Electronic Supplementary Information (ESI) for Organic & Biomolecular Chemistry

Refinement of Labile Hydrogen Position of Enol-Enol Tautomers of *β*-Dicarbonyl Compounds Based on DFT Calculations of ^{1}H NMR Chemical Shifts in Solution: Comparison with X-Ray and Neutron Diffraction Methods

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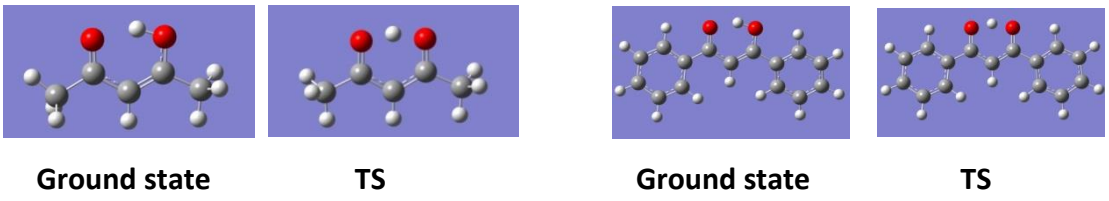


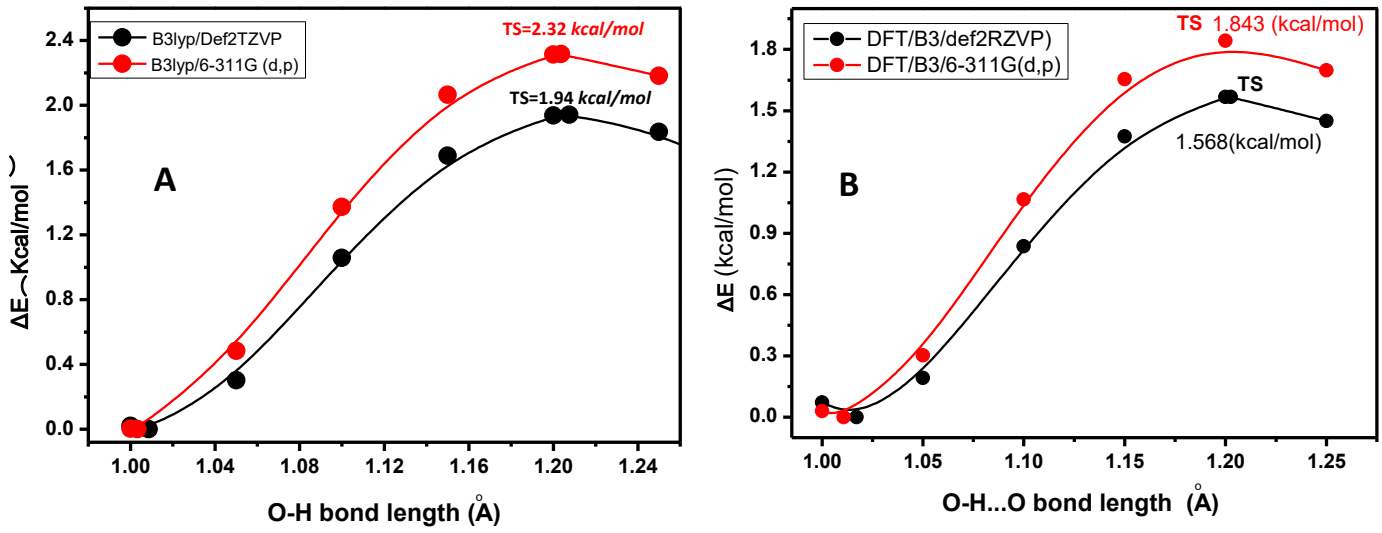


Fig. S1 Potential curves of the enolic form of acetyacetone (A) and dibenzoylmethane (B) as a function of the O–H bond length calculated at the B3LYP/6-311G(d,p) and B3LYP/def2TZVP level of theory.

