Supporting info for:

Conformational analysis a of supramolecular synthon: a case study of 8-hydroxyquinoline

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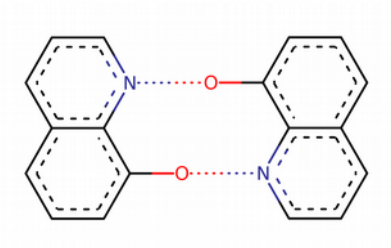
1. CSD search

The search was performed in Cambridge Structural Database version 5.38 with updates up to May 2017.

The query used for the search of all non-zwitterionic structures of 8HQ derivatives:



The following restrictions were applied:

1. N···O distance less than sum of vdW radii of O and N atoms +0.3Å;
2. Only organic structures were considered;
3. Ions were not considered;
4. Only one-component crystals were considered.

The results were reviewed manually to exclude all structures with annelated cycles and to choose a “best representative” [J. van de Streek, Acta Crystallogr. B, 2006, 62, 567–579] for structures determined multiple times and/or at different temperatures. Results are given in TS1.

Table TS1. List of CSD refcodes of unique non-zwitterionic crystal structures of **8HQ** derivatives with an H-bonded dimer and without annelated cycles. The angle φ is the angle between the average planes of 8HQ heterocycles in the dimer, multiple values of φ are given for cyrstallographicaly independent dimers.

Refcode	**φ**	**sp. gr.**
Structures with zero on nearly zero φ		
ACETOS	0	$P2_1/c$
ASAFUV	0	*Pbca*
CAHZES	0	$P\bar{1}$
HAHJAC	0	$P2_1/c$
HODSOI	0	*Pbca*
HXQUIN14	0	$P2_1/n$
HXQUIN15	0 0.03	$P\bar{1}$
IHUVIS	0	$P2_1/c$
MENDAL01	0	$P2_1/c$
REKYUC	0	$P\bar{1}$
RIHGIZ	0	$P\bar{1}$
HANDEI	0	$P2_1/c$
HANDOS	0	$P2_1/c$
HANDUY	0	*Pbca*
PIQPIO	0.02	$P2_1/n$
WUJXAA	0.02	$P2_1/n$
FAMDIG02	0.03	$P2_1/c$
GIRZUD	0.03	$P2_1/c$
HAHJEG	0.03	$P\bar{1}$
IFEHIK	0.03	$P2_1/c$
HANCIL	0.03	$P\bar{1}$
OVAKOM	0.04	$P2_1/c$
Structures with intermediate values of φ		
VIFLAX	0.76	$Pbc2_1$
NUBKEA	0.92	$P2_1$
ACETOS	6.32	$P2_1/c$
HANDAE	19.07	$P\bar{1}$
PEHCIP	20.33	$P\bar{1}$
IFEHEG	27.78	$P4_12_12$

Table TS1 (continued)

Refcode	φ	sp. gr.
	Structures with high values of φ	
YOKQAQ	44.846	*Fdd*2
NEQNEE	46.467	*Aba*2
FAMDIG01	50.341	*Fdd*2
HXQUIN13	52.273	*Fdd*2
MOSXUO	54.378	*P*2/*c*
EJEREQ	59.575	*C*2/*c*
DBHXQU02	59.954	*P*2/*c*
UNUDOX	61.671	*C*2/*c*
CIQUOL01	62.038	*P*2/*a*
KUVQEY	62.409	*C*2/*c*
HOFZOR	62.492	*Pbcn*
CIBCEV	65.901 64.879	$P\bar{1}$
NEVMOR	70.469	*P*2/*c*
CIBCIZ	70.719	*C*2/*c*
RELPED	73.517	$P\bar{1}$
WOFZIC	74.41	$P2_1/c$
YIRKOA01	79.917	*Pbca*
WOFZEY	82.257	*C*2/*c*
WOFZAU	85.383	*C*2/*c*
HUKTOY	86.826	$P2_1/c$

