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Supplementary Materials

Intramolecular Hydrogen Bond Energy and Its Decomposition - O-H···O Interactions

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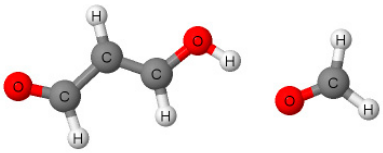
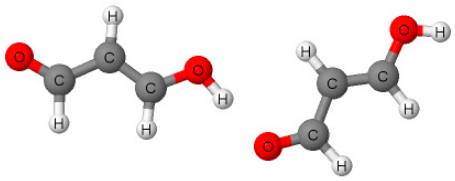
Abstract: The method to calculate the energy of intramolecular hydrogen bond is proposed that is tested for the sample of malonaldehyde and its fluorine derivatives; the corresponding calculations were performed at the ωB97XD/aug-cc-pVTZ level. This method that is based on relationships found for related intermolecular hydrogen bonds is compared with other approaches which may be applied to estimate the intramolecular hydrogen bond energy. Particularly methods based on the comparison of the system that contains the intramolecular hydrogen bond with corresponding conformations where such interaction does not occur are discussed. The function based energy decomposition analysis, FB-EDA, of the intramolecular hydrogen bonds is also proposed here.

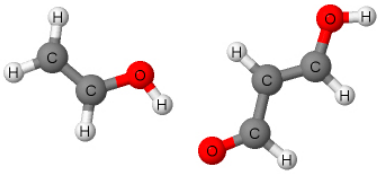
Keywords: intramolecular hydrogen bond; strength of interaction; hydrogen bond energy; function based energy decomposition analysis; malonaldehyde conformations



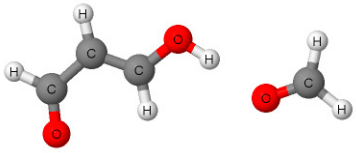
1 malonaldehyde-formaldehyde



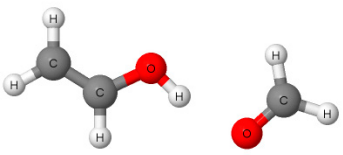
2 malonaldehyde-malonaldehyde



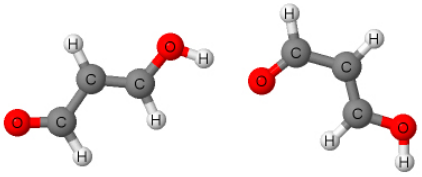
3 ethenol-malonaldehyde



4 malonaldehyde-formaldehyde



5 ethenol-formaldehyde



6 malonaldehyde-malonaldehyde

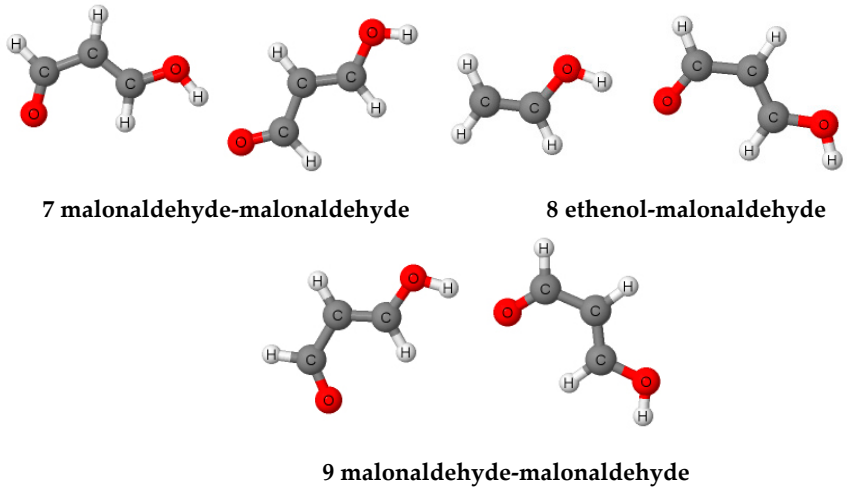


Figure S1. Complexes linked by the intermolecular O-H···O hydrogen bonds.

