Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

PCl_3-C_6H_6 heterodimer: Evidence for P…π *phosphorus bonding* at low temperatures

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Electronic Supplementary Information

Table S1. Thermodynamics of formation of various PCl_3-Benzene heterodimers

Dimer	Thermodyanamic parameters			
	ΔE (kcal/mol)	**ΔH (kcal/mol)**	**ΔS (kcal/mol/k)**	**ΔG (kcal/mol)**
Dimer-**I**	-9.87	-9.97	-0.031	-8.41
Dimer-**II**	-7.67	-7.77	-0.032	-6.19
Dimer-**III**	-6.05	-6.15	-0.032	-4.57
Dimer-**IV**	-4.52	-4.61	-0.028	-3.19

Table S2. The structures of PCl_3-Benzene heterodimers along with its ZPE corrected relative energies (kcal/mol) calculated at MP2/6-311++G(d,p) level of theory.

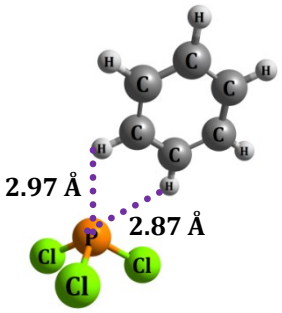
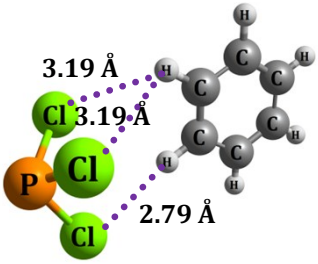
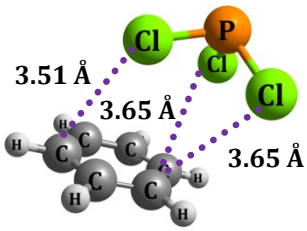
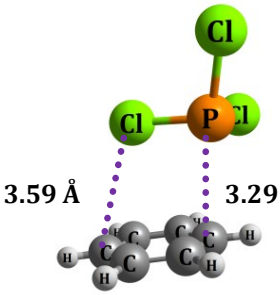
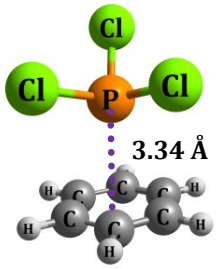
Structure of the adduct	Relative energy (kcal/mol)
 V	6.77
 IV	5.06
 III	2.88
 II	1.96
 I	0.00

Table S3. The structures of PCl_3-Benzene heterodimers along with its relative energies (kcal/mol) calculated at dispersion corrected B3LYP/aug-cc-pVDZ level of theory.

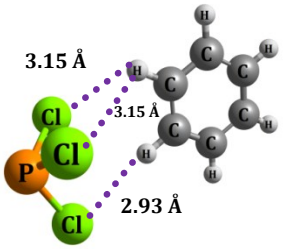
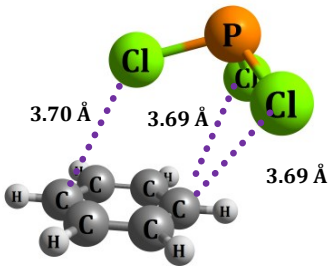
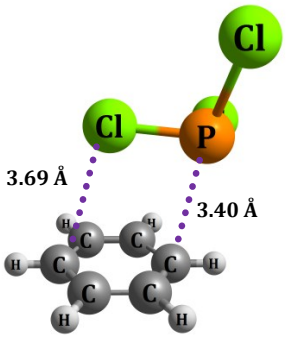
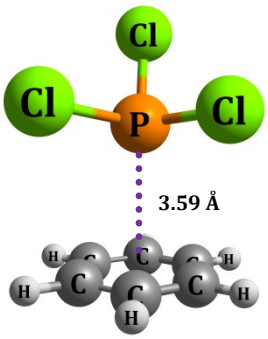
Structure of the adduct	Relative energy (kcal/mol)
 IV	2.38
 III	1.73
 II	0.88
 I	0.00

Table S4. The structures of PCl_3-Benzene heterodimers along with its ZPE corrected relative energies (kcal/mol) calculated at dispersion corrected B3LYP/6-311++G(d,p) level of theory

