Supporting Information

Competing and directing interactions in new phosphoramide/thiophosphoramide structures: energy considerations and evidence for CH···HC contacts and aliphatic-aromatic stacking

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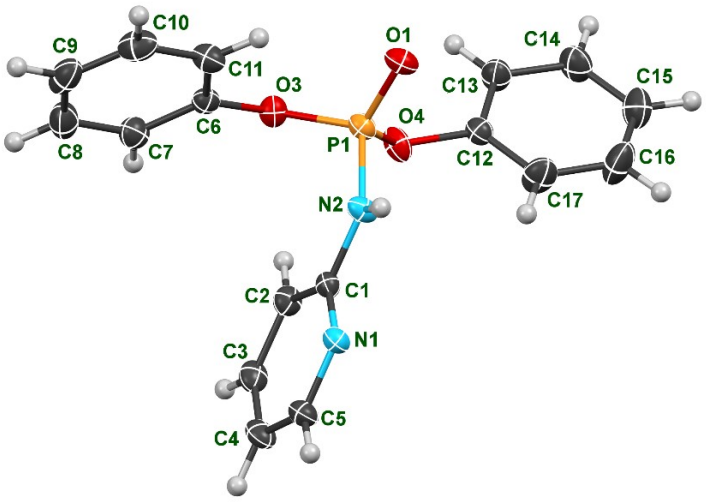

Fig. S1 The molecular structure and atom-labeling scheme for I. Displacement ellipsoids are drawn at the 50% probability level.

Table S1 Selected geometric parameters of structure I (Å, °).

P1—O1	1.4618 (10)	O3—C6	1.4031 (15)
P1—O3	1.5808 (10)	O4—C12	1.4054 (15)
P1—O4	1.5843 (10)	N1—C1	1.3331 (17)
P1—N2	1.6327 (12)	N2—C1	1.4039 (15)
O1—P1—O3	117.56 (6)	O4—P1—N2	109.17 (6)
O1—P1—O4	115.37 (5)	C6—O3—P1	124.68 (9)
O1—P1—N2	110.96 (6)	C12—O4—P1	121.68 (8)
O3—P1—O4	94.55 (5)	C1—N2—P1	129.39 (9)
O3—P1—N2	107.96 (6)	N1—C1—N2	114.18 (11)

Table S2 Hydrogen-bond geometry of structure I (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.84 (2)	2.08 (2)	2.9229 (16)	174.7 (18)
C5—H5···O1^{i}	0.95	2.53	3.3365 (19)	142
C10—H10···O1^{ii}	0.95	2.55	3.4416 (18)	156
C11—H11···O1	0.95	2.63	3.2819 (18)	126
C13—H13···O1^{iii}	0.95	2.77	3.3965 (18)	124

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) −*x*+2, −*y*+1, −*z*; (iii) −*x*+2, −*y*+1, −*z*+1.

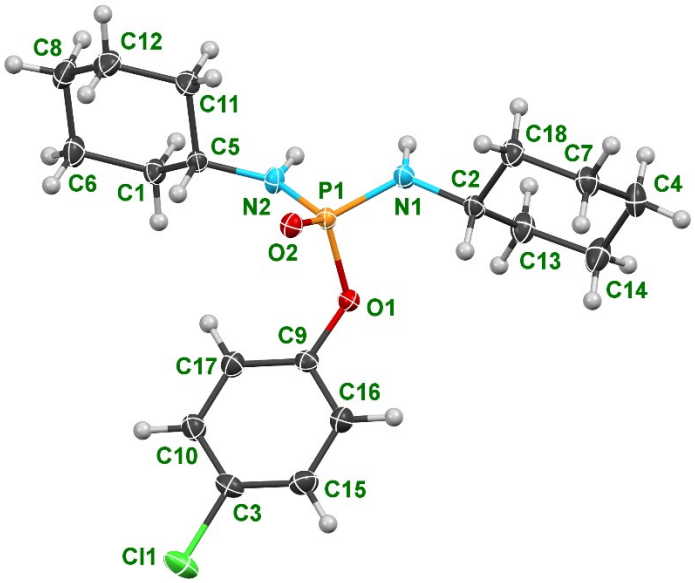

Fig. S2 The molecular structure and atom-labeling scheme for II. Displacement ellipsoids are drawn at the 50% probability level.

Table S3 Selected geometric parameters of structure II (Å, °).

P1—O2	1.4785 (11)	O1—C9	1.3839 (18)
P1—N1	1.6219 (13)	N1—C2	1.4700 (18)
P1—N2	1.6254 (12)	N2—C5	1.4658 (19)
O2—P1—N1	119.63 (6)	P1—N1—C2	124.16 (10)
O2—P1—N2	113.41 (6)	P1—N2—C5	124.94 (10)
N1—P1—N2	104.60 (6)		

Table S4 Hydrogen-bond geometry of structure II (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1n2···O2^{i}	0.86 (2)	2.08 (2)	2.8878 (17)	157.1 (16)
N1—H1n1···O2^{i}	0.86 (2)	2.180 (18)	2.9812 (15)	154.7 (17)

Symmetry code: (i) *x*, −*y*+5/2, *z*+1/2.

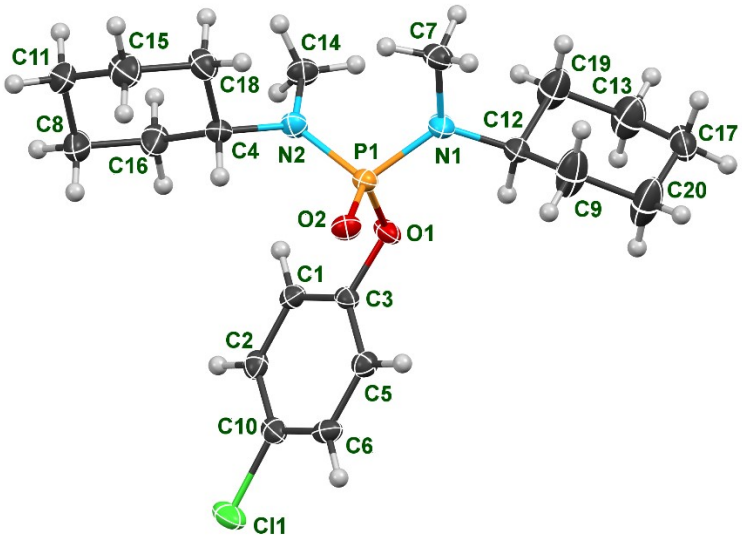

Fig. S3 The molecular structure and atom-labeling scheme for III. Displacement ellipsoids are drawn at the 50% probability level.

Table S5 Selected geometric parameters of structure III (Å, °).

