H/F Replacement in secondary alcohols of sydnones as examples of isostructural OH···O=C hydrogen bonded dimer structures

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-=SUPPLEMENTARY MATERIAL=-

1. Relevant secondary alcohol dimers from the literature

Table 1S. Secondary alcohols identified through CCDC search and dimeric –like structures identified

Index	CCD Ref.	DIMER	Fragment	ANG1 O-H···O >150◦	ANG2 O-H···O >150◦	DIST1 H···O <vdW	DIST2 H···O <vdW
1	ADOHUY	YES	1	175.498	173.071	1.937	1.933
	ADUNAP	NO	1	173.506	168.773	1.923	1.917
2	ADUNAP	NO	2	173.506	151.576	1.923	2.031
	ADUNAP	NO	3	151.576	168.773	2.031	1.917
3	AKUFIX	NO	1	160.313	178.159	1.993	1.951
4	ARAFPY10	NO	1	158.146	154.245	1.947	1.991
5	AZELAV	NO	1	177.711	154.421	1.969	1.934
6	BARJOX	NO	1	163.534	154.156	2.006	2.024
7	BUQDIC	NO	1	160.662	160.103	2.009	2.09
8	BUVFAA	NO	1	169.063	158.963	2.033	1.913
9	CAQRUH	NO	1	164.587	173.054	2.012	1.948
10	CEHDAX	NO	1	152.591	172.274	2.036	2.008
11	COBQEP	NO	1	158.045	167.558	2.036	1.982
	COKKIY		1	170.713	159.461	2.088	2.02
12	COKKIY		2	170.62	159.461	2.051	2.02
	COKKIY	YES	3	170.62	170.713	2.051	2.088
13	CUQJII	NO	1	173.469	169.002	1.948	1.987
	DUNFEY	NO	1	171.677	155.669	1.922	2.095
	DUNFEY	NO	2	154.725	171.677	2.04	1.922
14	DUNFEY	NO	3	154.725	155.669	2.04	2.095
	EBOPOE	NO	1	153.469	156.929	1.972	1.931
	EBOPOE	NO	2	155.407	153.469	2.241	1.972
	EBOPOE	NO	3	155.407	156.929	2.241	1.931
15	EDEMOR	YES	1	153.18	162.555	2.028	1.975
16	EGALAB	YES	1	172.271	178.141	1.942	1.923
17	ELEJUB01	YES	1	164.113	174.283	1.897	1.864
18	ELEKAI01	YES	1	179.295	177.757	1.83	1.83
19	EZEPEF	YES	1	152.996	150.364	2.105	2.179
	FELNIU	NO	1	168.236	168.524	1.927	1.89
20	FELNIU	NO	2	168.236	164.13	1.927	1.99
	FELNIU	NO	3	164.13	168.524	1.99	1.89
21	FIBMIQ	NO	1	174.141	176.153	1.977	1.936
22	FIDSES	NO	1	154.691	177.031	1.999	2.104
23	FIQDOZ	YES	1	150.797	150.797	2.244	2.244
24	FLOCOS	NO	1	154.383	154.383	2.21	2.21
25	FUHYAL	YES	1	168.845	178.438	2.022	1.992
26	GEGRAP	NO	1	166.971	158.007	2.001	2.108
27	GEJPUH	NO	1	166.812	161.227	2.049	2.049
28	GOGQEZ	NO	1	164.571	163.096	2	2.064
29	HBMHPO10	YES	1	153.947	156.697	2.316	2.182
30	HIJBEK	NO	1	170.71	174.596	1.973	1.969
31	HIKWEG	YES	1	166.685	160.122	1.916	1.982
	HIWREM	NO	1	169.477	169.258	1.947	1.929
	HIWREM	NO	2	169.477	167.815	1.947	1.963
	HIWREM	NO	3	169.258	167.815	1.929	1.963

	HIWREM	NO	4	163.33	169.258	2.004	1.929
32	HIWREM	NO	5	163.33	167.815	2.004	1.963
	HIWREM	NO	6	163.33	169.477	2.004	1.947
	IBAQEL	NO	1	151.872	156.975	2.32	2.3
	IBAQEL	NO	2	151.872	155.538	2.32	2.269
	IBAQEL	NO	3	155.538	156.975	2.269	2.3
33	ILAROF	NO	1	162.603	158.672	1.973	1.977
34	IQONIO	NO	1	160.758	168.136	2.029	1.839
35	IRAGEP	NO	1	170.403	168.492	1.939	1.995
36	ISAFEQ	**YES**	1	171.085	161.617	1.953	2.08
37	JEVPAF	NO	1	169.297	170.141	1.952	1.946
38	JONZUJ	NO	1	154.333	154.582	2.121	2.157
39	JUXKAR	NO	1	150.414	162.309	2.288	2.027
40	KEBTUK	NO	1	173.742	166.247	1.969	2.253
41	KEXSIS	**YES**	1	178.354	170.954	2.035	2.23
42	KIHNOF	**YES**	1	176.458	164.305	1.871	1.927
	KIWPAL	**YES**	1	159.895	158.1	1.993	2.012
	KIWPAL		2	152.897	159.895	2.022	1.993
43	KIWPAL		3	152.897	158.1	2.022	2.012
	KIWPAL		4	152.897	150.345	2.022	2.07
	KIWPAL		5	150.345	159.895	2.07	1.993
	KIWPAL		6	150.345	158.1	2.07	2.012
44	KUPYOM	**YES**	1	172.655	170.026	2.069	2.048
	LAGQES	NO	1	170.92	160.577	1.869	1.858
	LAGQES	NO	2	170.92	174.909	1.869	1.859
	LAGQES	NO	3	170.92	174.707	1.869	1.969
	LAGQES	NO	4	174.909	160.577	1.859	1.858
45	LAGQES	NO	5	174.707	160.577	1.969	1.858
	LAGQES	NO	6	174.707	174.909	1.969	1.859
	LAPDEO	NO	1	173.678	169.447	1.906	1.911
	LAPDEO	NO	2	173.678	170.579	1.906	1.946
	LAPDEO	NO	3	169.447	170.579	1.911	1.946
46	LEDGEK	NO	1	172.205	155.546	1.957	2.107
47	LETNOR	NO	1	172.561	172.246	2.167	2.168
48	LIGVUT	NO	1	156.498	159.741	2.04	2.012
49	LISSUE	**YES**	1	168.183	167.225	2.033	2.056
	LONVUI	NO	1	163.136	164.581	2.012	2.009
	LONVUI	NO	2	171.122	164.581	1.943	2.009
	LONVUI	NO	3	160.109	164.581	2.077	2.009
50	LONVUI	NO	4	171.122	163.136	1.943	2.012
	LONVUI	NO	5	160.109	163.136	2.077	2.012
	LONVUI	NO	6	171.122	160.109	1.943	2.077
51	LUQHUD	NO	1	153.35	163.566	1.996	1.901
52	LUYHAR	NO	1	175.718	171.487	1.881	2.018
53	LUZJUL	**YES**	1	151.001	151.001	2.193	2.193
54	MEHNPQ	NO	1	173.418	173.488	1.965	1.956
55	MEQCEU	NO	1	163.359	164.122	1.95	2.19
56	MIDMUK	NO	1	172.647	168.294	2.188	2.097
57	MOJPUW	**YES**	1	153.171	157.485	2.116	2.211
58	MOYPUO	NO	1	158.19	168.659	1.963	2.017
59	NANFOB	NO	1	158.33	174.119	2.081	1.989
60	NOQKIO	NO	1	179.118	168.245	1.877	1.857

