Estimating the Binding Ability of Onium Ions with CO_2 and π Systems: A Computational Investigation

M. Althaf Hussain, A. Subha Mahadevi and G. Narahari Sastry*

Centre for Molecular Modeling, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad, Andhra Pradesh, India, 500607.

Supporting Information

(25 Pages including contents page)

Contents Page No

Table S1. Calculated topological properties at the (3,-1) critical points of various $CO_2\cdots\pi$ complexes, obtained from M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All values are in au.

Complex	Interaction	ρ(r)	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)	-G(r)/V(r)	Type of Interaction
BC	**1**	0.0061	0.0052	0.0044	-0.0036	0.0008	1.2172	(B)$C_1\cdots O(CO_2)$
	2	0.0081	0.0071	0.0057	-0.0042	0.0014	1.3402	(B)$C_4\cdots O(CO_2)$
RC	**1**	0.0188	0.0166	0.0153	-0.0139	0.0014	1.0973	(R)N$\cdots C(CO_2)$
QC	**1**	0.0081	0.0072	0.0057	-0.0043	0.0014	1.3376	(Q)$C_3\cdots O(CO_2)$
UC	**1**	0.0069	0.0061	0.0052	-0.0043	0.0009	1.2141	(U)P-H$\cdots O(CO_2)$
	2	0.0087	0.0082	0.0066	-0.0049	0.0016	1.3323	(U)C_4-$C_5\cdots O(CO_2)$
ZC	**1**	0.0078	0.0070	0.0063	-0.0055	0.0007	1.1343	(Z)N$\cdots O(CO_2)$
	2	0.0090	0.0080	0.0065	-0.0050	0.0015	1.2971	(Z)C_4-$C_5\cdots O(CO_2)$
FC	**1**	0.0148	0.0158	0.0140	-0.0122	0.0018	1.1478	(F)O$\cdots C(CO_2)$
TC	**1**	0.0066	0.0062	0.0053	-0.0044	0.0009	1.2011	(T)S$\cdots O(CO_2)$
N0C	**1**	0.0268	0.0299	0.0266	-0.0232	0.0033	1.1436	(N0)H$\cdots O(CO_2)$
N1C	**1**	0.0232	0.0267	0.0229	-0.0190	0.0038	1.2019	(N1)H$\cdots O(CO_2)$
N2C	**1**	0.0203	0.0235	0.0197	-0.0159	0.0038	1.2386	(N2)H$\cdots O(CO_2)$
N3C	**1**	0.0189	0.0217	0.0181	-0.0145	0.0036	1.2453	(N3)H$\cdots O(CO_2)$
N4C	**1**	0.0092	0.0084	0.0071	-0.0058	0.0013	1.2273	(N4)C-H$\cdots O(CO_2)$
	2	0.0091	0.0083	0.0070	-0.0057	0.0013	1.2265	(N4)C-H$\cdots O(CO_2)$
	3	0.0091	0.0083	0.0070	-0.0057	0.0013	1.2266	(N4)C-H$\cdots O(CO_2)$
P0C	**1**	0.0139	0.0134	0.0120	-0.0105	0.0015	1.1386	(P0)P$\cdots O(CO_2)$
P1C	**1**	0.0119	0.0116	0.0103	-0.0089	0.0014	1.1553	(P1)P$\cdots O(CO_2)$
	2	0.0093	0.0089	0.0075	-0.0060	0.0015	1.2403	(P1)C-H$\cdots O(CO_2)$
P2C	**1**	0.0102	0.0102	0.0087	-0.0072	0.0015	1.2067	(P2)P-H$\cdots O(CO_2)$
	2	0.0085	0.0079	0.0067	-0.0055	0.0012	1.2244	(P2)C-H$\cdots O(CO_2)$
	3	0.0086	0.0080	0.0067	-0.0055	0.0012	1.2243	(P2)C-H$\cdots O(CO_2)$
P3C	**1**	0.0091	0.0091	0.0077	-0.0063	0.0014	1.2224	(P3)P-H$\cdots O(CO_2)$
	2	0.0088	0.0081	0.0068	-0.0056	0.0012	1.2197	(P3)C-H$\cdots O(CO_2)$
	3	0.0087	0.0080	0.0068	-0.0056	0.0012	1.2197	(P3)C-H$\cdots O(CO_2)$
P4C	**1**	0.0088	0.0079	0.0067	-0.0055	0.0012	1.2146	(P4)C-H$\cdots O(CO_2)$
	2	0.0089	0.0079	0.0067	-0.0055	0.0012	1.2153	(P4)C-H$\cdots O(CO_2)$
	3	0.0090	0.0080	0.0068	-0.0056	0.0012	1.2153	(P4)C-H$\cdots O(CO_2)$
O0C	**1**	0.0560	0.0400	0.0508	-0.0616	-0.0108	0.8253	(O0)H$\cdots O(CO_2)$
O1C	**1**	0.0412	0.0383	0.0402	-0.0420	-0.0019	0.9550	(O1)H$\cdots O(CO_2)$
O2C	**1**	0.0361	0.0367	0.0362	-0.0357	0.0005	1.0129	(O2)H$\cdots (CO_2)$
O3C	**1**	0.0096	0.0087	0.0074	-0.0060	0.0013	1.2241	(O3)H$\cdots O(CO_2)$
	2	0.0096	0.0087	0.0074	-0.0060	0.0013	1.2235	(O3)H $\cdots O(CO_2)$
	3	0.0095	0.0087	0.0074	-0.0060	0.0013	1.2241	(O3)H $\cdots O(CO_2)$
S0C	**1**	0.0272	0.0292	0.0255	-0.0217	0.0038	1.1736	(S0)H$\cdots O(CO_2)$
S1C	**1**	0.0134	0.0144	0.0124	-0.0104	0.0020	1.1922	(S1)S$\cdots O(CO_2)$
	2	0.0100	0.0098	0.0082	-0.0066	0.0016	1.2420	(S1)C-H$\cdots O(CO_2)$

S2C	**1**	0.0141	0.0141	0.0119	-0.0096	0.0023	1.2352	(S2)S-H···O(CO_2)
	2	0.0082	0.0076	0.0065	-0.0053	0.0011	1.2140	(S2)C-H···O(CO_2)
	3	0.0082	0.0076	0.0065	-0.0053	0.0011	1.2141	(S2)C-H···O(CO_2)
S3C	**1**	0.0099	0.0098	0.0086	-0.0073	0.0012	1.1646	(S3)S···O(CO_2)
	2	0.0099	0.0094	0.0079	-0.0064	0.0015	1.2373	(S3)C-H···O(CO_2)
	3	0.0099	0.0094	0.0079	-0.0064	0.0015	1.2375	(S3)C-H···O(CO_2)

Table S2. Calculated topological properties at the (3,-1) critical points of various ammonium ion···π complexes obtained from M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All values are in au.

Complex	Interaction	ρ(r)	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)	-G(r)/V(r)	Type of Interaction
BN0	**1**	0.0146	0.0113	0.0093	-0.0074	0.0019	1.2572	(N0)N-H···C(B)
	2	0.0146	0.0112	0.0093	-0.0074	0.0019	1.2586	(N0)N-H···C(B)
BN1	**1**	0.0138	0.0106	0.0089	-0.0072	0.0017	1.2428	(N1)N-H···C(B)
	2	0.0142	0.0109	0.0091	-0.0073	0.0018	1.2466	(N1)N-H···C(B)
BN2	**1**	0.0141	0.0108	0.0091	-0.0073	0.0017	1.2385	(N2)N-H···C(B)
	2	0.0141	0.0108	0.0091	-0.0073	0.0017	1.2385	(N2)N-H···C(B)
BN3	**1**	0.0133	0.0119	0.0100	-0.0080	0.0020	1.2464	(N3)N-H···C(B)
	2	0.0132	0.0119	0.0099	-0.0079	0.0020	1.2487	(N3)N-H···C(B)
	3	0.0132	0.0119	0.0099	-0.0079	0.0020	1.2458	(N3)N-H···C(B)
	4	0.0132	0.0119	0.0099	-0.0079	0.0020	1.2486	(N4)N-H···C(B)
BN4	**1**	0.0071	0.0045	0.0038	-0.0031	0.0007	1.2155	(N1)C-H···C(B)
	2	0.0090	0.0072	0.0060	-0.0047	0.0013	1.2669	(N1)C-H···C(B)
	3	0.0073	0.0047	0.0039	-0.0032	0.0007	1.2198	(N1)C-H···C(B)
RN1	**1**	0.0118	0.0094	0.0079	-0.0064	0.0015	1.2305	(N0)N-H···C(R)
	2	0.0118	0.0094	0.0079	-0.0064	0.0015	1.2305	(N0)N-H···C(R)
	3	0.0119	0.0095	0.0081	-0.0066	0.0015	1.2193	(N1)C-H···N(R)
RN2	**1**	0.0729	0.0194	0.0454	-0.0715	-0.0261	0.6354	(N2)N-H···N(R)
RN3	**1**	0.0658	0.0219	0.0425	-0.0632	-0.0206	0.6731	(N3)N-H···N(R)
RN4	**1**	0.0113	0.0083	0.0073	-0.0062	0.0011	1.1686	(N4)C-H···N(R)
	2	0.0134	0.0102	0.0088	-0.0074	0.0014	1.1852	(N4)C-H···N(R)
	3	0.0132	0.0100	0.0087	-0.0073	0.0014	1.1852	(N4)C-H···N(R)
QN0	**1**	0.0349	0.0090	0.0144	-0.0198	-0.0054	0.7272	(N0)N-H···P(Q)
QN1	**1**	0.0128	0.0100	0.0081	-0.0063	0.0018	1.2942	(N1)N-H···C(Q)
	2	0.0130	0.0096	0.0080	-0.0064	0.0016	1.2523	(N1)N-H···C(Q)
	3	0.0057	0.0038	0.0032	-0.0025	0.0007	1.2634	(N1)C-H···P(Q)
QN2	**1**	0.0127	0.0099	0.0085	-0.0070	0.0015	1.2070	(N2)N-H···C(Q)
QN3	**1**	0.0128	0.0092	0.0081	-0.0070	0.0011	1.1548	(N3)N-H···P(Q)
QN4	**1**	0.0068	0.0042	0.0036	-0.0030	0.0006	1.1938	(N4)C-H···C(Q)
	2	0.0079	0.0059	0.0080	-0.0041	0.0040	1.9710	(N4)C-H···C(Q)
	3	0.0068	0.0041	0.0035	-0.0029	0.0006	1.2159	(N4)C-H···P(Q)
UN0	**1**	0.0136	0.0097	0.0080	-0.0064	0.0017	1.2621	(N0)N-H···C(U)
	2	0.0136	0.0097	0.0080	-0.0064	0.0017	1.2621	(N0)N-H···C(U)
	3	0.0097	0.0087	0.0075	-0.0063	0.0012	1.1976	(N0)N···P(U)
UN1	**1**	0.0130	0.0093	0.0077	-0.0061	0.0016	1.2545	(N1)N-H···C(U)
	2	0.0130	0.0093	0.0077	-0.0061	0.0016	1.2545	(N1)N-H···C(U)
	3	0.0068	0.0046	0.0039	-0.0031	0.0008	1.2408	(N1)N···P(U)
UN2	**1**	0.0130	0.0093	0.0078	-0.0063	0.0015	1.2406	(N0)N-H···C(U)
	2	0.0130	0.0093	0.0078	-0.0063	0.0015	1.2408	(N0)N-H···C(U)

