Inter- and Intramolecular Interactions in Crystalline 2-Nitrobenzoic Acid – an Experimental and Theoretical QTAIM Analysis

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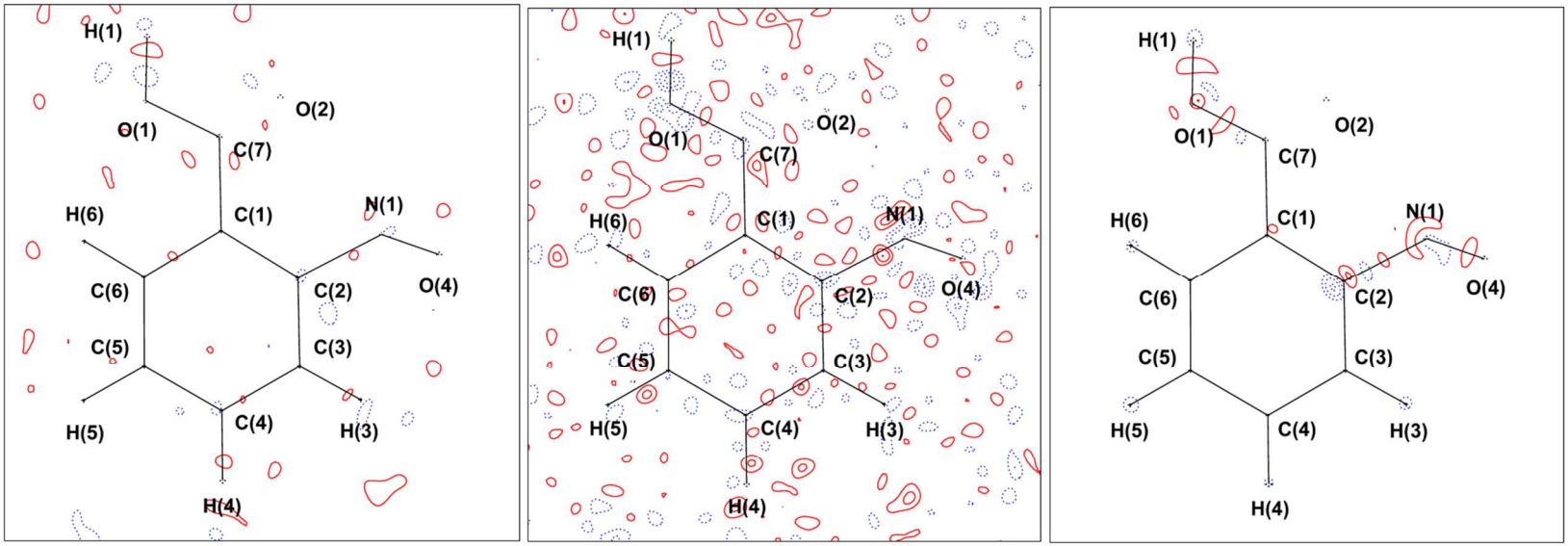
ABSTRACT

We have quantified the inter- and intramolecular interactions in crystalline 2-nitrobenzoic acid from QTAIM analysis of the topology of the electron density distribution obtained from both a low temperature (20K) X-ray diffraction experiment and from theoretical calculations. The covalent bonds have been characterized by the properties at their (3,-1) bond critical points; in particular the nature of the aromatic/nitro group C – N bond is discussed. All non-covalent bonds of the type O···H (both strong and weak), C···C, O···O, and O···C have also been characterized. Intermolecular interactions may be roughly divided into three types, the formation of a classical carboxylic acid hydrogen bonded dimer, an unusual ribbon of O···O interactions parallel to *a*, and a number of predominantly O···H interactions perpendicular to *a*. Integrated atomic charges (in particular for the acidic hydrogen, (~+0.6) and the derived molecular dipole moment are reported.



a) b) c)

Figure S1. a) Experimental residual density ($\sin\theta/\lambda_{max}$ = 1.0 Å^{-1}), b) experimental residual density (all data), c) theoretical residual density. Contour interval 0.05 eÅ^{-3}.

