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Substituent Effect on the Enthalpies of Formation of CH/π Complexes of Aromatic π-Bases

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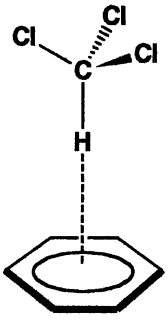
The formation constants and the enthalpies of formation of CH/π complexes were determined for a series of ternary chloroform/aromatic π-base/carbon tetrachloride (solvent) systems. The enthalpies showed that the interaction is favored by the electron-releasing substituent on the aromatic ring. Electronegative substituents on the CH donor also strengthen the interaction. The fact renders a support on the hydrogen-bond-like nature of the CH/π interaction.

Recent investigations by the present authors[1—10] revealed the fact that an alkyl group often prefers to take a position contiguous to the aromatic π-electrons in certain molecules. As a result, folded conformations become more favorable. It appears that the folding tendency of the chain is quite general in a wide variety of aralkyl molecules. The preference for alkyl/aryl contiguous (i.e., usually synclinal) conformation has been rationalized by assuming an attractive interaction between alkyl and aryl groups. Dispersive force is sure to contribute to a large extent to such attractive interaction.[6,8] However, contribution of a weak hydrogen-bond-like interaction became very probable by our recent work concerning the substituent effect on an intramolecularly CH/π interacted system, namely 4-aryl-2-methyl-3-pentanones-2-*d* $XC_6H_4CHMeCOCDMe_2$.[9,10]

On the other hand, intermolecularly CH/π interacted systems have been investigated and discussed rather extensively in relation to the aromatic-solvent-induced shift (ASIS) of ^1H NMR spectra. In the pioneering works by Zurcher[11,12] and Williams,[13,14] the ASIS was explained in terms of the formation of a complex in which a CH group approaches from the perpendicular direction of the plane of the aromatic ring (**1**) (Chart 1).



(1)

Chart 1.

Independently to the investigations on ASIS, possibility of CH/π hydrogen bonding was discussed by Allerhand and Schleyer,[15] who concluded that the CH/π hydrogen bond is persistent only in some limited cases where a strongly acidic CH-hydrogen donor is involved. On the other hand, attractive force originating from the intermolecular CH hydrogen bonding has been ascribed to the increase in s-character of the CH bonding orbital induced by the approach of the π-electrons by Olympia, Jr.[16] The enthalpies of chloroform/benzene complex formation were also determined by using NMR technique.[17] The values of the enthalpy were collected in a review article.[18] However, the substituent electronic effect was not so far studied systematically.

In this report, we determined the enthalpies of formation for the CH/π complexes of a series of substituted benzenes by the conventional method and discussed the substituent effect on the intermolecularly CH/π interacted system with the aim of comparing them with the intramolecular case.

Experimental

Materials. All CH hydrogen donors and π-bases, mostly perdeuterated, are known compounds and purchased commercially. Except for the deuterium-labeled compounds, the reagents were further purified by distillation.

Spectral Measurement. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer using a 10-mm-probe. The measurements were carried out on the CH-donor(D)/π-acceptor(A)/CCl_4 (solvent) ternary system by using deuterium-labeled π-bases in order to avoid the interference by the signals of protons on the aromatic ring. Their deuterium signals were conveniently used as the internal lock signals. The concentrations of the π-bases (A) were kept to be 2.0 mol kg^{-1} (except for hexamethylbenzene (0.2 mol kg^{-1} and for octadeuterionaphthalene (1.0 mol kg^{-1}), while those of hydrogen-donors (D) were changed in the range from 0.1 to 0.8 mol kg^{-1} (except for the experiments with hexamethylbenzene where they are maintained in the range from 0.008 to 0.04 mol kg^{-1}. Temperature-dependent NMR spectra were measured with an aid of JES-VT-3 variable temperature apparatus.