UN3	**1**	0.0152	0.0131	0.0110	-0.0089	0.0021	1.2344	(N0)N-H···C(U)
	2	0.0152	0.0131	0.0110	-0.0089	0.0021	1.2344	(N0)N-H···C(U)
UN4	**1**	0.0072	0.0049	0.0041	-0.0034	0.0008	1.2258	(N4)C-H···C(U)
	2	0.0084	0.0058	0.0049	-0.0039	0.0009	1.2340	(N4)C-H···C(U)
	3	0.0084	0.0048	0.0042	-0.0035	0.0007	1.1933	(N4)C-H···P(U)
	4	0.0075	0.0055	0.0048	-0.0041	0.0007	1.1703	(N4)C-H···P(U)
ZN0	**1**	0.0188	0.0136	0.0117	-0.0098	0.0019	1.1911	(N0)N-H···C(Z)
	2	0.0167	0.0124	0.0105	-0.0086	0.0019	1.2193	(N0)N-H···C(Z)
ZN1	**1**	0.0184	0.0135	0.0116	-0.0097	0.0019	1.1962	(N1)N-H···C(Z)
	2	0.0151	0.0114	0.0096	-0.0078	0.0018	1.2251	(N1)N-H···C(Z)
ZN2	**1**	0.0166	0.0124	0.0106	-0.0087	0.0019	1.2126	(N2)N-H···C(Z)
	2	0.0166	0.0124	0.0106	-0.0087	0.0019	1.2126	(N2)N-H···C(Z)
ZN3	**1**	0.0217	0.0171	0.0152	-0.0133	0.0019	1.1396	(N3)N-H···C(Z)
NZ4	**1**	0.0099	0.0086	0.0071	-0.0057	0.0014	1.2526	(N4)C-H···C(Z)
	2	0.0082	0.0055	0.0046	-0.0038	0.0009	1.2252	(N4)C-H···C(Z)
	3	0.0087	0.0054	0.0046	-0.0039	0.0007	1.1899	(N4)C-H···C(Z)
FN0	**1**	0.0183	0.0137	0.0117	-0.0097	0.0020	1.2097	(N0)N-H···C(F)
	2	0.0131	0.0127	0.0110	-0.0092	0.0018	1.1918	(N0)N-H···O(F)
FN1	**1**	0.0125	0.0094	0.0080	-0.0065	0.0014	1.2199	(N1)N-H···C(F)
	2	0.0175	0.0128	0.0110	-0.0092	0.0018	1.1984	(N1)N-H···C(F)
	3	0.0092	0.0077	0.0068	-0.0059	0.0009	1.1605	(N2)C-H···O(F)
FN2	**1**	0.0176	0.0129	0.0111	-0.0093	0.0018	1.1970	(N2)N-H···C_5(F)
	2	0.0122	0.0091	0.0078	-0.0065	0.0013	1.2035	(N2)N-H···C_2-C_3(F)
	3	0.0082	0.0069	0.0061	-0.0052	0.0009	1.1638	(N3)C-H···O(F)
FN3	**1**	0.0172	0.0142	0.0121	-0.0100	0.0021	1.2115	(N3)N-H···C_3(F)
	2	0.0077	0.0074	0.0063	-0.0053	0.0010	1.1937	(N3)C···O(F)
FN4	**1**	0.0085	0.0052	0.0044	-0.0036	0.0008	1.2264	(N4)C-H···C(F)
	2	0.0085	0.0052	0.0044	-0.0036	0.0008	1.2264	(N4)C-H···C(F)
	3	0.0121	0.0104	0.0090	-0.0076	0.0014	1.1813	(N4)C-H···O(F)
TN0	**1**	0.0152	0.0113	0.0094	-0.0076	0.0018	1.2392	(N0)N-H···C_2(T)
	2	0.0152	0.0113	0.0094	-0.0076	0.0018	1.2392	(N0)N-H···C_5(T)
TN1	**1**	0.0147	0.0110	0.0092	-0.0075	0.0017	1.2314	(N1)N-H···C_2(T)
	2	0.0147	0.0110	0.0092	-0.0075	0.0017	1.2313	(N1)N-H···C_5(T)
TN2	**1**	0.0144	0.0108	0.0091	-0.0074	0.0017	1.2273	(N2)N-H···C_2(T)
	2	0.0144	0.0108	0.0091	-0.0074	0.0017	1.2270	(N2)N-H···C_5(T)
TN3	**1**	0.0156	0.0139	0.0117	-0.0095	0.0022	1.2337	(N3)N-H···C_3(T)
	2	0.0156	0.0139	0.0117	-0.0095	0.0022	1.2348	(N3)N-H···C_4(T)
	3	0.0122	0.0119	0.0102	-0.0086	0.0017	1.1939	(N3)N-H···S(T)
TN4	**1**	0.0070	0.0041	0.0036	-0.0030	0.0006	1.1824	(N4)C-H···C_4(T)
	2	0.0096	0.0075	0.0062	-0.0048	0.0013	1.2779	(N4)C-H···C_3(T)
	3	0.0071	0.0047	0.0040	-0.0032	0.0007	1.2289	(N4)C-H···C_2(T)

Table S3. Calculated topological properties at the (3,-1) critical points of various phosphonium ion···π complexes obtained from M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All values are in au.

Complex	Interaction	ρ(r)	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)	-G(r)/V(r)	Type of Interaction
BP0	**1**	0.0145	0.0111	0.0091	-0.0072	0.0020	1.2752	(P0)H···C(B)
	2	0.0110	0.0081	0.0070	-0.0060	0.0011	1.1801	(P0)P···C(B)
BP1	**1**	0.0136	0.0106	0.0087	-0.0068	0.0019	1.2841	(P1)H···C(B)
	2	0.0098	0.0078	0.0067	-0.0055	0.0012	1.2134	(P1)P-H···C(B)
BP2	**1**	0.0125	0.0098	0.0080	-0.0063	0.0017	1.2737	(P2)P-H···C_1(B)
	2	0.0093	0.0077	0.0065	-0.0053	0.0012	1.2190	(P2)P-H···C_4(B)
	3	0.0064	0.0047	0.0039	-0.0031	0.0008	1.2654	(P2)C-H···C_2(B)
	4	0.0064	0.0047	0.0039	-0.0031	0.0008	1.2648	(P2)C-H···C_6(B)
BP3	**1**	0.0119	0.0093	0.0077	-0.0061	0.0016	1.2662	(P3)P-H···C_1(B)
	2	0.0091	0.0076	0.0064	-0.0053	0.0011	1.2176	(P3)P-H···C_4(B)
	3	0.0061	0.0044	0.0036	-0.0029	0.0007	1.2579	(P3)C-H···C_2(B)
	4	0.0061	0.0044	0.0036	-0.0029	0.0007	1.2579	(P3)C-H···C_6(B)
BP4	**1**	0.0070	0.0047	0.0039	-0.0032	0.0008	1.2458	(P4)C-H···C1(B)
	2	0.0069	0.0046	0.0039	-0.0031	0.0008	1.2419	(P4)C-H···C_3(B)
	3	0.0089	0.0070	0.0057	-0.0045	0.0012	1.2766	(P4)C-H···C_5(B)
RP0	**1**	0.0597	0.0129	0.0301	-0.0473	-0.0172	0.6361	(P0)P···N(R)
RP1	**1**	0.0499	0.0159	0.0260	-0.0360	-0.0101	0.7200	(P1)P···N(R)
RP2	**1**	0.0186	0.0129	0.0124	-0.0119	0.0005	1.0429	(P2)P···N(R)
RP3	**1**	0.0143	0.0106	0.0098	-0.0090	0.0008	1.0934	(P3)P-H···N(R)
	2	0.0115	0.0092	0.0080	-0.0068	0.0012	1.1827	(P3)C-H···N(R)
	3	0.0115	0.0092	0.0080	-0.0068	0.0012	1.1827	(P3)C-H ···N(R)
RP4	**1**	0.0098	0.0073	0.0064	-0.0055	0.0009	1.1659	(P4)C-H···N(R)
	2	0.0123	0.0094	0.0081	-0.0068	0.0013	1.1893	(P4)C-H···N(R)
	3	0.0114	0.0087	0.0075	-0.0064	0.0012	1.1848	(P4)C-H···N(R)
QP0	**1**	0.0095	0.0064	0.0055	-0.0047	0.0009	1.1831	(P0)P-H···P-C_2(Q)
	2	0.0126	0.0096	0.0078	-0.0059	0.0018	1.3080	(P0)H···C_3(Q)
QP1	**1**	0.0116	0.0089	0.0073	-0.0056	0.0017	1.3009	(P1)H···C_3(Q)
	2	0.0086	0.0062	0.0053	-0.0044	0.0009	1.2037	(P1)P-H···P(Q)
	3	0.0068	0.0044	0.0037	-0.0030	0.0007	1.2421	(P1)C-H···P(Q)
QP2	**1**	0.0086	0.0086	0.0055	-0.0046	0.0009	1.1913	(P2)P-H···P(Q)
	2	0.0111	0.0084	0.0069	-0.0055	0.0015	1.2697	(P2)H···C_4(R)
	3	0.0060	0.0040	0.0033	-0.0026	0.0007	1.2680	(P3)C-H···P(Q)
	4	0.0060	0.0040	0.0033	-0.0026	0.0007	1.2680	(P3)C-H···P(Q)
QP3	**1**	0.0084	0.0063	0.0054	-0.0046	0.0009	1.1873	(P3)H···P(Q)
	2	0.0104	0.0078	0.0065	-0.0052	0.0013	1.2538	(P3)H···C_4(Q)
	3	0.0058	0.0038	0.0032	-0.0025	0.0006	1.2571	(P3)C-H···P(R)
	4	0.0057	0.0039	0.0032	-0.0025	0.0007	1.2720	(P3)C-H···C_2(P)
QP4	**1**	0.0074	0.0044	0.0038	-0.0031	0.0007	1.2092	(P4)C-H···P(Q)
	2	0.0059	0.0037	0.0031	-0.0025	0.006	1.2385	(P4)C-H···C_2(Q)
	3	0.0075	0.0055	0.0046	-0.0038	0.008	1.2149	(P4)C-H···C_6(Q)