2. Multipole refinement

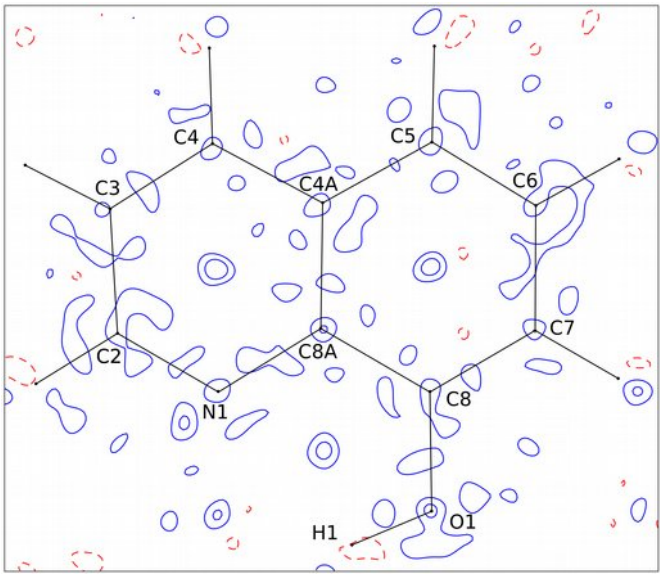


Fig. S1. Residual electron density map in the average planes of quinoline moiety in the **orthorhombic** polymorph of **8HQ**, for reflection data with sin θ/λ ≤ 1.219 Å^{-1}. Contours step is 0.05 e Å^{-3}, positive contours are drawn with a solid blue line and negative with a dashed red line.

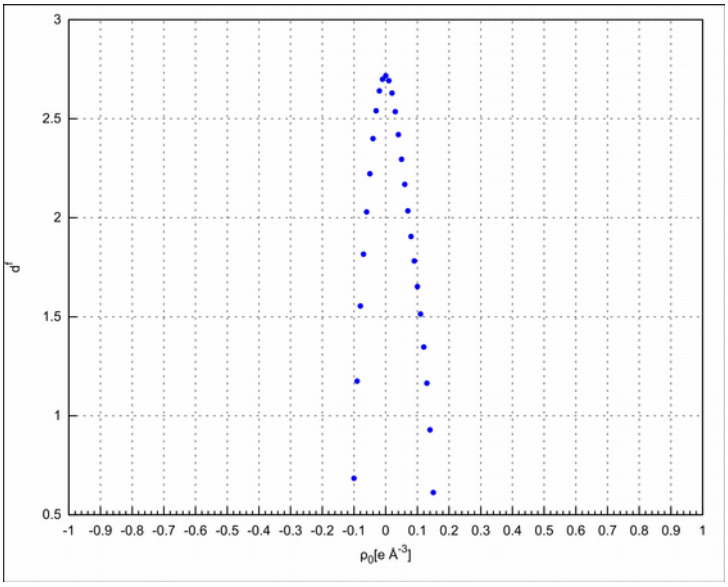


Fig. S2. Fractal dimension plot of the residual electron density after multipole refinement of the **orthorhombic** polymorph of **8HQ**.

The plot is calculated with in-house software that re-implements algorithms from jnk2RDA program. Descriptive numerical parameters are: d'(0) =2.717224; ρ_{min} = –0.096, ρ_{max} = 0.149, Δρ =0.228 e A^{-3}, e_{gross} = 23.86 e. All values are calculated for reflection data with sin θ/λ ≤ 1.2185 Å^{-1}.

For details, see [K. Meindl, J. Henn, Foundations of residual-density analysis, *Acta Crystallogr. Sect. A.*, 2008, 64, 404-418;doi:10.1107/S0108767308006879]

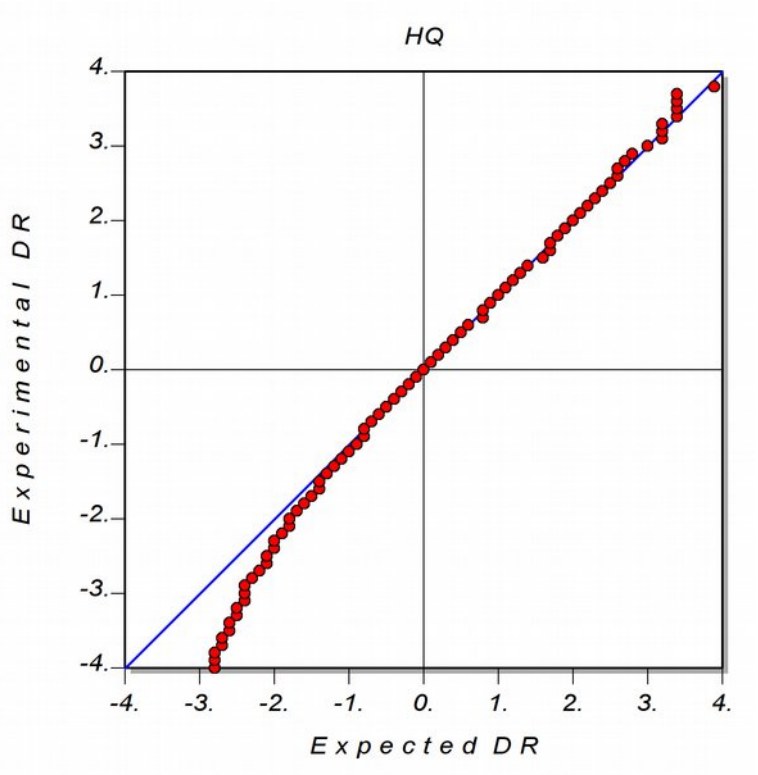


Fig. S3. Normal probability plot, plotted against full dataset of the **orthorhombic** polymorph of **8HQ**.