Calculations.[19] Molecular mechanics calculations were performed by using the MM2(91) program. Semiempirical molecular orbital calculations were carried out with MOPAC version 6. All calculations were done using SUN SPARC station IPC.

Table 1. Chemical Shifts (δ/ppm) of the CH Hydrogen-Donors in CH Donor (D)/π-Acceptor(A)/CCl_4 Ternary System as a Function of Temperature (t/°C) [a)]

1)	t/°C	49.8	45.1	39.9	35.2	25.8	19.1	14.9	10.1
	δ_{obsd}	6.862	6.853	6.842	6.830	6.804	6.788	6.776	6.765
2)	t/°C	49.8	45.1	39.9	35.2	25.8	19.1	14.9	10.1
	δ_{obsd}	6.853	6.842	6.828	6.817	6.793	6.775	6.760	6.750
3)	t/°C	49.8	45.1	39.9	35.2	25.8	19.1	14.9	10.1
	δ_{obsd}	6.861	6.851	6.836	6.828	6.803	6.786	6.772	6.759
4)	t/°C	49.4	44.9	40.4	35.4	24.0	20.6	15.2	9.5
	δ_{obsd}	6.863	6.850	6.842	6.834	6.801	6.793	6.776	6.763
5)	t/°C	50.0	45.3	40.2	35.3	25.2	20.6	15.4	9.8
	δ_{obsd}	7.061	7.060	7.058	7.054	7.051	7.049	7.045	7.039
6)	t/°C	50.0	45.3	40.2	35.3	25.2	20.6	15.4	9.8
	δ_{obsd}	7.057	7.054	7.051	7.051	7.045	7.043	7.040	7.038
7)	t/°C	50.0	45.3	40.2	35.3	25.2	20.6	15.4	9.8
	δ_{obsd}	7.063	7.062	7.059	7.057	7.052	7.049	7.046	7.041
8)	t/°C	50.0	44.9	39.8	34.3	25.3	20.3	14.7	9.3
	δ_{obsd}	6.808	6.793	6.778	6.765	6.735	6.710	6.684	6.668
9)	t/°C	50.0	44.9	39.8	34.3	25.3	20.3	14.7	9.3
	δ_{obsd}	6.809	6.796	6.777	6.765	6.735	6.714	6.689	6.672
10)	t/°C	50.0	44.9	39.8	34.3	25.3	20.3	14.7	9.3
	δ_{obsd}	6.811	6.801	6.785	6.771	6.743	6.716	6.695	6.678
11)	t/°C	49.7	44.6	39.8	34.8	24.9	20.3	14.7	9.7
	δ_{obsd}	6.718	6.699	6.683	6.665	6.624	6.596	6.561	6.534
12)	t/°C	49.7	44.6	39.8	34.8	24.9	20.3	14.7	9.7
	δ_{obsd}	6.716	6.698	6.682	6.663	6.622	6.594	6.559	6.531
13)	t/°C	49.7	44.6	39.8	34.8	24.9	20.3	14.7	9.7
	δ_{obsd}	6.725	6.706	6.692	6.673	6.633	6.603	6.572	6.545
14)	t/°C	49.9	45.4	40.5	34.5	24.8	20.7	14.8	9.6
	δ_{obsd}	6.733	6.722	6.703	6.699	6.665	6.633	6.604	6.583
15)	t/°C	49.9	45.4	40.5	34.5	24.8	20.7	14.8	9.6
	δ_{obsd}	6.741	6.728	6.711	6.704	6.667	6.644	6.607	6.588
16)	t/°C	49.9	45.4	40.5	34.5	24.8	20.7	14.8	9.6
	δ_{obsd}	6.735	6.722	6.703	6.702	6.667	6.637	6.606	6.585