UP0	**1**	0.0132	0.0090	0.0080	-0.0070	0.0010	1.1456	(P0)P-H···C_2(U)
	2	0.0182	0.0126	0.0108	-0.0089	0.0019	1.2127	(P0)H···C_5(U)
UP1	**1**	0.0118	0.0082	0.0075	-0.0067	0.0007	1.1109	(P1)P-H···P(U)
	2	0.0120	0.0084	0.0070	-0.0055	0.0014	1.2594	(P1)H···C_2-C_3(U)
UP2	**1**	0.0109	0.0080	0.0072	-0.0064	0.0008	1.1243	(P2)P-H···P(U)
	2	0.0110	0.0080	0.0067	-0.0053	0.0013	1.2466	(P2)H···C_3(U)
	3	0.0068	0.0050	0.0042	-0.0033	0.0009	1.2576	(P2)C-H···P(U)
UP3	**1**	0.0133	0.0097	0.0081	-0.0065	0.0016	1.2479	(P3)P-H···C_2(U)
	2	0.0097	0.0078	0.0066	-0.0055	0.0012	1.2114	(P3)P-H···C_5(U)
	3	0.0049	0.0040	0.0032	-0.0024	0.0008	1.3321	(P3)C···H-P(U)
	4	0.0063	0.0044	0.0036	-0.0029	0.0007	1.2486	(P3)C-H···C_3(U)
	5	0.0063	0.0042	0.0036	-0.0030	0.0006	1.1915	(P3)C-H···C_4(U)
UP4	**1**	0.0071	0.0042	0.0035	-0.0029	0.0006	1.2130	(P4)C-H···P(U)
	2	0.0074	0.0057	0.0050	-0.0042	0.0007	1.1755	(P4)C-H···P(U)
	3	0.0086	0.0061	0.0051	-0.0040	0.010	1.2521	(P4)C-H···C_2-C_3(Z)
	4	0.0073	0.0046	0.0039	-0.0033	0.0006	1.1938	(P4)C-H···P(U)
ZP0	**1**	0.0213	0.0153	0.0134	-0.0114	0.0019	1.1686	(P0)P···C_2(Z)
	2	0.0145	0.0105	0.0093	-0.0081	0.0012	1.1505	(P0)H···C_5(Z)
ZP1	**1**	0.0176	0.0136	0.0117	-0.0098	0.0019	1.1959	(P1)P-H···C_2(Z)
	2	0.0123	0.0098	0.0085	-0.0073	0.0013	1.1729	(P1)P-H···C_4(Z)
ZP2	**1**	0.0138	0.0128	0.0108	-0.0087	0.0021	1.2399	(P2)H···N(Z)
	2	0.0114	0.0096	0.0082	-0.0068	0.0014	1.2011	(P2)H···C_3(Z)
ZP3	**1**	0.0129	0.0119	0.0100	-0.0081	0.0019	1.2326	(P3)H···N(Z)
	2	0.0128	0.0112	0.0096	-0.0079	0.0017	1.2115	(P3)P-H···C_2(Z)
	3	0.0072	0.0055	0.0046	-0.0036	0.0009	1.2584	(P3)C-H···C_3-C_4(Z)
ZP4	**1**	0.0105	0.0088	0.0073	-0.0059	0.0015	1.2537	(P4)C-H ···C_2(Z)
FP0	**1**	0.0169	0.0159	0.0137	-0.0115	0.0022	1.1885	(P0)P-H···O(F)
FP1	**1**	0.0160	0.0121	0.0102	-0.0083	0.0019	1.2329	(P1)P-H···C_2(F)
	2	0.0118	0.0092	0.0081	-0.0070	0.0011	1.1562	(P1)P···C_5(F)
FP2	**1**	0.0127	0.0123	0.0109	-0.0095	0.0014	1.1445	(P2)H···O(F)
	2	0.0119	0.0107	0.0092	-0.0077	0.0015	1.1959	(P2)H···C_2(F)
FP3	**1**	0.0118	0.0115	0.0102	-0.0088	0.0013	1.1495	(P3)H···O(F)
	2	0.0113	0.0100	0.0086	-0.0072	0.0014	1.1958	(P3)H···C_2(F)
	3	0.0113	0.0100	0.0086	-0.0072	0.0014	1.1958	(P3)H···C_5(F)
FP4	**1**	0.0097	0.0094	0.0082	-0.0071	0.0012	1.1664	(P4)C-H···O(F)
	2	0.0106	0.0092	0.0080	-0.0068	0.0012	1.1804	(P4)C-H···O(F)
	3	0.0060	0.0049	0.0043	-0.0037	0.0006	1.1677	(P4)C-H···O(F)
	4	0.0093	0.0086	0.0073	-0.0060	0.0013	1.2223	(P4)C-H···C_2(F)
	5	0.0098	0.0085	0.0071	-0.0058	0.0014	1.2380	(P4)C-H···C_5(F)
TP0	**1**	0.0163	0.0121	0.0100	-0.0079	0.0021	1.2658	(P0)P···C_2-C_3(T)
	2	0.0117	0.0090	0.0077	-0.0064	0.0013	1.2001	(P0)H···C_4-C_5(T)
TP1	**1**	0.0147	0.0111	0.0091	-0.0072	0.0020	1.2728	(P1)H···C_2(T)
TP2	**1**	0.0137	0.0105	0.0087	-0.0068	0.0018	1.2707	(P2)H···C_2(F)

TP3	**1**	0.0128	0.0098	0.0081	-0.0064	0.0017	1.2666	(P3)H···C_2(T)
	2	0.0060	0.0043	0.0036	-0.0029	0.0007	1.2444	(P3)H···C_5(T)
TP4	**1**	0.0070	0.0050	0.0041	-0.0033	0.0008	1.2576	(P4)C-H···S(T)
	2	0.0068	0.0041	0.0036	-0.0030	0.0006	1.1930	(P4)C-H···C_2(T)
	3	0.0098	0.0075	0.0061	-0.0047	0.0014	1.2921	(P4)C-H···C_4(T)

Table S4. Calculated topological properties at the (3,-1) critical points of various hydronium ion···π complexes obtained from M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All values are in au.

Complex	Interaction	ρ(r)	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)	-G(r)/V(r)	Type of Interaction
BO0	**1**	0.0145	0.0110	0.0095	-0.0079	0.0015	1.1951	(O0)H···C_1-C_2(B)
	2	0.0145	0.0110	0.0095	-0.0079	0.0015	1.1951	(O0)H···C_3-C_4(B)
	3	0.0145	0.0110	0.0095	-0.0079	0.0015	1.1951	(O0)H···C_5-C_6(B)
BO1	**1**	0.0180	0.0131	0.0114	-0.0097	0.0017	1.1746	(O1)H···C_1(B)
	2	0.0190	0.0133	0.0119	-0.0105	0.0014	1.1335	(O1)H···C_3(B)
BO2	**1**	0.0259	0.0161	0.0157	-0.0152	0.0004	1.0291	(O2)H···C_1-C_2(B)
BO3	**1**	0.0078	0.0068	0.0060	-0.0052	0.0008	1.1502	(O3)O···C_1(B)
	2	0.0077	0.0068	0.0060	-0.0053	0.0007	1.1496	(O3)O···C_5(B)
	3	0.0078	0.0067	0.0059	-0.0052	0.0008	1.1392	(O3)O···C_2(B)
	4	0.0070	0.0064	0.0052	-0.0041	0.0007	1.2884	(O3)C···C_1(B)
	5	0.0078	0.0068	0.0060	-0.0052	0.0008	1.1503	(O3)O···C_3(B)
	6	0.0070	0.0064	0.0052	-0.0040	0.0012	1.2887	(O3)C_2···C_3(B)
	7	0.0077	0.0066	0.0059	-0.0052	0.0012	1.1392	(O3)O···C_4(B)
	8	0.0070	0.0063	0.0052	-0.0040	0.0012	1.2889	(O3)C_4···C_5(B)
RO0	**1**	0.0177	0.0128	0.0111	-0.0094	0.0017	1.1802	(O0)H···C_2-C_3(R)
	2	0.0177	0.0128	0.0111	-0.0094	0.0017	1.1802	(O0)H···C_5-C_6(R)
RO1	**1**	0.0102	0.0080	0.0068	-0.0057	0.0012	1.2041	(O1)C-H···N(R)
	2	0.0159	0.0120	0.0103	-0.0085	0.0017	1.2050	(O1)H···C_2(R)
	3	0.0159	0.0120	0.0103	-0.0085	0.0017	1.2050	(O1)H···C_6(R)
RO2	**1**	0.0223	0.0155	0.0145	-0.0134	0.0010	1.0760	(O2)H···C_2(R)
	2	0.0094	0.0076	0.0065	-0.0054	0.0011	1.2044	(O2)C-H···N(R)
	3	0.0062	-0.0046	0.0038	-0.0030	0.0008	1.2699	O2(CH3)H…C6(R)
RO3	**1**	0.0116	0.0087	0.0076	-0.0065	0.0011	1.1682	(O3)C-H···N(R)
	2	0.0136	0.0105	0.0089	-0.0075	0.0014	1.1841	(O3)C-H···N(R)
	3	0.0134	0.0103	0.0089	-0.0075	0.0014	1.1841	(O3)C-H···N(R)
QO0	**1**	0.0191	0.0126	0.0113	-0.0100	0.0013	1.1268	(O0)H···C_2(Q)
	2	0.0191	0.0126	0.0113	-0.0100	0.0013	1.1268	(O0)H···C_6(Q)
QO1	**1**	0.0672	-0.0055	0.0208	-0.0471	-0.0263	0.4415	(O1)H···P(Q)
QO2	**1**	0.0580	0.0010	0.0203	-0.0396	-0.0193	0.5124	(O2)H···P(Q)
QO3	**1**	0.0070	0.0042	0.0036	-0.0030	0.0006	1.2037	(O3)C-H···P(Q)
	2	0.0064	0.0038	0.0032	-0.0027	0.0006	1.2049	(O3)C-H···P(Q)
	3	0.0084	0.0062	0.0052	-0.0043	0.0010	1.2274	(O3)C-H···C_2(Q)
UO0	**1**	0.0107	0.0096	0.0087	-0.0078	0.0009	1.1145	(O0)O···P(U)
	2	0.0208	0.0129	0.0118	-0.0107	0.0011	1.0986	(O0)H···C_2-C_3(U)
	3	0.0208	0.0129	0.0118	-0.0107	0.0011	1.0985	(O0)H···C_4-C_5(U)
UO1	**1**	0.0362	0.0145	0.0194	-0.0243	-0.0049	0.7985	(O1)H···C_2(U)
	2	0.0147	0.0107	0.0094	-0.0080	0.0014	1.1709	(O1)H···C_5(U)
UO2	**1**	0.0647	-0.0036	0.0204	-0.0444	-0.0240	0.4596	(O2)H···P(U)
UO3	**1**	0.0106	0.0083	0.0079	-0.0075	0.0004	1.0495	(O3)O···P(U)
	2	0.0068	0.0054	0.0045	-0.0035	0.0009	1.2625	(O3)C-H···C_3(U)