3. Geometrical parameters of **8HQ** molecule in crystal structures and isolated dimers.

Table TS2. Bond lengths in crystals of polymorphs and dimers.

	X-ray[1]	DFT periodic calculation[2]				Isolated systems[3]		
Bond	***Fdd*2**	***Fdd*2**	$P2_1/n$	$P\bar{1}(1)$	$P\bar{1}(2)$	dimer, C_2	dimer, C_{2h}	molecule
O1-C8	1.34897(18)	1.354	1.359	1.360	1.361	1.339	1.341	1.347
N1-C2	1.3220(2)	1.319	1.321	1.320	1.320	1.314	1.316	1.313
N1-C8A	1.36346(18)	1.364	1.368	1.367	1.367	1.358	1.358	1.355
C2-C3	1.4121(2)	1.406	1.408	1.409	1.407	1.408	1.409	1.411
C3-C4	1.3743(2)	1.366	1.366	1.367	1.367	1.368	1.368	1.370
C4-C4A	1.4161(2)	1.411	1.414	1.412	1.413	1.412	1.412	1.412
C4A-C5	1.4173(2)	1.412	1.414	1.412	1.414	1.411	1.412	1.413
C4A-C8A	1.42084(18)	1.425	1.426	1.425	1.428	1.427	1.426	1.420
C5-C6	1.3761(2)	1.370	1.370	1.368	1.367	1.372	1.372	1.376
C6-C7	1.4132(2)	1.404	1.404	1.405	1.406	1.404	1.405	1.409
C7-C8	1.3813(2)	1.375	1.373	1.374	1.373	1.380	1.378	1.374
C8-C8A	1.42868(19)	1.426	1.424	1.423	1.425	1.428	1.425	1.424
O1···N1	2.79216(17)	2.745	2.814	2.863	2.860	2.737	2.829	
H1···N1	1.912	1.827	1.990	2.060	2.053	1.817	2.041	

Notes:
1. Experimental values after multipole refinement.
2. Results of B3LYP-D2/POB-TZVP periodic calculation.
3. Results of B3LYP-D3/def2-TZVPP calculations.

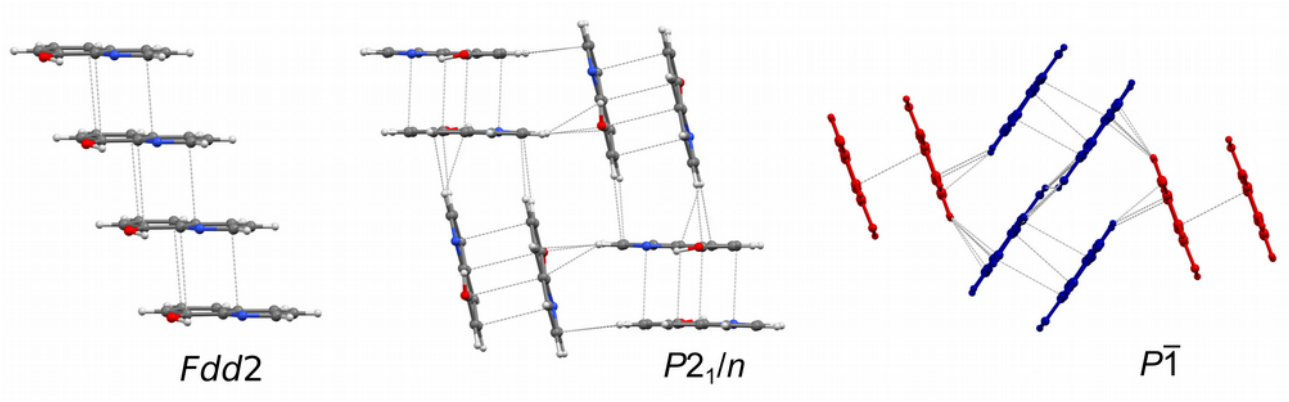


Fig. S4. Fragments of crystal packing of **8HQ** polymorphs demonstrating different patterns in different forms (stacks and dimers). The shortest contacts with interatomic distances less than the sum of vdW radii+0.1 Å are shown with dotted lines.

