Keto Forms of Salicylaldehyde Schiff Bases: Structural and Theoretical Aspects

Spyros D. Chatziefthimiou, Yannis G. Lazarou, Eugene Hadjoudis, Tereza Dziembowska[1] and Irene M. Mavridis[*]

Institute of Physical Chemistry, National Center for Scientific Research "Demokritos", P.O. Box 60228, Aghia Paraskevi 15310, Greece

SUPPORTING INFORMATION

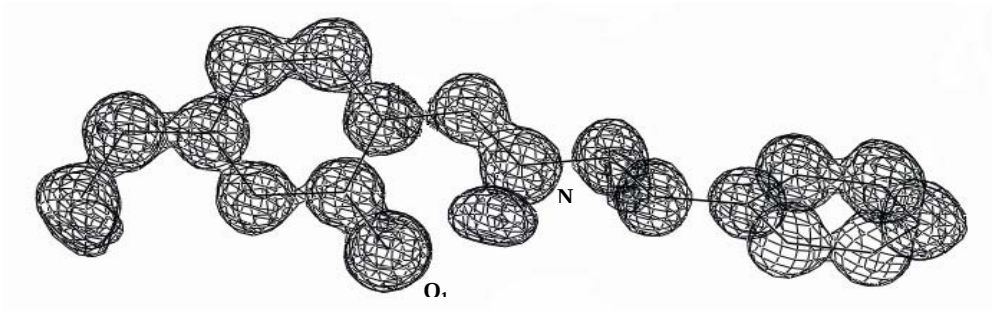
[1] Institute of Chemistry and Environmental Protection, Technical University of Szczecin Al. Piastów 42, 71-065 Szczecin, Poland
[*] E-mail: mavridi@chem.demokritos.gr, fax: +30 210 6511766

Table S1. Least square planes of monomers and deviations from them of atoms involved in hydrogen bonds (O1, N and H_N or $H_{O)}$. Last column shows least square planes of keto-dimers (based on the two phenyl rings).

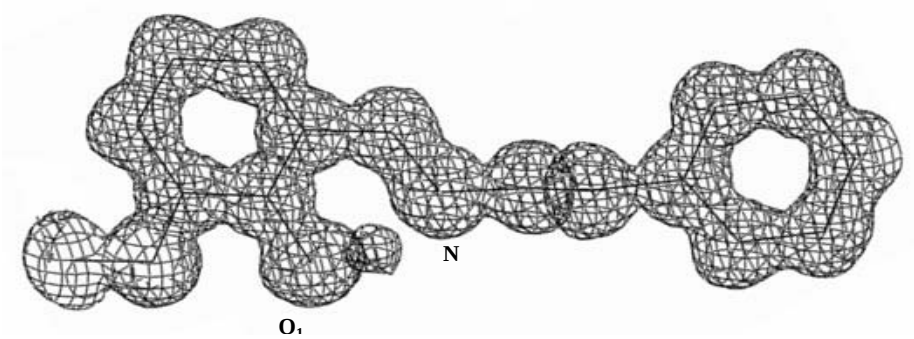
Compound	Plane through atoms C_1-C_6				Planes through atoms C_1-C_6 in dimers
	rms deviation	O_1	N	H_N / H_O	rms deviation
1	0.009	0.028(2)	0.074(3)	0.04(2)	0.1094
2	0.012	0.059(3)	0.159(3)	0.12(2)	0.0543
3	0.011	0.029(2)	0.140(3)	0.11 (2)	0.0748
4	0.006	0.014(3)	0.127(4)	0.09(3)	0.5955
5	0.006	0.039(4)	0.132(6)	0.11(5)/0.07(6)	
6	0.003	0.006(2)	0.063(3)	- /0.01(2)	
7	0.005	0.001(3)	0.016(3)	- / 0.04(3)	
8	0.010	0.058(4)	0.030(6)	- / 0.07(4)	
9	0.005	0.032(6)	0.133(6)	- / 0.02(5)	
10	0.003	0.016(4)	0.071(5)	- / 0.08(4)	

Table S2. Electronic energy differences ΔE between the syn-enol and cis-keto forms of dimers (without zero-point energies, in kJ/mol) at the B3P86/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory, for the compounds **1**, **4**, and **10**.

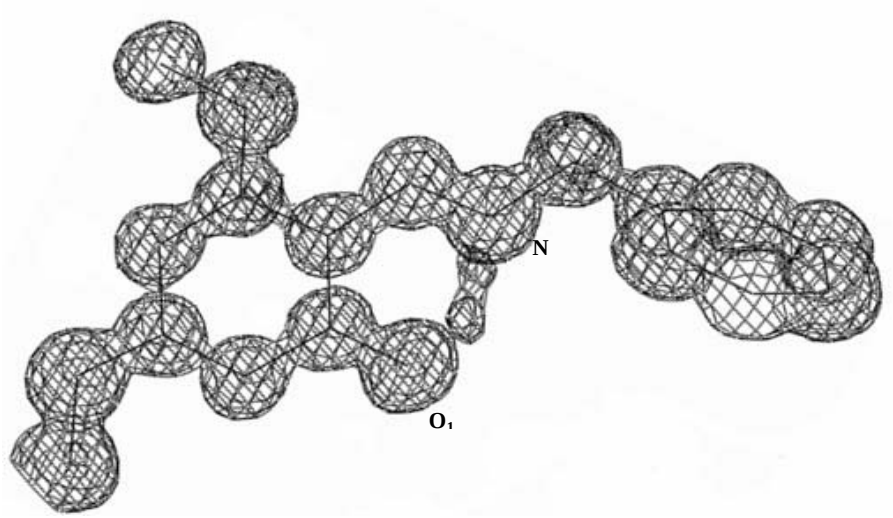
Compound	dimer-1	dimer-4	dimer-10a	dimer-10b	Level of theory
1	18.0	-	-8.2	-18.4	B3P86/ aug-cc-pVDZ
	18.3	-	-6.5	-18.0	B3LYP/ aug-cc-pVDZ
4	4.5	0.6	0.6	-16.9	B3P86/ aug-cc-pVDZ
	2.8	-0.6	2.8	-16.8	B3LYP/ aug-cc-pVDZ
10	-4.5	0.6	-25.2	-25.8	B3P86/ aug-cc-pVDZ
	-6.7	-2.5	-25.5	-26.4	B3LYP/ aug-cc-pVDZ