	3	0.0068	0.0054	0.0045	-0.0035	0.0009	1.2622	(O3)C-H···C_4(U)
	4	0.0061	0.0048	0.0040	-0.0032	0.0008	1.2396	(O3)C-H···C_2(U)
	5	0.0061	0.0048	0.0040	-0.0032	0.0008	1.2396	(O3)C-H···C_5(U)
ZO1	**1**	0.0638	0.0037	0.0285	-0.0533	-0.0248	0.5350	(O1)H···C_3(Z)
ZO2	**1**	0.0510	0.0102	0.0254	-0.0406	-0.0152	0.6256	(O2)H···C_4(Z)
	2	0.0054	0.0040	0.0034	-0.0028	0.0006	1.2157	(O2)C-H···C_2(Z)
ZO3	**1**	0.0109	0.0093	0.0077	-0.0061	0.0016	1.2610	(O3)C-H···C_2(Z)
	2	0.0078	0.0051	0.0044	-0.0036	0.0008	1.2158	(O3)C-H···C_3(Z)
	3	0.0109	0.0093	0.0077	-0.0061	0.0016	1.2610	(O3)C-H···C_4(Z)
FO0	**1**	0.1752	-0.1199	0.0865	-0.2929	-0.2064	0.2953	(O0)H···O(F)
FO1	**1**	0.1047	0.0257	0.0777	-0.1298	-0.0521	0.5988	(O1)H···O(F)
FO2	**1**	0.0838	0.0370	0.0672	-0.0975	-0.0303	0.6894	(O2)H···O(F)
FO3	**1**	0.0111	0.0113	0.0103	-0.0094	0.0009	1.1008	(O3)O···O(F)
	2	0.0088	0.0077	0.0070	-0.0064	0.0009	1.1034	(O3)O···S(T)
	3	0.0064	0.0052	0.0043	-0.0034	0.0009	1.2561	(O3)C-H···C_3(F)
	4	0.0082	0.0071	0.0063	-0.0055	0.0007	1.1357	(O3)O···C_2(T)
	5	0.0066	0.0052	0.0043	-0.0034	0.0008	1.2506	(O3)C-H···C_4(F)
	6	0.0081	0.0070	0.0062	-0.0055	0.0007	1.1354	(O3)O···C_3(T)
	7	0.0065	0.0052	0.0044	-0.0035	0.0008	1.2417	(O3)C-H···C_2(T)
	8	0.0066	0.0056	0.0046	-0.0036	0.0009	1.2479	(O3)C-H···C_3(T)
TO0	**1**	0.0491	0.0113	0.0232	-0.0350	-0.0118	0.6619	(O0)H···C_2-C_3(T)
TO1	**1**	0.0200	0.0137	0.0123	-0.0108	0.0014	1.1327	(O1)H···C_2(T)
	2	0.0200	0.0137	0.0123	-0.0108	0.0014	1.1327	(O1)H···C_5(T)
TO2	**1**	0.0341	0.0155	0.0187	-0.0218	-0.0031	0.8560	(O2)H···C_3(T)
	2	0.0065	0.0050	0.0041	-0.0033	0.0009	1.2636	(O2)C-H···C_4(T)
TO3	**1**	0.0066	0.0054	0.0044	-0.0035	0.0009	1.2679	(O3)C-H···C_4(T)
	2	0.0067	0.0055	0.0046	-0.0036	0.0010	1.2761	(O3)C-H···C_5(T)

Table S5. Calculated topological properties at the (3,-1) critical points of various sulfonium ion···π complexes obtained from M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All values are in au.

Complex	Interaction	ρ(r)	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)	-G(r)/V(r)	Type of Interaction
BS0	**1**	0.0154	0.0107	0.0090	-0.0072	0.0017	1.2411	(S0)H···C_1(B)
	2	0.0188	0.0124	0.0108	-0.0092	0.0016	1.1781	(S0)H···C_4(B)
BS1	**1**	0.0154	0.0106	0.0090	-0.0074	0.0016	1.2188	(S1)H···C_1(B)
	2	0.0154	0.0106	0.0090	-0.0074	0.0016	1.2191	(S1)H···C_4(B)
	3	0.0055	0.0037	0.0031	-0.0026	0.0006	1.2217	(S1)C-H···C_2-C_3(B)
BS2	**1**	0.0186	0.0139	0.0116	-0.0092	0.0024	1.2553	(S2)H···C_1(B)
BS3	**1**	0.0083	0.0058	0.0050	-0.0041	0.0009	1.2157	(S3)S···C_1(B)
	2	0.0072	0.0048	0.0040	-0.0033	0.0008	1.2313	(S3)C-H···C_1(B)
	3	0.0092	0.0073	0.0060	-0.0046	0.0014	1.2955	(S3)C-H···C_3(B)
RS0	**1**	0.0372	0.0234	0.0245	-0.0255	-0.0010	0.9595	(S0)S···N(R)
RS1	**1**	0.0276	0.0195	0.0192	-0.0188	0.0004	1.0187	(S1)S···N(R)
RS2	**1**	0.0215	0.0154	0.0148	-0.0143	0.0005	1.0369	(S2)S···N(R)
	2	0.0131	0.0111	0.0096	-0.0081	0.0015	1.1864	(S2)C-H···N(R)
	3	0.0131	0.0111	0.0096	-0.0081	0.0015	1.1864	(S2)C-H···N(R)
RS3	**1**	0.0174	0.0128	0.0122	-0.0116	0.0006	1.0510	(S3)S···N(R)
	2	0.0130	0.0106	0.0092	-0.0078	0.0014	1.1834	(S3)C-H···N(R)
	3	0.0130	0.0106	0.0092	-0.0077	0.0014	1.1833	(S3)C-H···N(R)
QS0	**1**	0.0087	0.0076	0.0062	-0.0048	0.0014	1.3000	(S0)H···P(Q)
	2	0.0266	0.0102	0.0114	-0.0126	-0.0012	0.9045	(S0)S···C_4(Q)
QS1	**1**	0.0202	0.0121	0.0107	-0.0093	0.0014	1.1502	(S1)S-H···C_2(Q)
	2	0.0063	0.0044	0.0037	-0.0030	0.0007	1.2256	(S1)C-H ···C_4(Q)
QS2	**1**	0.0417	0.0085	0.0154	-0.0224	-0.0069	0.6900	(S2)H···P(Q)
QS3	**1**	0.0074	0.0049	0.0042	-0.0034	0.0008	1.2199	(S3)S···P(Q)
	2	0.0074	0.0046	0.0039	-0.0032	0.0007	1.2160	(S3)C-H···P(Q)
	3	0.0082	0.0059	0.0050	-0.0040	0.0010	1.2401	(S3)C-H···C_2(Q)
US0	**1**	0.0102	0.0088	0.0076	-0.0064	0.0012	1.1877	(S0)S···P(U)
	2	0.0162	0.0102	0.0086	-0.0070	0.0016	1.2238	(S0)H···C_2(U)
	3	0.0162	0.0101	0.0086	-0.0070	0.0016	1.2241	(S0)H···C_5(U)
US1	**1**	0.0146	0.0094	0.0079	-0.0065	0.0015	1.2243	(S1)H···C_2(Q)
	2	0.0146	0.0094	0.0079	-0.0065	0.0015	1.2243	(S1)H···C_5(Q)
US2	**1**	0.0522	0.0049	0.0173	-0.0298	-0.0125	0.5818	(S2)H···P(U)
US3	**1**	0.0132	0.0083	0.0080	-0.0077	0.0003	1.0389	(S3)S···P(U)
ZS1	**1**	0.0455	0.0146	0.0225	-0.0304	-0.0079	0.7407	(S1)H···C_3(U)
ZS2	**1**	0.0316	0.0171	0.0176	-0.0182	-0.0006	0.9689	(S2)H···C_3(Z)
ZS3	**1**	0.0104	0.0094	0.0079	-0.0064	0.0015	1.2312	(S3)C-H···N(Z)
	2	0.0094	0.0067	0.0058	-0.0049	0.0009	1.1935	(S3)S···C_3(Z)
	3	0.0079	0.0052	0.0045	-0.0037	0.0008	1.2016	(S3)C-H···C_3(Z)
FS0	**1**	0.0548	0.0110	0.0247	-0.0384	-0.0137	0.6431	(S0)S···C2(Z)
FS1	**1**	0.0117	0.0078	0.0068	-0.0059	0.0010	1.1632	(S1)S···C_2-C_3(F)
	2	0.0127	0.0104	0.0086	-0.0067	0.0018	1.2692	(S1)C-H···C_2(F)

FS2	**1**	0.0240	0.0156	0.0141	-0.0127	0.0014	1.1139	(S2)H···C_2(F)
	2	0.0115	0.0104	0.0088	-0.0072	0.0016	1.2244	(S2)H···C_5(F)
FS3	**1**	0.0099	0.0086	0.0079	-0.0072	0.0007	1.0996	(S3)S···O(F)
	2	0.0108	0.0093	0.0081	-0.0069	0.0012	1.1752	(S3)C-H···O(F)
	3	0.0114	0.0094	0.0078	-0.0063	0.0015	1.2443	(S3)C-H···C_2(F)
TS0	**1**	0.0131	0.0087	0.0074	-0.0061	0.0013	1.2159	(S0)H···C_2(T)
	2	0.0264	0.0144	0.0137	-0.0131	0.0006	1.0492	(S0)H···C_5(T)
TS1	**1**	0.0279	0.0161	0.0153	-0.0146	0.0008	1.0539	(S1)S-H···C_2(T)
TS2	**1**	0.0168	0.0130	0.0108	-0.0087	0.0022	1.2496	(S2)H···C_3(T)
	2	0.0060	0.0044	0.0037	-0.0029	0.0008	1.2653	(S2)C-H···S(T)
	3	0.0060	0.0045	0.0036	-0.0029	0.0008	1.2710	(S2)C-H···S(T)
TS3	**1**	0.0084	0.0058	0.0051	-0.0044	0.0007	1.1660	(S3)S···C_2(T)
	2	0.0100	0.0079	0.0064	-0.0050	0.0015	1.2949	(S3)C-H···C_3(T)
	3	0.0071	0.0045	0.0039	-0.0032	0.0007	1.2122	(S3)C-H···C_4-C_5(T)

Table S6. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for the $CO_2 \cdots \pi$ complexes.

Complex	ES	EX	REP	POL	DISP	TE
BC	-1.99	-0.94	8.27	-1.66	-7.37	-3.69
RC	-7.15	-3.67	14.66	-3.66	-6.81	-6.63
QC	-1.84	-0.94	8.02	-1.66	-7.13	-3.55
UC	-3.16	-1.85	11.05	-2.05	-8.59	-4.59
ZC	-3.57	-1.56	10.06	-2.13	-8.04	-5.23
FC	-3.62	-1.32	7.97	-2.07	-5.24	-4.27
TC	-2.49	-1.57	9.92	-1.96	-7.88	-3.99
N0	-7.76	-2.63	10.47	-7.86	-2.93	-10.71
N1	-6.91	-2.16	9.54	-6.50	-3.76	-9.79
N2	-6.29	-1.81	9.12	-5.66	-4.63	-9.29
N3	-5.87	-1.71	8.84	-5.22	-4.7	-8.66
N4	-4.22	-1.43	7.54	-3.72	-4.31	-6.14
P0	-6.6	-2.33	9.59	-5.59	-4.22	-9.15
P1	-5.76	-1.91	9.13	-4.89	-4.88	-8.31
P2	-5.03	-1.63	8.6	-4.38	-5.29	-7.73
P3	-4.49	-1.5	8.13	-3.88	-5.12	-6.86
P4	-4.09	-1.45	7.98	-3.79	-4.9	-6.25
O0	-12.49	-6.57	23.92	-18.16	-4.61	-17.91
O1	-10.38	-4.54	17.36	-12.73	-4.36	-14.65
O2	-9.36	-3.95	15.24	-10.8	-4.09	-12.96
O3	-4.73	-1.76	8.57	-4.15	-4.64	-6.73
S0	-8.79	-5.33	16.28	-8.34	-3.53	-9.71
S1	-6.1	-1.93	9.24	-4.99	-4.77	-8.56
S2	-5.73	-2.05	9.55	-4.77	-5.35	-8.34
S3	-4.71	-1.69	8.69	-3.99	-5.16	-6.86

Table S7. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for the ammonium ion···π complexes.