P1—O2	1.4701 (18)	N2—C4	1.477 (3)
P1—N2	1.629 (2)	N2—C14	1.465 (3)
P1—N1	1.640 (2)	N1—C7	1.459 (3)
O1—C3	1.392 (3)	N1—C12	1.474 (3)
O2—P1—N2	111.22 (10)	C4—N2—C14	118.00 (19)
O2—P1—N1	120.01 (10)	P1—N1—C7	117.32 (17)
N2—P1—N1	106.27 (11)	P1—N1—C12	124.38 (16)
P1—N2—C4	122.13 (16)	C7—N1—C12	116.97 (19)
P1—N2—C14	119.62 (17)		

Table S6 Hydrogen-bond geometry of structure III (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1c1···O2^{i}	0.96	2.30	3.243 (3)	166.36
C4—H1c4···O2	0.96	2.42	2.953 (3)	114.55
C12—H1c12···O1	0.96	2.22	2.807 (3)	118.83

Symmetry code: (i) *x*−1, *y*, *z*.

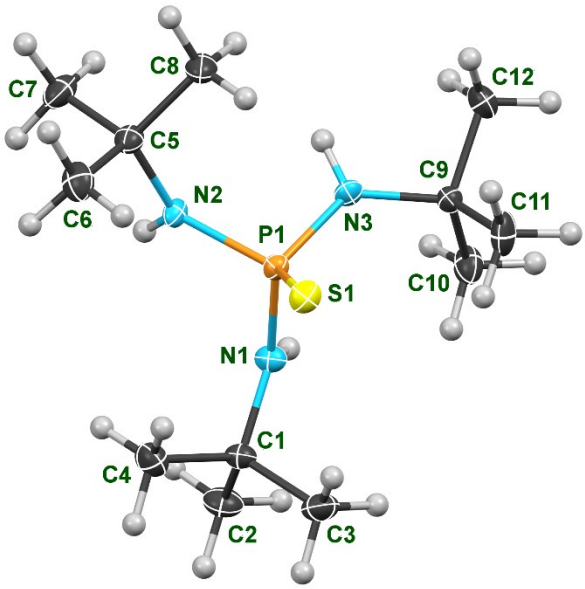

Fig. S4 The molecular structure and atom-labeling scheme for IV. Displacement ellipsoids are drawn at the 50% probability level.

Table S7 Selected geometric parameters of structure IV (Å, °).

S1—P1	1.9535 (10)	N1—C1	1.489 (4)
P1—N1	1.649 (3)	N2—C5	1.489 (4)
P1—N3	1.657 (3)	N3—C9	1.483 (5)
P1—N2	1.660 (3)		
N1—P1—N3	106.41 (14)	N2—P1—S1	115.89 (10)
N1—P1—N2	103.89 (14)	C1—N1—P1	130.7 (2)
N3—P1—N2	100.31 (14)	C5—N2—P1	129.1 (2)
N1—P1—S1	114.16 (11)	C9—N3—P1	131.0 (2)
N3—P1—S1	114.64 (10)		

Table S8 Hydrogen-bond geometry (Å, °)

D—*H*···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···S1^{i}	0.88	2.89	3.692 (3)	152

Symmetry code: (i) *x*−1/2, −*y*+1/2, *z*.

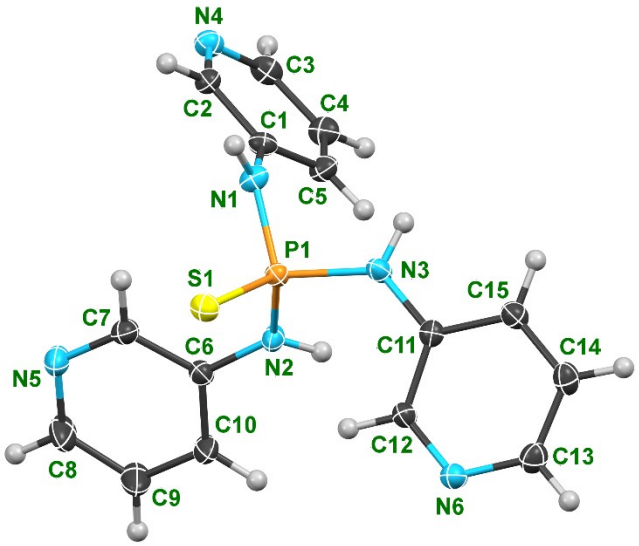

Fig. S5 The molecular structure and atom-labeling scheme for V. Displacement ellipsoids are drawn at the 50% probability level.

Table S9 Selected geometric parameters of structure V (Å, °).

S1—P1	1.9331 (9)	N1—C1	1.410 (3)
P1—N2	1.652 (2)	N2—C6	1.404 (3)
P1—N1	1.655 (2)	N3—C11	1.403 (3)
P1—N3	1.660 (2)		
N2—P1—N1	109.18 (10)	N3—P1—S1	118.17 (8)
N2—P1—N3	101.02 (11)	C1—N1—P1	128.41 (16)
N1—P1—N3	103.02 (11)	C6—N2—P1	126.97 (17)
N2—P1—S1	114.22 (9)	C11—N3—P1	128.05 (18)
N1—P1—S1	110.25 (8)		

Table S10 Hydrogen-bond geometry of structure V (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···N4^{i}	0.88	2.17	3.038 (3)	167.0
N2—H2A···N6^{ii}	0.88	2.03	2.888 (3)	164.7
N3—H3A···N5^{iii}	0.88	1.96	2.838 (3)	173.5

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*; (ii) *x*+1/2, −*y*+1/2, *z*; (iii) −*x*+1, −*y*+1, *z*+1/2.

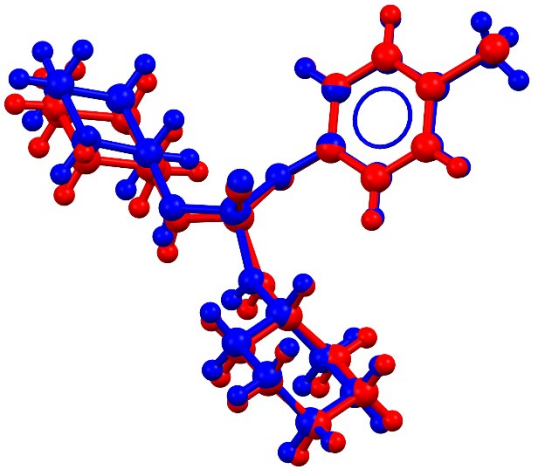

Fig. S6 The molecular overlay of II and EVOSUE.

