## Controlled tautomerism – a switching caused by an "underground" anionic effect

Liudmil Antonov<sup>a,\*</sup>, Vera Deneva<sup>a</sup>, Vanya Kurteva<sup>a</sup>, Daniela Nedeltcheva<sup>a</sup>, Aurelien Crochet<sup>b</sup> and Katharina M. Fromm<sup>b</sup>

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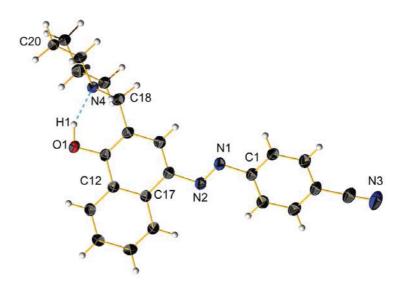


Figure S1. View of the molecular structure of the enol form of compound 3, ellipsoids are drown with 50% probability. N atoms are in blue, O in red, C in black and H in white.

<sup>&</sup>lt;sup>a</sup> Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl.9, BG-1113 Sofia, Bulgaria

<sup>&</sup>lt;sup>b</sup> Chemistry Department, University of Fribourg, Chemin du Muse CH-1700 Fribourg, Switzerland

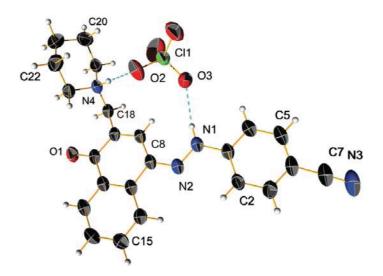


Figure S2. View of the molecular structure of the keto form of compound **3** with perchloric acid, ellipsoids are drown with 50% probability. N atoms are in blue, O in red, C in black, H in white and Cl in green.

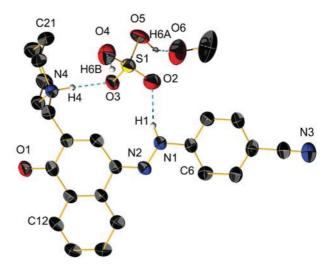


Figure S3. View of the molecular structure of the keto form of compound 3 with sulfuric acid. Ellipsoids are drown with 50% probability, some hydrogen atoms are omitted for clarity. N atoms are in blue, O in red, C in black, H in white and S in yellow.

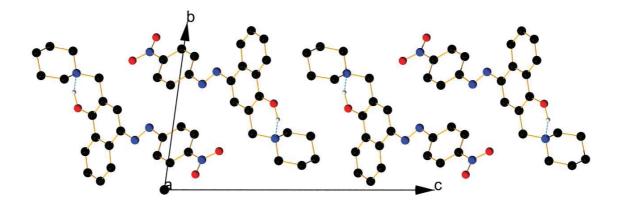


Figure S4. View of the packing along a axis in the enol form of compound 4.

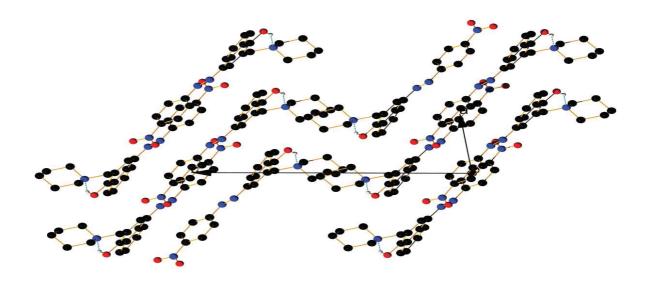


Figure S5. View of the packing along b axis in the enol form of compound 4.

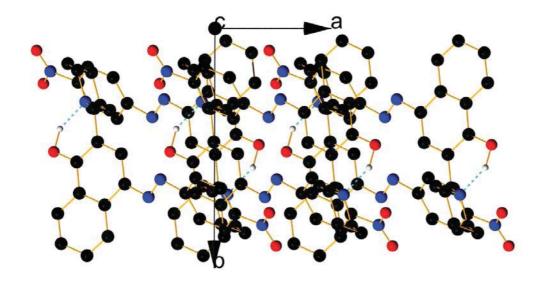


Figure S6. View of the packing along c axis in the enol form of compound 4.