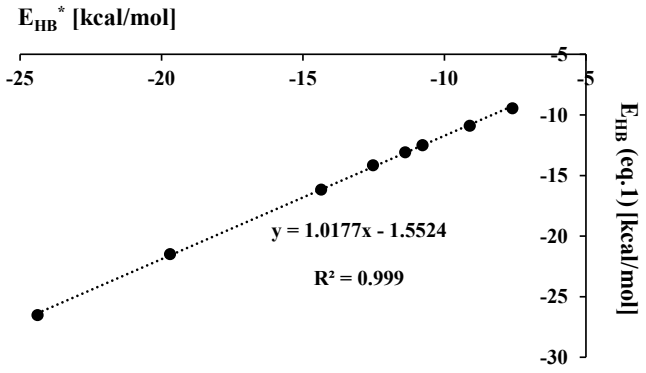


Figure S2. The linear relationship between the E_{HB}^{*} and E_{HB} (Equation 1) energies (see caption of Table 7).

Table S1. QTAIM parameters, characteristics of the RCP (in au) for malonaldehyde and its fluoro derivatives (designations as in Table 1); ρ_{RCP} – electron density at RCP, $\nabla^2\rho_{RCP}$ – Laplacian of electron density, H_{RCP} – total electron energy density at RCP, and its potential and kinetic components, V_{RCP} and G_{RCP}, respectively.

Species	ρ_{RCP}	$\nabla^2\rho_{RCP}$	V_{RCP}	G_{RCP}	H_{RCP}
Malonaldehyde	0.0213	0.1333	-0.0240	0.0287	0.0047
M-1	0.0248	0.1576	-0.0294	0.0344	0.0050
M-2	0.0199	0.1217	-0.0217	0.0261	0.0043
M-3	0.0198	0.1177	-0.0210	0.0252	0.0042
M-12	0.0230	0.1443	-0.0266	0.0313	0.0048
M-13	0.0217	0.1299	-0.0237	0.0281	0.0044
M-23	0.0187	0.1086	-0.0193	0.0233	0.0039
M-123	0.0205	0.1203	-0.0218	0.026	0.0041

Table S2. Geometrical parameters of intermolecular O-H···O hydrogen bonds (Å, degrees), numeration of complexes corresponds to that one of Figure S1.

Complex	OH	H···O	O···O	O-H…O
1	0.971	1.805	2.776	177.9
2	0.980	1.711	2.691	176.9
3	0.973	1.789	2.752	170.1
4	0.971	1.806	2.777	178.1
5	0.967	1.863	2.806	164.1
6	0.980	1.711	2.690	178.3
7	0.980	1.715	2.693	175.5
8	0.972	1.783	2.753	175.5
9	0.979	1.719	2.693	173.3

Table S3. QTAIM parameters, characteristics of the H···O BCP (in au) for complexes considered here; ρ_{BCP} – electron density at H···O BCP, $\nabla^2\rho_{BCP}$ – Laplacian of electron density, H_{BCP} – total electron energy density at H···O BCP, and its potential and kinetic components, V_{BCP} and G_{BCP}, respectively. The numeration of complexes follows Figure S1.

Complex	ρ_{BCP}	$\nabla^2\rho_{BCP}$	V_{BCP}	G_{BCP}	H_{BCP}
1	0.035	0.093	-0.033	0.028	-0.005
2	0.045	0.100	-0.045	0.035	-0.010
3	0.038	0.095	-0.035	0.029	-0.006
4	0.035	0.093	-0.032	0.028	-0.005
5	0.031	0.089	-0.027	0.025	-0.003
6	0.045	0.100	-0.045	0.035	-0.010
7	0.045	0.100	-0.044	0.034	-0.010
8	0.038	0.095	-0.036	0.030	-0.006
9	0.044	0.102	-0.043	0.034	-0.009

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