POLYCHLORINATED FLUORENES (PCFLs): A CLASS OF POSSIBLE DIOXIN ANALOGUES - EVALUATION OF SOME PHYSICO-CHEMICAL PROPERTIES

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Introduction

Fluorene is tricyclic aromatic molecule composed of two benzene rings fused to five element carbon skeleton and is found among major PAHs formed during municipal solid waste incineration (1). PCFLs (Cl-Flo) are an example of the environmental contaminants and their source can be unintended formation during various anthropogenic processes. PCFLs belong to a larger group of unintentionally produced chlorinated polycyclic aromatic compounds (Cl-PAHs) (2-4). In a recent study mono- to tri-CFLs were found in urban air, tri- to tertra- in the settling particulate matter sample, tri- to tetra- in sediment collected outside pulp and paper mill, tri- to tetra- in sediment collected close to magnesium and chlorine plants, and from mono- to hepta- in fly ash from the municipal solid waste incinerator (5). PCFLs are planar compounds and can be considered as stereoisomers to highly toxic TCDD.

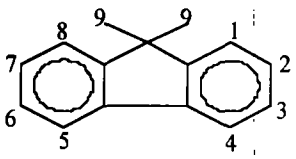

Fig. 1. Generalized structure and numbering system for fluorene.

There is extremely limited number or lack of data available on sources, possible mechanism of formation, occurrence, analytical chemistry, properties, environmental features or effects of PCFLs. In this work some selected thermodynamic and physicochemical properties of PCFLs were computed using semiempirical methods and differences/similarities between the congeners were examined using multivariate classification and QASR analysis.

Materials and Methods

The values of the heat of formation (ΔH), entropy (ΔS), heat capacity (Cp), energy of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), ionisation potential, dipole moment (D) and geometry optimisation of all theoretically possible congeners of chlorofluorene were generated on the level of the semiempirical AM1 and PM3 methods using EF technique implemented in the MOPAC 93 program package and UNIX operational system (6).

Results and Discussion

The congeners of CFL nos. 12, 18, 23, 25, 94, 108, 115, 129, 137, 142, 150, 151, 156, 157, 270, 280, 297, 299, 314, 318, 321, 330, 332, 333, 382, 397, 401, 406 and 415 have c2v point group symmetry (rotation by 180°) and two vertical planes, while other have one plane and cs or c1 symmetry. All CFLs are thermodynamically unstable and their absolute values of ΔH decrease (persistency increase) with increasing degree of chlorination. There is 10 homologue groups of CFL and 415 theoretically possible congeners (Table 1). The values of ΔH and ΔS are slightly different for isomers of CFL within a particular homologue group, and with an increase of the degree of chlorination the values of ΔH decrease, while of ΔS increase (Table 2). The energies of HOMO differ slightly while of LUMO slightly increase toward higher chlorinated congeners, and dipole moments are more dependent on the constitution than on a degree of chlorination of the fluorene molecule. The data on the results of PCA and QASR analysis will be further discussed.

Table 1. Homologue groups, chemical formulas, number of isomers and congeners and molecular weight of chlorofluorenes

Homologue group	Chemical formula	Number of isomers	Molecular weight
Mono-	$C_{13}H_9Cl$	5	200
Di-	$C_{13}H_8Cl_2$	22	234
Tri-	$C_{13}H_7Cl_3$	48	268
Tetra-	$C_{13}H_6Cl_4$	82	302
Penta-	$C_{13}H_5Cl_5$	94	336
Hexa-	$C_{13}H_4Cl_6$	82	370
Hepta-	$C_{13}H_3Cl_7$	48	404
Octa-	$C_{13}H_2Cl_8$	25	438
Nona-	$C_{13}H_1Cl_9$	8	472
Deca-	$C_{13}Cl_{10}$	1	506

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Table 2. Selected physico-chemical properties of chlorofluorenes (minimum and maximum values within homologue group)