(a)



(b)



(c)

Figure S1. Electron density maps and models of: (a) **3**, belonging to the keto group (b) **9**, belonging to the enol group and (c) **5**, belonging to the group with a mixture of the two forms, calculated with coefficients $2F_o$-F_c for the non-hydrogen atoms (contoured at 1.5σ) and F_o-F_c for the OH and/or NH hydrogen atoms (contoured at 3σ).

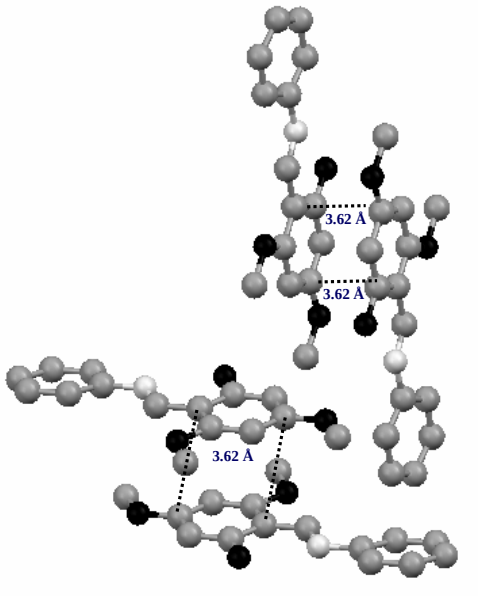


Figure S2. π…π interactions in **7** (colour code as in Figure 1).

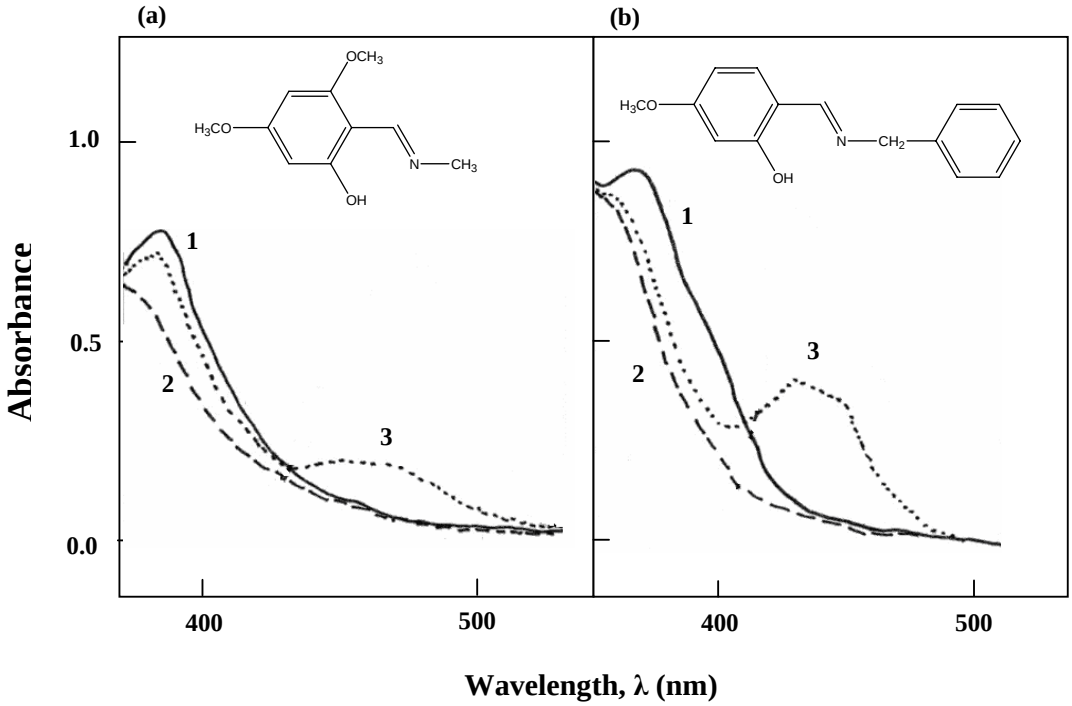


Figure S3. Absorption spectra of thin polycrystalline films of compounds **1** and **8**. Curve 1 at room temperature, 2 at liquid nitrogen temperature (it turns back to 1 at room temperature), and 3 after irradiation with 365 nm light at liquid nitrogen temperature (it turns back to 1 at room temperature in the dark).