17)	t/°C	49.7	44.9	40.1	34.5	24.6	20.0	15.0	10.5
	δ_{obsd}	7.054	7.042	7.032	7.024	7.000	6.989	6.964	6.946
18)	t/°C	49.7	44.9	40.1	34.5	24.6	20.0	15.0	10.5
	δ_{obsd}	7.052	7.040	7.030	7.023	6.996	6.986	6.960	6.945
19)	t/°C	49.7	44.9	40.1	34.5	24.6	20.0	15.0	10.5
	δ_{obsd}	7.041	7.031	7.022	7.010	6.981	6.967	6.947	6.932
20)	t/°C	65.3	59.9	54.6	50.3	44.8	40.3	35.4	25.2
	δ_{obsd}	6.904	6.899	6.891	6.887	6.880	6.874	6.866	6.847
21)	t/°C	65.3	59.9	54.6	50.3	44.8	40.3	35.4	25.2
	δ_{obsd}	6.902	6.893	6.888	6.883	6.877	6.869	6.863	6.845
22)	t/°C	65.3	59.9	54.6	50.3	44.8	40.3	35.4	25.2
	δ_{obsd}	6.906	6.899	6.891	6.888	6.881	6.874	6.869	6.849
23)	t/°C	50.0	45.0	40.0	35.0	25.0	20.0	15.0	10.0
	δ_{obsd}	7.231	7.233	7.237	7.239	7.242	7.242	7.245	7.248
24)	t/°C	50.0	45.0	40.5	34.2	29.8	23.8	17.8	10.0
	δ_{obsd}	4.806	4.806	4.804	4.803	4.802	4.800	4.799	4.797
25)	t/°C	50.0	44.5	40.0	34.0	29.2	23.0	17.5	11.8
	δ_{obsd}	4.803	4.801	4.800	4.800	4.797	4.795	4.795	4.793
26)	t/°C	49.7	45.0	40.9	34.5	30.5	23.2	14.3	10.0
	δ_{obsd}	4.798	4.798	4.797	4.795	4.795	4.793	4.790	4.788
27)	t/°C	49.3	45.4	40.2	35.5	29.2	23.0	17.5	13.2
	δ_{obsd}	6.528	6.520	6.515	6.504	6.490	6.479	6.463	6.452
28)	t/°C	46.0	39.7	34.9	31.2	26.1	21.0	19.0	13.0
	δ_{obsd}	6.509	6.498	6.485	6.477	6.466	6.458	6.447	6.430
29)	t/°C	46.0	39.7	34.9	31.2	26.1	21.0	19.0	13.0
	δ_{obsd}	6.507	6.496	6.485	6.477	6.466	6.458	6.441	6.428
30)	t/°C	59.8	55.0	49.9	44.5	40.0	35.8	30.5	24.9
	δ_{obsd}	8.801	8.793	8.787	8.779	8.773	8.765	8.760	8.746
31)	t/°C	59.8	55.0	49.9	44.5	40.0	35.8	30.5	24.9
	δ_{obsd}	8.793	8.784	8.776	8.770	8.763	8.757	8.749	8.735
32)	t/°C	59.8	55.0	49.9	44.5	40.0	35.8	30.5	24.9
	δ_{obsd}	8.784	8.776	8.768	8.763	8.754	8.746	8.741	8.727
33)	t/°C	25.4	19.8	14.7	10.0	5.1	0.6	-5.1	-9.8
	δ_{obsd}	4.896	4.886	4.877	4.868	4.858	4.848	4.836	4.826
34)	t/°C	25.4	19.8	14.7	10.0	5.1	0.6	-5.1	-9.8
	δ_{obsd}	4.910	4.900	4.891	4.882	4.871	4.861	4.850	4.840
35)	t/°C	25.4	19.8	14.7	10.0	5.1	0.6	-5.1	-9.8
	δ_{obsd}	4.898	4.891	4.879	4.869	4.859	4.848	4.837	4.836

a) Numbers 1) to 35) designate the runs of measurement and correspond to those in Table 2.