4. Topological analysis of $\rho(\mathbf{r})$

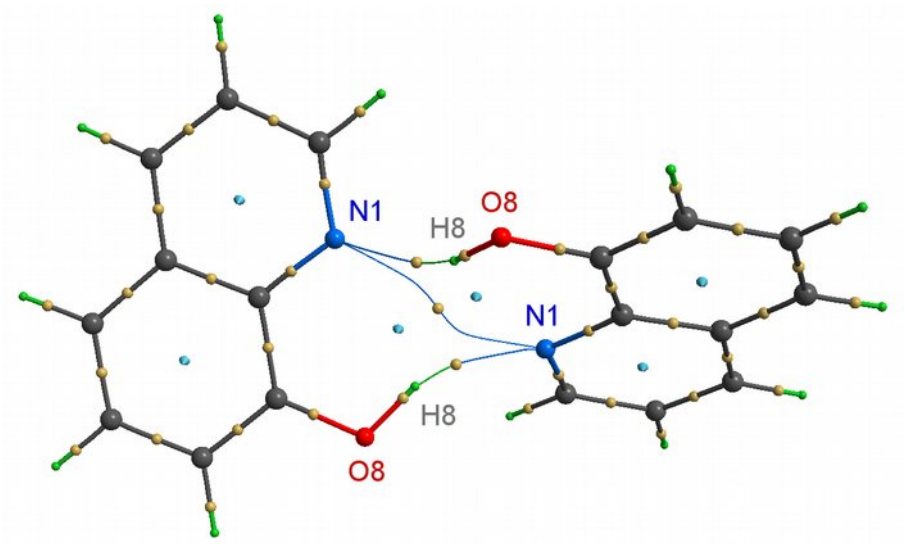
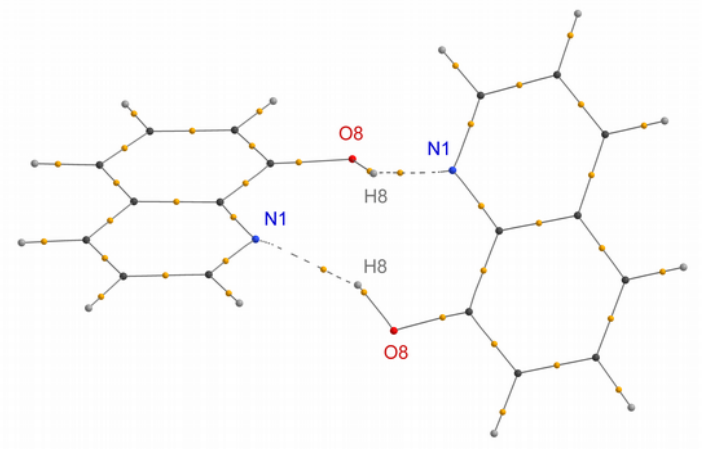
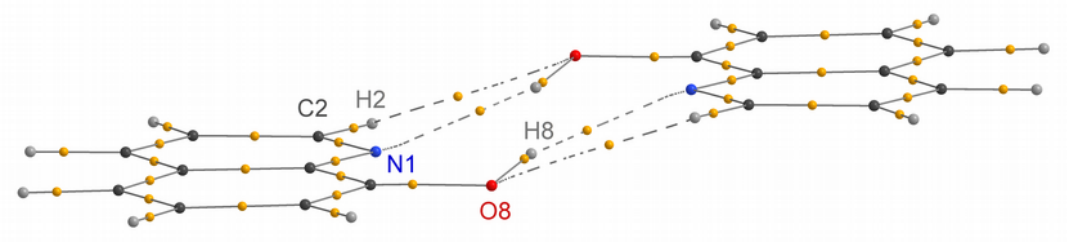
5. 

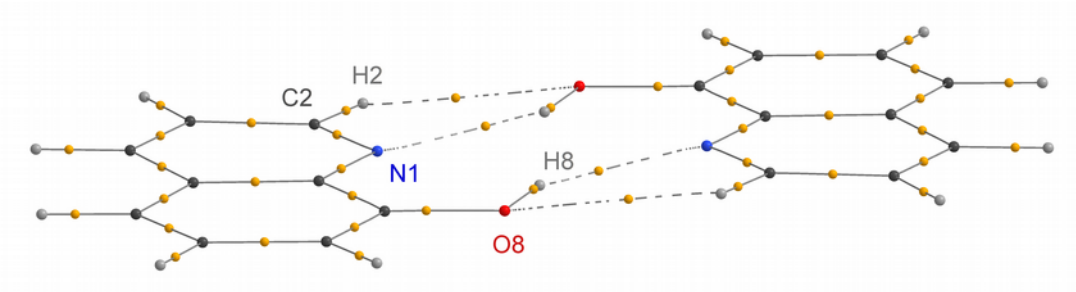
Fig. S5. The topological graph of the dimer in **orthorhombic** polymorph of **8HQ** from analysis of $\rho(\mathbf{r})$ obtained by multipole refinement against experimental data. Bond critical points are shown as small orange spheres, and (3,+1) are shown as small turquoise cones.