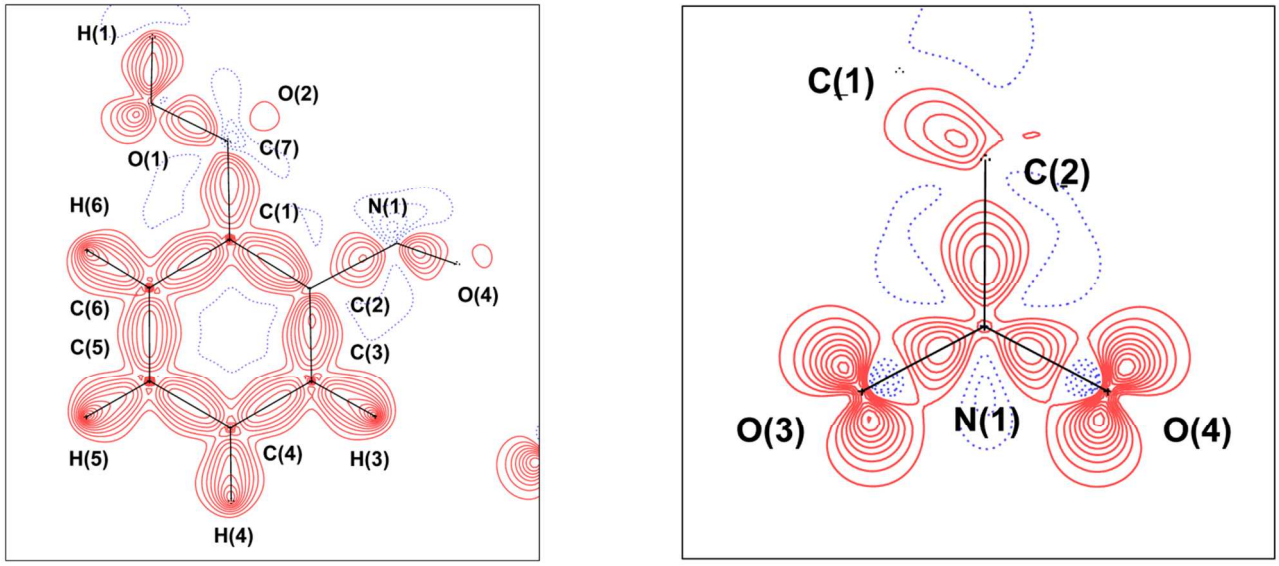


Figure S2. Experimental deformation density in the aromatic plane and in the plane of the nitro group. Contour interval 0.1 eÅ^{-3}.

