Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The MC-QTAIM analysis reveals an exotic bond in the coherently quantum superposed Malonaldehyde

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Table of contents

The optimized geometry of **1** (or **3**) at the CCSD(T)/cc-pVQZ level				
Atom	Number	Coordinates [Bohr]		
		X	Y	Z
C	1	0.000000	2.077361	0.000000
C	2	2.339522	0.675322	0.000000
C	3	-2.236791	0.811101	0.000000
O	4	2.439903	-1.657362	0.000000
O	5	-2.441842	-1.681011	0.000000
H	6	0.019948	4.116154	0.000000
H	7	4.109976	1.763188	0.000000
H	8	-4.041823	1.778489	0.000000
H*	9	-0.688985	-2.333555	0.000000

* The coordinates of the quantum hydrogen atom

The optimized geometry of **2** at the CCSD(T)/cc-pVQZ level				
Atom	Number	Coordinates [Bohr]		
		X	Y	Z
C	1	0.000000	0.000000	2.130982
C	2	0.000000	-2.239563	0.731188
C	3	0.000000	2.239563	0.731188
O	4	0.000000	-2.229682	-1.682393
O	5	0.000000	2.229682	-1.682393
H	6	0.000000	0.000000	4.166644
H	7	0.000000	-4.079697	1.658786
H	8	0.000000	4.079697	1.658786
H*	9	0.000000	0.000000	-2.126078

* The coordinates of the quantum hydrogen atom

The averaged geometry of **4**				
Atom	Number	Coordinates [Bohr]		
		X	Y	Z
C	1	0.000000	0.000000	4.458367
C	2	2.288822	0.000000	3.124956
C	3	-2.288822	0.000000	3.124956
O	4	2.439951	0.000000	0.711995
O	5	-2.439951	0.000000	0.711995
H	6	0.000000	0.000000	6.497257
H	7	4.077565	0.000000	4.152645
H	8	-4.077565	0.000000	4.152645
Bq*	9	-0.564373	0.000000	0.132820
Bq*	10	0.564373	0.000000	0.132820

* The coordinates of the "ghost atoms" used as the centers of expansion for the electronic basis functions of the quantum hydrogen atom coinciding with the maxima of the ground state protonic orbital.

The averaged geometry of **5**				
Atom	Number	Coordinates [Bohr]		
		X	Y	Z
C	1	0.000000	0.000000	4.458367
C	2	2.288822	0.000000	3.124956
C	3	-2.288822	0.000000	3.124956
O	4	-2.439951	0.000000	0.711995
O	5	2.439951	0.000000	0.711995
H	6	0.000000	0.000000	6.497257
H	7	4.077565	0.000000	4.152645
H	8	-4.077565	0.000000	4.152645
Bq*	9	-0.582494	0.000000	0.121241
Bq*	10	0.582494	0.000000	0.121241

* The coordinates of the "ghost atoms" used as the centers of expansion for the electronic basis functions of the quantum hydrogen atom coinciding with the maxima of the excited state protonic orbital.

The regression procedure: Transforming the numerical protonic wavefunctions into the Gaussian-type orbitals

The numerical ground and excited protonic orbitals, obtained by the 3D Numerov method, were fitted by linear combinations of [6s6p6d] Cartesian Gaussian-type shells which were placed on the molecular symmetry plane of the averaged geometry that contains all the clamped nuclei. This is called the xz plane where the x-axis is the C_2 geometrical symmetry axis with respect to the rotation of the clamped nuclei. In the fitting procedure, the protonic orbital is explicitly shown by:

$$\Psi_{ground\ state} = \sum_{i=1}^{15}\left[c_i\varphi_{\alpha_i}(x_i, y_i, z_i) + c_i\varphi_{\alpha_i}(-x_i, y_i, z_i)\right],$$

and,

$$\Psi_{excited\ state} = \sum_{i=1}^{15}\left[c_i\varphi_{\alpha_i}(x_i, y_i, z_i) - c_i\varphi_{\alpha_i}(-x_i, y_i, z_i)\right],$$

where c_i, α_i and (x_i, y_i, z_i) are the coefficients, exponents and coordinates of the center of *i-th normalized* Gaussian function in these series, respectively. It must be noted that only non-zero contributions, due to the molecular symmetry, were included in the wavefunction expansions and offered in the forthcoming tables of the optimal parameters. The following tables gather the optimized parameters of the protonic orbitals, which were derived after the fitting of the Gaussian expansions to the 3D grid of the protonic wavefunctions.

