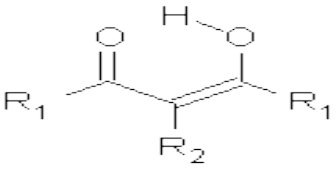
MALONALDEHYDES: SEARCHING FOR SHORT HYDROGEN BONDS

Malonaldehyde **1** possesses a very short intramolecular hydrogen bond. Its potential energy surface has two local minima (the two mirror image hydrogen-bonded structures) separated by a C_{2v}transition state. Schaefer reports a high-level computational study for the search for even shorter hydrogen bonds that might even lead to a single well on the PES.[1]



1	R_1	R_2
2	H	H
3	H	CN
4	H	NO_2
5	H	BH_2
6	NH_2	H
7	OCH_3	H
8	$C(CH_3)_3$	H

NH_2 NO_2

The hydrogen bond distance is characterized by the non-bonding separation between the two oxygen atoms. Table 1 shows the O···O distance for a number of substituted malonaldehydes computed at B3LYP/DZP++. Electron withdrawing groups on C_2 reduce the O··O distance (see trend in **1** → **4**). Electron donating groups on C_1 and C_3 also reduce this distance (see **5** and **6**). Bulky substituents on the terminal carbons also reduce the O···O distance (see **7**). Combining all of these substituent effects in **8** leads to the very short O···O distance of 2.380 Å.

Table 1. Distance (Å) between the two oxygen atoms and the barrier for hydrogen transfer of substituted malonaldehydes .[1]

Compound	r(O···O)	ΔE^a	ΔE^b
1	2.546	3.92	1.54
2	2.526	3.56	1.24
3	2.521	3.34	1.04
4	2.499	2.62	0.40
5	2.474	2.02	-0.06
6	2.498		

7	2.466		
8	2.380	0.43	-0.78

[a]Focal point energy. [b]Focal point energy and corrected for zero-point vibrational energy.

A shorter O···O distance might imply a smaller barrier for hydrogen transfer between the two oxygens. The structures of **8** and the transition state for its hydrogen transfer are shown in Figure 1. The energies of a number of substituted malonaldehydes were computed using the focal point method, and the barriers for hydrogen transfer are listed in Table 1. There is a nice correlation between the O···O distance and the barrier height. The barrier for **8** is quite small, suggesting that with some bulkier substituents, the barrier might vanish altogether, leaving only a symmetric structure. In fact, the barrier appears to vanish when zero-point vibrational energies are included.

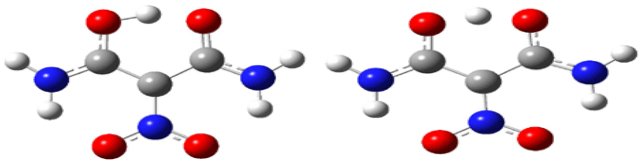


Figure 1. B3LYP/DZP++ optimized geometries of **8** and the transition state for hydrogen transfer**8TS**.[1]

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