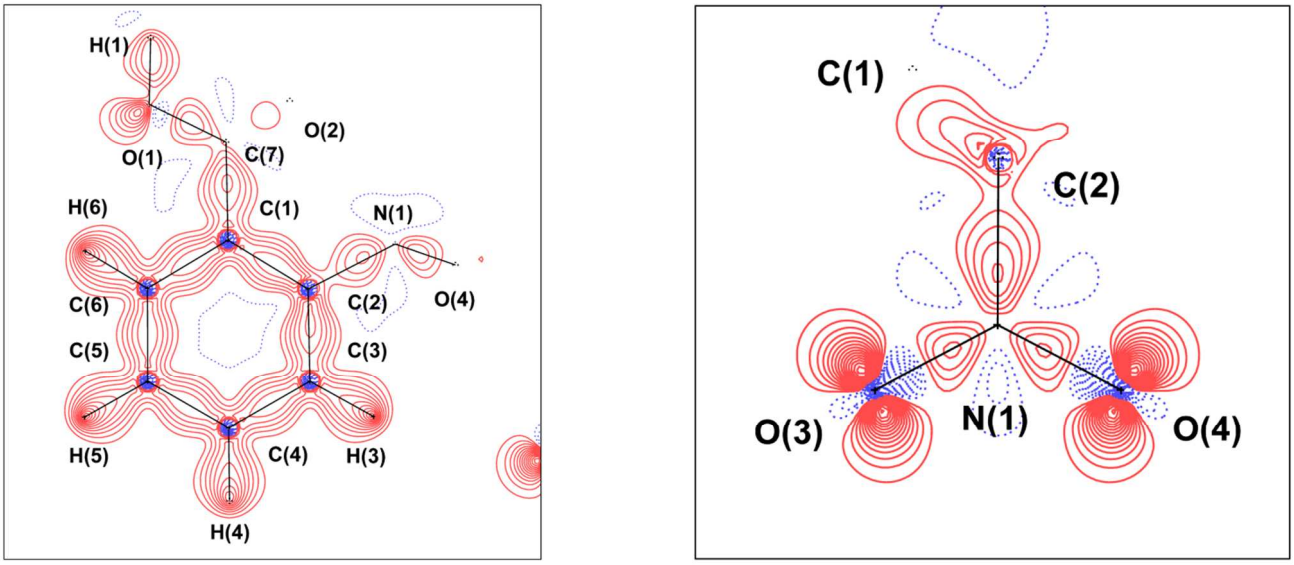


Figure S3. Deformation density from theoretical structure factors in the aromatic plane and in the plane of the nitro group. Contour interval 0.1 eÅ^{-3}.

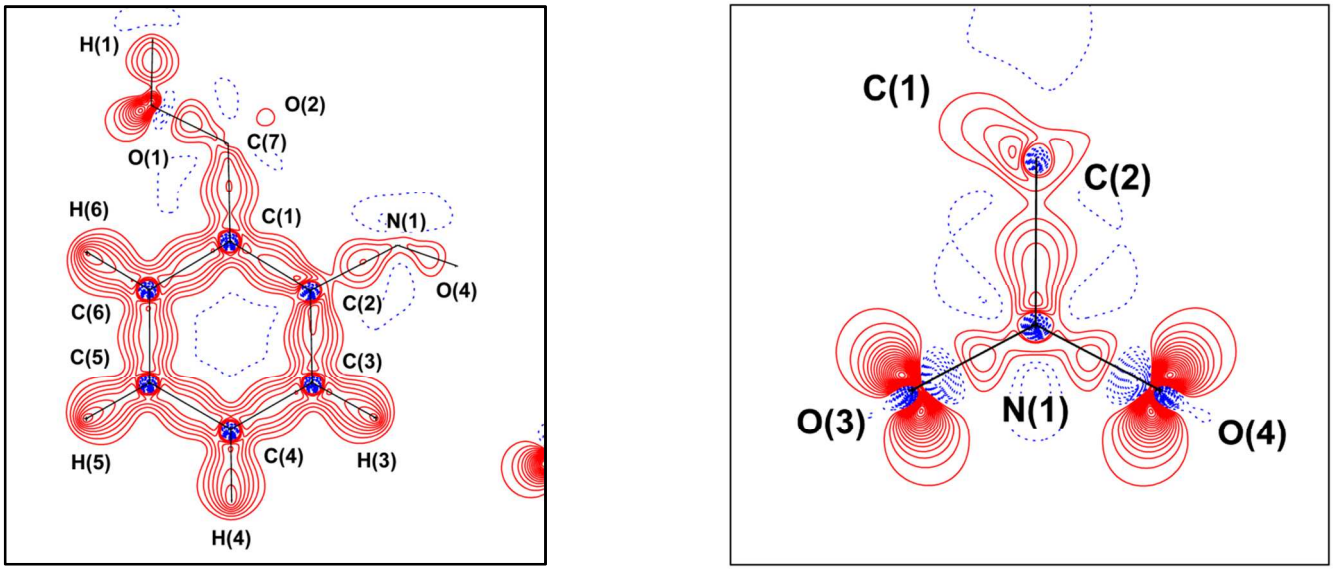


Figure S4. Theoretical deformation density in the aromatic plane and in the plane of the nitro group. Contour interval 0.1 eÅ^{-3}.