61	OGIXIO	NO	1	167.028	159.771	1.967	1.987
62	OHUKIO	NO	1	174.923	174.773	1.975	1.934
63	OMAFEP	**YES**	1	172.359	172.085	1.989	1.964
64	PAVQEI	NO	1	176.158	178.751	1.846	1.913
65	PESPOT	NO	1	168.206	175.445	2.148	2.088
	QETZUL	NO	1	152.467	156.298	1.943	2.002
	QETZUL	NO	2	152.467	164.434	1.943	1.975
66	QETZUL	NO	3	152.467	164.576	1.943	1.989
	QETZUL	NO	4	156.298	164.434	2.002	1.975
	QETZUL	NO	5	164.576	156.298	1.989	2.002
	QETZUL	NO	6	164.576	164.434	1.989	1.975
67	QOMBUS	NO	1	156.679	161.65	2.097	1.874
68	QULBII	NO	1	165.907	168.249	2.042	2.005
69	QUWZEQ	NO	1	150.846	159.578	2.194	2.154
70	RAGDEM	NO	1	172.31	165.237	2.086	2.031
71	REPDEX	**YES**	1	169.627	169.627	1.889	1.889
72	REXHEI	NO	1	172.477	169.539	2.002	2.071
73	RUVSOS	NO	1	175.306	175.847	1.898	2.108
74	RUVSOS01	NO	1	167.71	176.547	2.101	1.885
75	RUVVEL	NO	1	179.731	173.373	2.131	1.975
76	SAKJOG	NO	1	166.899	171.21	1.924	1.869
77	SAKKAT	NO	1	163.959	172.888	1.916	1.927
78	SAZRUK	NO	1	173.774	177.79	1.954	1.953
79	SEHLEA	NO	1	167.812	164.378	2.021	2.078
80	SELTEM	**YES**	1	173.587	175.25	1.97	1.862
81	SEWFAD	NO	1	162.661	162.661	2.038	2.038
82	SIMDUR	NO	1	162.888	159.881	2.208	2.395
83	SIMKAE	NO	1	159.653	166.154	1.996	2.019
84	SUQBIR	NO	1	172.554	178.027	1.959	2.066
85	SUQBUD	NO	1	174.527	176.254	1.974	2.252
86	TANFUJ	**YES**	1	152.333	150.407	2.031	2.153
87	TESTON10	NO	1	167.368	163.324	1.993	1.805
	TUDSOD	NO	1	156.036	160.699	2.037	2.015
	TUDSOD	NO	2	159.683	160.699	2.059	2.015
	TUDSOD	NO	3	159.683	156.036	2.059	2.037
	UMAHAT	NO	1	158.59	157.93	1.954	1.959
	UMAHAT	NO	2	158.59	151.965	1.954	1.964
	UMAHAT	NO	3	151.965	157.93	1.964	1.959
88	UMAHAT	NO	4	155.613	158.59	1.974	1.954
	UMAHAT	NO	5	155.613	157.93	1.974	1.959
	UMAHAT	NO	6	155.613	151.965	1.974	1.964
	UMAHAT	NO	7	152.498	158.59	1.975	1.954
	UMAHAT	NO	8	152.498	157.93	1.975	1.959
	UMAHAT	NO	9	152.498	151.965	1.975	1.964
	UMAHAT	NO	10	152.498	155.613	1.975	1.974
89	UTILUG	NO	1	156.55	169.581	2.108	1.869
90	UVEMOA	NO	1	167.727	167.064	2.067	2.037
91	UYOQAB	NO	1	151.568	158.035	2.038	2.042
	UZIPIF	NO	1	155.614	160.608	2.084	2.002
92	UZIPIF	NO	2	155.614	150.688	2.084	2.166
	UZIPIF	NO	3	150.688	160.608	2.166	2.002
93	VAHCOZ	NO	1	167.597	164.638	1.972	1.986

94	VAWMUF	**YES**	1	158.743	159.337	2.049	2.109
95	VEMNUA	NO	1	174.254	159.785	1.985	1.974
96	VIQQUK	NO	1	164.847	173.271	2.016	2.037
97	VUYYUJ	**YES**	1	165.327	166.589	1.908	1.902
98	WAKWIQ	NO	1	175.416	172.22	1.94	1.955
99	WAQYUI	NO	1	156.392	164.152	1.957	1.933
100	WEGLON	NO	1	166.39	167.065	1.942	1.942
101	WIMLEL	NO	1	171.104	163.447	2.022	2.043
102	WIPVOG	**YES**	1	166.45	173.316	2.142	1.99
103	XIDZES	NO	1	175.446	172.468	2.02	1.983
104	XIFSIP	NO	1	155.345	159.686	1.975	2.029
105	XODQAL	NO	1	151.498	154.53	2.112	2.067
106	YOFWEW	NO	1	155.35	172.702	1.808	1.646
107	YOWPAE	NO	1	179.44	177.965	1.955	2.148
108	ZEPZEB	NO	1	164.303	157.868	1.845	1.969
109	ZIBTEN	NO	1	150.853	157.537	2.058	2.013
110	ZIBTUB	NO	1	171.072	168.115	2.06	2.014
111	ZICZEQ	NO	1	168.909	164.796	1.705	1.831
112	ZOYMOP03	NO	1	170.911	170.671	2.068	1.912
	ZUDKAM	NO	1	158.352	157.084	2.044	2.047
	ZUDKAM		2	158.352	157.802	2.044	2.052
113	ZUDKAM		3	157.433	158.352	2.045	2.044
	ZUDKAM		4	157.433	157.084	2.045	2.047
	ZUDKAM		5	157.433	157.802	2.045	2.052
	ZUDKAM		6	157.084	157.802	2.047	2.052
114	ZUKRUS	NO	1	165.281	168.839	1.94	1.817
115	JOCVAC	**YES**	1	154.769	163.307	2.053	1.936
116	KUHRIR	NO					
117	TIMFAA	NO					
118	UFABUC	NO					
119	UHUDAD	NO					
120	UZIPEB	NO					
121	XEJAO	NO					
122	XEZJES	NO					
123	YIQMUJ	**YES**					
124	YOVWOX	NO					

Identified separately from the search

2. IR spectroscopy revealing the O-H···O=C interaction

The ATR-IR spectra for compounds **Alc-1, Alc-2**, **Keto-1** and **Keto-2** show that the CO exocyclic group in the sydnone presents a redshift in the frequency from 1752-1771 cm^{-1} (Figure 1S) in ketones down to 1722 cm^{-1} for **Alc-2** and 1719 cm^{-1} **Alc-1**.