Table 2. Enthalpies of CH/π Complex Formation

No.	CH-Donor (D)	π-Acceptor (A)	c_A mol kg^{-1}	c_D mol kg^{-1}	δ_C ppm	K_{298}	$-\Delta H$[a] kcal mol^{-1}	$-\Delta S$[a] cal mol^{-1} K^{-1}
1	$CHCl_3$	C_6D_6	1.990	0.067	6.059	0.302	1.84	8.55
2			2.070	0.097	6.010	0.286	1.87	8.76
3			2.014	0.200	6.040	0.301	1.90	8.76
4			2.000	0.406	6.049	0.316	1.94	8.80
	Average						1.89	8.72
5	$CHCl_3$	C_6D_5Cl	1.963	0.226	6.895	0.673	1.51	5.85
6			2.025	0.325	6.903	0.707	1.47	5.62
7			1.985	0.416	6.890	0.683	1.59	6.09
	Average						1.52	5.85
8	$CHCl_3$	$C_6D_5CD_3$	1.967	0.316	5.684	0.261	2.07	9.62
9			2.012	0.407	5.711	0.267	2.08	9.60
10			2.030	0.767	5.729	0.278	2.13	9.69
	Average						2.09	9.64
11	$CHCl_3$	o-$C_6D_4(CD_3)_2$	1.996	0.397	5.250	0.242	2.18	10.13
12			1.999	0.519	5.235	0.245	2.22	10.24
13			1.981	0.621	5.280	0.253	2.24	10.25
	Average						2.21	10.21
14	$CHCl_3$	p-$C_6D_4(CD_3)_2$	2.000	0.318	5.538	0.273	1.99	9.26
15			2.001	0.472	5.528	0.276	2.06	9.47
16			2.002	0.644	5.552	0.291	2.06	9.37
	Average						2.04	9.37
17	$CHCl_3$	$C_6(CH_3)_6$	0.197	0.0079	6.215	1.59	2.97	9.04
18			0.200	0.0103	6.210	1.60	2.94	8.93
19			0.198	0.0397	6.150	1.67	3.03	9.15
	Average						2.98	9.04
20	$CHCl_3$	$C_{10}D_8$[b]	0.979	0.101	6.436	1.04	1.71	5.66
21			1.018	0.160	6.447	1.07	1.71	5.60
22			1.005	0.214	6.447	1.10	1.76	5.72
	Average						1.73	5.66
23	$CHCl_3$	C_6Cl_6[c]	0.006	0.020	7.412	—	—	
24	$CH(OCH_3)_3$	C_6D_6	2.027	0.797	4.730	6.36	1.04	0.19
25			1.990	0.599	4.721	5.44	0.97	0.11
26			1.964	0.396	4.718	5.09	0.97	0.02
	Average						0.99	0.09
27	$CHBr_3$	C_6D_6	1.943	0.593	5.856	0.534	2.01	7.99
28			1.989	0.389	5.759	0.497	2.01	8.13
29			1.982	0.200	5.750	0.488	1.95	7.97
	Average						1.99	8.10
30	CCl_3CHO	C_6D_6	2.022	0.596	8.305	0.605	2.15	8.21
31			2.012	0.396	8.275	0.603	2.15	8.22
32			1.997	0.200	8.260	0.607	2.23	8.48
	Average						2.18	8.30
33	CH_2Cl_2	C_6D_6	1.998	0.320	4.301	0.353	1.56	7.30
34			1.968	0.385	4.312	0.348	1.61	7.50
35			2.007	0.546	4.327	0.382	1.59	7.25
	Average						1.59	7.33

a) 1 cal_{th}=4.184 J. b) Naphthalene-d_8. c) The values for CH/Cl interaction.