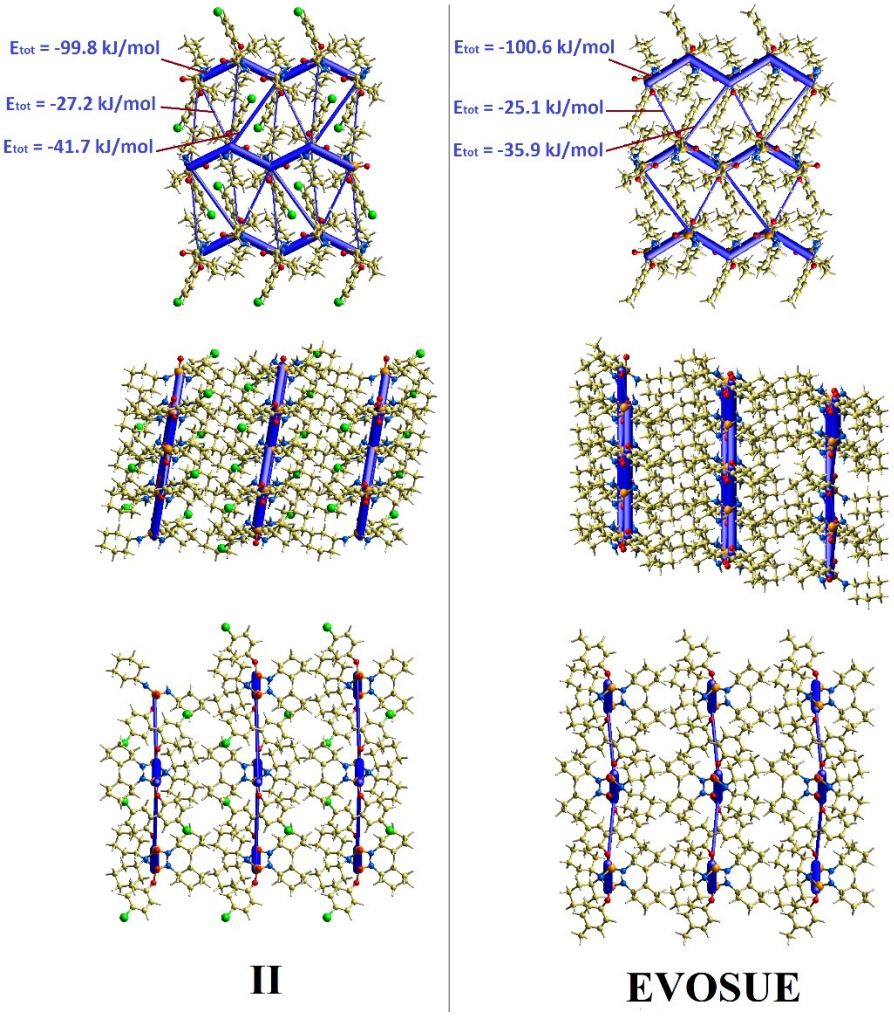

Fig. S7 Comparison of the packing maps and energy frameworks of structures II and EVOSUE (energy cutoff = –20 kJ/mol).

Table S11 The interaction energies for the different molecular pairs in structure I (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
1	*–x*, *–y*, *–z*	11.68	–2.9	–0.4	–9.6	5.7	–8.2
2	*x*, *y*, *z*	9.01	–5.4	–3	–20.6	12.7	–18
2	*x*, *y*, *z*	10.41	–0.5	–0.4	–8.6	3.6	–6.1
1	*–x*, *–y*, *–z*	9.17	–8.8	–1.4	–51.5	38.8	–31.2
2	*x*, *y*, *z*	10.02	–2.7	–0.6	–15.1	10.6	–9.9
1	*–x*, *–y*, *–z*	6.47	–100.9	–20	–36.1	119.3	–79.2
2	*x*, *y*, *z*	10.47	0.3	–0.2	–9	3.4	–5.5
1	*–x*, *–y*, *–z*	5.04	–17.8	–2.7	–54.7	32.2	–48.5
1	*–x*, *–y*, *–z*	8.56	–9.2	–0.8	–42	29.3	–28.9
1	*–x*, *–y*, *–z*	8.89	–14.3	–5.2	–15.6	15.6	–22.9
1	*–x*, *–y*, *–z*	7.93	–15.8	–5.4	–38	29.1	–35.8
1	*–x*, *–y*, *–z*	13.56	–1.9	–0.3	–5.2	1	–6.2
	$\sum \frac{1}{2} E.N$		**–94.1**	**–22.3**	**–179.65**	**165.8**	**–169.95**

Table S12 The interaction energies for the different molecular pairs in structure II (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
1	*–x*, *–y*, *–z*	14.83	0	–0.1	–4	0.3	–3.3
2	*x*, *–y*+1/2, *z*+1/2	11.97	–0.1	–0.2	–8.6	2.6	–6.2
2	*x*, *y*, *z*	11.27	–3.1	–0.5	–28.1	17.3	–17.4
2	*x*, *–y*+1/2, *z*+1/2	13.27	–0.4	–0.1	–10.2	3.8	–7
2	*x*, *–y*+1/2, *z*+1/2	5.73	–67.1	–22.7	–75.4	86.9	–99.8
1	*–x*, *–y*, *–z*	7.52	–19.3	–6.9	–46.8	39.7	–41.7
2	*–x*, *y*+1/2, *–z*+1/2	9.58	–5.4	–1.1	–29.6	18.9	–20.7
1	*–x*, *–y*, *–z*	7.45	–8.2	–1	–37.4	24	–27.2
2	*–x*, *y*+1/2, *–z*+1/2	14.05	–2.7	–0.4	–7.2	7.5	–4.7
	$\sum \frac{1}{2} E.N$		**–92.55**	**–29**	**–203.2**	**169**	**–191.9**

Table S13 The interaction energies for the different molecular pairs in structure III (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
2	–*x*, *y*+1/2, –*z*+1/2	9.26	–7.8	0	–44.7	26.8	–30.5
1	–*x*, –*y*, –*z*	13.17	–0.7	–0.1	–6	0.6	–5.6
2	*x*, *y*, *z*	6.05	–23.4	–10.5	–55.1	45.5	–52.4
2	*x*, –*y*+1/2, *z*+1/2	11.18	–4.2	–0.8	–28.9	18.9	–18.5
2	*x*, –*y*+1/2, *z*+1/2	9.73	–6.9	–2.1	–42.2	23.3	–31.2
2	–*x*, *y*+1/2, –*z*+1/2	9.83	–3	–0.3	–23.7	11.5	–16.9
1	–*x*, –*y*, –*z*	14.78	–2.5	–0.2	–4.1	12.5	1.4
	$\sum \frac{1}{2} E.N$		**–46.9**	**–13.85**	**–199.65**	**132.55**	**–151.6**

Table S14 The interaction energies for the different molecular pairs in structure IV (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
2	*x*+1/2, –*y*+1/2, *z*	9.56	–3.1	–1.4	–12.8	8.4	–10.3
2	–*x*, –*y*, *z*+1/2	8.83	–2.4	–0.4	–17.3	7.3	–13.4
2	*x*+1/2, –*y*+1/2, *z*	5.9	–17.7	–6.1	–53.8	40.8	–44.9
2	–*x*, –*y*, *z*+1/2	10.70	–0.5	–0.1	–10	5.2	–6.1
2	*x*, *y*, *z*	9.65	–0.5	–0.4	–14.9	8.5	–8.5
2	–*x*+1/2, *y*+1/2, *z*+1/2	9.22	–4.4	–0.7	–17.1	8.1	–15.1
2	–*x*+1/2, *y*+1/2, *z*+1/2	9.22	–5	–1	–18.8	9.9	–16.3
	$\sum \frac{1}{2} E.N$		**–33.6**	**–10.1**	**–144.7**	**88.2**	**–114.6**