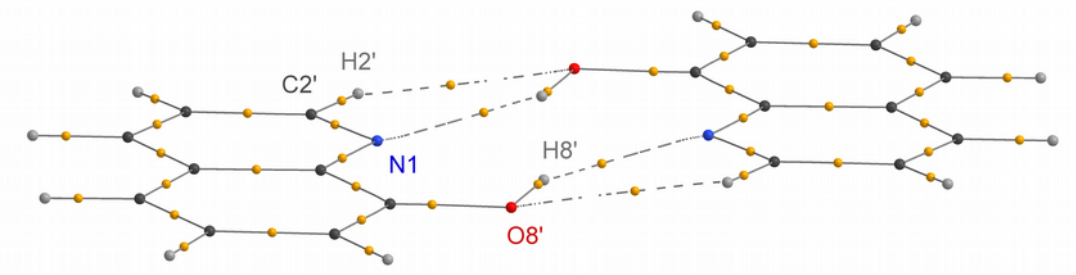
a: orthorhombic polymorph



b: monoclinic polymorph



c: triclinic polymorph, the first independent molecule



d: triclinic polymorph, the second independent molecule

Fig. S6. Topological graphs of the dimers in polymorphic modifications of **8HQ**, based on wavefunctions of B3LYP-D2/POB-TZVP optimized crystal structures. Bond critical points are shown as small orange spheres. The search for (3,+1) and (3,+3) critical points was not performed, since it is relatively time-consuming for a periodic structure.

The images were drawn with the AIMStudio program from the AIMAll software package [T. A. Keith, *AIMAll (Version 17.01.25)*, TK Gristmill Software, Overland Park KS, USA, 2017]. The output of TOPOND14 was converted to the *.sumviz format with an in-house program *topond2sumviz*.

Table TS3. Independent bonding intermolecular interactions in **orthorhombic** polymorph of **8HQ**, results of multipole refinement of the experimental data. The hydrogen bond is highlighted with the bold blue font.

Contact	$\rho(\mathbf{r})$, e Å^{-3}	$\nabla^2\rho(\mathbf{r})$, e Å^{-5}	ε	$v(\mathbf{r})$, a.u.	E_{EML}, kcal/mol
O1···H2	0.022	0.43	1.97	-0.00190	-0.6
O1···H4	0.017	0.30	1.14	-0.00130	-0.4
N1···H1	**0.188**	**1.00**	**0.22**	**-0.01814**	**-5.7**
C2···H5	0.036	0.32	0.29	-0.00204	-0.6
C3···H7	0.022	0.37	1.24	-0.00171	-0.5
C6···H6	0.033	0.34	0.28	-0.00197	-0.6
H2···H4	0.025	0.23	0.18	-0.00131	-0.4
H2···H5	0.017	0.30	1.14	-0.00130	-0.4
H3···H5	0.022	0.43	1.97	-0.00190	-0.6
H3···H6	0.026	0.37	0.88	-0.00180	-0.6
H3···H7	0.018	0.22	0.39	-0.00107	-0.3
N1···C2	0.032	0.37	1.86	-0.00203	-0.6
C4···C4A	0.036	0.40	0.89	-0.00232	-0.7
C5···C6	0.035	0.39	0.78	-0.00226	-0.7
C8···C8A	0.038	0.41	0.62	-0.00241	-0.8
N1···N1	0.062	0.33	0.96	-0.00348	-1.1

Table TS4. Independent bonding intermolecular interactions in **orthorhombic** polymorph of **8HQ**, results of B3LYP-D2/POB-TZVP periodic calculation. The hydrogen bond is highlighted with the bold blue font.

