Quantum-Mechanical Calculations on Chlorinated Aromatics for Determination of Molecular Constants Relevant for New Laser Based Analytical Methods:
Comparison of Semiempirical Methods

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1 Abstract

The applicability of new laser based analytical methods as resonance-enhanced laser mass spectrometry is supported by the knowledge of molecular parameters (e.g. ionization potentials, electronic transition energies etc.) of the compounds to be analyzed. In principle these data can be obtained by molecular orbital calculations on the molecules of interest. In this work different semiempirical quantum-mechanical methods are tested on their reliability to calculate of ionization potentials (IP) of all chlorinated benzene congeners. By comparison of calculated results with experimental IP data (photoelectron spectroscopy) it is possible to find out which method describes chlorinated aromatic compounds with best accuracy. The best agreement between calculated and experimental data has been observed for the AM1 method. Further on, the AM1 hamiltonian has been used for exemplary calculations on three chlorinated debenzodioxins (PCDD).

2 Introduction

The high toxicity of many chlorinated aromatic pollutants (e.g. PCDD) makes it difficult to measure their molecular constants experimentally. However, the recent developements in computational chemistry open new ways to obtain molecular constants as e.g. electron affinities, ionization potentials, dipole moments or geometrical parameters. The knowledge of such molecular parameters is interesting for modeling of derivated physical-chemical properties as e.g. GC retention indices /1,2/, standard reduction potentials /3/ or biochemical properties (e.g. receptor-bonding affinities) /4,5/. Especially the calculation of ionization potentials and IR as well as UV/VIS spectral data is important as "software" for new laser based analytical techniques as resonance-enhanced laser ionization-mass spectrometry /6,7,8/. However, the reliability of the primary molecular data is fundamental for accurate derivated results.

Ab initio quantum mechanical calculations (using an adequately good basis set) give accurate results but are far to expensive (i.e. need extremely long calculation times) for extensive studies on larger chlorinated aromatics as PCDD/F or PCB. Of course, semiempirical methods allow fast calculations on these molecules, but the reliability of the chosen method has to be tested previously. The accuracy of a semiempirical method for describing molecular properties of substance class can be proofed by comparision of computed results of representative compounds with experimental data.

In this work the reliability of 7 semiempirical methods for describing chlorinated aromatics

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is investigated. The fundamental representative compounds for chlorinated aromatics (the chlorinated benzenes) are chosen for this investigation.

3 Calculations

The MINDO3, AM1, MNDO and PM3 calculations were performed on a Silicon Graphics Iris workstation with the MOPAC 6.0 /9/ molecular orbital program. The INDO, CNDO, ZINDO/1 and some of the PM3 and MNDO work has been done on a personal computer with the Hyper-Chem 3.0 /10/ program. All methods are based on the Hartree-Fock self consistent field (SCF) approach but using different approximations for integral evaluation. AM1 and PM3 represent new parametrisations of the MNDO method. The theoretical background and the specific aproximations used in the different methods are described elsewhere /11/. All calculations were done with full geometry optimisation. The ionization potentials were calculated according to Koopman's theorem ($IP = -E_{HOMO}$).For each semiempirical method the averaged differences between the experimental ionization potentials /12/and the calculated ones (table 1) were taken as of-set parameter (table 2) for calculating the corrected IP's (table 3). The averaged differences (table 2) between the experimental IP data and the corrected IP's are an indicator parameter for the reliability of the respective method. The AM1 results for dibenzodioxin, 2,3,7,8-tetrachlorodibenzodioxin and octachlorodibenzodioxin are subsumarized in table 4 as an example for application on larger chlorinated molecules.

4 Results

In this section the calculated results are tabulated. The discussion of the results is given in the next section.

Table 1
Ionization potentials of chlorinated benzenes obtained by different semiempirical quantum mechanical methods. Experimental IP's (photoelectron data) are taken from reference /12/