Results and Discussion

Intermolecular CH/π complex is generally formed between a CH hydrogen donor (D) and a hydrogen-accepting π-base (A). The complex formation induces an ASIS, which causes a considerable high field shift of the proton NMR signal of the relevant hydrogen atom in the hydrogen donating molecule. The shift is known as the effect of diamagnetic field induced by the aromatic ring and becomes very predominant when the CH group approaches from the direction perpendicular to the plane of the aromatic ring of the π-acceptor (A) forming the CH/π complex (as illustrated by Eq. 1).

$$\mathrm{HCXYZ(D)} + \mathrm{ArH(A)} \rightleftharpoons \mathrm{HCXYZ{\cdot}ArH(C)} \qquad (1)$$

From this point of view, intermolecular CH/π interaction was studied by measuring the ^{1}H NMR signal of the CH donor (D) in the ternary system consisting of a CH-hydrogen-donor (D), an aromatic π-base (A), and

Table 3. Electron Densities on the Hydrogen Atoms and the Energies of Anti-Bonding CH Orbitals by PM3 Calculations

CH-Donor	Formal charge (ζ_H)	σ^*_{CH} Energy	$-\Delta H_{CH/\pi}$
	e[a)]	eV	kcal mol^{-1} [b)]
CCl_3CHO	0.081	1.55	2.2
$CHBr_3$	0.138	2.71	2.0
$CHCl_3$	0.104	2.59	1.9
CH_2Cl_2	0.075	3.09	1.6
$CH(OCH_3)_3$ CH	0.069	2.82	1.0
CH_3	0.474—0.016	—	

a) 1 e=1.602×10^{-19} C. b) 1 cal$_{th}$=4.184 J.

carbon tetrachloride (solvent). The observed chemical shifts are given in Table 1.

The method for the NMR spectroscopic determination of the formation constant is well established and has long been known.[17,18,20,21] If we assume that only the 1 : 1 complex is formed by the CH/π interaction,[22] the formation equilibrium constant (K) of the complex can be evaluated by the quantitative treatment of the high field shift. In this situation, the formation constant K is given by Eq. 2, where c_D and c_A are the initial stoichiometric concentrations of the CH donor (D) and the π-acceptor (A), respectively, and p represents the mole fraction of the CH/π complexed hydrogen donor.

$$K = pc_D/[c_D(1-p)(c_A - pc_D)] \qquad (2)$$

Since the observed chemical shift (δ) of the CH donor in the CH/π interacting system is easily expressible by the chemical shift of the free CH donor (D) and the CH/π complex (C), the mole fraction (p), and hence the formation constant (K), of the complex can be obtained from the observed chemical shift, if we could estimate the intrinsic chemical shift of the CH/π complex (δ_C in Eq. 3).

$$p = (\delta_D - \delta)/(\delta_D - \delta_C) \qquad (3)$$

The δ_C values are practically evaluated by the extrapolation to the absolute zero temperature of the observed chemical shift (δ) as described in the review by Laszolo.[18] The formation constants (K) at various temperatures from the temperature dependence measurement gives the enthalpy (ΔH) of the CH/π complex formation by use of the ln K vs. $1/T$ plot.[23] The results are summarized in Table 2.

The enthalpies of complex formation decreases in the order of $C_6D_5Cl > C_6D_6 > p\text{-}C_6D_4(CD_3)_2 > C_6D_5CD_3 > o\text{-}C_6D_4(CD_3)_2 > C_6(CH_3)_6$. Methyl group(s) can be expected to donate electrons to the aromatic ring; while chlorine atom is electron-withdrawing. Thus, the order is roughly in accord with the order of increasing electron density of the aromatic ring. As a whole, the CH/π interacted complexes are shown to be formed more favorably when the aromatic ring of the π-acceptor (A) becomes more electron-rich. This is convincing evidence for the hydrogen-bond-like nature of the CH/π interaction, since hydrogen bonding is generally favored by the increase in electron density on the hydrogen-acceptor.