Regression parameters of the ground state protonic orbital							
Function Number	Shell Number	Function Type	Exponent	Coefficient	Coordinates [Bohr]		
					X	Y	Z
1	1	S	5.92536	-0.667308	0.098133	0.000000	-0.042515
2	2	S	4.90609	0.103662	0.831002	0.000000	-0.082282
3	3	S	5.53872	0.971034	0.256124	0.000000	-0.022740
4	4	Pz	9.99765	-0.025588	0.894294	0.000000	-0.102668
5	5	Pz	5.98643	0.277155	0.488342	0.000000	-0.086228
6	6	Pz	8.71275	-0.067002	0.668808	0.000000	0.221253
7	7	Dxx	6.17956	0.583140	0.559992	0.000000	0.043214
8	7	Dyy	6.17956	-0.405039	0.559992	0.000000	0.043214
9	7	Dzz	6.17956	0.505316	0.559992	0.000000	0.043214
10	8	Dxx	6.97638	0.417660	0.736994	0.000000	0.148422
11	8	Dyy	6.97638	-0.295682	0.736994	0.000000	0.148422
12	8	Dzz	6.97638	0.230332	0.736994	0.000000	0.148422
13	9	Dxx	6.33365	-0.999577	0.649366	0.000000	0.093094
14	9	Dyy	6.33365	0.756131	0.649366	0.000000	0.093094
15	9	Dzz	6.33365	-0.587118	0.649366	0.000000	0.093094

Regression parameters of the excited state protonic orbital							
Function Number	Shell Number	Function Type	Exponent	Coefficient	Coordinates [Bohr]		
					X	Y	Z
1	1	S	7.94753	-0.995443	0.063433	0.000000	-0.199071
2	2	S	8.43716	0.469871	0.967696	0.000000	0.165908
3	3	S	6.71810	0.999654	0.280224	0.000000	-0.116529
4	4	Pz	6.37756	-0.778184	0.720576	0.000000	0.060806
5	5	Pz	7.81809	0.835965	0.545553	0.000000	0.019451
6	6	Pz	7.93854	0.155353	0.834297	0.000000	0.249593
7	7	Dxx	7.17292	0.272671	0.498309	0.000000	0.080944
8	7	Dyy	7.17292	0.310717	0.498309	0.000000	0.080944
9	7	Dzz	7.17292	0.434034	0.498309	0.000000	0.080944
10	8	Dxx	6.66305	-0.207159	0.560419	0.000000	0.028372
11	8	Dyy	6.66305	-0.999654	0.560419	0.000000	0.028372
12	8	Dzz	6.66305	-0.402189	0.560419	0.000000	0.028372
13	9	Dxx	6.30875	-0.468891	0.618625	0.000000	0.067678
14	9	Dyy	6.30875	0.861386	0.618625	0.000000	0.067678
15	9	Dzz	6.30875	0.019168	0.618625	0.000000	0.067678

Table S1- Summary of the ab initio NEO-DFT results.

Method/basis set	**B3LYP-EPC17-1/[cc-pVTZ:10s10p10d]**	
System	**2**	**1 and 3**
Electronic kinetic energy	265.577772	265.554369
Proton's kinetic energy	0.007718	0.007746
Electron-electron potential energy	261.422933	258.206955
Proton-electron potential energy	-13.233539	-12.654149
electron-clamped nuclei potential energy	-949.386639	-943.531760
Proton-clamped nuclei potential energy	12.255060	11.684860
Clamped Nuclei-clamped Nuclei potential energy	156.082444	153.453666
Total energy	-267.274253	-267.278314
Virial ratio	2.006359	2.006463
Method/basis set	**B3LYP/[cc-pVTZ:6s6p6d]**	
System	**4**	**5**
Electronic kinetic energy	265.443959	265.454513
Proton's kinetic energy	0.005092	0.005817
Electron-electron potential energy	258.213390	258.215910
Proton-electron potential energy	-12.401579	-12.396164
electron-clamped nuclei potential energy	-943.513438	-943.531044
Proton-clamped nuclei potential energy	11.709815	11.712679
Clamped Nuclei-clamped Nuclei potential energy	153.388670	153.388670
Total energy	-267.154092	-267.149620
Virial ratio	2.006423	2.006364