Complex	ES	EX	REP	POL	DISP	TE
BN0	-14.15	-4.65	19.58	-11.47	-10.80	-21.50
BN1	-13.11	-4.45	19.62	-10.41	-11.93	-20.28
BN2	-12.56	-4.48	19.92	-9.88	-12.46	-19.46
BN3	-11.10	-4.10	20.63	-8.38	-15.95	-18.90
BN4	-6.81	-2.91	14.01	-4.81	-10.78	-11.30
RN1	-10.12	-3.56	16.91	-9.04	-11.16	-16.96
RN2	-32.08	-19.06	56.15	-26.72	-9.31	-31.01
RN3	-29.33	-17.3	50.73	-23.29	-9.03	-28.21
RN4	-12.38	-4.03	15.82	-6.99	-8.60	-16.17
QN0	-15.66	-7.97	25.51	-18.36	-4.30	-20.78
QN1	-10.37	-4.44	19.38	-10.46	-11.95	-17.84
QN2	-8.57	-3.91	18.98	-8.85	-14.34	-16.70
QN3	-8.26	-3.88	20.38	-8.58	-16.46	-16.79
QN4	-5.41	-2.99	14.17	-4.81	-10.89	-9.94
UN0	-12.09	-4.43	18.74	-11.9	-10.50	-20.17
UN1	-11.49	-4.57	19.27	-10.65	-11.36	-18.80
UN2	-10.52	-4.28	19.04	-9.98	-12.16	-17.90
UN3	-9.22	-4.57	21.62	-8.99	-15.66	-16.82
UN4	-7.27	-3.51	14.67	-5.12	-9.74	-10.98
ZN0	-19.52	-6.12	23.53	-13.23	-10.64	-25.96
ZN1	-18.14	-5.83	23.12	-11.80	-11.74	-24.39
ZN2	-17.00	-5.80	22.93	-11.18	-11.92	-22.97
ZN3	-15.25	-5.62	23.57	-10.22	-14.07	-21.59
ZN4	-9.98	-3.87	16.26	-5.60	-11.06	-14.26
FN0	-12.12	-4.35	18.43	-10.45	-10.05	-18.55
FN1	-11.52	-4.21	18.94	-10.15	-10.99	-17.93
FN2	-13.56	-6.87	24.18	-7.86	-11.26	-15.37
FN3	-9.96	-4.71	21.64	-10.11	-15.13	-18.28
FN4	-6.48	-2.47	12.30	-5.03	-8.47	-10.15
TN0	-13.52	-4.96	19.98	-11.68	-10.28	-20.47
TN1	-12.36	-4.73	19.78	-10.51	-11.29	-19.11
TN2	-11.91	-4.77	20.08	-9.79	-11.79	-18.18
TN3	-10.07	-4.33	20.23	-8.61	-14.54	-17.32
TN4	-6.37	-3.12	14.09	-4.99	-10.33	-10.72

Table S8. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for the phosphonium ion···π complexes.

Complex	ES	EX	REP	POL	DISP	TE
BP0	-13.08	-7.32	24.82	-11.01	-12.16	-18.75
BP1	-11.43	-6.54	23.28	-9.13	-13.11	-16.92
BP2	-10.13	-6.00	22.55	-7.77	-14.38	-15.74
BP3	-9.13	-5.58	21.04	-6.74	-13.77	-14.17
BP4	-6.15	-2.63	13.80	-4.67	-11.19	-10.84
RP0	-49.59	-38.44	109.44	-42.87	-13.62	-35.08
RP1	-39.72	-30.01	86.97	-32.29	-15.28	-30.33
RP2	-17.27	-6.88	25.20	-10.55	-11.38	-20.88
RP3	-14.07	-4.80	18.77	-7.99	-10.11	-18.20
RP4	-11.65	-3.69	15.85	-6.75	-9.81	-16.06
QP0	-9.99	-6.39	22.56	-10.77	-11.86	-16.46
QP1	-9.30	-6.10	21.98	-8.94	-12.68	-15.05
QP2	-8.46	-5.74	21.83	-7.63	-14.13	-14.13
QP3	-7.55	-5.34	20.19	-6.51	-13.53	-12.73
QP4	-5.81	-3.16	14.60	-4.74	-11.01	-10.12
UP0	-12.63	-9.37	30.22	-13.82	-12.71	-18.30
UP1	-11.26	-6.61	22.89	-9.46	-11.67	-16.11
UP2	-10.12	-6.08	22.07	-7.68	-13.02	-14.84
UP3	-7.56	-6.12	22.26	-7.25	-13.87	-12.54
UP4	-7.25	-3.56	15.30	-4.86	-10.50	-10.88
ZP0	-19.05	-11.19	34.83	-15.65	-12.88	-23.94
ZP1	-16.26	-8.72	28.64	-11.40	-13.29	-21.02
ZP2	-14.11	-7.09	25.06	-8.62	-14.43	-19.20
ZP	-12.53	-6.45	23.17	-7.44	-13.94	-17.19
ZP4	-9.40	-3.46	15.84	-5.39	-11.53	-13.94
FP0	-11.13	-6.27	22.20	-10.11	-10.84	-16.15
FP1	-10.28	-6.81	23.56	-9.85	-11.98	-15.36
FP2	-9.23	-5.58	22.09	-7.30	-14.07	-14.10
FP3	-8.31	-5.15	20.58	-6.37	-13.65	-12.91
FP4	-6.41	-3.11	15.84	-4.70	-11.96	-10.34
TP0	-12.68	-7.98	26.24	-12.06	-11.76	-18.23
TP1	-10.91	-6.91	23.64	-9.69	-12.30	-16.16
TP2	-9.70	-6.42	22.95	-7.99	-13.67	-14.84
TP3	-8.68	-5.89	21.27	-6.86	-13.12	-13.29
TP4	-5.90	-2.93	14.11	-4.86	-10.74	-10.32

Table S9. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for the hydronium ion···π complexes.

Complex	ES	EX	REP	POL	DISP	TE
BO0	-18.67	-4.98	23.04	-17.09	-12.55	-30.25
BO1	-16.84	-5.69	25.06	-16.72	-13.62	-27.81
BO2	-14.05	-5.59	25.41	-14.50	-15.34	-24.07
BO3	-7.55	-2.74	17.39	-4.49	-15.64	-13.03
RO0	-11.88	-4.45	20.76	-17.29	-11.44	-24.31
RO1	-11.93	-4.47	21.44	-14.53	-13.14	-22.64
RO2	-9.93	-4.14	20.93	-12.29	-14.05	-19.47
RO3	-13.48	-4.56	17.50	-7.65	-9.28	-17.47
QO0	-14.81	-6.00	25.56	-20.48	-12.91	-28.64
QO1	-23.34	-16.64	50.58	-39.30	-7.04	-35.75
QO2	-21.34	-14.67	44.83	-31.46	-7.43	-30.06
QO3	-6.62	-3.64	15.76	-5.73	-11.16	-11.39
UO0	-16.47	-6.36	26.72	-21.70	-12.61	-30.42
UO1	-18.12	-8.95	34.13	-22.05	-13.81	-28.80
UO2	-23.85	-18.16	53.76	-35.21	-8.78	-32.24
UO3	-9.05	-4.14	20.44	-4.99	-15.87	-13.61
ZO1	-25.00	-13.81	46.67	-33.97	-12.15	-38.27
ZO2	-22.51	-10.92	40.00	-24.93	-14.30	-32.66
ZO3	-11.10	-4.27	17.41	-6.24	-11.36	-15.56
FO0	-35.09	-31.21	94.30	-72.45	-9.43	-53.88
FO1	-27.31	-19.21	60.30	-36.63	-8.54	-31.39
FO2	-23.35	-15.00	47.84	-26.88	-8.00	-25.39
FO3	-6.75	-2.29	15.69	-4.29	-14.20	-11.84
TO0	-19.22	-10.15	37.17	-28.44	-11.66	-32.29
TO1	-16.96	-6.45	26.52	-17.18	-12.82	-26.89
TO2	-14.56	-7.19	29.31	-17.32	-14.17	-23.92
TO3	-7.39	-3.00	17.16	-4.47	-14.63	-12.32

Table S10. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for the sulfonium ion···π complexes.

Complex	ES	EX	REP	POL	DISP	TE
BS0	-16.21	-9.60	31.35	-15.60	-12.77	-22.84
BS1	-14.22	-8.30	28.19	-12.63	-13.47	-20.44
BS2	-12.52	-8.29	27.61	-11.09	-13.50	-17.79
BS3	-7.62	-3.61	16.69	-5.64	-12.54	-12.73
RS0	-27.93	-14.12	43.37	-18.93	-9.04	-26.66
RS1	-21.92	-9.27	30.82	-13.24	-9.96	-23.58
RS2	-17.92	-6.97	25.05	-10.55	-10.84	-21.23
RS3	-15.26	-5.76	21.07	-8.35	-10.17	-18.47
QS0	-12.12	-11.48	36.26	-20.60	-12.87	-20.82
QS1	-11.30	-9.09	30.50	-14.34	-14.34	-18.57
QS2	-18.06	-17.33	47.05	-23.24	-7.34	-18.92
QS3	-6.92	-3.94	16.95	-5.65	-11.99	-11.56
US0	-13.92	-9.23	30.70	-16.82	-12.73	-22.00
US1	-11.76	-7.87	27.21	-13.26	-13.44	-19.12
US2	-11.42	-7.27	25.28	-9.73	-13.89	-17.03
US3	-9.50	-6.37	22.23	-6.54	-12.32	-12.51
ZS1	-24.62	-20.36	58.07	-26.96	-13.80	-27.68
ZS2	-19.93	-14.19	42.73	-17.74	-14.38	-23.50
ZS3	-11.15	-4.50	18.59	-6.30	-12.62	-15.97
FS0	-19.88	-21.27	61.64	-33.53	-13.09	-26.13
FS1	-9.03	-4.69	18.90	-8.30	-11.25	-14.37
FS2	-11.95	-9.49	30.56	-12.85	-12.59	-16.33
FS3	-7.95	-3.69	17.09	-5.57	-11.93	-12.04
TS0	-16.66	-11.73	36.64	-18.3	-12.68	-22.73
TS1	-15.09	-11.98	36.95	-16.34	-13.35	-19.80
TS2	-11.50	-7.28	25.05	-9.20	-13.83	-16.76
TS3	-7.54	-4.12	17.31	-5.83	-12.05	-12.23

Table S11. Binding energies (BE in kcal/mol) and NPA charge transfer (CT*10^2 in au.) of ammonium ion (N), phosphoniumion (P), hydronium ion (O), sulfonium ion (S) and CO_2 complexes computed at M06-2X/6-311++G(d,p) //M06-2X/6-31G(d) level of theory.

