

Electronic supplementary information (ESI) for

Covalency of hydrogen bonds in solids revisited

Volker L. Deringer,^a Ulli Englert,^{a,*} and Richard Dronskowski^{a,b,*}

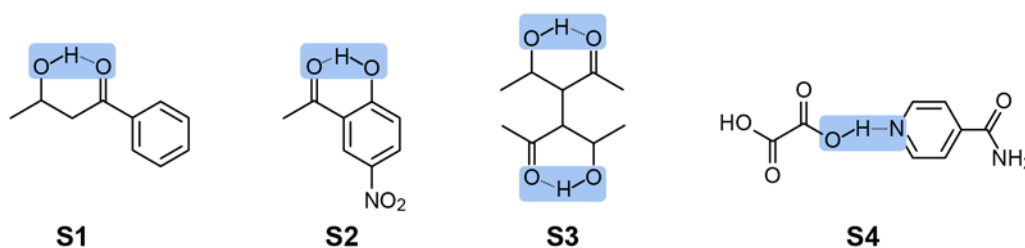
^aInstitute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany, and ^bJülich–Aachen Research Alliance (JARA-HPC), RWTH Aachen University, 52056 Aachen, Germany.

*E-mail: ullrich.englert@ac.rwth-aachen.de; drons@HAL9000.ac.rwth-aachen.de.

Overview of systems and HB contacts studied

Initial studies were performed on *N,N*-dimethylbiguanidinium bis(hydrogensquarate) (Ref. 11 in the main text) which offers itself as a fitting example because the *entire* dataset of atomic contacts and charge-density values can be derived from a single experiment.

In a next step, we searched the Cambridge Structural Database (version 5.35, 658007 entries) for additional structures with a focus on short hydrogen-bonded contacts investigated by neutron diffraction. The articles were then manually inspected as to the presence of *charge-density* analyses. Some contributions had to be excluded, *e.g.*, because they contained no reliable data. Finally, we arrived at four compounds which are shown below:



Scheme S1: Schematic structural drawings of the additional molecular systems whose crystal structures are studied here. The respective shortest O–H···acceptor contacts have been indicated by shading. The boldface labels correspond to the references in this ESI document.

Table S1: Overview of experimental parameters. In some cases, several datasets are available in the cited studies, and we refer here to the respective lowest-temperature experiment.

| Ref. | Compound | CSD refcode | Structure determination | X-ray/Charge density |
|-----------|---|-------------|-------------------------|--------------------------|
| S1 | benzoylacetone | BZOYAC03 | Neutrons, 20(1) K | Ag K α , 8.4(4) K |
| S2 | 1-(2-hydroxy-5-nitrophenyl)ethanone | GADBAP | Neutrons, 100(2) K | Mo K α , 100(2) K |
| S3 | tetraacetyethane | TACETA | Neutron-TOF, 20(1) K | Mo K α , 20(2) K |
| S4 | isonicotinamide···oxalic acid complex (2:1) | ULAWAF | Neutron-TOF, 100(2) K | Mo K α , 100(2) K |

Table S2: List of intermolecular contacts from the above-cited works. In some of the latter, longer C–H···O bonds are given, too, but these have been excluded here because their ρ_{bcp} and ICOHP values are close to zero. Standard deviations are taken from the experimental reports, where available.

| Ref. | Type | $d(\text{H}\cdots\text{A})$ (expt.; Å) | $d(\text{H}\cdots\text{A})$ (relaxed; Å) | ρ_{bcp} , (expt.; e Å ⁻³) | –ICOHP (eV) |
|-----------|---------|---|---|--|----------------|
| S1 | O–H···O | 1.329(11) | 1.494 | 0.76(3) | 1.476 |
| S2 | O–H···O | 1.648(2) | 1.643 | 0.32(5) | 0.865 |
| | C–H···O | 2.184(1) | 2.190 | 0.04(1) | 0.114 |
| S3 | O–H···O | 1.416(2) | 1.425 | 0.681 | 1.637 |
| | C–H···O | 2.293(2) | 2.282 | 0.062 | 0.084 |
| S4 | O–H···N | 1.398(3) | 1.419 | 0.77 | 1.570 |
| | N–H···O | 1.894(2) | 1.888 | 0.16 | 0.526 |
| | N–H···O | 1.997(3) | 1.988 | 0.13 | 0.237 |