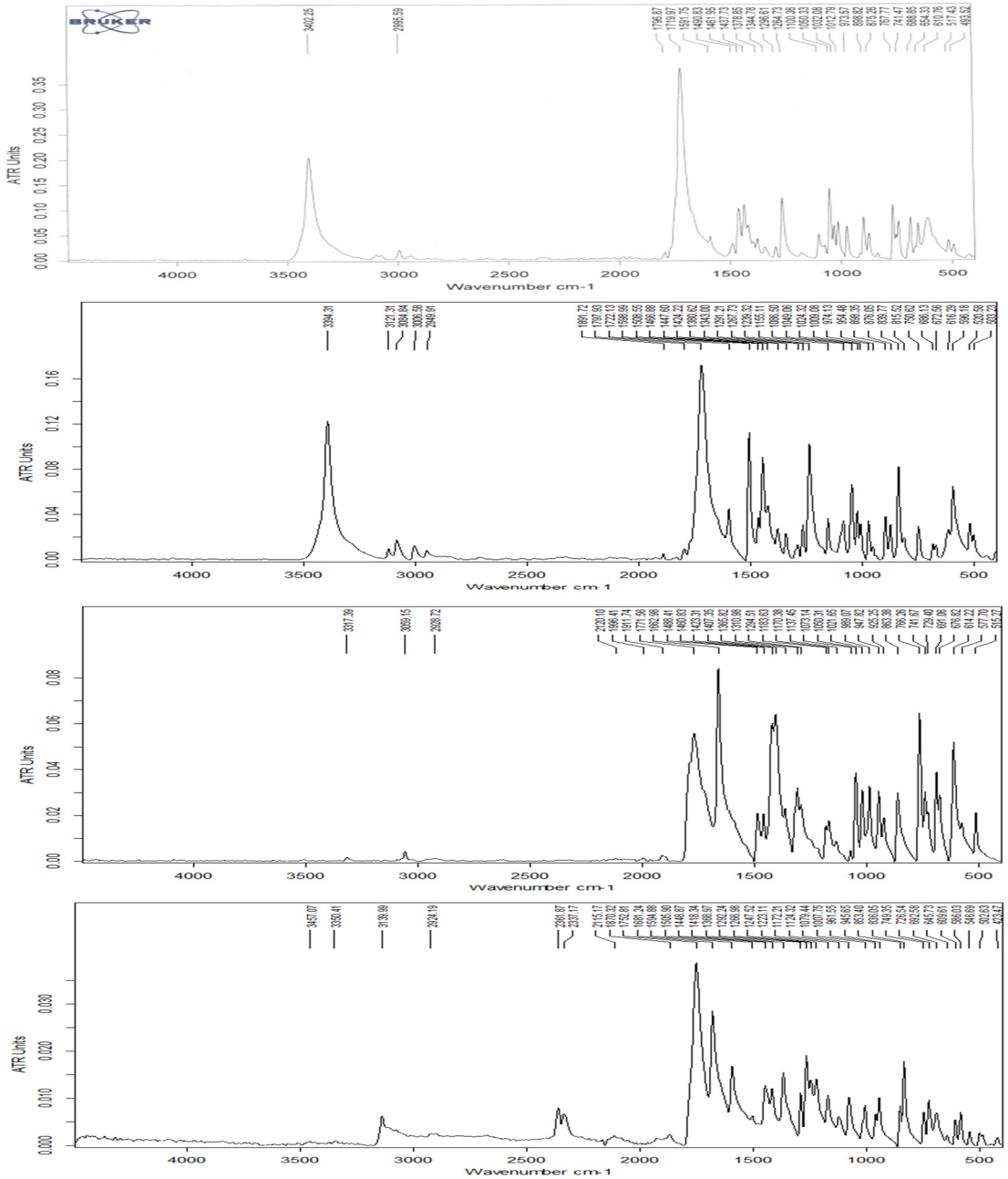
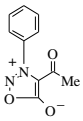
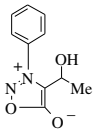
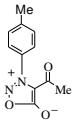
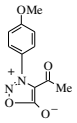
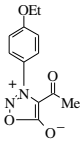
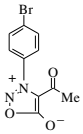
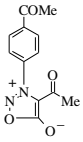
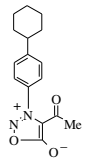
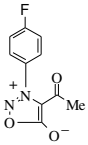


Figure 1S. ATR-IR Spectra of **Alc-1**, **Alc-2**, **Keto-1** and **Keto-2** (from top)

Table 2S also confirms such a trend with literature IR data. However, to gain more insight we performed DFT simulated spectra for **Alc-1** and **Keto-1** as models. For the purpose of the calculation we have employed the monomer of **Keto-1** and for **Alc-1** we have envisaged three scenarios: monomer extracted from the .cif file (optimized or used as is), the O-H···O=C H bonded dimer (optimized or used as is) and the most stable configuration presenting an intramolecular H-bond between the O-H and C=O groups of the sydnone.

Table 2S. Literature data-mining on the IR spectra of certain ketones and analogous alcohols

No.	Ketone	Other	CO	Alcohol	OH	CO
1		3060 1426 1053	1780 1662 1793 1665 1771*		3402*	1719*
2		2933 1509 1316 1050	1783 1686		3436	1770
3		N/A	1780		3418	1725
4		N/A	1780 1658		3412	1734
5		N/A	1792 1660		3442	1725
6		N/A	1790 1655		3406	1731
7		- N/A	1762 1664		3394	1728
8		N/A	1791 1734 1668		3340	1707
9		1752*			3394*	1722*

*Current study ATR-IR-Figure 1S
J. Chin. Chem. Soc. **1995**, 42, 987-989
J. Chin. Chem. Soc. **1992,** 39, 107-110
J. Org. Chem. **1983**, 48, 1382-1384
Bull. Chem. Soc. Jpn. **1972**, 45, 2944-2945
Synth. Commun. **1996**, 26, 2757-2764

Figure 2S presents the stacked simulated spectra. The band at 1791 cm^{-1} for the Keto-1 corresponds to the 1752-1771 cm^{-1} range for ATR IR spectra (**Keto-1** and **Keto-2**). All the alcohol configurations, in either monomer or dimeric forms, present the CO sydnone vibration at a lower frequency confirming that IR vibration is correlated with the H-bond. For the optimized monomer and the intramolecular H-bonded monomer the CO bond vibrates at a higher frequency due to more relaxed configuration obtained by optimization. For the dimer form (either optimized or not) and monomer (non-optimized) the CO band ranges from 1692.5 to 1703.7 cm^{-1}. All three structures adopt the configurations constrained by the crystalline packing. These bands are analogous to the 1722 cm^{-1} bands from the ATR IR spectra. The conclusion is that historically the H-bonds between OH and sydnone CO could be predicted by IR spectroscopy and are confirmed by X-ray diffraction analysis.

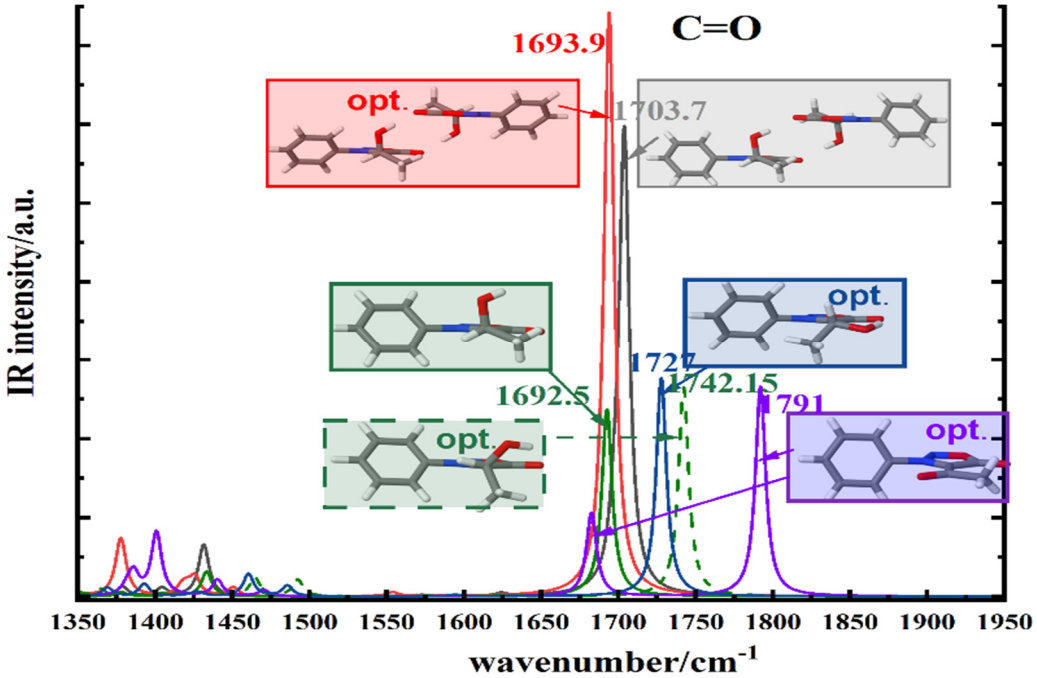


Figure 2S. Calculated IR spectra of **Alc-1 and Keto-1:** Alc1- dimeric form as extracted from the X-Ray spectra (solid red) **, Alc1**-dimeric form as extracted from the X-ray spectra – optimized (solid dark gray), **Alc-1** monomer as extracted from X-ray spectra (solid green), Alc-1-monomer as extracted from X-Ray spectra – optimized (dash green), **Alc1-**monomer – proposed structure to form intramolecular H bond - optimized (solid blue), **Keto-1** monomer as extracted from the X-Ray optimized (solid purple).