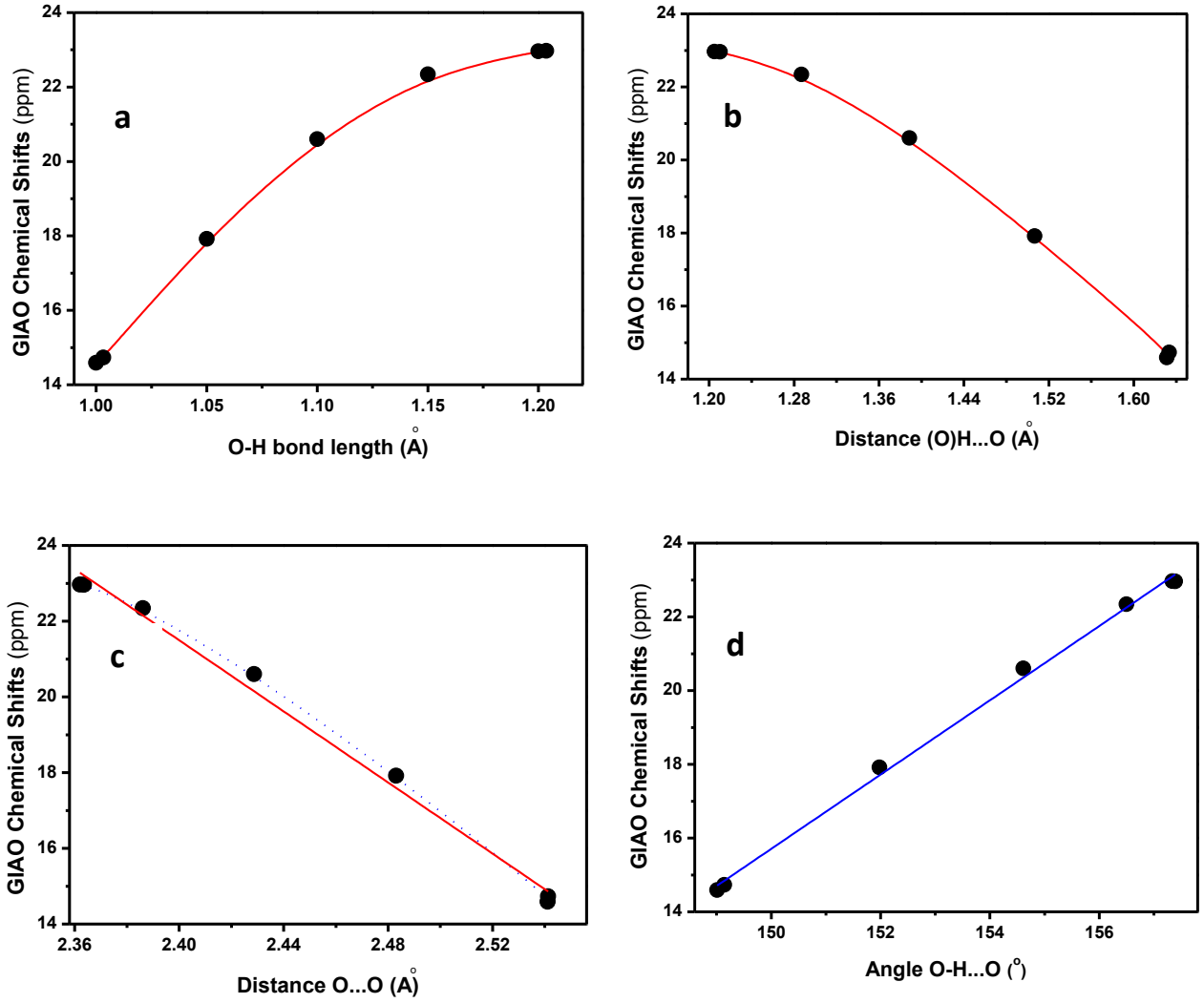


Fig. S2 Calculated ^{1}H chemical shifts at the GIAO DFT/B3LYP/6-311+G(2d,p) level of theory of the enolic form of acetylacetone *vs*. the O-H bond length **(a)**, (O)H···O bond length **(b)**, O•••O distance **(c)** (the dotted line represents a slightly curved second order polynomial fit)**,** and O-H•••O angle **(d)** (scan with minimization at the B3LYP/6-311G(d,p) level of theory).