Table S3: As Table S2, but for intermolecular contacts in *N,N*-dimethylbiguanidinium bis(hydrogensquarate) **1** (Ref. 11 in the main text).

| Type | $d(\text{H}\cdots\text{A})$ (expt.; Å) | $d(\text{H}\cdots\text{A})$ (relaxed; Å) | ρ_{bcp} , (expt.; e Å ⁻³) | –ICOHP (eV) |
|--|---|---|--|----------------|
| O–H···O | 1.421(4) | 1.410 | 0.64(2) | 1.498 |
| | 1.569(4) | 1.559 | 0.37(2) | 1.138 |
| ^{imine} N–H···O | 1.779(4) | 1.764 | 0.24(2) | 0.679 |
| ^{amine} N–H···O | 1.788(4) | 1.773 | 0.23(2) | 0.609 |
| | 1.849(4) | 1.824 | 0.23(2) | 0.619 |
| | 1.893(4) | 1.884 | 0.18(2) | 0.392 |
| | 1.838(4) | 1.826 | 0.18(2) | 0.564 |
| | 1.900(4) | 1.881 | 0.17(2) | 0.474 |
| | 2.068(5) | 2.047 | 0.090(9) | 0.352 |
| C–H···O | 2.265(7) | 2.236 | 0.072(4) | 0.105 |
| | 2.531(6) | 2.507 | 0.027(3) | 0.018 |
| Additional C–H···O contacts in 1 with $d < 2.75$ Å | | 2.375 | <i>not determined</i> | 0.026 |
| | | 2.661 | <i>not determined</i> | 0.020 |
| | | 2.745 | <i>not determined</i> | 0.015 |

Computational details

Computations were performed using density-functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP). “Hard” projector augmented wave (PAW) potentials (C_h, H_h *etc.*) were employed together with a high cutoff energy of 800 eV, exceeding the VASP authors’ recommendation for “accurate” settings in all cases. Exchange and correlation were modelled using the generalised gradient approximation (GGA) after Perdew, Burke, and Ernzerhof. The theoretical computations followed a three-step procedure:

1. First, an initial structural relaxation of the H atoms’ positions was performed whereas the lattice vectors and positions of the heavier atoms were kept locked. A test computation for **1** with full structural optimisation was performed, too, but led to no significant changes in interpretation (see Fig. S1 below).
2. Next, a single-point computation was performed from scratch on the thus optimised structure, in which the **k** mesh was increased from $2\times 2\times 2$ to $4\times 4\times 4$ for **1**.
3. Finally, the plane-wave/PAW coefficients from VASP were projected onto a minimal local basis of Slater type orbitals, in which then chemical-bonding analysis was carried out; all these steps were performed using the LOBSTER code, as described in detail in the original literature (Ref. 17b in the main text).

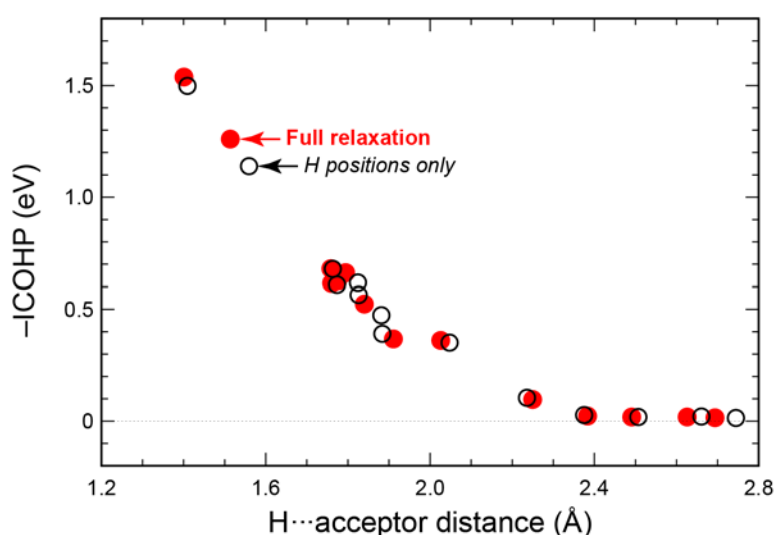


Fig. S1: Plot akin to Fig. 2 in the main text, but comparing the effect of full vs. “selective” structural optimisation. The full optimisation (red circles) included Grimme dispersion corrections (Ref. S5) in the implementation of Bučko et al. (Ref. S6) and leads to appreciable, qualitatively superimposable results.