Table S15 The interaction energies for the different molecular pairs in structure V (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
2	*x*+1/2, –*y*+1/2, *z*	6.6	–58	–16	–51.5	85.6	–65.2
2	–*x*+1/2, *y*+1/2, *z*+1/2	10.01	3.4	–1.3	–9	1.6	–4.3
2	–*x*, –*y*, *z*+1/2	10.86	–4.7	–1.1	–6.5	7.4	–6.9
2	*x*, *y*, *z*	9.45	–4	–3.4	–22.6	23.3	–11.9
2	–*x*, –*y*, *z*+1/2	7.62	–66.1	–17.3	–38.8	89.1	–61.6
2	–*x*+1/2, *y*+1/2, *z*+1/2	10.01	–1.7	–0.9	–6.6	1.3	–7.4
2	–*x*+1/2, *y*+1/2, *z*+1/2	11.39	–2	–0.8	–13.7	15.8	–4.8
2	*x*+1/2, –*y*+1/2, *z*	8.86	–40.4	–9.6	–18.7	43.5	–39.2
	$\sum \frac{1}{2} E.N$		**–173.5**	**–50.4**	**–167.4**	**267.6**	**–201.3**

Table S16 Topological parameters and estimated energies (E_{Esp}) for dihydrogen interactions in the different pairs of structures I–IV with normalized/non-normalized hydrogen atoms position (*N*/*NN*) at the basis set 6-311G(d,p). The codes indicate the interactions shown in Fig. S8.

pair	code	(*N*/*NN*)	$\rho(r)$ (e/Å^3)	$\nabla^2\rho(r)$ (e/Å^5)	$G(r)$	$V(r)$	E_{Esp} (kJ/mol)
I*f*	1	*N*	0.0040	0.0134	0.0028	–0.0022	–2.9
		NN	0.0027	0.0101	0.0020	–0.0015	–2.0
II*a*	2	*N*	0.0026	0.0079	0.0016	–0.0012	–1.6
		NN	0.0017	0.0058	0.0011	–0.0008	–1.0
	3	*N*	0.0047	0.0124	0.0027	–0.0023	–3.0
		NN	0.0031	0.0091	0.0019	–0.0015	–2.0
	4	*N*	0.0035	0.0099	0.0021	–0.0017	–2.3
		NN	0.0023	0.0072	0.0015	–0.0011	–1.5
	5	*N*	0.0025	0.0075	0.0015	–0.0011	–1.5
		NN	0.0021	0.0064	0.0013	–0.0009	–1.2
	6	*N*	0.0044	0.0117	0.0025	–0.0022	–2.8
		NN	0.0030	0.0088	0.0018	–0.0015	–1.9
	7	*N*	0.0031	0.0086	0.0018	–0.0015	–1.9
		NN	0.0017	0.0056	0.0011	–0.0008	–1.0
	8	*N*	0.0051	0.0150	0.0031	–0.0025	–3.3
		NN	0.0038	0.0117	0.0024	–0.0019	–2.5
	9	*N*	0.0062	0.0196	0.0042	–0.0035	–4.5
		*	—	—	—	—	—
II*c*	10	*N*	0.0037	0.0114	0.0024	–0.0019	–2.5
		NN	0.0025	0.0089	0.0018	–0.0014	–1.8
	11	*N*	0.0048	0.0139	0.0030	–0.0025	–3.3
		NN	0.0033	0.0103	0.0022	–0.0017	–2.3
	12	*N*	0.0086	0.0283	0.0059	–0.0048	–6.3
		NN	0.0066	0.0233	0.0048	–0.0037	–4.8
	13	*N*	0.0063	0.0204	0.0043	–0.0034	–4.5
		NN	0.0047	0.0172	0.0035	–0.0027	–3.5
III*a*	14	*N*	0.0060	0.0166	0.0036	–0.0030	–4.0
		NN	0.0037	0.0114	0.0024	–0.0019	–2.5
	15	*N*	0.0055	0.0153	0.0033	–0.0028	–3.7
		NN	0.0040	0.0122	0.0026	–0.0021	–2.8
	16	*N*	0.0038	0.0132	0.0026	–0.0019	–2.4
		NN	0.0032	0.0116	0.0022	–0.0016	–2.1
	17	*N*	0.0053	0.0182	0.0037	–0.0029	–3.7
		NN	0.0041	0.0159	0.0031	–0.0023	–3.0
	18	*N*	0.0021	0.0067	0.0013	–0.0010	–1.3

		NN	0.0013	0.0049	0.0009	–0.0006	–0.8
	19	*N*	0.0019	0.0063	0.0012	–0.0009	–1.2
		*	—	—	—	—	—
III*b*	20	*N*	0.0029	0.0093	0.0019	–0.0015	–1.9
		NN	0.0029	0.0085	0.0018	–0.0015	–1.9
	21	*N*	0.0046	0.0122	0.0027	–0.0023	–3.0
		NN	0.0007	0.0028	0.0005	–0.0003	–0.4
III*c*	22	*N*	0.0074	0.0216	0.0046	–0.0038	–5.0
		NN	0.0051	0.0156	0.0033	–0.0026	–3.4
	23	*N*	0.0041	0.0135	0.0027	–0.0021	–2.8
		NN	0.0032	0.0113	0.0022	–0.0017	–2.2
	24	*N*	0.0036	0.0117	0.0024	–0.0019	–2.5
		NN	0.0027	0.0097	0.0019	–0.0015	–1.9
	25	*N*	0.0042	0.0137	0.0028	–0.0022	–2.8
		NN	0.0032	0.0115	0.0023	–0.0017	–2.2
	26	*N*	0.0028	0.0094	0.0019	–0.0015	–1.9
		*	—	—	—	—	—
IV*a*	27	*N*	0.0023	0.0076	0.0015	–0.0011	–1.4
		NN	0.0018	0.0061	0.0012	–0.0008	–1.1
	28	*N*	0.0051	0.0137	0.0030	–0.0026	–3.4
		NN	0.0036	0.0105	0.0022	–0.0019	–2.5
	29	*N*	0.0056	0.0185	0.0037	–0.0027	–3.6
		NN	0.0039	0.0140	0.0028	–0.0020	–2.6
	30	*N*	0.0029	0.0089	0.0018	–0.0014	–1.8
		NN	0.0021	0.0071	0.0014	–0.0010	–1.3
	31	*N*	0.0053	0.0178	0.0036	–0.0028	–3.7
		NN	0.0044	0.0150	0.0030	–0.0023	–3.0
	32	*N*	0.0029	0.0089	0.0018	–0.0014	–1.9
		NN	0.0021	0.0071	0.0014	–0.0010	–1.4
	33	*N*	0.0055	0.0157	0.0033	–0.0027	–3.6
		NN	0.0041	0.0126	0.0026	–0.0021	–2.7
	34	*N*	0.0030	0.0087	0.0018	–0.0014	–1.8
		NN	0.0022	0.0071	0.0014	–0.0010	–1.3

* The interaction is absent in the QTAIM diagram, in the case of using non-normalized (original X-ray structure) as the input file.