Contact	$\rho(\mathbf{r})$, e Å^{-3}	$\nabla^2\rho(\mathbf{r})$, e Å^{-5}	ε	$v(\mathbf{r})$, a.u.	E_{EML}, kcal/mol
H2···O1	0.039	0.47	0.24	-0.00318	1.0
H4···O1	0.065	0.75	0.07	-0.00514	1.6
H1···N1	**0.264**	**2.18**	**0.03**	**-0.03137**	**9.8**
H5···C2	0.022	0.25	0.66	-0.00148	0.5
H7···C3	0.032	0.44	1.99	-0.00251	0.8
H2···H5	0.030	0.36	0.26	-0.00229	0.7
H3···H6	0.016	0.20	1.84	-0.00120	0.4
H3···H7	0.038	0.36	0.06	-0.00270	0.8
H2···H4	0.027	0.30	0.12	-0.00200	0.6
H5···H3	0.028	0.34	0.21	-0.00223	0.7
H6···H6	0.058	0.61	0.61	-0.00440	1.4
O1···O1	0.013	0.18	1.11	-0.00105	0.3
C2···N1	0.029	0.43	0.42	-0.00199	0.6
C4···C4A	0.032	0.47	1.64	-0.00209	0.7
C5···C6	0.036	0.50	0.78	-0.00251	0.8
C8···C8A	0.031	0.48	1.75	-0.00203	0.6

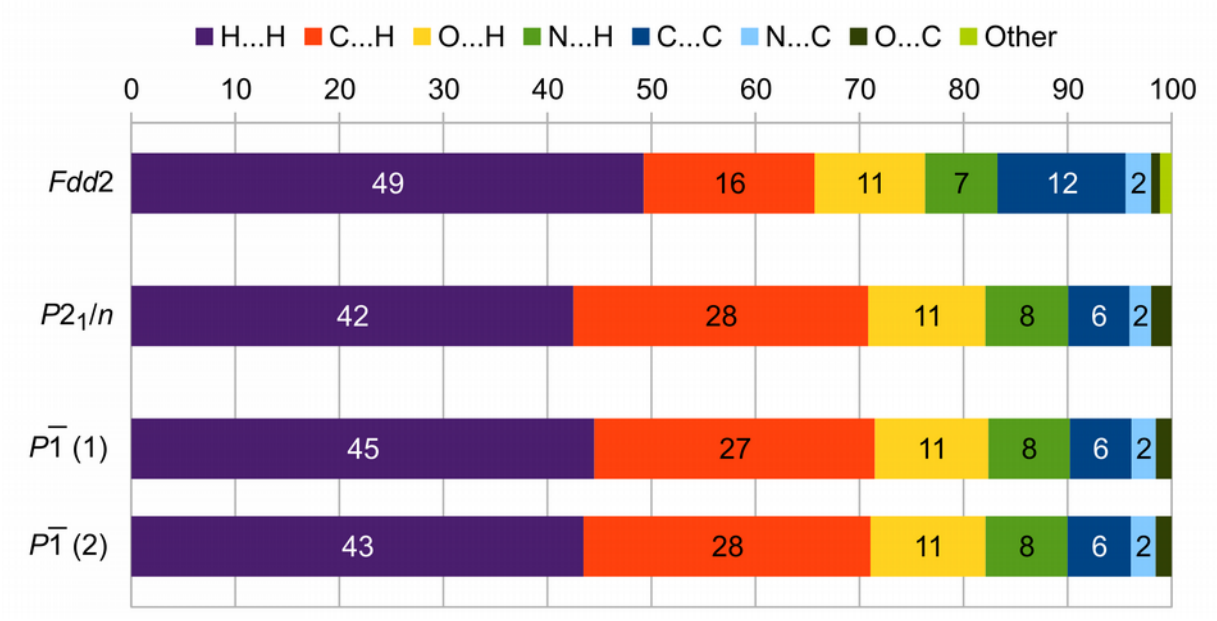
Table TS5. Independent bonding intermolecular interactions in **monoclinic** polymorph of **8HQ**, results of B3LYP-D2/POB-TZVP periodic calculation. The hydrogen bond is highlighted with the bold blue font.

Contact	$\rho(\mathbf{r})$, e Å^{-3}	$\nabla^2\rho(\mathbf{r})$, e Å^{-5}	ε	$v(\mathbf{r})$, a.u.	E_{EML}, kcal/mol
H2···O1	0.063	1.00	1.91	-0.00639	2.0
H6···O1	0.029	0.34	0.39	-0.00224	0.7
H1···N1	**0.181**	**1.90**	**0.02**	**-0.01918**	**6.0**
H5···N1	0.031	0.37	0.32	-0.00218	0.7
H3···C8	0.040	0.48	0.27	-0.00315	1.0
H7···C2	0.020	0.24	0.35	-0.00127	0.4
H2···C4A	0.047	0.53	1.93	-0.00344	1.1
H6···C3	0.031	0.34	0.21	-0.00213	0.7
H5···C3	0.028	0.38	0.79	-0.00220	0.7
H4···C6	0.019	0.28	1.59	-0.00140	0.4
H4···H2	0.009	0.13	0.22	-0.00062	0.2
H3···H6	0.018	0.25	0.20	-0.00146	0.5
H4···H7	0.031	0.34	0.08	-0.00231	0.7
H5···H7	0.036	0.36	0.02	-0.00257	0.8
C7···C3	0.031	0.49	3.68	-0.00234	0.7
C8···C4A	0.050	0.64	0.06	-0.00388	1.2
O1···C4	0.031	0.40	0.62	-0.00250	0.8
O1···C5	0.022	0.32	2.11	-0.00173	0.5
N1···C6	0.047	0.63	0.86	-0.00378	1.2