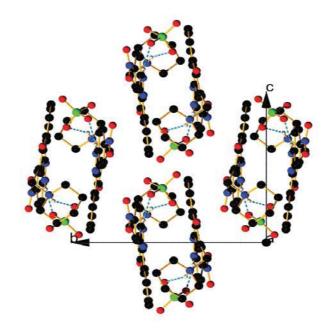


Figure S7. View of the packing along a axis in the keto form of compound 4 with perchloric acid.

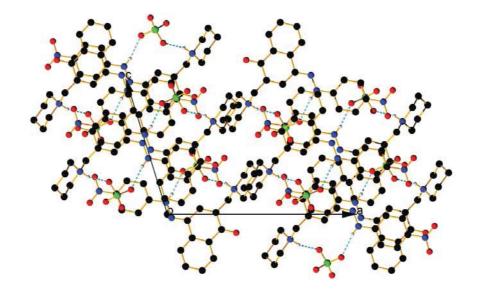


Figure S8. View of the packing along b axis in the keto form of compound 4 with perchloric acid.

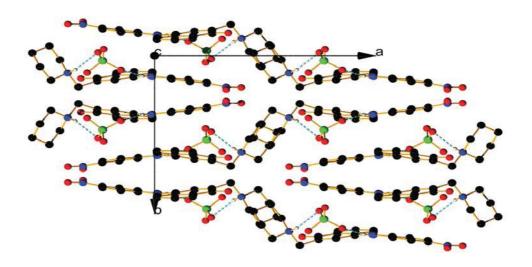


Figure S9. View of the packing along c axis in the keto form of compound 4 with perchloric acid.

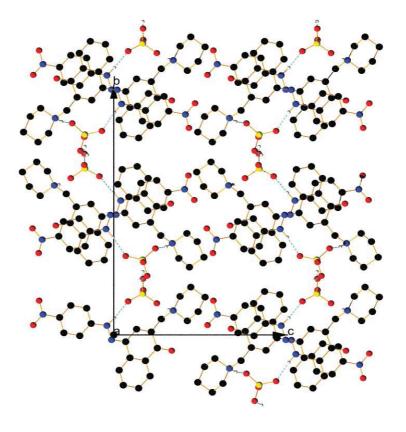


Figure S10. View of the packing along a axis in the keto form of compound 4 with sulfuric acid.

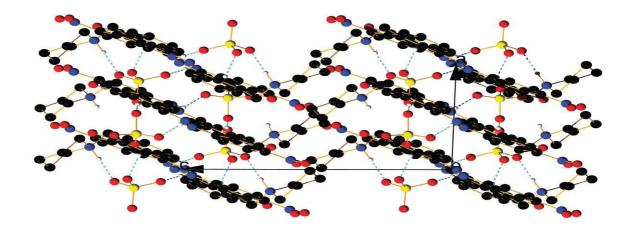


Figure S11. View of the packing along b axis in the keto form of compound 4 with sulfuric acid.

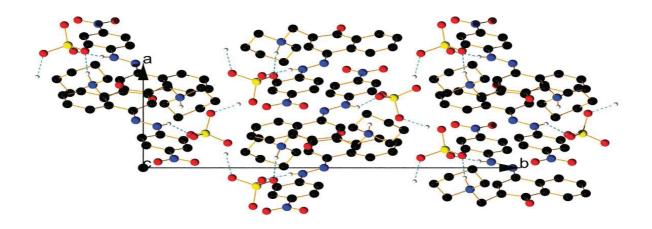


Figure S12. View of the packing along c axis in the keto form of compound 4 with sulfuric acid.

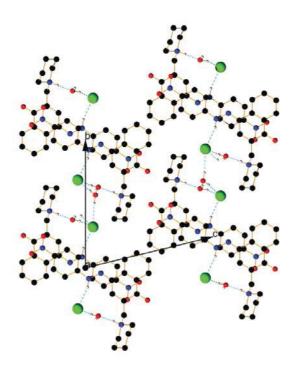


Figure S13. View of the packing along a axis in the keto form of compound 4 with hydrochloric acid.

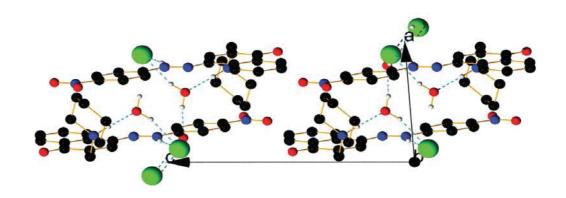


Figure S14. View of the packing along b axis in the keto form of compound **4** with hydrochloric acid.