N	BE	CT	P	BE	CT	O	BE	CT	S	BE	CT	CO_2	BE	CT
BN0	3.470	0.121	**BP0**	17.44	4.440	**BO0**	25.12	3.910	**BS0**	20.89	7.640	**BC**	3.20	0.170
BN1	2.960	0.117	**BP1**	15.85	3.400	**BO1**	24.19	5.130	**BS1**	18.82	5.650	**RC**	5.48	1.330
BN2	2.930	0.116	**BP2**	14.73	2.550	**BO2**	22.12	5.790	**BS2**	16.54	4.680	**QC**	3.15	0.040
BN3	3.040	0.101	**BP3**	13.30	2.220	**BO3**	12.26	0.910	**BS3**	12.01	1.370	**UC**	4.15	0.030
BN4	1.510	0.072	**BP4**	10.03	1.300	**RO0**	20.81	5.100	**RS0**	24.75	6.920	**ZC**	4.54	0.520
RN1	2.260	0.094	**RP0**	26.38	15.420	**RO1**	19.34	3.970	**RS1**	21.70	4.060	**FC**	3.54	0.300
RN2	12.740	0.169	**RP1**	21.78	11.890	**RO2**	17.67	4.370	**RS2**	19.65	2.680	**TC**	3.51	0.400
RN3	11.480	0.162	**RP2**	18.79	2.640	**RO3**	16.14	1.950	**RS3**	16.94	1.720	**N0C**	9.66	2.070
RN4	1.970	0.067	**RP3**	16.57	1.840	**QO0**	24.95	6.660	**QS0**	18.85	15.090	**N1C**	8.64	1.410
QN0	13.860	0.186	**RP4**	14.37	1.410	**QO1**	25.98	30.230	**QS1**	17.13	8.250	**N2C**	8.06	0.920
QN1	3.160	0.109	**QP0**	15.65	5.220	**QO2**	22.92	26.500	**QS2**	14.48	20.880	**N3C**	7.56	0.800
QN2	3.240	0.103	**QP1**	14.37	4.070	**QO3**	11.26	2.470	**QS3**	11.41	1.990	**N4C**	4.98	0.560
QN3	4.040	0.107	**QP2**	13.70	3.160	**UO0**	25.83	7.100	**US0**	19.80	9.060	**P0C**	8.30	0.880
QN4	1.990	0.068	**QP3**	12.33	2.670	**UO1**	23.89	9.260	**US1**	17.44	6.450	**P1C**	7.42	0.640
UN0	3.760	0.115	**QP4**	9.85	1.970	**UO2**	23.70	30.230	**US2**	16.09	4.190	**P2C**	6.56	0.470
UN1	3.530	0.107	**UP0**	15.95	6.390	**UO3**	13.05	1.730	**US3**	11.95	2.450	**P3C**	5.87	0.460
UN2	3.180	0.103	**UP1**	15.11	4.780	**ZO1**	29.57	16.550	**ZS1**	22.71	15.710	**P4C**	4.93	0.480
UN3	3.840	0.103	**UP2**	14.08	3.430	**ZO2**	26.77	12.880	**ZS2**	20.61	10.190	**O0C**	16.08	6.380
UN4	2.540	0.060	**UP3**	11.40	2.810	**ZO3**	14.06	2.350	**ZS3**	14.43	1.930	**O1C**	12.98	4.030
ZN0	5.390	0.137	**UP4**	10.39	2.250	**FO0**	31.88	22.860	**FS0**	19.25	19.200	**O2C**	11.44	3.240
ZN1	4.580	0.127	**ZP0**	20.80	8.310	**FO1**	24.49	13.870	**FS1**	12.10	3.500	**O3C**	5.74	0.540
ZN2	4.380	0.125	**ZP1**	18.71	5.360	**FO2**	21.08	10.720	**FS2**	14.35	6.990	**S0C**	8.79	2.540
ZN	4.720	0.112	**ZP2**	17.17	3.390	**FO3**	10.64	1.210	**FS3**	11.19	1.440	**S1C**	7.73	0.540
ZN4	2.190	0.077	**ZP**	15.40	2.890	**TO0**	27.67	12.910	**TS0**	20.41	10.540	**S2C**	7.56	0.600
FN0	3.740	0.101	**ZP4**	12.35	1.930	**TO1**	23.75	6.190	**TS1**	17.83	9.300	**S3C**	5.93	0.320
FN1	3.740	0.112	**FP0**	14.39	4.470	**TO2**	21.60	2.440	**TS2**	16.02	3.840			
FN2	3.560	0.107	**FP1**	13.55	4.740	**TO3**	11.82	1.960	**TS3**	11.36	2.080			
FN3	3.490	0.095	**FP2**	12.77	2.480									
FN4	2.060	0.077	**FP3**	11.67	2.220									
TN0	4.170	0.115	**FP4**	9.22	1.430									
TN1	3.570	0.107	**TP0**	16.51	5.700									
TN2	3.520	0.104	**TP1**	14.86	4.450									
TN3	4.100	0.096	**TP2**	13.70	3.560									
TN4	2.300	0.068	**TP3**	12.44	3.120									
			TP4	9.42	2.100									

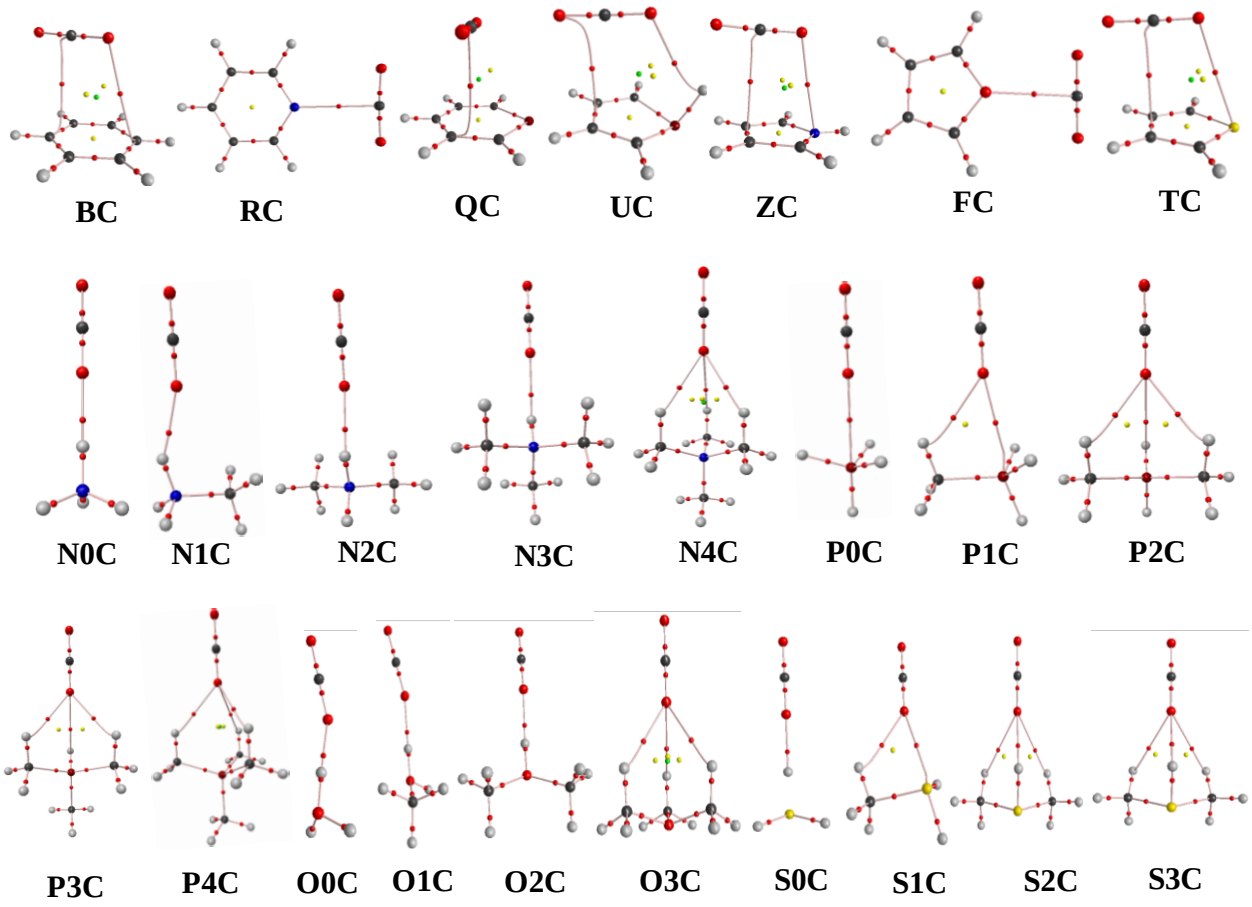

Figure S1. Molecular topological graphs obtained from QTAIM analysis for CO_2···π complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