	exp.	MINDO3	MNDO	AM1	PM3	INDO	CNDO	ZINDO/1
benzene	9.25	9.18	9.39	9.65	9.75	13.89	13.48	9.84
MCB	9.07	9.07	9.62	9.55	9.39	12.94	14.31	9.49
12DCB	9.08	9.14	9.85	9.60	9.29	12.93	15.04	9.63
13DCB	9.14	9.25	9.89	9.68	9.42	13.08	15.35	9.89
14DCB	8.97	9.03	9.82	9.52	9.23	12.71	15.01	9.43
123T$_3$CB	9.16	9.39	10.11	9.78	9.38	13.22	15.97	10.13
124T$_3$CB	9.04	9.17	10.04	9.62	9.24	12.85	15.73	9.75
135T$_3$CB	9.32	9.57	10.20	9.92	9.59	13.45	16.34	10.58
1234T$_4$CB	9.23	9.31	10.22	9.73	9.28	13.52	16.28	10.09
1245T$_4$CB	9.15	9.21	10.21	9.66	9.19	12.84	16.22	9.87
1235T$_4$CB	9.26	9.36	10.26	9.76	9.30	13.07	16.53	10.15
PCB	9.21	9.38	10.39	9.78	9.25	13.05	16.83	10.26
HCB	9.19	9.53	10.56	9.91	9.31	13.25	17.36	10.63

Table 2
The obtained off-set values and averaged deviations between the corrected and experimental IP's.
The averaged deviations between the experimental IP data and the corrected IP's are an indicator
prameter for the reliability of the respective method (smaller deviation $===>$ better reliability of
the method)

Method	MINDO3	MNDO	AM1	PM3	INDO	CNDO	ZINDO/1
off-set$_1$	0.137	0.884	0.537	0.201	6.562	3.982	0.819
middeld deviation$_2$	0.089	0.181	0.055	0.105	0.795	0.202	0.245
middeld deviation$_3$	0.068	0.081	0.037	0.070	0.522	0.118	0.176

  1   averaged off-set between experimental and calculated ionization potentials
  2   averaged deviation between off-set corrected calculated values and experimental data
  3   averaged deviation between off-set corrected calculated values and experimental data under exclusion of benzene
      and hexachlorobenzene

Table 3
Off-set corrected calculated ionization potentials of chlorinated benzenes

	exp.	MINDO3	MNDO	AM1	PM3	INDO	CNDO	ZINDO/1
benzene	9.25	9.04	8.51	9.11	9.55	6.92	9.91	9.02
MCB	9.07	8.93	8.74	9.01	9.19	7.74	8.96	8.67
12DCB	9.08	9.00	8.97	9.06	9.09	8.48	8.95	8.81
13DCB	9.14	9.11	9.01	9.14	9.22	8.79	9.10	9.07
14DCB	8.97	8.89	9.94	8.98	9.03	8.45	8.73	8.54
123T$_3$CB	9.16	9.25	9.23	9.24	9.18	9.41	9.24	9.31
124T$_3$CB	9.04	9.03	9.16	9.08	9.04	9.17	8.87	8.93
135T$_3$CB	9.32	9.43	9.32	9.38	9.39	9.78	9.47	9.76
1234T$_4$CB	9.23	9.17	9.34	9.19	9.08	9.72	9.57	9.27
1245T$_4$CB	9.15	9.07	9.33	9.12	8.99	9.66	8.86	9.05
1235T$_4$CB	9.26	9.22	9.38	9.22	9.10	9.96	9.09	9.33
PCB	9.21	9.24	9.51	9.24	9.05	10.27	9.07	9.44
HCB	9.19	9.39	9.68	9.35	9.11	10.80	9.27	9.81

Beside of chlorinated benzenes three dibenzo-p-dioxin derivatives have been investigated with the
AM1 method. The geometry optimization has beem started from a slightly folded conformation. If
a planar starting geometry is used the calculation give planar structures for dibenzodioxins (local
minimum at the potential hypersurface) which not represents the correct minimum conformation. The
results of the calculations are tabulated in table 4.

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Table 4
Calculated molecular parameters (AM1 method, MOPAC) of dibenzodioxin and two polychlorinated
dibenzodioxins (PCDD)

AM1 molecular parameters		dibenzodioxin	2378-T$_4$CDD	O$_8$CDD
ionization potential$_1$	[eV]	8.59	9.00	9.43
corrected ionization pot.$_2$	[eV]	7.78	8.19	8.62
electron affinity$_1$	[eV]	0.14	0.91	1.28
Heat of formation	[$^{kcal}/_{mole}$]	2.7	-19.4	-26.2
dipole moment	[D]	0.163	0.125	0.543
dihedral angle	[°]	3.2	5.8	20.3
bondlength C-Cl (3 posit.)	[A]	-	1.694	1.692
molecular dimension$_3$	[AxA]	4.60 x 8.48	5.02 x 10.05	6.22 x 10.00

1 The ionization potentials and electron affinities were calculated according to Koopman's theorem (IP= - E_{HOMO}, EA= -E_{LUMO}).
2 The off-set constant (0.81 eV) for the corrected IP's has been taken as the difference between the experimental /13/ and the AM1 IP value of dibenzodioxin.
3 Distance between the 1 and 4 as well as between the 2 and 8 substituents. For realistic molecular dimension the respective van-der-Waals radii have to be added.