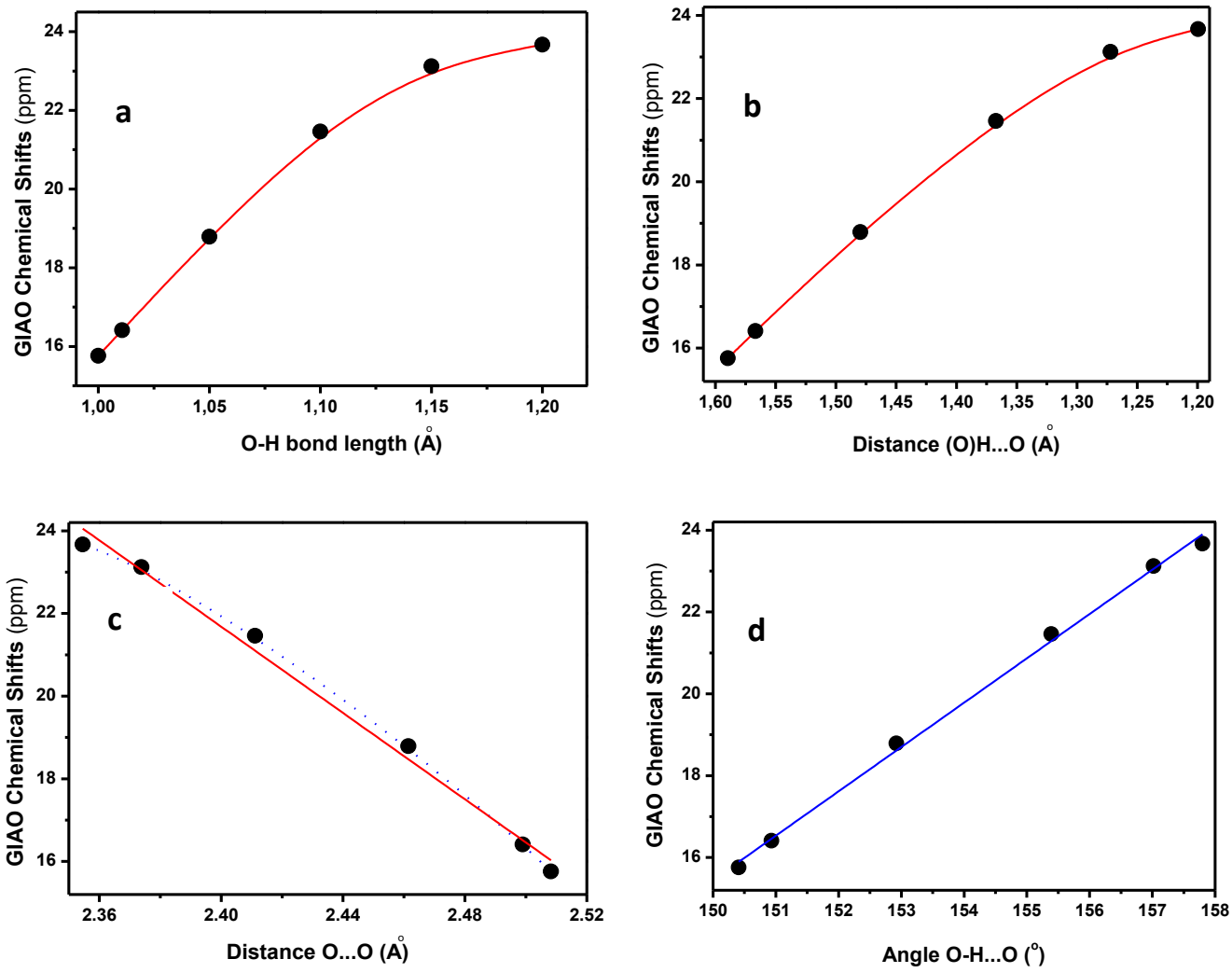
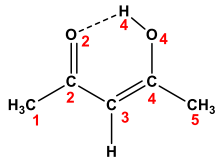