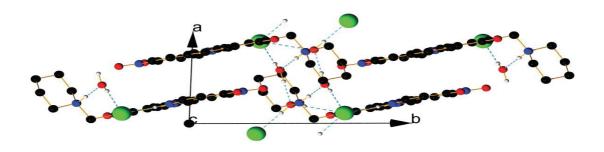


Figure S15. View of the packing along c axis in the keto form of compound 4 with hydrochloric acid.

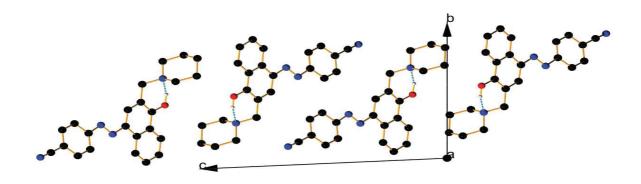


Figure S16. View of the packing along a axis in the enol form of compound 3.

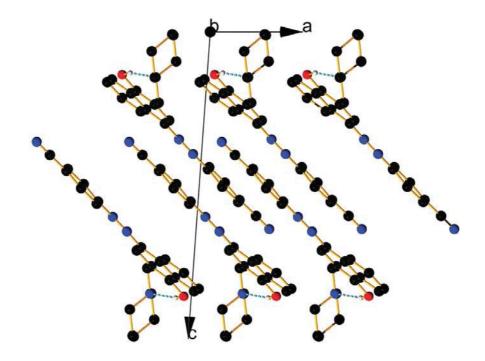


Figure S17. View of the packing along b axis in the enol form of compound 3.

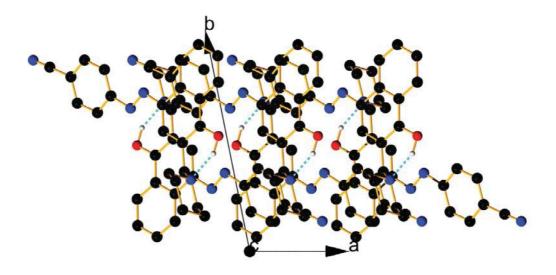


Figure S18. View of the packing along c axis in the enol form of compound 3.

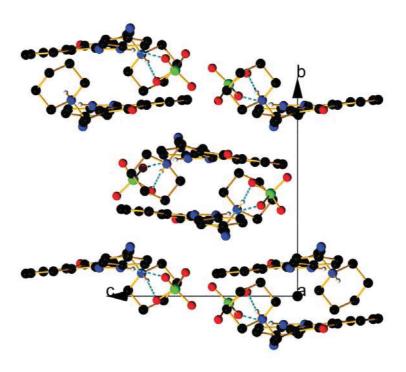


Figure S19. View of the packing along a axis in the keto form of compound 3 with perchloric acid.

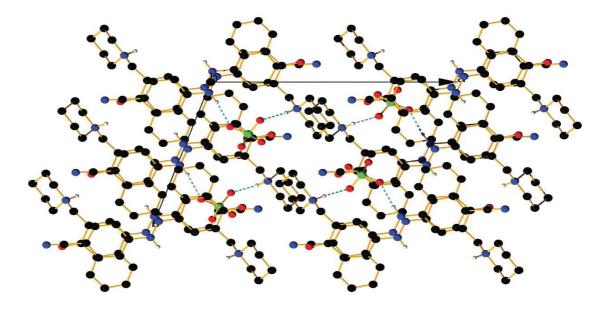


Figure S20. View of the packing along b axis in the keto form of compound 3 with perchloric acid.

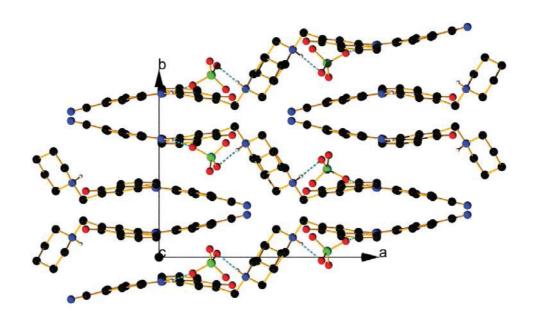


Figure S21. View of the packing along c axis in the keto form of compound 3 with perchloric acid.