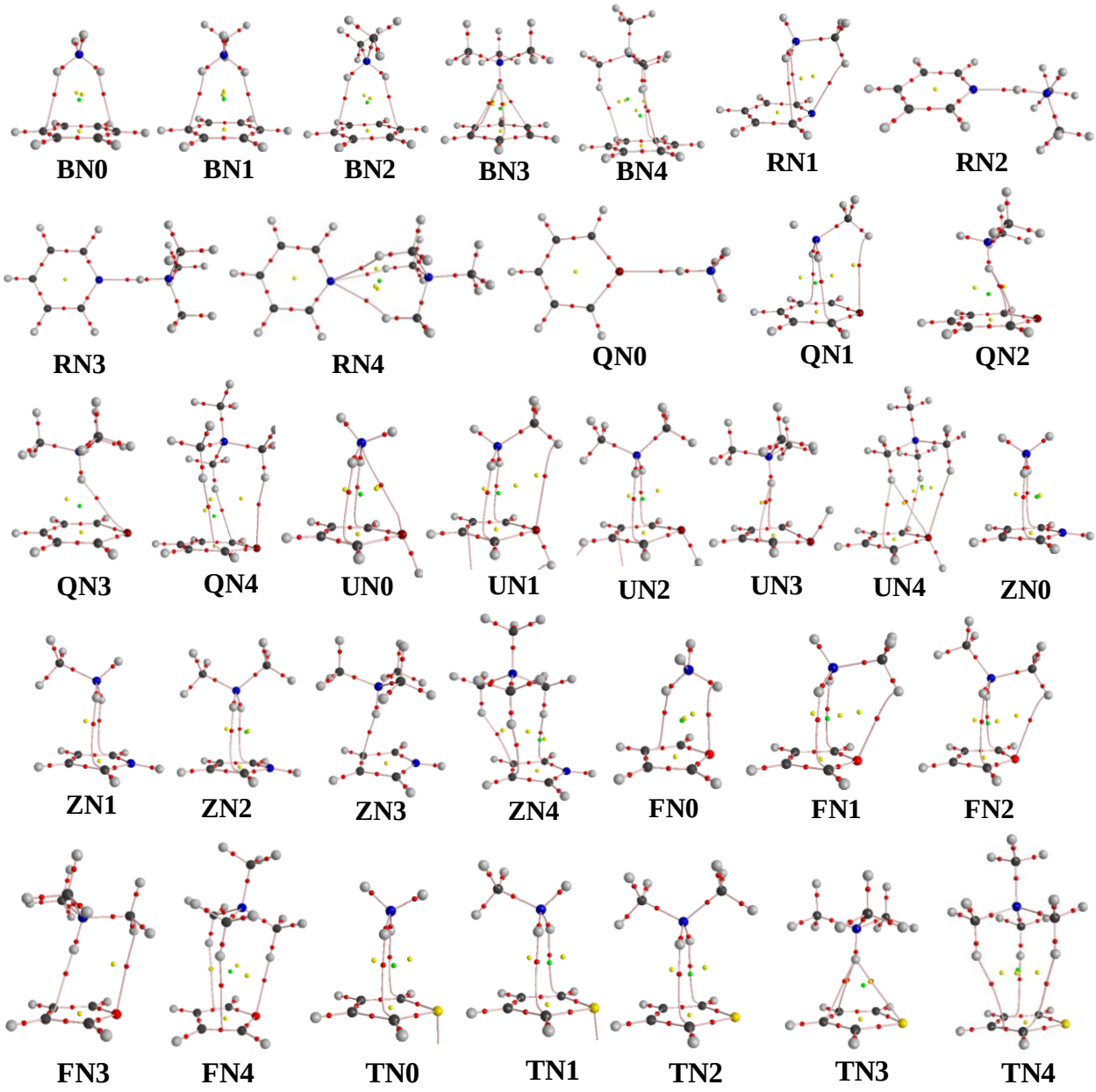

Figure S2. Molecular topological graphs obtained from QTAIM analysis for ammonium ion···π complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

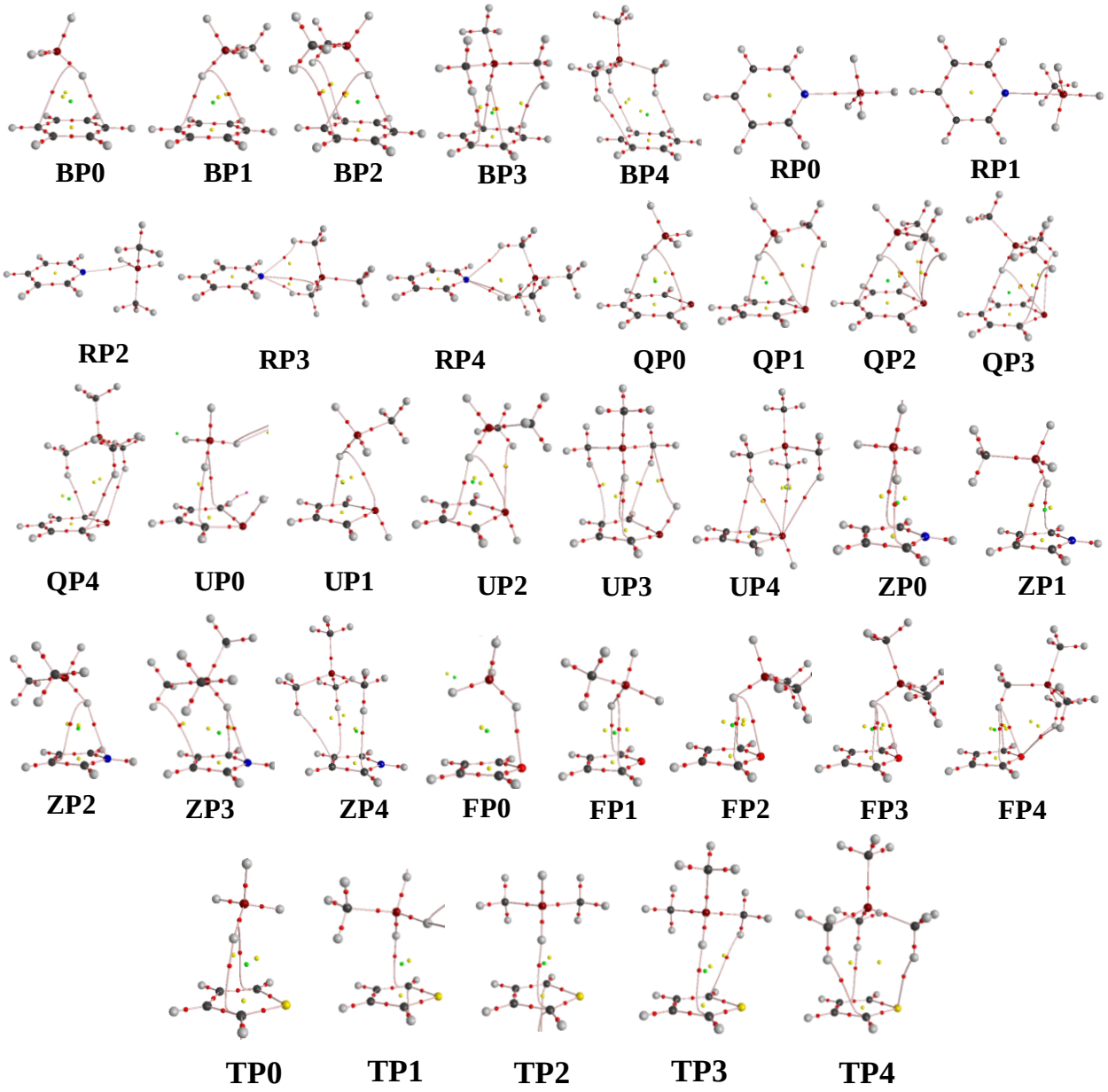

Figure S3. Molecular topological graphs obtained from QTAIM analysis for phosphonium ion···π complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

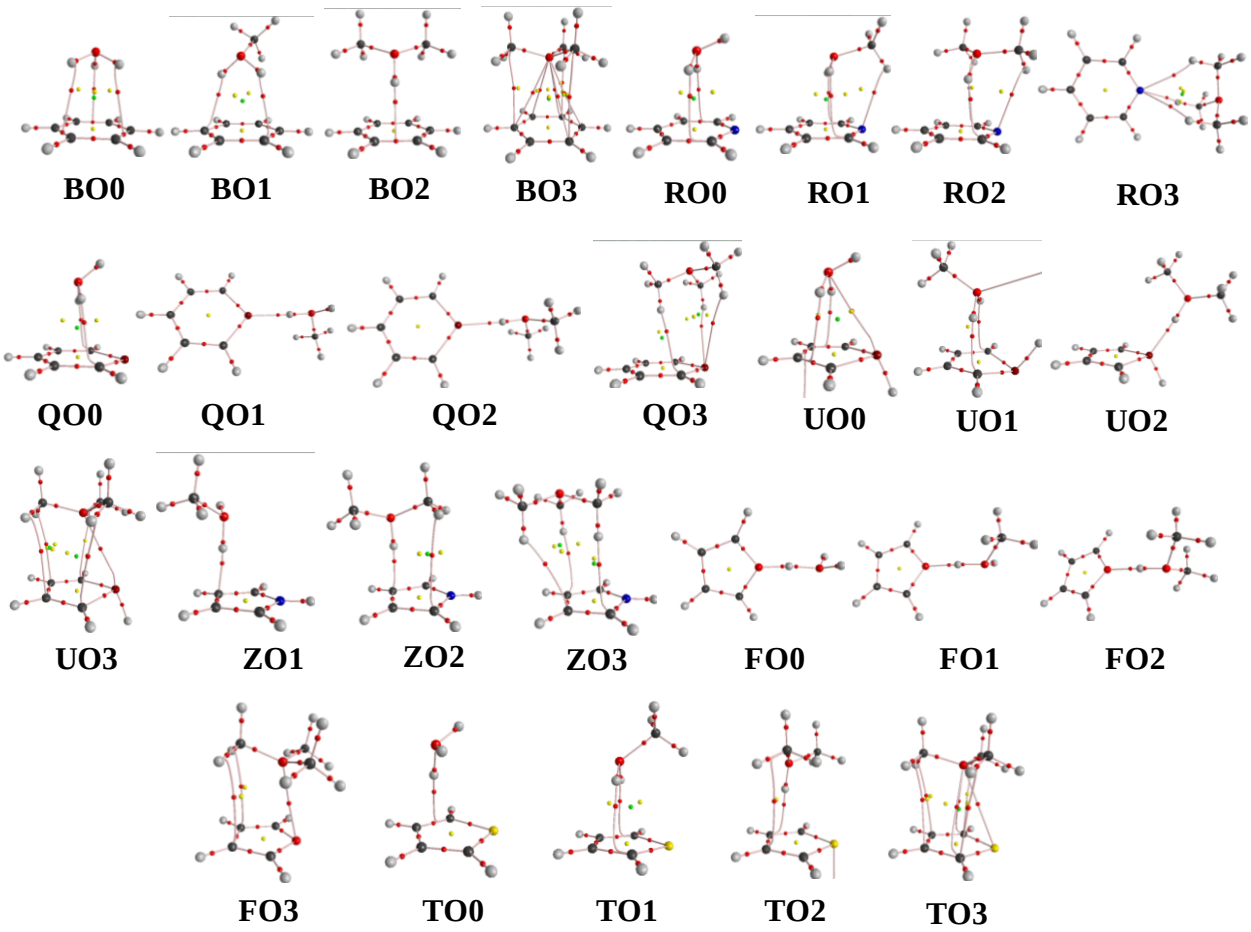

Figure S4. Molecular topological graphs obtained from QTAIM analysis for hydronium ion···π complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