Fig. S3 Calculated ^{1}H chemical shifts at the GIAO DFT/B3LYP/6-311G+(2d,p) level of theory of the enolic form of dibenzoylmethane *vs*. the O-H bond length **(a)**, (O)H···O bond length **(b)**, O···O distance **(c)** (the dotted line represents a slightly curved second order polynomial fit)**,** and O-H···O angle **(d)** (scan with minimization at the B3LYP/6-311G(d,p) level of theory).

Table S1 Statistical data of calculated *vs*. experimental OH ^{1}H chemical shifts of the compounds **1** to **22** of Figure 1 determined from various minimized geometries

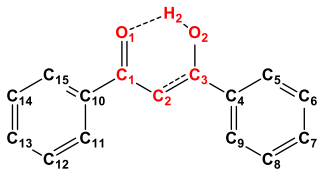
Method	Correlation coefficient (R^2)	Intercept	Slope	Mean square error
B3LYP/6-31+G(d)	0.9532	-2.8142	1.2542	0.0910
B3LYP/6-311G(d,p)	0.9342	-0.0683	1.0405	0.1279
B3LYP/def2TZVP	0.9419	-0.4060	1.0295	0.1128

Table S2 Comparison of structural data of X-ray and DFT calculations of the enol tautomer of acetylacetone.



	X-ray 210 K[21]	X-ray 110 K[21]	X-ray (complex)[22]	GED T = 300 K[23]	GED T = 671 K[23]	Electron diffraction 294 K[24]	Electron diffraction 290 K[25a]	Electron diffraction 378 K[25b]	Ultrafast Electron diffraction 428 K[26]	DFT/B3LYP/ 6-31+G(d)	DFT/B3LYP/ 6-311G(d,p)	DFT/B3LYP/ Def2TZVP
Bond distance (Å)												
O(2)-C(2)	1.283(2)	1.291(1)	1.238	1.248(3)	1.240(4)	1.243(9)	1.2867(54)	1.315(7)	1.262(5)	1.253	1.244	1.244
C(1)-C(2)	1.486(3)	1.497(1)	1.478	1.509(3)	1.511(3)	1.493(9)	1.4049(51)	1.497(10)	1.518(23)	1.514	1.513	1.508
C(2)-C(3)	1.397(2)	1.402(1)	1.412	1.441(3)	1.443(3)	1.430(8)		1.416(10)	1.443(19)	1.445	1.444	1.440
C(3)-C(4)			1.338	1.368(3)	1.370(3)	1.382(7)			1.359(34)	1.375	1.370	1.368
C(4)-O(4)H			1.331	1.326(3)	1.318(4)	1.319(3)			1.321(21)	1.330	1.325	1.323
C(4)-C(5)			1.554	1.492(3)	1.494(3)	1.525(7(			1.504(21)	1.497	1.495	1.491
O(4)-H(4)	0.91(5)	0.89(3)	1.03	1.007(3)	1.013(4)	1.049(15)	1.2595(117)	1.191(10)		1.001	1.003	1.008
H(4)···O(2)	1.74(5)	1.78(3)	1.66							1.647	1.627	1.609
O(2)···O(4)	2.547(1)	2.541(2)	2.535	2.521(9)	2.453(15)	2.512(8)	2.519(24)	2.381(20)	2.592	2.559	2.541	2.530
Bond angle (°)												
C(1)-C(2)-O(2)	117.2(2)	117.0(1)	117.3				123.23 (1.70)	120.0 (1.3)	118.7(3.1)	119.28	119.66	119.71
O(2)-C(2)-C(3)	121.5(2)	121.8(1)	120.5	121.0 (2.0)	120.3(1.5)	123.0(7)		120.0 (1.3)		121.53	121.74	121.61
C(1)-C(2)-C(3)	121.3(2)	121.2(1)	122.1	119.4(1.0)	118.0(2.0)	118.1(7)	118.29 (1.85)	120.0 (1.3)	118.2(1.0	119.18	118.59	118.67
C(2)-C(3)-C(4)	121.6(3)	121.0(1)	122.2	121.1 (0.8)	120.0(1.0)	119.7(5)		118.0 (2.5)	120.4(1.0	121.03	120.46	120.64
C(3)-C(4)-C(5)			124.5	123.5 (1.0)	123.6(1.2)	124.1(7)			123.6(1.1	124.27	124.13	124.24
C(3)-C(4)-O(4)			122.8	121.3(1.2)	120.4(1.3)	121.0(8)				122.05	122.16	121.76
C(5)-C(4)-O(4)			112.7						112.9(2.7)	113.68	113.71	114.01
C(4)-O(4)-H(4)	110(3)	113(2)	96	105.9	105.9					106.36	105.81	105.86
O(2)-H(4)-O(4)	147(5)	155(2)	141			137 (7)	178.5(9.2)	175		148.13	149.14	149.39