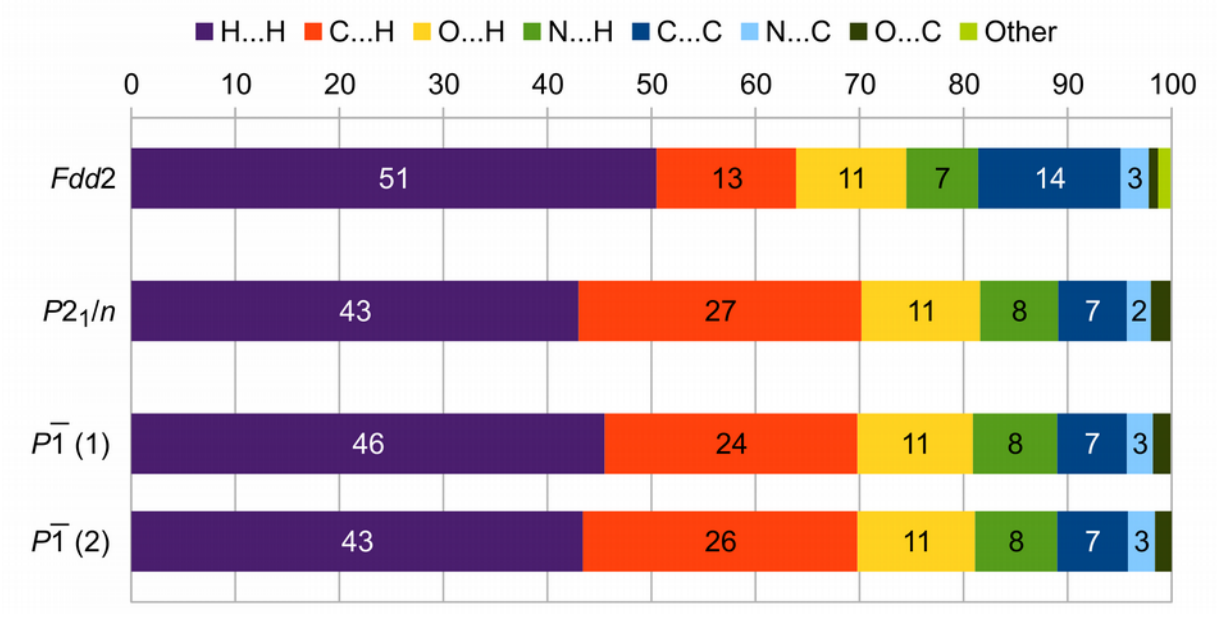
Table TS6. Independent bonding intermolecular interactions in **triclinic** polymorph of **8HQ**, results of B3LYP-D2/POB-TZVP periodic calculation. Labels with a prime (') belong to the second independent molecule. The hydrogen bonds are highlighted with the bold blue font.