And with overlap populations (pCOOPs)?

Finally, we are interested in whether the crystal orbital overlap population indicator (Ref. S7) can likewise capture the chemical-bonding information as presented in the Communication. It can, indeed, and the results are shown below.

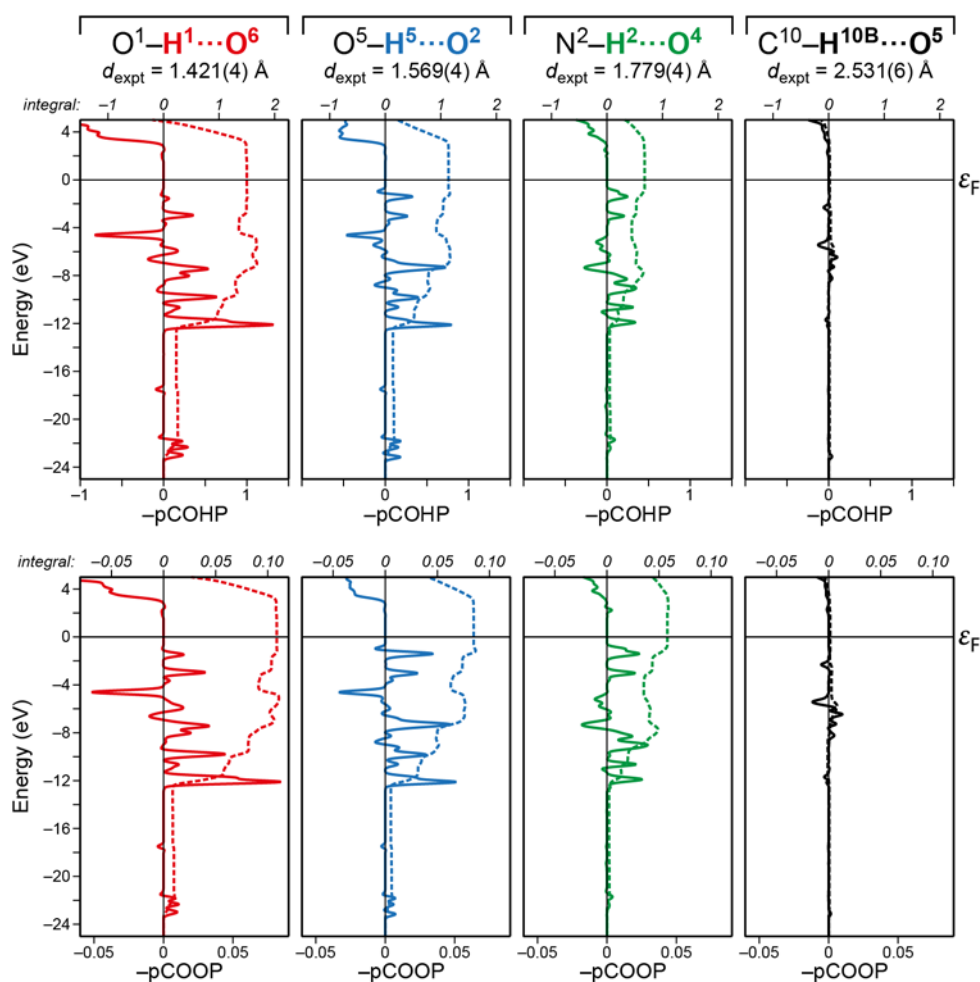


Fig. S2: Comparison of four representative types of contacts in the crystal structure of **1**. The first two panels correspond to Fig. 1b in the main text but here contain the entire range of electronic states. In the *top* row pCOHPs are shown, and in the *bottom* row the corresponding pCOOPs. Dashed lines denote the integrated values (in eV and electrons, respectively), for which axes are given at the top of each panel. Aside from trivial differences in *absolute* values, the shape of pCOHP and pCOOP curves are strikingly similar; this holds true for the entire range from strong covalent (*left*) to clearly noncovalent (*right*) bonds.

Supplementary references

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- S6 T. Bučko, J. Hafner, S. Lebègue and J. G. Ángyán, *J. Phys. Chem. A*, 2010, **114**, 11814–11824.
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