Table S17 Topological parameters and estimated energies (E_{Esp}) for dihydrogen interactions in the different pairs of structures I–IV with normalized hydrogen atoms position at the basis set 6-311++G(d,p). The codes indicate the interactions shown in Fig. S8.

pair	code	$\rho(r)$ (e/Å^3)	$\nabla^2\rho(r)$ (e/Å^5)	$G(r)$	$V(r)$	E_{Esp} (kJ/mol)
If	1	0.0041	0.0133	0.0028	–0.0022	–2.9
IIa	2	0.0026	0.0079	0.0016	–0.0012	–1.6
	3	0.0047	0.0126	0.0027	–0.0023	–3.0
	4	0.0035	0.0100	0.0021	–0.0017	–2.2
	5	0.0025	0.0075	0.0015	–0.0011	–1.5
	6	0.0043	0.0118	0.0025	–0.0021	–2.8
	7	0.0031	0.0087	0.0018	–0.0014	–1.9
	8	0.0051	0.0150	0.0031	–0.0025	–3.3
	9	0.0061	0.0195	0.0041	–0.0034	–4.5
IIc	10	0.0036	0.0115	0.0024	–0.0019	–2.5
	11	0.0048	0.0139	0.0030	–0.0025	–3.3
	12	0.0086	0.0283	0.0059	–0.0048	–6.3
	13	0.0063	0.0204	0.0043	–0.0035	–4.5
IIIa	14	0.0060	0.0166	0.0036	–0.0030	–4.0
	15	0.0055	0.0153	0.0033	–0.0028	–3.6
	16	0.0038	0.0132	0.0026	–0.0019	–2.5
	17	0.0053	0.0181	0.0037	–0.0029	–3.8
	18	0.0020	0.0067	0.0013	–0.0010	–1.3
	19	0.0018	0.0063	0.0012	–0.0009	–1.1
IIIb	20	0.0029	0.0092	0.0019	–0.0014	–1.8
	21	0.0011	0.0041	0.0008	–0.0005	–0.6
IIIc	22	0.0075	0.0215	0.0046	–0.0038	–5.0
	23	0.0041	0.0136	0.0027	–0.0021	–2.8
	24	0.0036	0.0117	0.0024	–0.0019	–2.5
	25	0.0042	0.0138	0.0028	–0.0022	–2.8
	26	0.0028	0.0094	0.0019	–0.0014	–1.9
IVa	27	0.0024	0.0076	0.0015	–0.0011	–1.4
	28	0.0051	0.0138	0.0030	–0.0026	–3.4
	29	0.0056	0.0186	0.0037	–0.0028	–3.6
	30	0.0029	0.0089	0.0018	–0.0014	–1.8
	31	0.0053	0.0178	0.0036	–0.0028	–3.7
	32	0.0028	0.0090	0.0018	–0.0014	–1.9
	33	0.0056	0.0158	0.0033	–0.0027	–3.6
	34	0.0030	0.0087	0.0018	–0.0014	–1.8

Table S18 Topological parameters and estimated energies (E_{Esp}) for selected interactions in the different pairs of structures I–V (using X-ray structure as input file) at the basis set 6-311G(d,p).

pair	interaction	$\rho(r)$ (e/Å^3)	$\nabla^2\rho(r)$ (e/Å^5)	$G(r)$	$V(r)$	E_{Esp} (kJ/mol)
I*a*	NH···N$^{\#}$	0.0221	0.0890	0.0191	–0.0159	–20.9
	CH···O═P$^{\#}$	0.0082	0.0282	0.0060	–0.0050	–6.6
I*b*	CH···O$^{\#}$	0.0063	0.0227	0.0048	–0.0040	–5.2
	CH···O$^{\#}$	0.0019	0.0087	0.0016	–0.0011	–1.4
	CH···O$^{\#}$	0.0031	0.0123	0.0025	–0.0019	–2.6
I*c*	CH···π$^{\#}$	0.0054	0.0167	0.0034	–0.0027	–3.5
	CH···O═P$^{\#}$	0.0048	0.0176	0.0037	–0.0029	–3.9
	CH···O═P$^{\#}$	0.0055	0.0205	0.0043	–0.0034	–4.5
I*d*	CH···N(π)$^{\#}$	0.0059	0.0180	0.0039	–0.0033	–4.3
	π···π$^{\#}$	0.0060	0.0157	0.0033	–0.0027	–3.5
I*e*	CH···π$^{\#}$	0.0062	0.0170	0.0036	–0.0030	–4.0
	π···π	0.0045	0.0121	0.0025	–0.0019	–2.5
I*f*	CH···O═P$^{\#}$	0.0068	0.0245	0.0051	–0.0041	–5.4
II*a*	NH···O═P	0.0147	0.0637	0.0132	–0.0106	–13.9
	NH···O═P	0.0180	0.0840	0.0174	–0.0139	–18.2
	CH···O	0.0037	0.0136	0.0028	–0.0023	–3.0
	CH···O	0.0037	0.0149	0.0030	–0.0023	–3.1
	CH···N	0.0030	0.0089	0.0019	–0.0015	–2.0
	CH···N	0.0024	0.0073	0.0015	–0.0012	–1.6
	CH···Cl	0.0027	0.0084	0.0017	–0.0013	–1.7
	CH···π	0.0033	0.0088	0.0018	–0.0015	–2.0
	CH···π	0.0042	0.0129	0.0026	–0.0021	–2.7
II*b*	CH···π$^{\#}$	0.0063	0.0176	0.0038	–0.0032	–4.1
	CH···π$^{\#}$	0.0039	0.0108	0.0023	–0.0018	–2.4
II*c*	CH···Cl	0.0021	0.0063	0.0012	–0.0009	–1.1
II*d*	CH···Cl$^{\#}$	0.0050	0.0174	0.0035	–0.0025	–3.4
	CH···Cl$^{\#}$	0.0060	0.0192	0.0038	–0.0029	–3.8
	Cl···O$^{\#}$	0.0021	0.0073	0.0014	–0.0009	–1.2
	CH···O═P$^{\#}$	0.0039	0.0136	0.0028	–0.0023	–3.0
	π···π$^{\#}$	0.0054	0.0143	0.0029	–0.0023	–3.0
III*a*	CH···O═P	0.0115	0.0451	0.0092	–0.0071	–9.3
	CH···O═P	0.0087	0.0276	0.0060	–0.0051	–6.6
III*b*	CH···Cl	0.0031	0.0106	0.0020	–0.0013	–1.8
	CH···Cl	0.0033	0.0102	0.0021	–0.0016	–2.1
	CH···π	0.0060	0.0167	0.0036	–0.0031	–4.1
	CH···π	0.0036	0.0103	0.0021	–0.0017	–2.3
	CH···π	0.0043	0.0124	0.0026	–0.0021	–2.8
	CH···π	0.0039	0.0109	0.0023	–0.0019	–2.5
III*c*	CH···Cl	0.0043	0.0143	0.0028	–0.0020	–2.6
	CH···Cl	0.0023	0.0069	0.0014	–0.0010	–1.3