Table S3 X-ray and neutron diffraction structural data of the enol form of dibenzoylmethane



	X-ray[28a] Metastable II	X-ray[28b] Polymorph (I)	X-ray[28c] Polymorph (III)	X-ray[28d]	Neutron diffraction[28e]	Neutron diffraction[28f]
Bond distance (Å)						
C(1)-O(1)	1.294(3)	1.287 (2)	1.284 (3)	1.292	1.273 (4)	1.292 (3)
C(1)-C(2)	1.387(4)	1.387(4)	1.389 (3)	1.413	1.422 (3)	1.412 (4)
C(2)-C(3)	1.383(4)	1.383(4)	1.383(4)	1.385	1.391(3)	1.373 (4)
C(3)-O(2)	1.299(3)	1.304 (2)	1.292 (3)	1.317	1.311 (4)	1.315 (3)
O(2)-H	1.22 (4)	1.22 (3)	1.257	1.18	1.161 (9)	1.185 (4)
O(1)-H	1.28(4)	1.28(3)	1.287	1.34	1.360 (9)	1.334 (4)
C(3)-C(4)	1.476(4)	1.479(2)	1.480(4)	1.475	1.480 (4)	1.467 (4)
C(1)-O(10)	1.478(4)	1.476(2)	1.481(4)	1.485	1.474 (3)	1.470 (3)
O(1)….O(2)	2.452	2.460 (2)	2.461 (4)	2.468	2.459 (4)	
Bond angle (°)						
O(1)….H…O(2)	158 (3)		150.7	154	154.7 (5)	
C(1)-C(2)-C(3)	121.2 (3)		121.4 (3)	120.1	120.4 (2)	121.7 (3)
C(2)-C(10-C(10)	123.6 (3)		123.1 (3)	122.2	122.2 (2)	124.0(3)
O(1)—C(1)—C(10)			116.3 (3)	117.3	117.6 (2)	116.5 (3)
O(1)—C(1)—C(2)			120.6 (3)	120.6	120.1 (2)	119.5 (3)
C(2)-C(3)-C(4)	124.3 (3)		124.2 (2)	124.1	124.0 (2)	124.7 (3)
O(2)—C(3)—C(4)			115.9 (3)	114.9	115.7 (2)	115.4 (3)
O(2)—C(3)—C(2)			119.9 (3)	121.1	120.3 (2)	119.9 (3)
Torsion angle (°)						
C(11)-C(10)-C(10)-C(2)	8		6.91	-3.9 (4.24)	3.9	2.0 ± 1
O(1)-C(1)-C(10)-C(15)	24		7.60	16.9(16.98)	17	17.5 ± 1