Contact	$\rho(\mathbf{r})$, e Å^{-3}	$\nabla^2\rho(\mathbf{r})$, e Å^{-5}	ε	$v(\mathbf{r})$, a.u.	E_{EML}, kcal/mol
H2···O1	0.059	0.91	0.74	-0.00580	1.8
H7···O1	0.057	0.66	0.07	-0.00450	1.4
H2'···O1'	0.063	0.96	0.64	-0.00617	1.9
H7'···O1'	0.048	0.54	0.08	-0.00370	1.2
H3'···O1'	0.028	0.38	10.19	-0.00244	0.8
H1···N1	**0.155**	**1.71**	**0.00**	**-0.01540**	**4.8**
H1'···N1'	**0.157**	**1.73**	**0.01**	**-0.01570**	**4.9**
H4'···C4	0.047	0.48	1.29	-0.00317	1.0
H3···C6'	0.038	0.46	0.65	-0.00299	0.9
H4···C3'	0.042	0.41	0.29	-0.00282	0.9
H5'···C5	0.057	0.59	1.28	-0.00409	1.3
H5···C4A'	0.048	0.50	0.53	-0.00337	1.1
H6···H2	0.041	0.45	0.22	-0.00310	1.0
H2···H2	0.018	0.19	0.08	-0.00126	0.4
H7···H3	0.056	0.70	1.18	-0.00474	1.5
H7···H7	0.046	0.56	0.32	-0.00366	1.1
H3'···H6	0.006	0.08	0.01	-0.00037	0.1
H2'···H2'	0.028	0.29	0.11	-0.00202	0.6
H6'···H2'	0.029	0.35	0.35	-0.00220	0.7
H3'···H7'	0.054	0.68	1.05	-0.00453	1.4
H7'···H7'	0.028	0.35	0.88	-0.00218	0.7
O1···C4	0.036	0.48	0.10	-0.00293	0.9
O1'···C4'	0.040	0.53	0.22	-0.00328	1.0
N1···C5	0.031	0.45	3.87	-0.00224	0.7
C7···C7	0.044	0.55	0.82	-0.00308	1.0
C8A···C8A	0.042	0.54	0.65	-0.00283	0.9
C2'···C7'	0.048	0.58	0.80	-0.00342	1.1
C8A'···C8A'	0.041	0.54	0.57	-0.00275	0.9

6. Intermolecular interactions from analysis of Voronoi-Dirichlet molecular polyhedra



a



b

Fig. S7. Relative contributions (%) of different types of intermolecular interactions in polymorphic modifications of **8HQ**. For the triclinic polymorph values are calculated separately for two independent molecules.

The values on the top chart (**a**) was calculated using molecular Voronoi−Dirichlet polyhedra using the methodology described in [V. N. Serezhkin and A. V. Savchenkov, *Cryst. Growth Des.*, 2015, **15**, 2878–2882, doi: 10.1021/acs.cgd.5b00326].

The lower chart (**b**) is a relative contributions for the various types of intermolecular contacts to the Hirshfeld surface area. It is a copy of the Fig. 3c from the main paper provided here for comparison.

7. Normal vibrational modes of the **8HQ** dimer in C_{2h} geometry

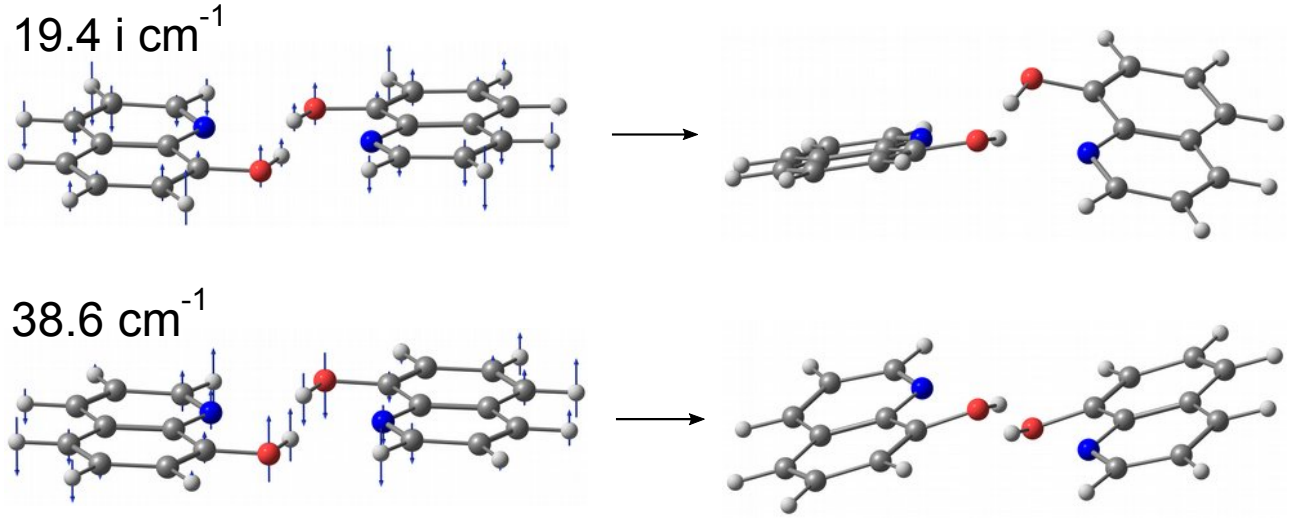


Fig. S8. Displacement vectors for selected vibrational modes of the **8HQ** dimer in C_{2h} conformation and geometries obtained by atomic displacements along these vectors.