Homologue group	Method	Heat of formation ΔH (kcal/mol)	Entropy ΔS (cal/molK)	Heat capacity Cp (cal/molK)	Energy of HOMO (eV)	Energy of LUMO (eV)	Dipole moment (D)	Ionization potential (eV)
Mono-	AM1	44.009	94.610	40.066	-9.005	-0.664	1.020	8.780
		48.134	97.625	41.412	-8.780	-0.407	1.739	9.005
	PM3	40.445	91.896	38.331	-9.030	-0.736	0.684	8.804
		43.093	98.018	41.602	-8.861	-0.489	1.368	9.030
Di-	AM1	40.026	94.859	41.410	-9.072	-0.579	0.098	8.847
		48.648	101.160	43.674	-8.847	-0.719	2.705	9.057
	PM3	35.318	95.045	39.958	-9.165	-0.796	0.037	8.792
		41.970	98.547	42.049	-8.844	-0.621	2.070	9.165
Tri-	AM1	33.948	96.313	41.848	-9.222	-0.926	0.231	8.937
		48.648	105.903	49.969	-8.937	-0.703	3.335	9.222
	PM3	29.528	96.802	42.049	-9.249	-0.961	0.209	8.826
		41.970	104.845	45.608	-8.826	-0.753	3.373	9.249
Tetra-	AM1	28.048	100.777	44.593	-9.523	-1.107	0.010	-9.358
		43.200	109.994	48.946	-9.025	-0.900	3.362	9.523
	PM3	23.926	102.960	45.089	-9.337	-1.114	0.045	-9.337
		34.778	111.947	51.299	-8.838	-0.868	2.499	9.327
Penta-	AM1	23.974	106.714	47.985	-9.498	-1.257	0.007	9.117
		38.730	112.122	51.284	-9.117	-1.058	0.999	9.498
	PM3	19.409	107.910	48.322	-9.400	-1.225	0.000	8.872
		30.486	115.052	53.096	-8.872	-0.994	0.992	9.400

Table 2, cont'd

Homologue group	Method	Heat of formation ΔH (kcal/mol)	Entropy ΔS (cal/molK)	Heat capacity Cp (cal/molK)	Energy of HOMO (eV)	Energy of LUMO (eV)	Dipole moment (D)	Ionization potential (eV)
Hexa-	AM1	20.174	109.011	49.614	-9.604	-1.396	0.007	9.196
		34.965	117.583	54.131	-9.196	-1.191	0.996	9.604
	PM3	14.906	111.021	50.929	-9.478	-1.326	0.017	8.904
		26.236	117.834	54.864	-8.904	-1.109	0.988	9.478
Hepta-	AM1	17.176	112.368	51.320	-9.625	-1.508	0.027	9.304
		32.033	119.494	56.221	-8.950	-1.218	0.985	9.625
	PM3	10.558	114.096	53.103	-9.408	-1.454	0.022	8.983
		21.113	120.378	56.538	-8.950	-1.218	0.998	9.346
Octa-	AM1	15.621	115.185	54.692	-9.590	-1.613	0.011	9.381
		27.897	122.118	58.347	-8.996	-1.316	0.888	9.590
	PM3	9.877	115.185	54.692	-9.521	-1.598	0.011	9.027
		16.805	122.118	58.236	-8.996	-1.316	0.888	9.257
Nona-	AM1	16.687	119.428	56.785	-9.589	-1.697	0.009	9.480
		11.739	124.584	59.970	-9.071	-1.466	0.909	9.180
	PM3	16.687	119.428	56.785	-9.589	-1.697	0.009	9.480
		11.739	124.584	59.970	-9.071	-1.466	0.909	9.180
Deca-	AM1	21.738	125.134	600.312	-9.576	-1.775	0.610	9.576
	PM3	7.455	125.665	61.717	-9.121	-1.583	0.654	9.121