IV*a*	NH···S═P	0.0063	0.0200	0.0041	–0.0032	–4.1
	CH···S═P	0.0041	0.0125	0.0024	–0.0018	–2.3
	CH···S═P	0.0046	0.0133	0.0027	–0.0021	–2.7
V*a*	NH···N	0.0249	0.0977	0.0216	–0.0188	–24.7
	CH···N	0.0069	0.0203	0.0044	–0.0037	–4.9
	CH···S═P	0.0051	0.0173	0.0034	–0.0024	–3.2
	CH···π	0.0053	0.0145	0.0031	–0.0025	–3.3
V*b*	NH···N	0.0176	0.0678	0.0141	–0.0113	–14.8
	CH···S═P	0.0070	0.0208	0.0042	–0.0032	–4.2
V*c*	NH···N	0.0288	0.1111	0.0256	–0.0235	–30.8
	CH···N	0.0066	0.0197	0.0042	–0.0035	–4.6
	CH···N	0.0062	0.0197	0.0042	–0.0036	–4.7
	C(π)···N	0.0045	0.0141	0.0029	–0.0023	–3.1

There are a couple of such interactions in the molecular pair, which one time is reported here.

Table S19 Topological parameters and estimated energies (E_{Esp}) for selected interactions in the different pairs of structures I–V obtained at the basis set 6-311G(d,p), considering the neutron-normalized structures.

pair	**Hydrogen bonds/contacts**	***ρ*(*r*) (e/Å³)**	**$\nabla^2\rho(r)$ (e/Å⁵)**	***G*(*r*)**	***V*(*r*)**	**E_{Esp} (kJ/mol)**
I*a*	CH···O═P#	0.0102	0.0337	0.0074	–0.0063	–8.3
	NH···N#	0.0318	0.0969	0.0244	–0.0246	–32.3
I*b*	CH···O#	0.0084	0.0296	0.0064	–0.0053	–7.0
	CH···O#	0.0023	0.0101	0.0019	–0.0014	–1.8
	CH···O#	0.0040	0.0143	0.0030	–0.0024	–3.2
I*c*	CH···π#	0.0073	0.0223	0.0046	–0.0036	–4.8
	CH···O═P#	0.0055	0.0190	0.0041	–0.0034	–4.5
	CH···O═P#	0.0064	0.0223	0.0048	–0.0040	–5.2
I*d*	CH···N(π)#	0.0075	0.0232	0.0050	–0.0042	–5.5
	π···π#	0.0060	0.0158	0.0033	–0.0027	–3.5
I*e*	CH···π#	0.0078	0.0217	0.0046	–0.0038	–5.0
	π···π	0.0046	0.0125	0.0025	–0.0020	–2.6
I*f*	CH···O═P#	0.0088	0.0311	0.0066	–0.0054	–7.1
II*a*	NH···O═P	0.0195	0.0799	0.0174	–0.0148	–19.4
	NH···O═P	0.0242	0.1042	0.0230	–0.0200	–26.3
	CH···O	0.0044	0.0151	0.0032	–0.0027	–3.5

	CH···O	0.0041	0.0158	0.0033	–0.0026	–3.4
	CH···N	0.0036	0.0101	0.0022	–0.0018	–2.4
	CH···N	0.0032	0.0089	0.0019	–0.0016	–2.1
	CH···Cl	0.0034	0.0105	0.0021	–0.0016	–2.1
	CH···π	0.0043	0.0115	0.0024	–0.0019	–2.6
	CH···π	0.0052	0.0155	0.0032	–0.0026	–3.4
	CH···π	0.0022	0.0062	0.0012	–0.0010	–1.2
II*b*	CH···π$^{\#}$	0.0076	0.0212	0.0046	–0.0039	–5.1
	CH···π$^{\#}$	0.0045	0.0121	0.0025	–0.0021	–2.7
II*c*	CH···Cl	0.0026	0.0079	0.0015	–0.0011	–1.4
II*d*	CH···Cl$^{\#}$	0.0060	0.0204	0.0041	–0.0031	–4.1
	CH···Cl$^{\#}$	0.0072	0.0226	0.0046	–0.0035	–4.6
	Cl···O$^{\#}$	0.0022	0.0074	0.0014	–0.0009	–1.2
	CH···O═P$^{\#}$	0.0050	0.0163	0.0035	–0.0029	–3.8
	π···π$^{\#}$	0.0055	0.0146	0.0030	–0.0024	–3.1
III*a*	CH···O═P	0.0147	0.0576	0.0120	–0.0097	–12.7
	CH···O═P	0.0111	0.0350	0.0078	–0.0068	–8.9
III*b*	CH···Cl	0.0035	0.0115	0.0022	–0.0015	–2.0
	CH···Cl	0.0039	0.0121	0.0025	–0.0020	–2.6
	CH···π	0.0074	0.0207	0.0045	–0.0038	–5.0
	CH···π	0.0042	0.0113	0.0024	–0.0019	–2.6
	CH···π	0.0053	0.0149	0.0031	–0.0026	–3.4
	CH···π	0.0051	0.0140	0.0030	–0.0025	–3.2
III*c*	CH···Cl	0.0031	0.0089	0.0018	–0.0013	–1.7
	CH···Cl	0.0074	0.0216	0.0046	–0.0038	–5.0
	CH···π	0.0036	0.0102	0.0021	–0.0016	–2.1
IV*a*	NH···S═P	0.0079	0.0236	0.0049	–0.0039	–5.2
	CH···S═P	0.0045	0.0133	0.0027	–0.0020	–2.6
	CH···S═P	0.0054	0.0153	0.0032	–0.0025	–3.3
V*a*	NH···N	0.0329	0.1039	0.0262	–0.0264	–34.6
	CH···N	0.0085	0.0247	0.0054	–0.0046	–6.1
	CH···S═P	0.0058	0.0185	0.0037	–0.0027	–3.6
	CH···π	0.0065	0.0175	0.0037	–0.0030	–4.0
	CH···π	0.0070	0.0227	0.0046	–0.0036	–4.7

V*b*	NH···N	0.0231	0.0780	0.0175	–0.0155	–20.4
	CH···S═P	0.0085	0.0242	0.0050	–0.0039	–5.2
V*c*	NH···N	0.0388	0.1124	0.0308	–0.0336	–44.1
	CH···N	0.0045	0.0150	0.0032	–0.0026	–3.4
	CH···N	0.0082	0.0237	0.0051	–0.0043	–5.6
	C(π)···N	0.0046	0.0147	0.0031	–0.0024	–3.2

There are a couple of such interactions in the molecular pair, which one time is reported here.