For the calculation of the IR spectra, the CAM-B3LYP [1] functional was used. This is one of the functionals that was proved reliable for the simulation of the IR spectra [2,3]**.** A scaling factor of 0.95 was applied to the calculated spectra [4]. Besides the conformations provided by the X-ray spectra, we have investigated a monomer conformation that provides an intramolecular hydrogen bonding.

[1] Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP) *Chem. Phys. Lett.* **2004**, *393*, 51-57. https://doi.org/10.1016/j.cplett.2004.06.011

[2] Srivastava, R.; Al-Omary, F.A.M.; El-Emam, A.A.; Pathak, S.K.; Karabacak, M.; Narayan, V.; Chand, S.; Prasad, O.; Sinha, L. A combined experimental and theoretical DFT (B3LYP, CAM-B3LYP and M06-2X) study on electronic structure, hydrogen bonding, solvent effects and spectral features of methyl 1H-indol-5-carboxylate *J. Mol. Struct.* **2017**, *1137*, 725-741. https://doi.org/10.1016/j.molstruc.2017.02.084

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[4] Jarota, A.; Drwal, D.; Pieta, J.; Pastorczak, E. Wide-range IR spectra of diarylethene derivatives and their simulation using the density functional theory *Sci. Rep.* **2022**, *12*, 16834. https://doi.org/10.1038/s41598-022-20264-x

3. Condensed sydnones with tertiary alcohol structure generating O-H···O=C dimers

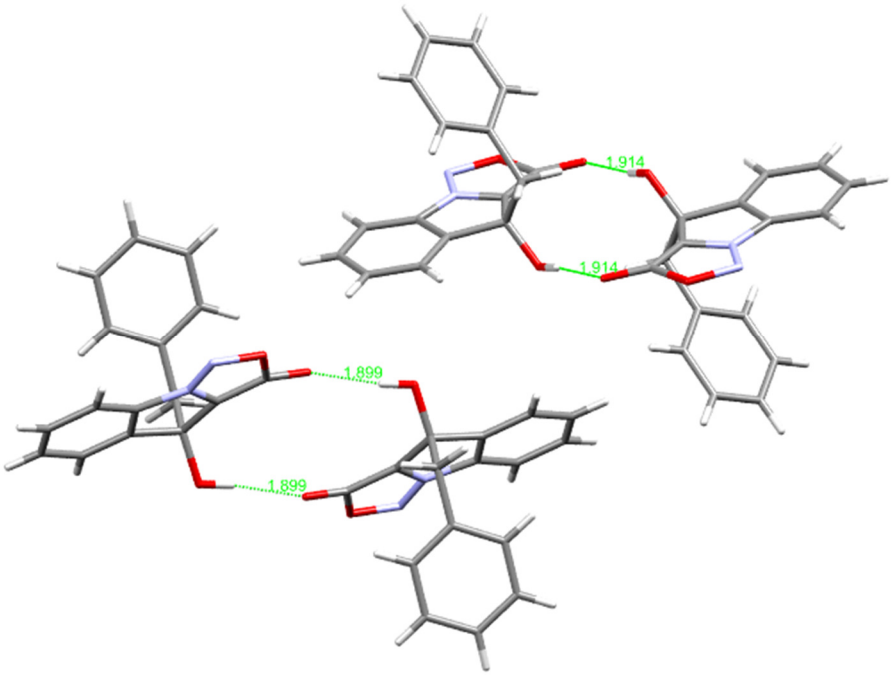

Figure 3S. OH···O=C dimers of ***ABELID*** [5] (two independent molecules)

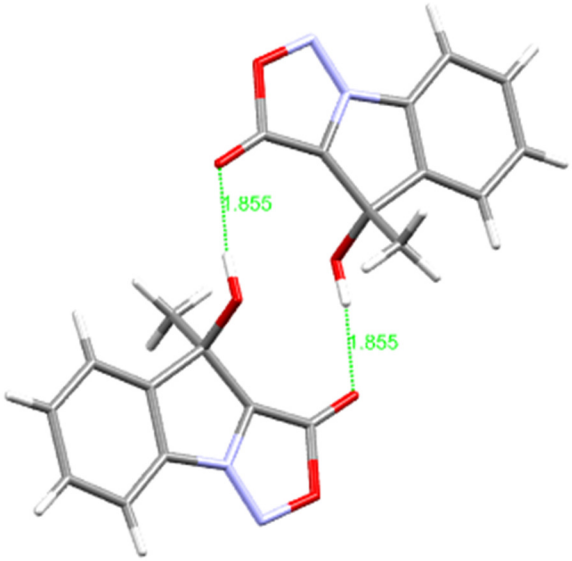

Figure 4S. OH···O=C dimers of ***TAPJUP*** [6]

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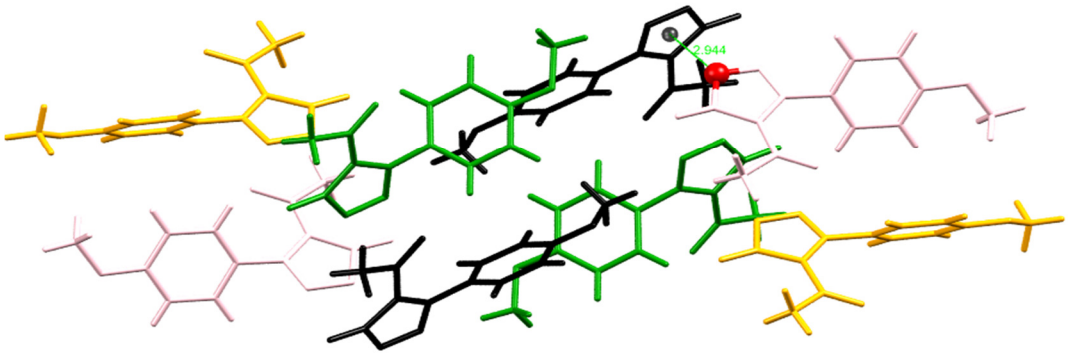
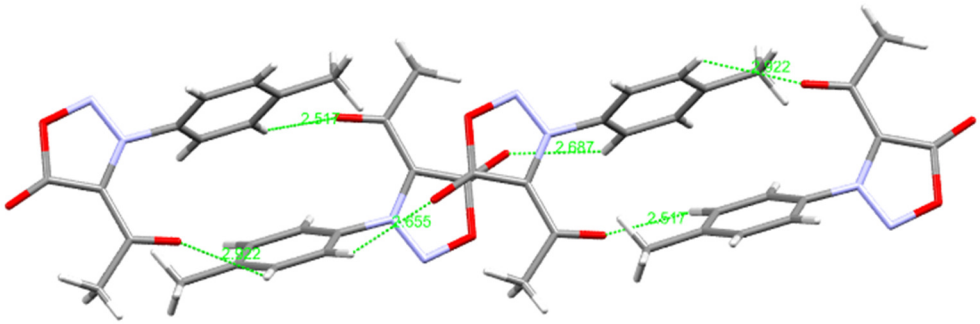
[5] Riddle, G.B.; Grossie, D.A.; Turnbull, K. The sydnone compound 4-hydroxy-4-benzyl-sydno-[3,4-a]-indole *Acta Cryst. E* **2004**, *60*, o1568-o1570. https://doi.org/10.1107/S1600536804020082