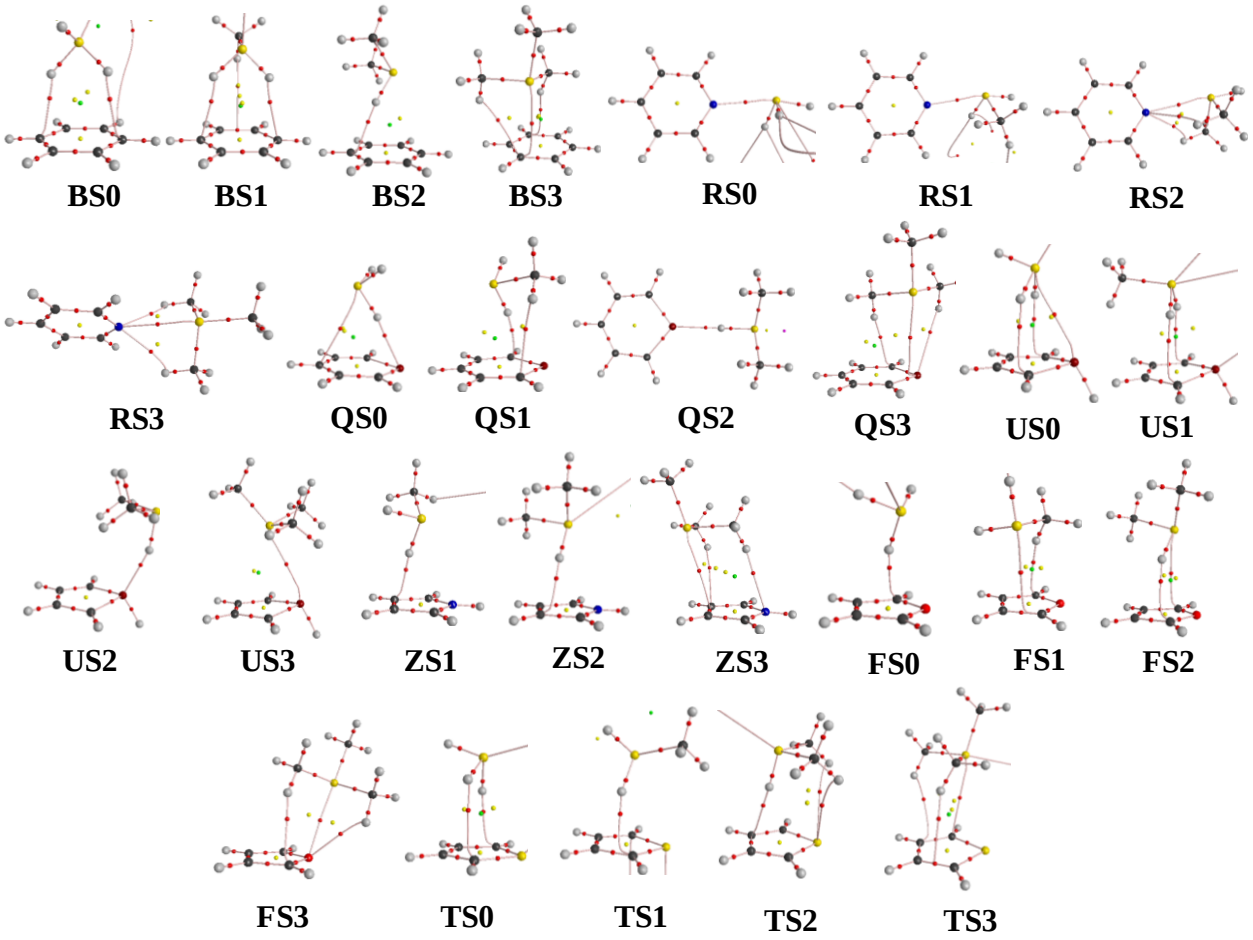

Figure S5. Molecular topological graphs obtained from QTAIM analysis for sulfonium ion···π complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

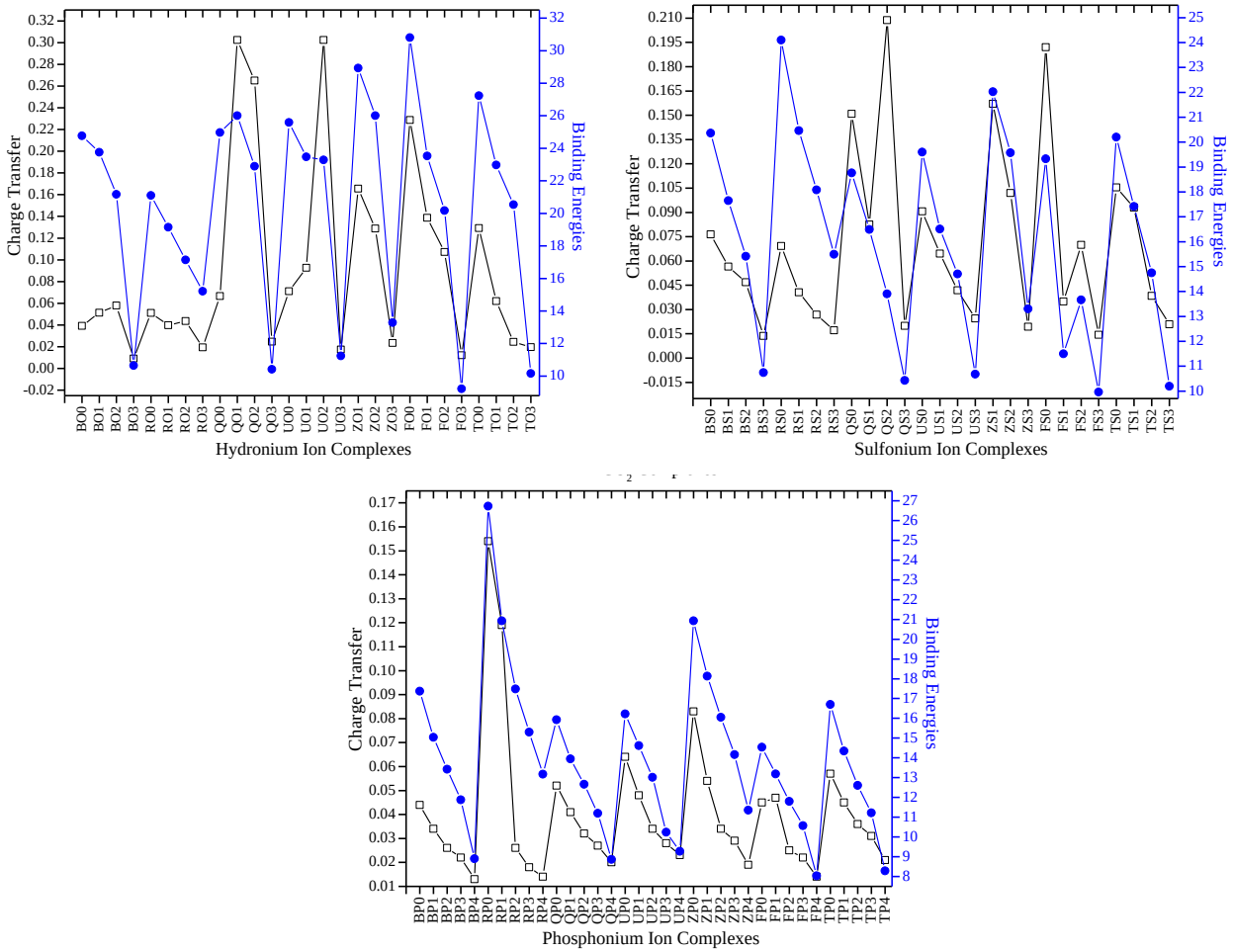

Figure S6. Variation of binding energies (BE in kcal/mol) and NPA charge transfer (in a.u) of phosphonium ion, hydronium ion and sulfonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. (Blue: Binding energy and Black: Charge transfer)

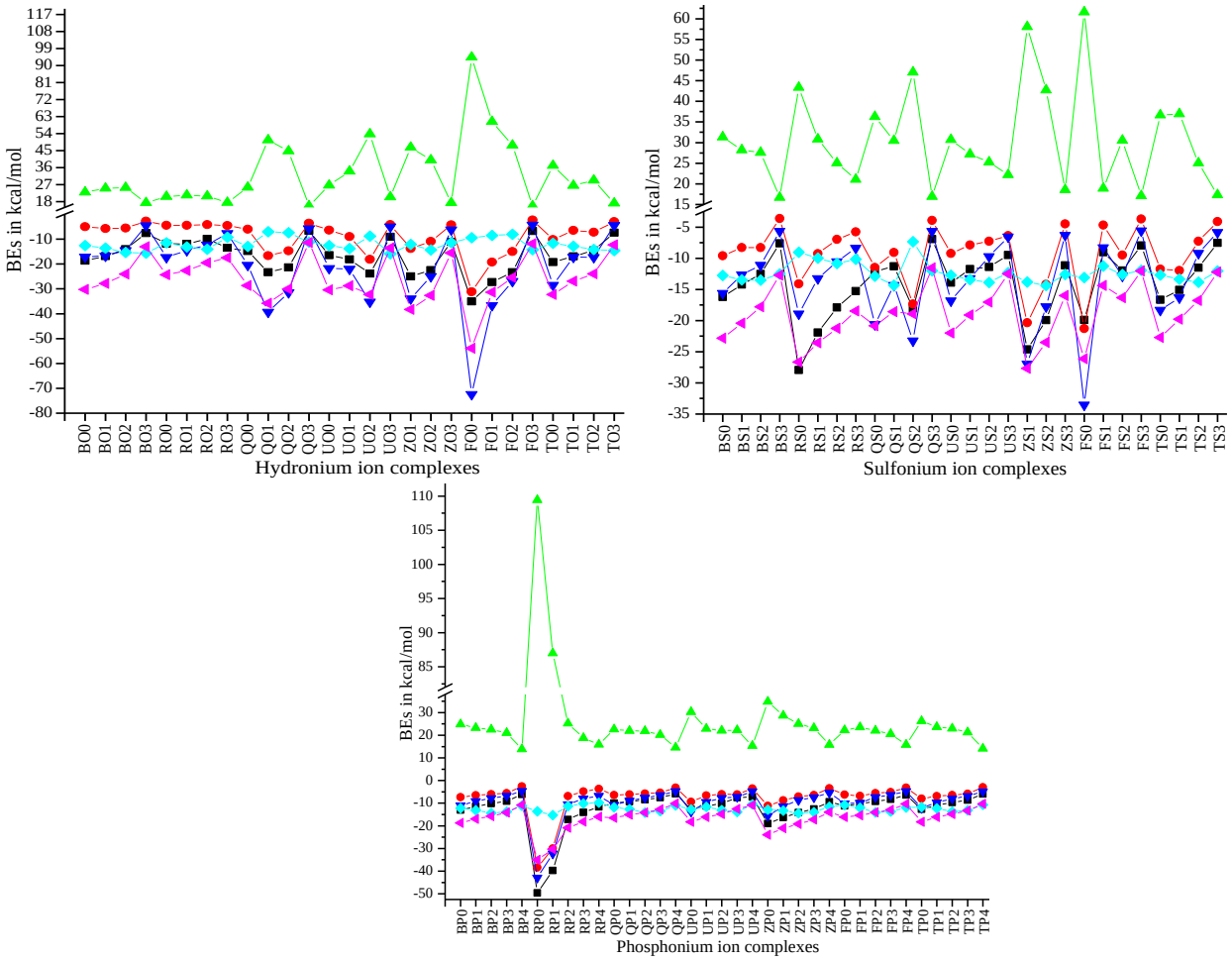

Figure S7. Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for phosphonium ion, hydronium ion and sulfonium ion complexes. (Black: Electrostatic, Red: Exchange, Green: Repulsion, Blue: Polarization, Cyan: Dispersion, Pink: Total Interaction Energy)