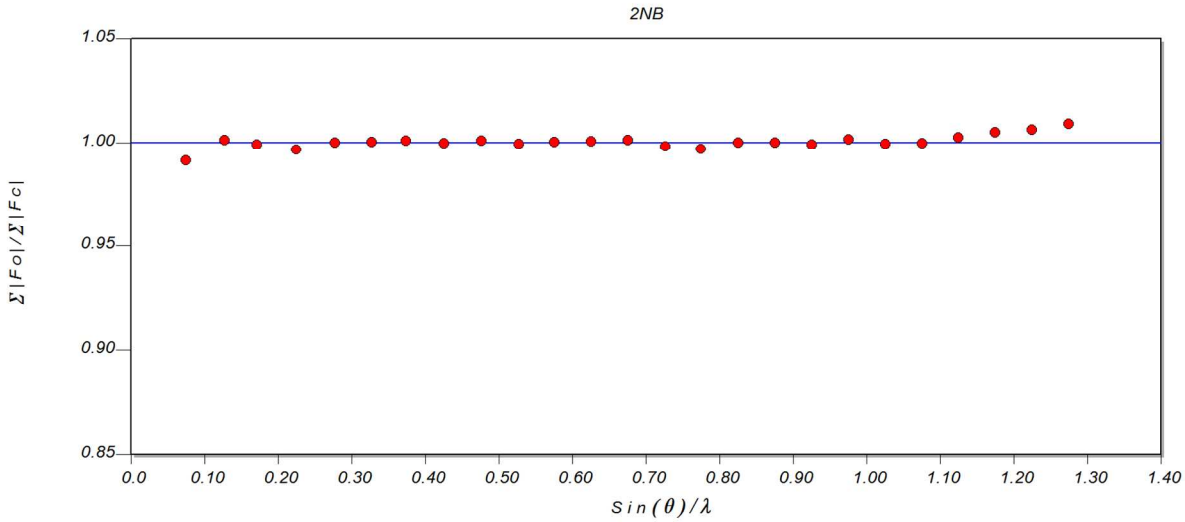


Figure S5. Experimental scale factor with respect to resolution.

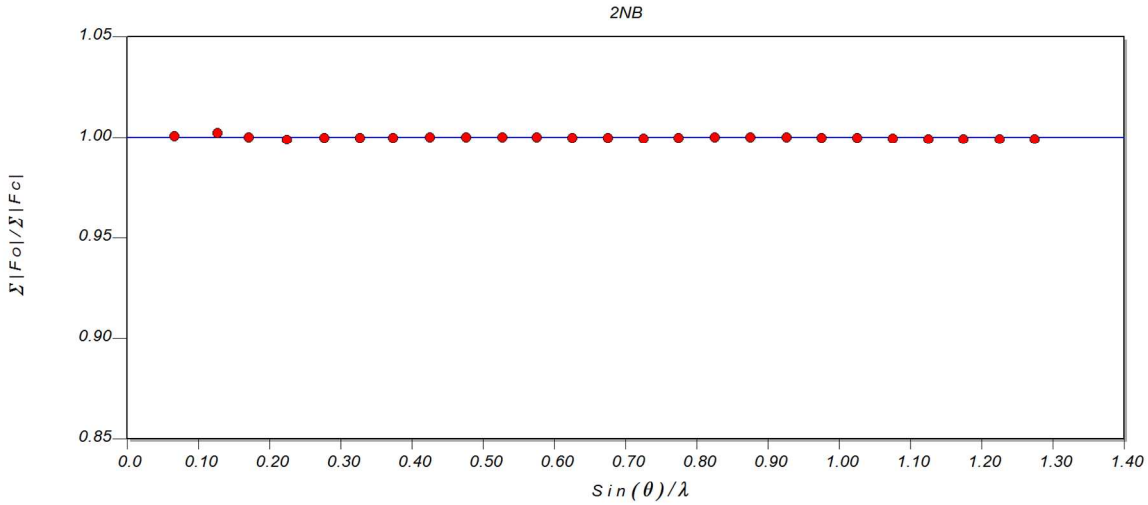


Figure S6. Theoretical scale factor with respect to resolution.

