomer set.

This study has shown that DFT calculations can provide not only support for additivity procedures in using experimental results to make predictions for related species which have not been examined (e.g., in this work, confirmation of interaction of adjacent chlorine atoms and non-interaction of chlorine atoms on different benzene rings), but also identify strong interactions, as in this case for the 1,9-chlorination, which may contribute significantly to relative equilibrium isomer concentrations and which is specific to the DF structure: weaker interactions such as the chlorine-oxygen bridge interaction and the secondary effect of the 1,9 substitution on 2- or 8-substitution can also be identified. To summarize, the study indicates that the combination of additivity principles with DFT calculations, where experimental data for extrapolation are of questionable accuracy or absent, or where the potential for additional interactions can be envisaged, can provide improved data and resolve uncertainties.

References and Notes

(1) Stockholm Convention on Persistent Organic Pollutants, United Nations Environment Programme, 2001; United Nations Environment Programme: Geneva, Switzerland, 2001.

(2) European Commission Regulation 850/2004 on Persistent Organic Pollutants, 2004, Official Journal of the EU, L158 of April 30, 2004.

(3) Papina, T. S.; Kolesov, V. P.; Vorobieva, V. P.; Golovkov, V. F. *J. Chem. Thermodyn.* **1996**, *28*, 307−311.

(4) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chemov, C. A.; Vorobieva, V. P. *Zh. Fiz. Khim.* **1998**, *72*, 7−10.

(5) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chemov, C. A.; Vorobieva, V. P. *J. Chem. Thermodyn.* **1998**, *30*, 431−436.

(6) Pimenova, S. M.; Melkhanova, S. V.; Kolesov, V. P.; Demyanov, P. I.; Fedotov, A N.; Vorobieva, V. P. *J. Chem. Thermodyn.* **2002**, *34*, 385−390.

(7) Unsworth, J. F.; Dorans, H. *Chemosphere* **1993**, *27*, 351−358.

(8) Saito, N.; Fuwa, A. *Chemosphere* **2000**, *40*, 131−145.

(9) Stewart, J. P. *J. Computer-Aided Mol. Des.* **1990**, *4*, 1−103.

(10) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York 1976.

(11) Shaub, W. M. *Thermochim. Acta* **1982**, *55*, 59−73.

(12) Thompson, D. *Thermochim. Acta* **1995**, *261*, 7−20.

(13) Dorofeeva, O. V.; Iorish, V. S.; Moiseeva, N. F. *J. Chem. Eng. Data* **1999**, *44*, 516−523.

(14) Ooi, T. C.; Ewan, B. C. R.; Cliffe K. R.; Thompson, D.; Anderson, D. R.; Fisher, R. *Abstracts of the 5th Materials Congress*, Apr 5−7, 2006 London; Institute of Materials, Minerals and Mining: London.

(15) Lee, J. E.; Choi, W.; Mhin, B. J. *J. Phys. Chem. A* **2003**, *107*, 2693−2699.

(16) Thompson, D.; Anderson, D. R.; Fisher, R. *Abstracts of the Industrial Advisory Group Meeting for AEA-NPL-DSTI-MIRO Project on'Thermodynamic Data for Safe, Energy Efficient High Temperature Processing of Complex Materials'*, Jan 29, 2004, AEAT Harwell, U.K.; Mineral Industry Research Organization: Birmingham, U.K.

(17) Lee, J. E.; Choi, W.; Mhin, B. J. *J. Phys. Chem. A* **2003**, *107*, 2693− (17) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian Inc. Publisher: Pittsburgh, 1996.

(18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(19) Parr, R. G.; Yang, W. *Density Functional theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(20) León, L. A.; Notario, R.; Quijano, J.; Sánchez, C. *J. Phys. Chem. A* **2002**, *106*, 6618−6627.

(21) Pedley, J. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center, Texas; CRC Press: Boca Raton, FL, 1994.

(22) Chirico, R. D.; Gammon, B. E.; Knipmeyer, S. E.; Nhuyen, A.; Strube, M. M.; Tsonopoulos, C.; Steele, W. V. *J. Chem. Thermodyn.* **1990**, *22*, 1075−1096.

(23) Cass, R. C.; Fletcher, S. E.; Mortimer, C. T.; Springall, H. D.; White, T. R. *J. Chem. Soc.* **1958**, 1406−1410.

(24) Wong, M. W. *Chem. Phys. Lett*. **1996**, *256*, 391−399.

(25) Dorofeeva, O. V.; Yungman, V. S. *J. Phys. Chem. A* **2003**, *107*, 2848−2854.

(26) Platonov, V. A.; Simulin, V. A. *Russ. J. Phys. Chem*. **1985**, *59*, 179−181.

(27) Platonov, V. A.; Simulin, V. A. *Russ. J. Phys. Chem*. **1984**, *58*, 1630−1632.