[6] Grossie, D.A.; Turnbull, K. 5-Hydroxy-5-methylsydno[3,4-a]indole *Acta Cryst. C* **1992**, *48*, 377-379. https://doi.org/10.1107/S0108270191009125

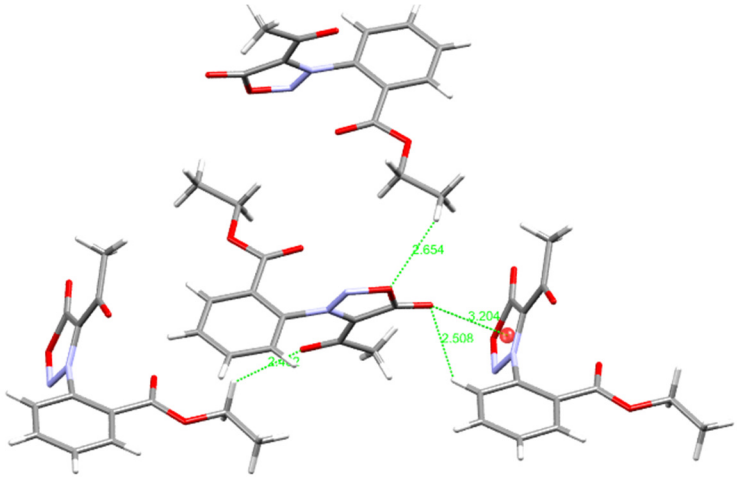
4. Primary interactions in 4-acetylsydnones deposited in the CSD



(a)



(b)



(c)

Figure 5S. Known CCDC 4-acetylsydnones: a. ***ERUCAW***-four independent molecules-highlight O···π contact; b. ***FIXPIL*** – Examples of H-bonds involving the C=O bonds; c. ***MIHTUU*** **–** Contacts involving the O atoms in the sydnone and acetyl moiety.

5. X-Ray-Diffraction supplementary data for Alc-1,2 and Keto-1,2

Table 3S. Bond lengths in crystals of the investigated compounds

Alc-1				**Alc-2**			
Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å
O1-N2	1.378(2)	C1-C6	1.366(3)	F1-C4	1.347(3)	C1-C6	1.370(3)
O1-C8	1.402(3)	C2-C3	1.373(4)	O1-N2	1.377(3)	C2-C3	1.373(4)
O2-C8	1.223(3)	C3-C4	1.359(4)	O1-C8	1.398(3)	C3-C4	1.360(4)
O3-C9	1.419(3)	C4-C5	1.374(3)	O2-C8	1.228(3)	C4-C5	1.363(4)
N1-N2	1.311(3)	C5-C6	1.371(3)	O3-C9	1.424(3)	C5-C6	1.377(4)
N1-C1	1.448(3)	C7-C8	1.396(3)	N1-N2	1.313(3)	C7-C8	1.402(3)
N1-C7	1.346(3)	C7-C9	1.496(3)	N1-C1	1.445(3)	C7-C9	1.502(4)
C1-C2	1.369(3)	C9-C10	1.511(3)	N1-C7	1.341(3)	C9-C10	1.507(4)
				C1-C2	1.366(3)	-	
Keto-1				**Keto-2**			
Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å
O1-N2	1.351(10)	C1-C6	1.367(12)	F1-C4	1.362(2)	C1-C6	1.373(3)
O1-C8	1.432(11)	C2-C3	1.367(13)	O1-N2	1.370(2)	C2-C3	1.381(3)
O2-C8	1.173(10)	C3-C4	1.369(17)	O1-C8	1.419(3)	C3-C4	1.358(3)
O3-C9	1.220(9)	C4-C5	1.377(16)	O2-C8	1.206(2)	C4-C5	1.372(3)
N1-N2	1.307(9)	C5-C6	1.365(14)	O3-C9	1.215(2)	C5-C6	1.383(3)
N1-C1	1.448(10)	C7-C8	1.445(11)	N1-N2	1.307(2)	C7-C8	1.418(3)
N1-C7	1.345(9)	C7-C9	1.458(10)	N1-C1	1.447(2)	C7-C9	1.459(3)
C1-C2	1.379(11)	C9-C10	1.495(12)	N1-C7	1.358(2)	C9-C10	1.500(3)
				C1-C2	1.379(3)	-	

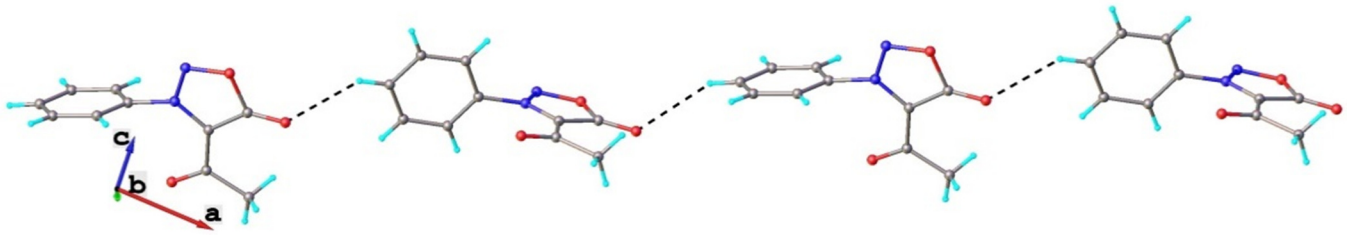


Figure 6S. View of 1D supramolecular chain showing the role of C-H---O hydrogen bonds in the crystal structure of keto-1. H-bond parameters (Å, °): C5-H---O2 [C5-H 0.930, H---O2 2.63, C5---O2(–0.5 + *x*, 1.5 – *y*, *z* – 0.5) 3.43(1), ∠C5HO2 145.2].

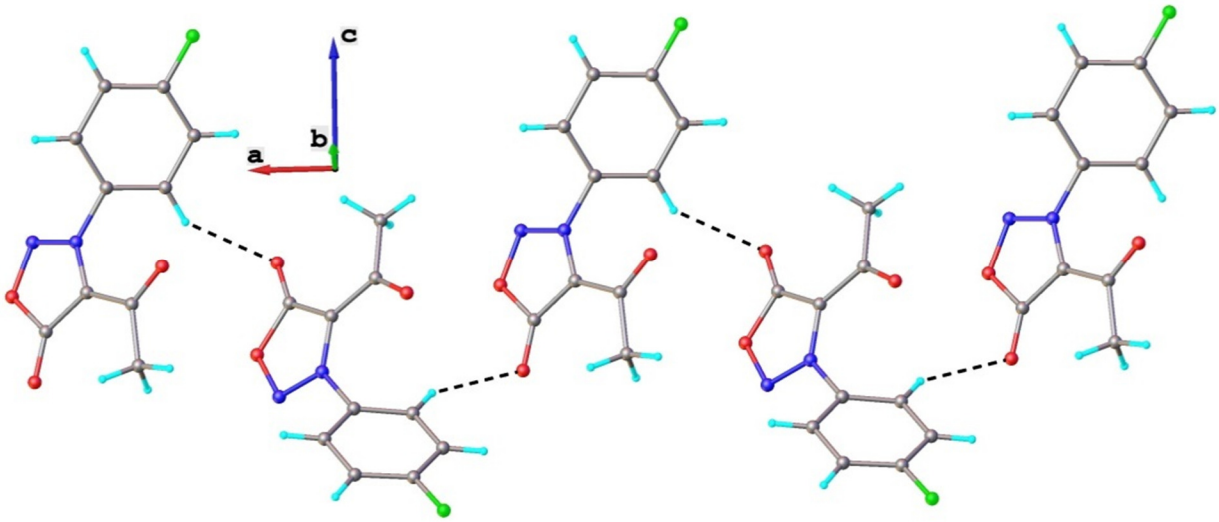


Figure 7S. View of 1D supramolecular chain showing the role of C-H---O hydrogen bonds in the crystal structure of keto-2. H-bond parameters (Å, °): C2-H---O2 [C2-H 0.952, H---O2 2.37, C2---O2(−0.5 + *x*, *y*, 0.5 − *z*) 3.191(2), ∠C2HO2 144.8].