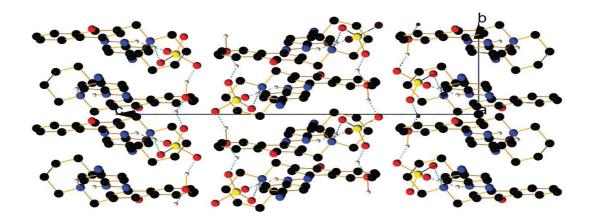


Figure S22. View of the packing along a axis in the keto form of compound 3 with sulfuric acid.

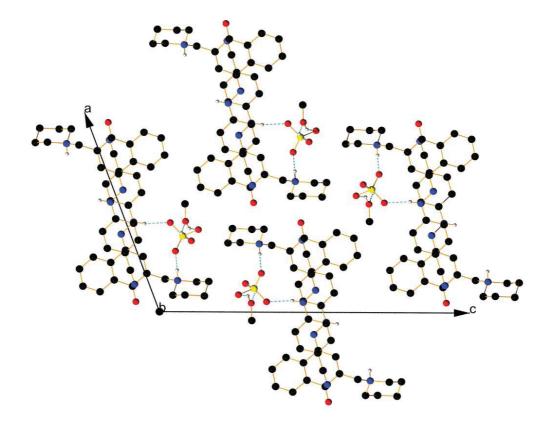


Figure S23. View of the packing along b axis in the keto form of compound 3 with sulfuric acid.

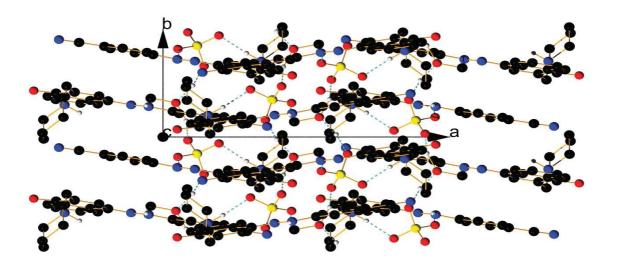


Figure S24. View of the packing along c axis in the keto form of compound 3 with sulfuric acid.

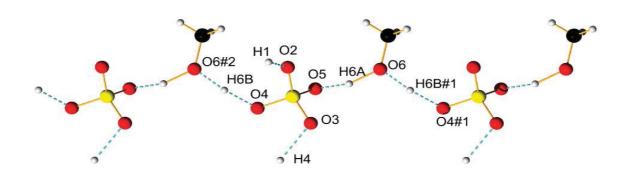


Figure S25. View of the counter anion chain in the packing of the keto form of compound **3** with sulfuric acid.

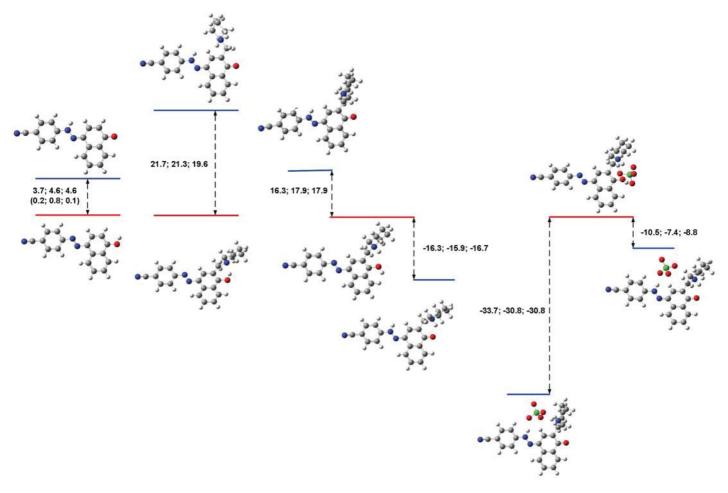


Figure S26. Change of the relative energy (M06-2X/def2TZVP) of the tautomers of the parent compound 1, 3,  $3H^+$  and  $3H^+ClO_4^-$ . The values of  $\Delta E$ ,  $\Delta E+ZPE$  and  $\Delta \Delta G$  are given in kJ/mol units.

Crystal data can be obtained on quoting the depository numbers CCDC- 928932 (3), 928933 (3H<sup>+</sup>ClO<sub>4</sub><sup>-</sup>), 928934 (3H<sup>+</sup>HSO<sub>4</sub><sup>-</sup>) (Fax: +44-1223-336-033; E-Mail:deposit@ccdc.cam.ac.uk).