The entropies of chloroform–arene complex formation are within a relatively narrow range from −8.7 to −10.2 cal mol^{-1} K^{-1}, except for the cases of chlorobenzene and naphthalene. Thus, the formation of CH/π complexes is governed to a greater extent by the enthalpies of their formation. The formation of chloroform/naphthalene-d_8 is considerably more favored entropically than chloroform/benzene-d_6 complex because the former π-base has two aromatic rings instead of one in the latter.

The similar treatment on chloroform/hexachlorobenzene/CCl_4 system gives a δ_C value in a lower field than δ_D (chemical shift of $CHCl_3$ in CCl_4). This can be attributed to the formation of a CH/Cl interacted species. The CH/Cl complex can also be formed in the case of chlorobenzene. The combined CH/π and CH/Cl interactions must result a larger formation constant than those for other π-bases. The entropy value with respect to chlorobenzene which is considerably less negative than those for benzene and the other methylbenzenes supports the additional formation of the CH/Cl interacted complex. Even if the CH/Cl interaction is mingled, the apparent ΔH value guarantees that the $-\Delta H$ of CH/π interaction for $CHCl_3/C_6H_5Cl$ system is less than 1.5 kcal mol^{-1}.

The electron densities and the anti-bonding CH orbital energies of the five CH donors are given in Table 3. Surveying the data on the benzene complexes of five different hydrogen donors, we can discern the tendency that the CH/π interaction becomes stronger as the positive charge on the hydrogen atom increases except for trichloroacetaldehyde (CCl_3CHO). This is in line with the electron-withdrawing ability of the substituents geminal to the CH bond. In the case of CCl_3CHO, polarizability may govern the feasibility of CH/π interaction because its formyl carbon atom is involved in a highly polarizable carbonyl bond. Its σ^*_{CH} energy which is considerably lower than others in Table 3 supports this interpretation.

Except for trichloroacetaldehyde, the enthalpy decreases in the decreasing order of the positive charge on the interacting hydrogen atom. However, the enthalpies could not be correlated confidently with the energies of the anti-bonding CH orbitals which can be a measure for the contribution of delocalization interaction. Thus the strength of the intermolecular CH/π interaction seems to be governed most predominantly by the electrostatic (dipole–quadrupole) attraction between the CH group and π-electrons quite similarly to the cases of weak hydrogen bonding. The exceptionally strong CH/π interaction in CCl_3CHO–C_6D_6 complex can be attributed to the larger stabilization due to the delocalization effect caused by the lower σ^*_{CH} energy. In the case of trimethoxymethane, the methoxyl hydrogen atoms can be enough acidic to interact with benzene, which, in turn, could increase the apparent formation constant of the CH/π complex.

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19) Following computer programs were employed in this research. (a) N. L. Allinger, MM2(91) (It is being distributed under a special agreement with Molecular Design Ltd. (MDL) of San Leandro, California and Prof. N. L. Allinger of the University of Georgia.). (b) K. Mislow, BIGSTRN-3 (QCPE # 514). (c) M. J. S. Dewar and J. J. P. Stewart, PM3 program (QCPE # 455).

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22) The concentration of the hydrogen donor (c_D) was kept lower than one third of that of the π-base (c_A) in order to suppress the formation of the 2 : 1 complex D_2A. Formation of the 1 : 1 complex was guaranteed by the constancy of ΔH and ΔS values while the concentration was varied. The 1 : 1 $CHCl_3/C_6H_6$ complex was also postulated in the previous investigations.[17,21]

23) The chemical shift of chloroform in carbon tetrachloride depends both on the temperature and the concentration of the solution. However, the influence of the temperature was almost negligible when the measurements were carried out at the concentrations lower than 0.5 mol kg^{-1}. Under the conditions of our experiments, the chemical shift moves towards upfield (from 7.250 ppm (at 10°C) to 7.227 ppm (at 65°C)) as the temperature increases. Thus, the δ_D values were corrected by taking the temperature of the solution into consideration.