5 Discussion

The substituent effects of chlorine on aromatic systems represents a somewhat difficult problem for theoretical methods. This is due to the ambivalence of the mesomeric electron donating (+M effect) and inductive electron withdrawing (-I) effects of aromatic bonded chlorine. In principle the mesomeric effects (electron donation) result in a destabilization of the highest occupied molecular orbital (HOMO) and therefore should be responsible for a decrease of the ionization potentials /13/. On the other hand an overestimation of the inductive effects (electron withdrawing) leads to increasing ionization potentials /14/. However, the experimental ionization potentials for the chlorinated benzenes (table 1 and 3) show no significant in- or decreasing tendency in dependence on the substituent number, implicating a well balanced character between the two effects.
Therefore the trend of the calculated ionization potentials of the chlorinated benzenes as a function of the chlorine substituent number is a good indicator for the reliability of a theoretical method in describing the electronic effects of aromatic bonded chlorine. An overestimation of electron withdrawing properties will cause increasing, an overestimation of electron donating effects decreasing ionization potentials /14/.
The ionization potentials calculated with MNDO, INDO, CNDO and ZINDO/1 (table 3) increase with rising number of chlorine substituents. On the other hand the ionization potentials calculated with PM3 decrease slightly as a function of the chlorine substituent number. Only MINDO3 and AM1 describe the ionzation potential curve correctly (except of hexachlorobenzene, which gives to high IP's for all methods, probably due to general difficulties in calculating such highly strained molecules). However, all methods give IP values which are shifted (positive off set) in relation to the experimental ones. If experimental IP data are available for some or at least one congener of the substance class under investigation, this off-set constant easily can be deteminated by comparision with the respective calculated IP values. Afterwards the other calculated IP's can be corrected by substraction of this off-set constant. If no experimental data exists at all, a MINDO/3

calculation -which have shown the smallest off-set in this study- may give an approximate value. Previosly published investigations exhibit that the AM1 method give the most accurate geometrical parameters (e.g. averaged error in C-Cl bondlength 0.033 A for AM1) of all MNDO-type parametrisations (MNDO, AM1, PM3) /15/. Thermodynamic properties are slightly better described by MNDO, followed by AM1 and PM3 /16/.

In table 4 the AM1 results for three representatives of the PCDD substance class are sumarized. An interesting result are the rising ionization potentials for increasing degree of chlorination. This is probably due to an increased electron withdrawing effect of the oxygen atoms caused by mesomeric interaction with the chlorine substituents in ortho/para position /17/. First experimental results confirm an increasing of the IP's of PCDD as a function of the chlorine substituent number /18/

6 Summary and Conclusion

Seven different semiempirical quantum-mechanical methods have been applied for calculation of ionization potentials (IP) of all chlorinated benzene congeners.

The (relative) accuracy of calculated ionization potentials represent an indicator parameter for the reliability of the description of the chlorinated aromatic system. All methods give to high values for the ionization potentials (i.e. are off-seted). If experimental data is available for at least one compound of the substance class under investigation, an off-set correction can be performed. The experimental ionization potentials are reproduced best by the AM1 hamiltonian (averaged deviation after off-set correction, $MD_{off} = 0.055$ eV) followed by MINDO/3 ($MD_{off} = 0.089$ eV) and PM3 ($MD_{off} = 0.105$ eV). All other methods are unsuitable for calculating electronic parameters of chlorinated benzens (and probably also for all other chlorinated aromatics). If no experimental data is achievable at all, the MINDO/3 (off-set: 0.137) and PM3 (off-set: 0.201) give the best absolute IP values without off-set correction. However, semiempirical quantum-mechanical calculations can generate molecular parameters, used for laser mass spectrometric analytical methods /6,7,8/ (e.g. IP data for setting up suitable ionization schematics) and other purposes. A prerequisite for accurate results is the carefully consideration of the reliability of the chosen methods on the substance classes under investigation. Results of some priviously published studies /9,11,19/ in combination with the results from this work suggest, that the use of the AM1 method for chlorinated aromatic compounds (possibly also MINDO/3 and PM3 for off-set determination) is favourable.

7 Acknowledgments

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