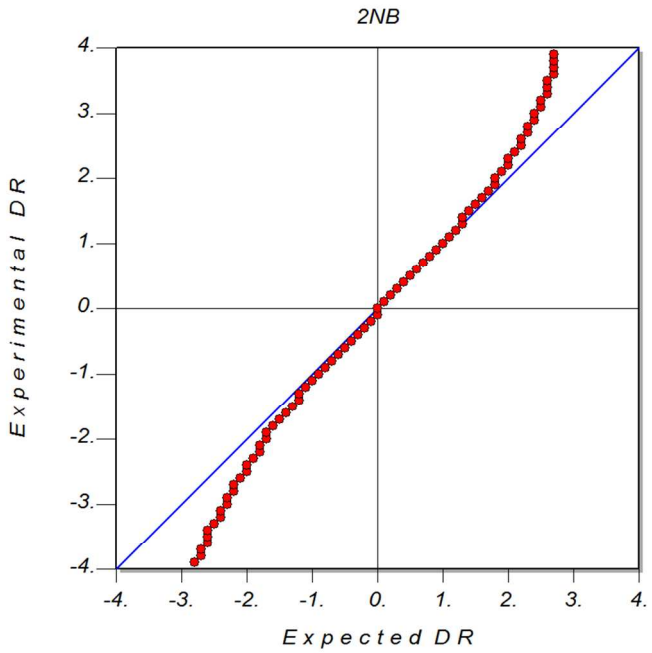


Figure S7. Normal probablity plot from experimental data.

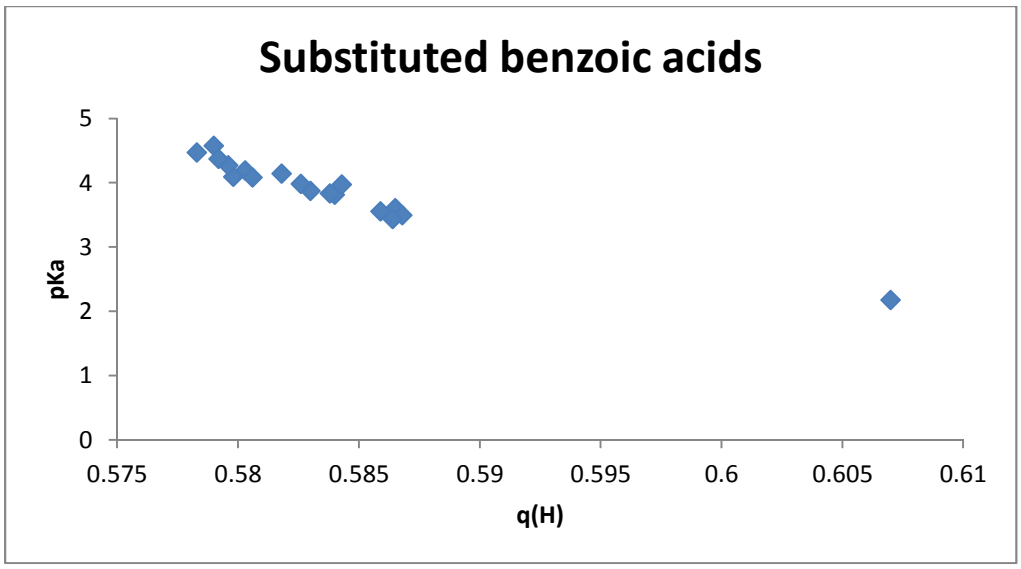


Figure S8. pKa vs q(H) from reference 70 and from TOPOND

Table S1. Comparison of ADPs for hydrogen atoms: 1st line – SHADE; 2nd line - refined

H1	0.020389	0.011901	0.022601	-0.005871	0.005463	-0.001478
	0.0213(7)					
H3	0.022185	0.021143	0.020954	-0.011175	0.012438	-0.007760
	0.0243(19)	0.0210(16)	0.0195(17)	-0.0103(15)	0.0134(10)	-0.0080(14)
H4	0.029688	0.011775	0.028492	-0.010717	0.009174	-0.005821
	0.0258(19)	0.0079(12)	0.0218(18)	-0.0051(15)	0.0014(14)	-0.0007(13)
H5	0.024040	0.014758	0.029241	-0.002841	0.010398	-0.012412
	0.0205(18)	0.0161(16)	0.0236(17)	-0.0025(11)	0.0074(13)	-0.0120(13)
H6	0.020268	0.020321	0.021783	-0.008693	0.012445	-0.007913
	0.0133(18)	0.0198(17)	0.0202(17)	-0.0042(13)	0.0096(10)	-0.0091(14)

Complete reference 29

Dovesi, R.; Saunders, V.R.; Roetti, C.; Orlando, T.; Zicovich-Wilson, C.M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N.M.; Bush, I.J.; D'Arco, Ph.; Llunell, M. *CRYSTAL09 User's Manual*, University of Torino, Torino, **2009.**