6. Hirshfeld surface analysis of keto-1 and keto-2

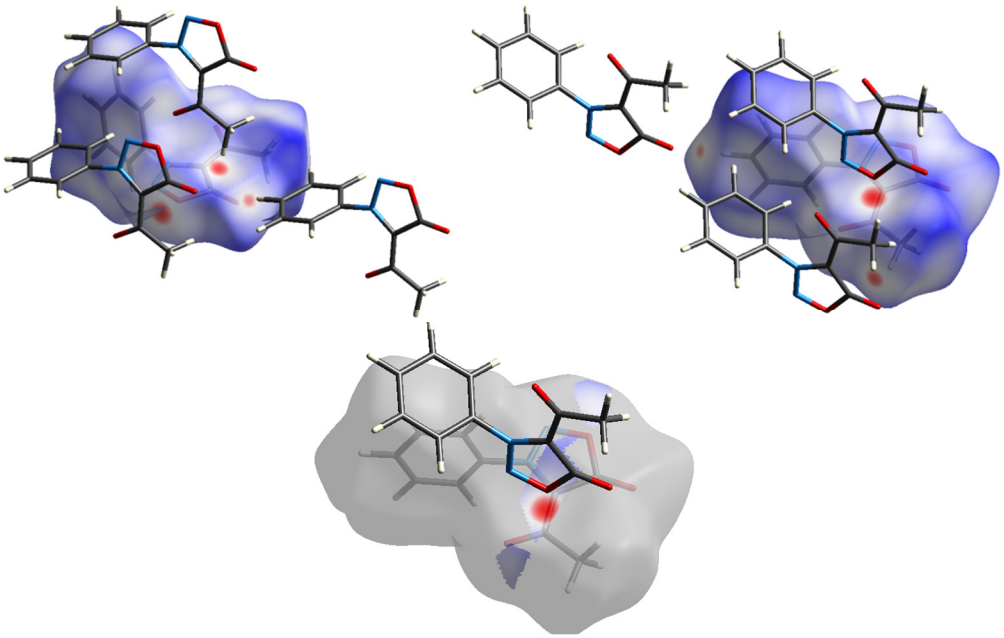


Figure 8S. –O–···C=O, CO···π, CH···π and C=O···H(*para*) contacts in **Keto-1**

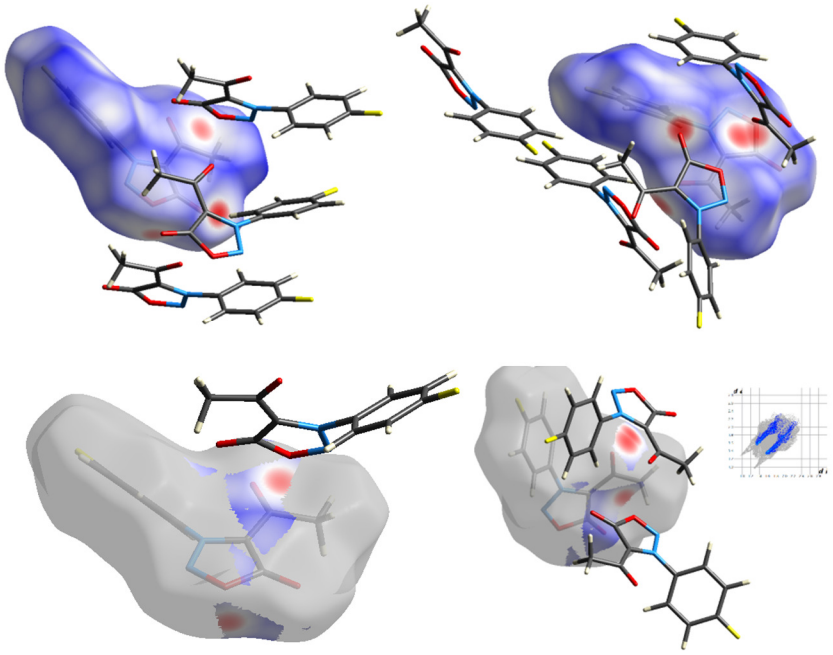


Figure 9S. –O–···C=O, CO···π, and C=O···H(*ortho*) contacts in **Keto-2**

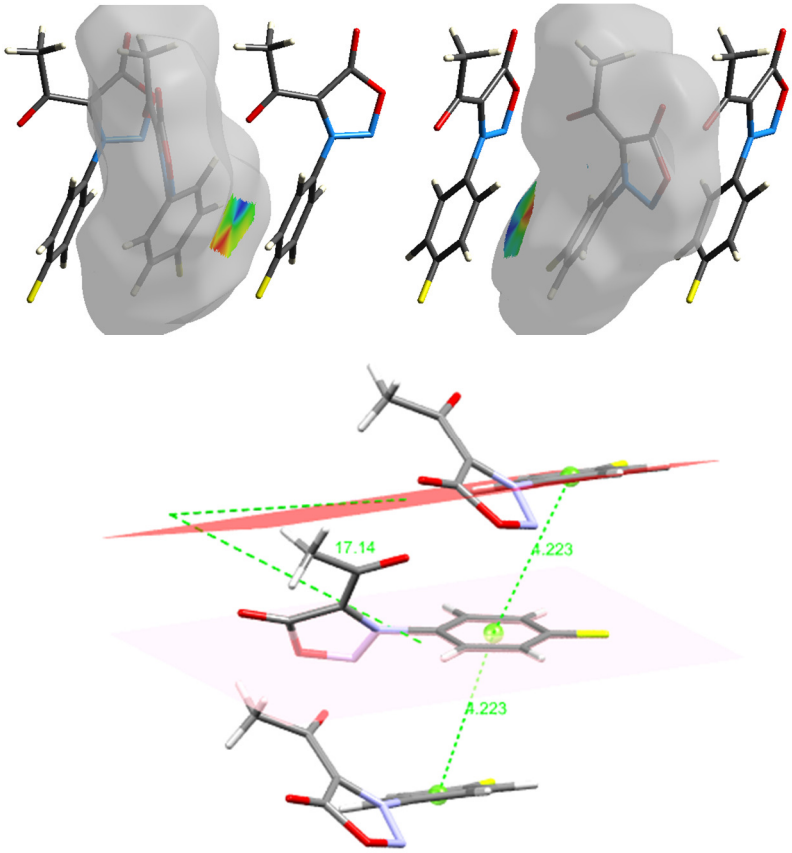


Figure 10S. HF surface Shape index mode presents complementarity surfaces indicating a π···π interaction. However, C_g···C_g distances of 4.22 Å and interplanar angles for benzene ring planes of 17° are not favorable