Table S20 The interaction energies for the different molecular pairs in the structure EVOSUE (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	$\mathbf{E_{ele}}$	$\mathbf{E_{pol}}$	$\mathbf{E_{dis}}$	$\mathbf{E_{rep}}$	$\mathbf{E_{tot}}$
2	*x*, *y*, *z*	11.29	–2.1	–0.2	–23.7	11.3	–16.1
2	*x*+1/2, –*y*+1/2, *z*	11.87	–0.2	–0.1	–7	1.4	–5.5
2	–*x*+1/2, *y*+1/2, –*z*	9.70	–2.6	–0.6	–26.7	14.1	–17.8
2	*x*+1/2, –*y*+1/2, *z*	13.19	–0.1	–0.1	–8.7	0	–7.7
2	–*x*+1/2, *y*+1/2, –*z*	14.42	0.5	0	–7.1	0	–5.6
2	*x*+1/2, –*y*+1/2, *z*	5.47	–65.8	–22.8	–68	72.9	–100.6
1	–*x*, –*y*, –*z*	7.84	–4.2	–1.2	–35.8	18.4	–25.1
1	–*x*, –*y*, –*z*	8.38	–8.9	–6.4	–43.3	25.8	–35.9
1	–*x*, –*y*, –*z*	14.81	–1	0	–3.5	0	–4.2
1	–*x*, –*y*, –*z*	14.16	–0.9	0	–1.9	0	–2.7
	$\sum \frac{1}{2} E.N$		**–77.8**	**–27.6**	**–183.5**	**121.8**	**–187.3**

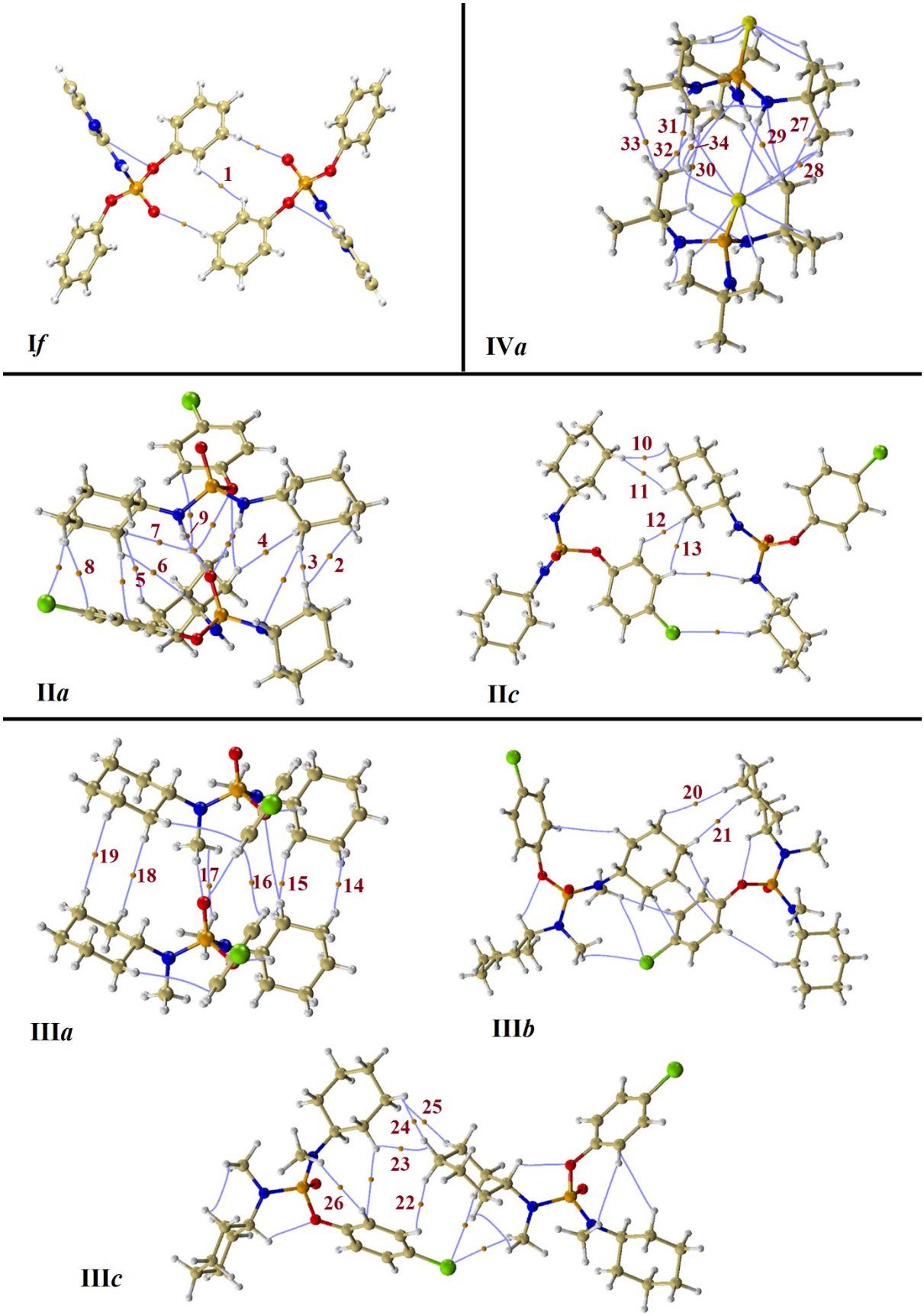

Fig. S8 QTAIM plots of the pairs having H···H interactions, which are encoded with numbers.

Table S21 The interaction energies for the different molecular pairs in the structure KESZIR (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	Symmetry operations	*R*	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
Molecule 1:							
1	–	8.34	1.7	–0.8	–12.8	5.7	–6.4
1	–	8.02	–12.1	–5.3	–16.2	17.4	–20.1
1	–	7.83	–15.7	–6.1	–16.3	22.3	–21.5
1	–	9.56	2.9	–0.2	–2.7	0	0.5
1	–	8.64	–2.7	–0.6	–10.4	6.1	–8.5
1	–	6.73	–20.9	–6.7	–31.8	21.5	–41.4
1	–	8.34	–1.1	–0.4	–21.4	10	–13.9
1	–	8.05	–0.2	–0.8	–15.8	7.3	–10.2
1	–*x*, –*y*, –*z*	9.01	–1.9	–0.3	–5	1.1	–6
2	–*x*, *y*+1/2, –*z*+1/2	7.37	–1.8	–1.8	–23.3	9.7	–17.5
1	–*x*, –*y*, –*z*	8.39	–7.6	–3.1	–8.4	3.5	–15.5
2	*x*, –*y*+1/2, *z*+1/2	6.93	–12.5	–5.2	–35.5	23.3	–33.6
	$E_1 = \sum \frac{1}{2} E.N$		–43.1	–19.15	–129.2	80.45	–122.6
Molecule 2:							
1	–	8.34	1.7	–0.8	–12.8	5.7	–6.4
1	–*x*, –*y*, –*z*	7.63	0.4	–1	–21.4	9.5	–13.1
1	–	8.02	–12.1	–5.3	–16.2	17.4	–20.1
1	–	7.83	–15.7	–6.1	–16.3	22.3	–21.5
1	–*x*, –*y*, –*z*	6.55	–18.3	–8.5	–33.3	22.6	–40.7