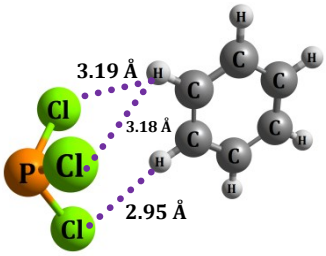
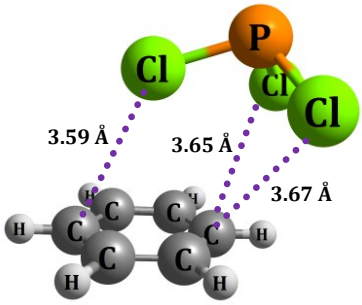
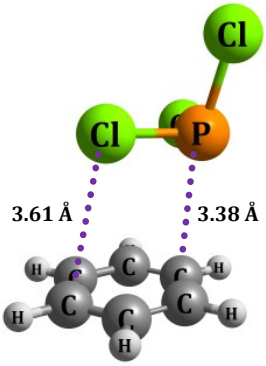
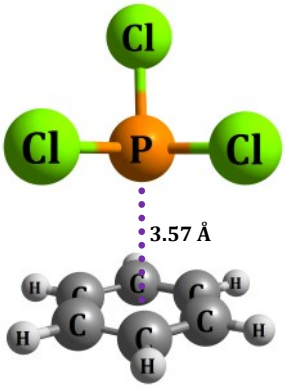
Structure of the adduct	Relative energy (kcal/mol)
 IV	3.24
 III	1.72
 II	0.91
 I	0.00

Table S5. Computed and experimental vibrational wavenumbers, shifts in the wavenumbers and mode assignments for PCl_3-C_6H_6 heterodimers calculated at MP2/aug-CC-pVDZ level of theory.

Vibrational wavenumbers *v* (cm^{-1})			Vibrational mode assignments
Computed[a]	**Shift with respect to the monomer**	**Experimental**[b] **(N_2 Matrix)**	
PCl_3 Region			
492.0 (146)	---	496.6	ν_3(P-Cl stretching, e)[c] in PCl_3
474.5 (150) 474.6 (116)	-17.5 -17.4	488.9 (-7.7) 487.0 (-7.2) 483.6 (-8.7)	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**I**
476.9 (187) 480.6 (121)	-15.1 -11.4	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**II**
483.2 (120) 491.2 (104)	-8.8 -0.8	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**III**
487.5 (124) 490.5 (117)	-4.5 -1.5	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**IV**
Benzene Region			
678.3 (116)	---	678.4	ν_4 out-of-plane bending of C_6H_6
686.6 (133)	+8.3	683.8 (+5.4)	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**I**
681.4 (130)	+3.1	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**II**
673.4 (128)	-4.9	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**III**
682.1 (100)	+3.8	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**IV**
680.8 (81) 685.2 (139)	+2.5 +6.9	679.8 (+1.4) 681.8 (+3.4)	out-of-plane bending in C_6H_6 sub-molecule of C_6H_6 dimer

[a] Intensities in km/mol given in parenthesis.
[b] Experimental shift with respect to the monomer given in parenthesis.
[c] P-Cl doubly degenerate vibrational stretching wavenumber.
[d]Features were not observed experimentally.

Table S6. Computed and experimental vibrational wavenumbers, shifts in the wavenumbers and mode assignments for PCl_3-C_6H_6 heterodimers calculated at dispersion corrected B3LYP/aug-CC-pVDZ level of theory.

Vibrational wavenumber ν (cm^{-1})			Vibrational mode assignments
Computed[a]	**Shift with respect to the monomer**	**Experimental[b] (N_2 Matrix)**	
PCl_3 Region			
464.1 (146)	---	496.6	ν_3(P-Cl stretching, e)[c] in PCl_3
453.7 (151) 454.4 (118)	-10.4 -9.7	488.9 (-7.7) 487.0 (-7.2) 483.6 (-8.7)	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**I**
453.1 (176) 462.5 (133)	-11.0 -1.6	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**II**
457.1 (120) 466.6 (109)	-7.0 +2.5	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**III**
461.6 (126) 464.7 (118)	-2.5 +0.6	-[d]	P-Cl stretching in PCl_3 sub-molecule of PCl_3-C_6H_6 dimer-**IV**
Benzene Region			
680.9 (113)	---	678.4	ν_4 out-of-plane bending of C_6H_6
683.5 (130)	+2.6	683.8 (+5.4)	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**I**
681.8 (130)	+0.9	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**II**
675.8 (125)	-5.1	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**III**
682.9 (97)	+2.0	-[d]	out-of-plane bending in C_6H_6 sub-molecule of PCl_3-C_6H_6 dimer-**IV**

[a] Intensities in km/mol given in parenthesis.

[b] Experimental shift with respect to the monomer given in parenthesis.

[c] P-Cl doubly degenerate vibrational stretching wavenumber.

[d]Features were not observed experimentally.

Table S7. The structure of $(C_6H_6)_2$ homodimer and interaction energy (kcal/mol) calculated at MP2/aug-cc-pVDZ level of theory

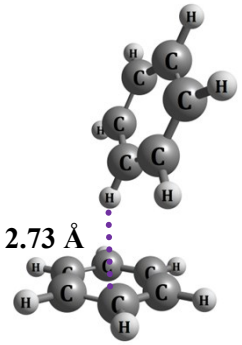
Structure of the $(C_6H_6)_2$ homodimer	Binding energy (ZPE/BSSE corrected) (kcal/mol)
	-6.02/-2.42

Fig S1. The AIM structure of C_6H_6-HCl dimer calculated at MP2/aug-cc-pVDZ level of theory