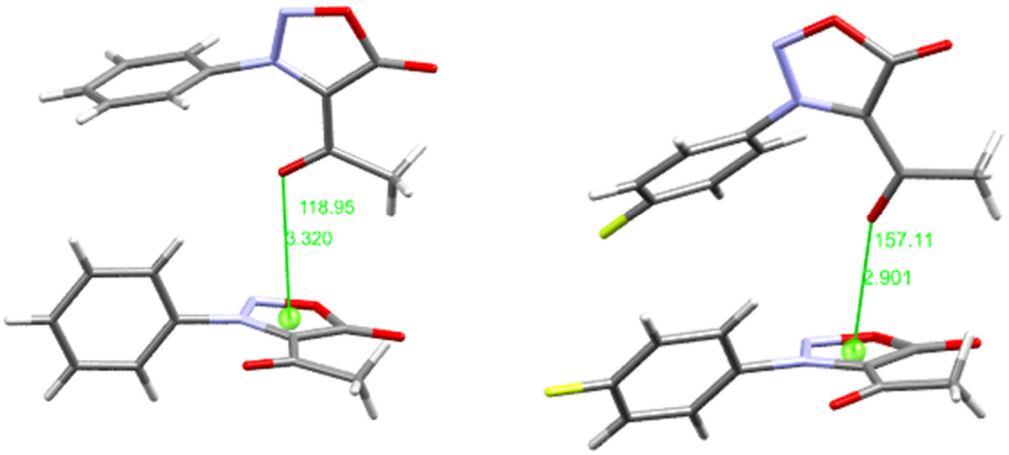
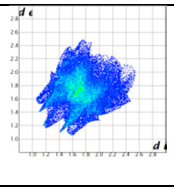
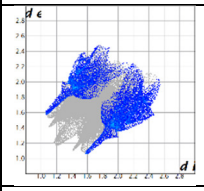
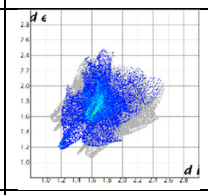
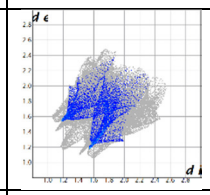
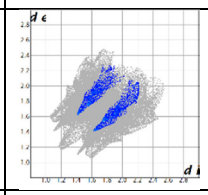
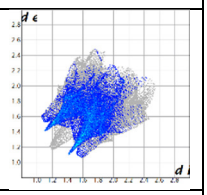
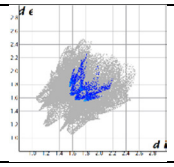
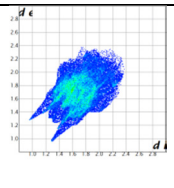
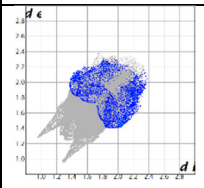
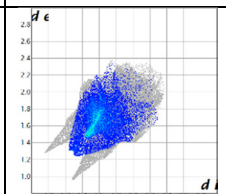
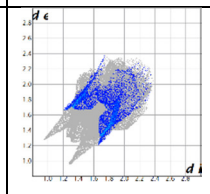
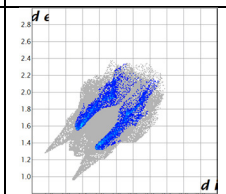
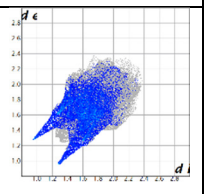
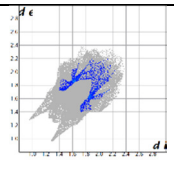
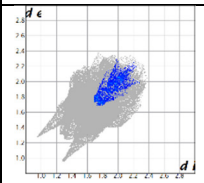
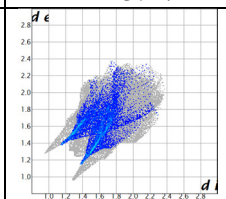
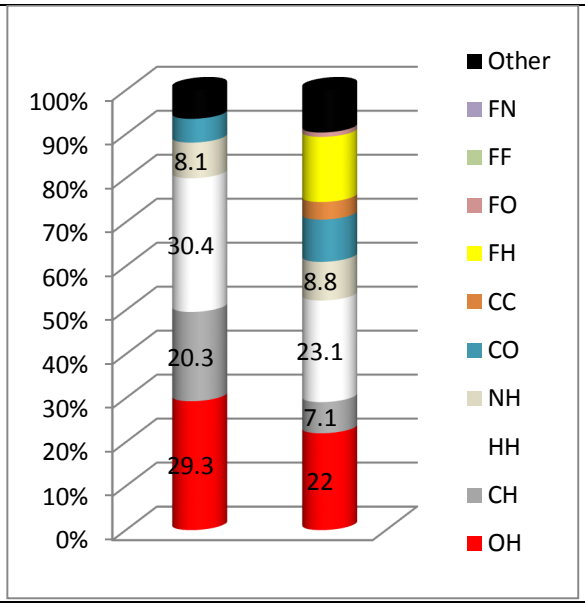


Figure 11S. Measurements of possible C=O···π interactions to justify increased O···C contacts in **Keto-2** (more favorable angle and vdW contact distance < 3.22 Å)

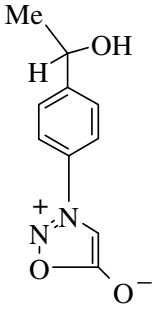
Table 4S. Fingerprint plots for ketones **Keto-1** and **Keto-2** and percentage interactions

Keto-1						
	All	C···H 20.3%	H···H 30.4%	N···H 8.1%	O···C 5.4%	O···H 20.9%
						
	O···N 3.9%					
Keto-2						
	All	C···H 7.1%	H···H 23.1%	N···H 8.8%	O···C 9.6%	O···H 22.0%
						
	O···N 3.1%	C···C 4.0%	F···H 14.8%			



7. Crystal features and analysis of Alc-3

Table 5S. Complete crystal data refinement for **Alc-3**



Empirical formula	$C_{10}H_{10}N_2O_3$
Formula weight	206.20
Temperature/K	288(19)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	41.5257(16)
b/Å	12.1880(5)
c/Å	7.6472(4)
α/°	90
β/°	90.053(4)
γ/°	90
Volume/Å^3	3870.4(3)
Z	16
ρ_{calc}g/cm^3	1.415
μ/mm^{-1}	0.894
F(000)	1728.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.386 to 133.192
Index ranges	$-42 \le h \le 49$, $-14 \le k \le 14$, $-9 \le l \le 9$

Reflections collected	30898
Independent reflections	6826 [R_{int}= 0.1163, R_{sigma}= 0.0644]
Data/restraints/parameters	6826/0/550
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1= 0.1196, wR_2= 0.2986
Final R indexes [all data]	R_1= 0.1703, wR_2= 0.3425
Largest diff. peak/hole / e Å^{-3}	0.67/-0.35