2	–*x*, *y*+1/2, –*z*+1/2	7.18	–3.6	–2.5	–24.4	10.3	–20.6
1	–	9.56	2.9	–0.2	–2.7	0	0.5
1	–	8.64	–2.7	–0.6	–10.4	6.1	–8.5
2	*x*, –*y*+1/2, *z*+1/2	9.03	0.7	–0.5	–7.3	2.5	–4.3
1	–	6.73	–20.9	–6.7	–31.8	21.5	–41.4
1	–	8.34	–1.1	–0.4	–21.4	10	–13.9
1	–	8.05	–0.2	–0.8	–15.8	7.3	–10.2
	$E_2 = \sum \frac{1}{2} E.N$		**–35.9**	**–18.2**	**–122.75**	**74**	**–112.55**
	$E_{average} = \frac{E_1 + E_2}{2}$		**–39.5**	**–18.675**	**–125.975**	**77.225**	**–117.575**

Table S22 The interaction energies for the different molecular pairs in the structure BOFHIQ (energy values are in kJ/mole). *R* is the distance between molecular centroids (Å).

N	**Symmetry operations**	***R***	**E_{ele}**	**E_{pol}**	**E_{dis}**	**E_{rep}**	**E_{tot}**
1	–*x*, –*y*, –*z*	8.51	–4.8	–0.4	–33.1	19.7	–22
2	*x*, *y*, *z*	9.28	–2.2	–1.3	–16.3	9.1	–11.9
2	–*x*, *y*+1/2, –*z*+1/2	10.62	–0.1	–0.1	–7.5	1.4	–5.8
2	*x*, –*y*+1/2, *z*+1/2	10.33	–0.8	–0.2	–12.3	5.7	–8.1
1	–*x*, –*y*, –*z*	7.81	–11.9	–5.9	–36.4	22.7	–34.6
2	–*x*, *y*+1/2, –*z*+1/2	7.97	–8.3	–3	–32.8	21.1	–26.5
1	–*x*, –*y*, –*z*	7.12	–6.5	–0.6	–54.8	33.4	–34.4
2	*x*, –*y*+1/2, *z*+1/2	7.64	–11	–5	–27.7	23.8	–24.7
1	–*x*, –*y*, –*z*	11.66	–1.9	–0.1	–11.7	6.3	–8.3
	$\sum \frac{1}{2} E.N$		**–34.95**	**–13.1**	**–164.6**	**102.15**	**–126.65**

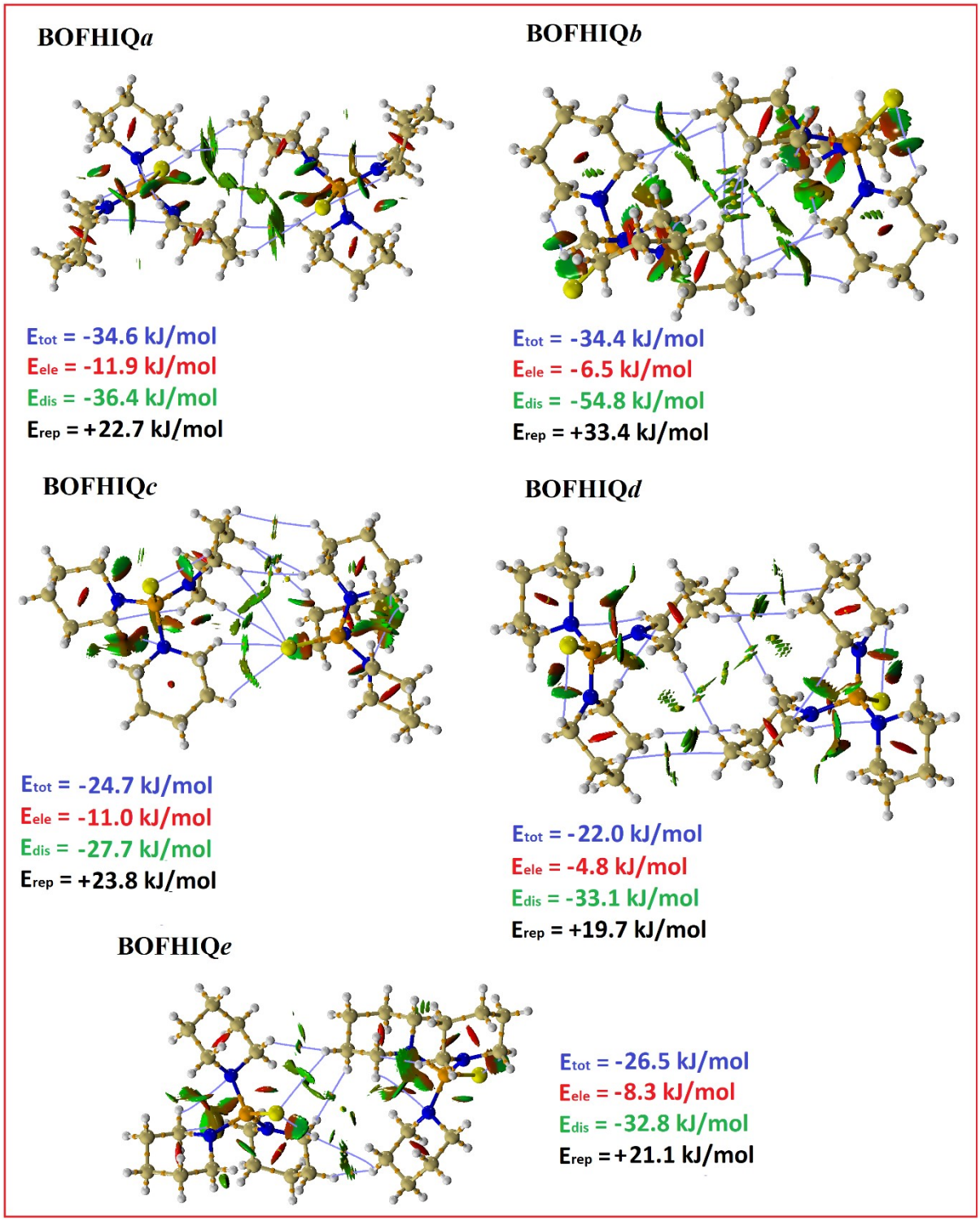

Fig. S9 The combined QTAIM/NCI plots of the selected molecular pairs (E_{tot} < –20 kJ/mol) of the structure BOFHIQ (atom color codes: P = orange, S = yellow, N = blue, C = light beige, H = white).

Table S23 The scale factors of energy components.

k_{ele}	k_{pol}	k_{dis}	k_{rep}
1.057	0.740	0.871	0.618