8. ISOS output diagram for isostructurality search

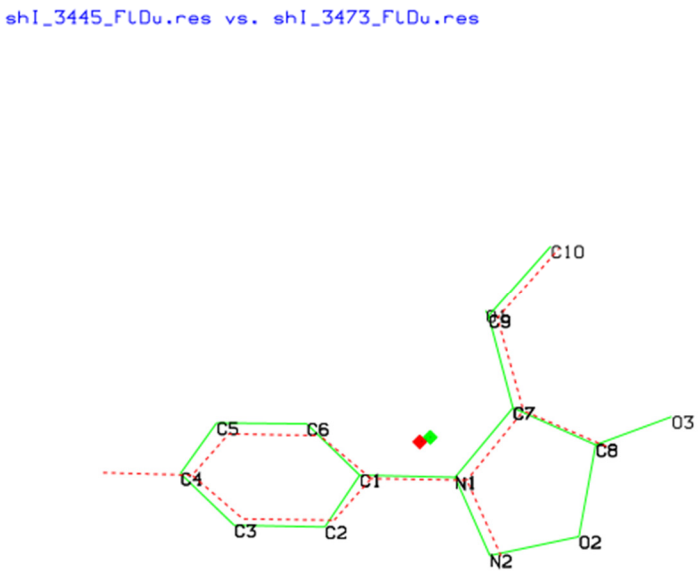


Figure 12S. ISOS output with superposition of 15 atoms with search mode ON

9. DFT – supplementary data

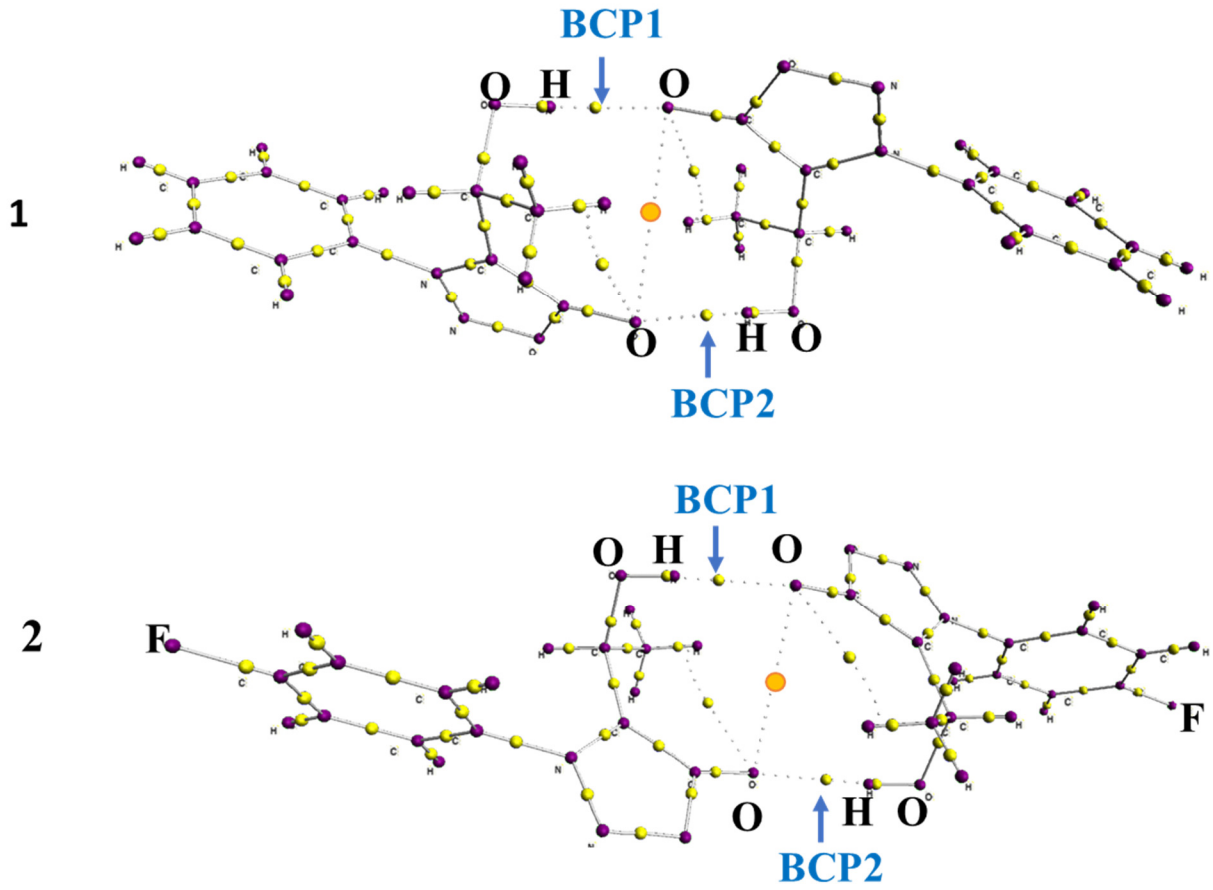


Figure 13S - Molecular graphs of HB dimeric complexes (-O-H···O-), showing positions of the two attractors (purple spheres) linking the bond paths (BPs) and the corresponding bond critical points (BCP) (yellow spheres) for **Alc-1** and **Alc-2**, obtained with M06-D3/6-311++G**. The orange mid-point represents the ring critical point. Graphs were performed with the aid of the QTAIM extension available in Avogadro

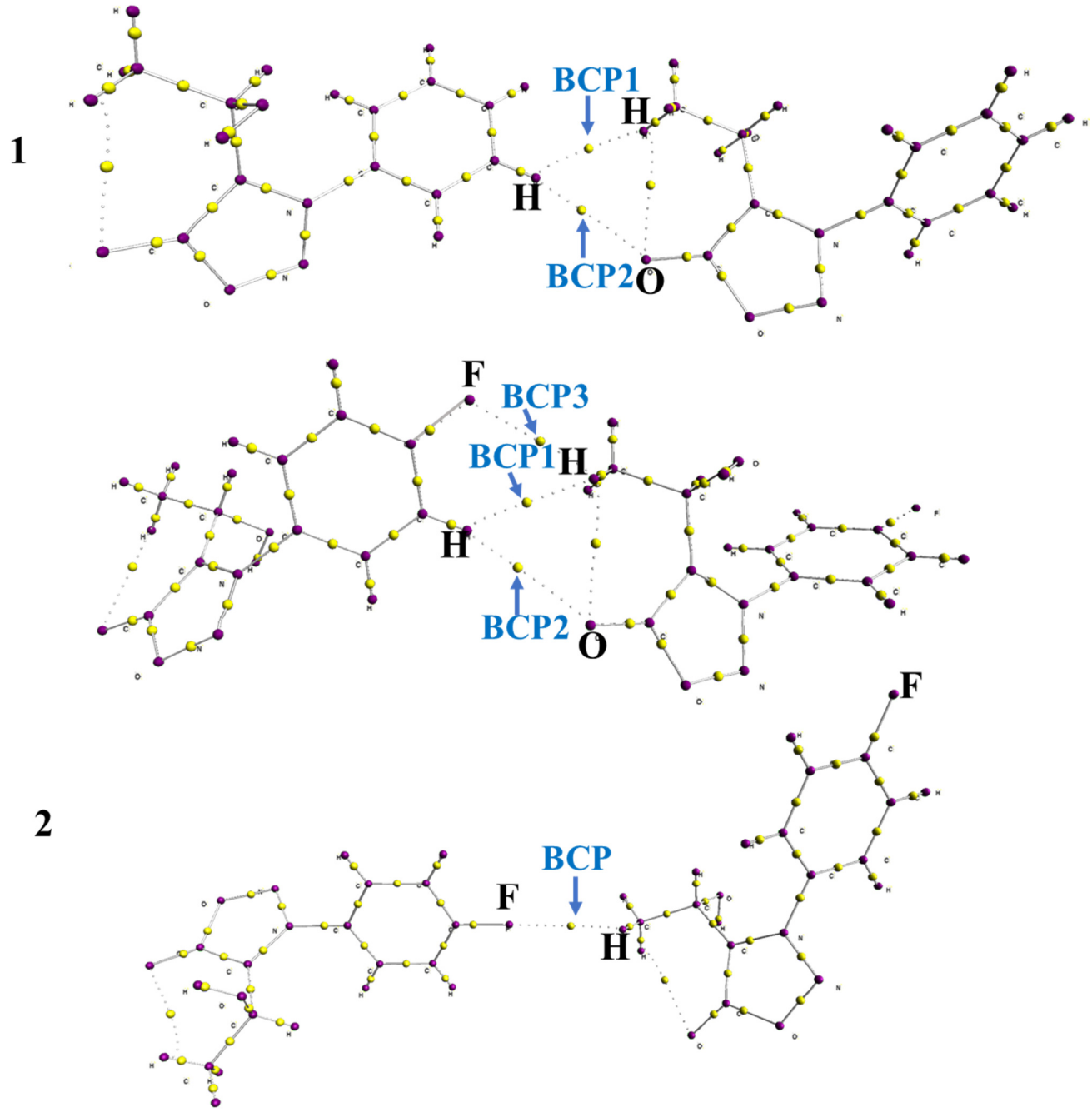


Figure 14S - Molecular graphs of HB dimeric complexes (C=O···H-C/C-H···H-C/C-F···H-C), showing positions of the two attractors (purple spheres) linking the bond paths (BPs) and the corresponding bond critical points (BCP) (yellow spheres) for **Alc-1** and **Alc-2**, obtained with M06-D3/6-311++G**. Graphs were performed with the aid of the QTAIM extension available in Avogadro