
Crystalline packings of diketoarylhydrazones controlled by a methyl for trifluoromethyl structural change

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Supporting Information

DFT calculations

Since the molecule under investigation contains an iodine atom, the quantum chemical description of the system is not trivial. Heavy elements like iodine have a large number of core electrons which are in general less important for the chemical reactivity and bonding modes. However, it needs a large number of basis functions to describe the corresponding orbitals. This makes computations with heavy elements very time consuming and expensive. Furthermore, relativistic effects should be taken into account for elements of the lower half of the periodic table. These two problems may be solved by using effective core potentials (ECP) which represent all core electrons.^{1, 2} This means the core electrons are modelled by a suitable function and only the valence electrons or the two outermost electron shells are treated explicitly. There are numerous computational studies involving iodine compounds in the literature containing recommendations for the treatment of such systems.³⁻⁷ Test calculations have been performed in order to reproduce the solid state geometry of **2** as good as possible. All calculations have been done at the density functional theory level (DFT), using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP).^{8, 9} The compilation of all tests is shown in Table S1 and Fig. S2.

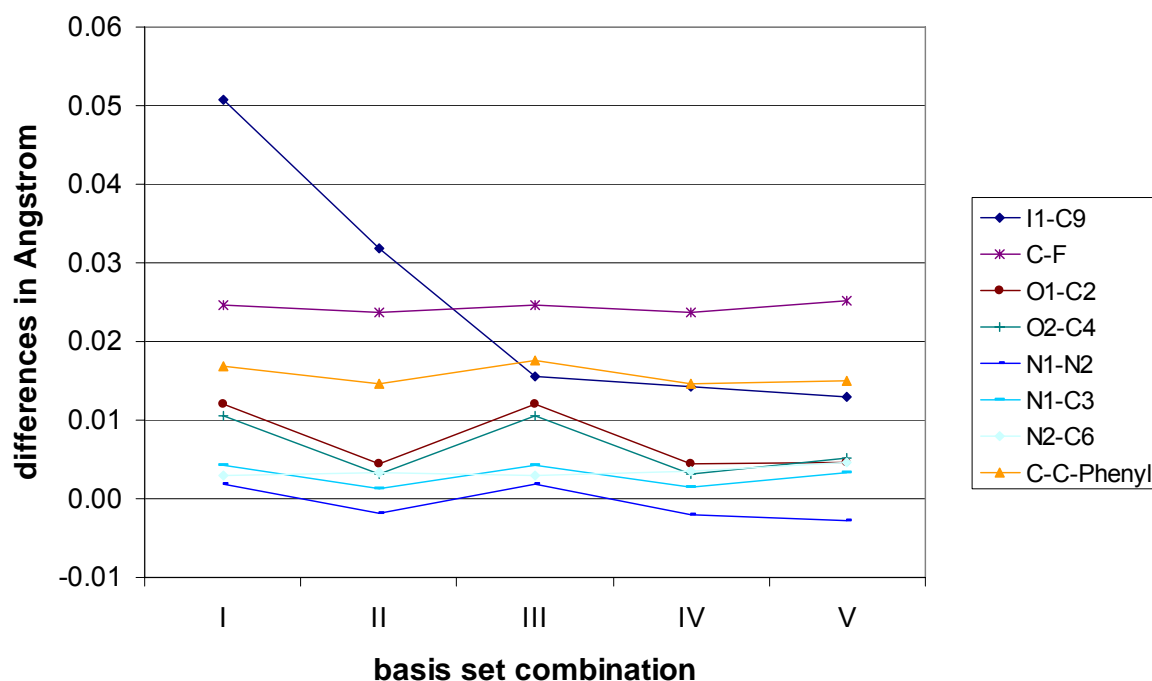
The all electron basis set 6-311G(d,p)¹⁰ and two different effective core potentials plus suitable basis sets were used at iodine. The largest deviation of the C-I bond length from the value of the solid state structure was observed with the small core Stuttgart-Dresden-pseudopotential basis set (**I**).¹¹ Better agreement was achieved with the all electron basis set (**II**) and best performance with the ECP / basis set combination SDB-cc-pVTZ at iodine (**III-V**). SDB-cc-pVTZ consists of the small core Stuttgart-Dresden-Bonn effective core potential which is augmented with a correlation consistent triple zeta valence basis set according to Martin and Sundermann.^{12, 13}

The elements C, N, O, H and F have been described with the standard Pople basis sets 6-31G(d,p),^{14, 15} 6-311G(d,p),¹⁶ and 6-311+G(d,p).^{16, 17} Going from double zeta quality for the valence shell (**III**) to triple zeta quality (**IV**) gives more accurate values for the bond lengths. Further computational effort by using triple zeta quality valence shell plus diffuse functions (**V**) does not pay off. The bond lengths do not get closer to the values of the X-ray structure, instead the CPU- time is increased more than ten fold! According to these test calculations we have decided to use the basis set combination **IV** for further calculations.

Tab. S1: Comparison of bond lengths between X-ray structure and calculated geometries of compound **2** with the basis set combinations **I** to **V** (all calculations with the B3LYP method; values of bond lengths in Å)

	I	II	III	IV	V	2
main group elements	6-31G(d,p)	6-311G(d,p)	6-31G(d,p)	6-311G(d,p)	6-311+G(d,p)	-
iodine	SDD	6-311G(d,p)	SDB-cc-pVTZ	SDB-cc-pVTZ	SDB-cc-pVTZ	-
I1-C9	2.1478	2.1288	2.1126	2.1113	2.1099	2.097
F1-C1	1.349	1.3486	1.349	1.3486	1.3504	1.318
F2-C1	1.3366	1.3351	1.3366	1.3351	1.3359	1.326
F3-C1	1.3491	1.3486	1.3491	1.3486	1.3504	1.317
C-F	1.345	1.344	1.345	1.344	1.346	1.320
O1-C2	1.2181	1.2105	1.2181	1.2105	1.2106	1.206
O2-C4	1.2406	1.2331	1.2406	1.2332	1.2351	1.230
N1-N2	1.2948	1.2911	1.2949	1.2909	1.2902	1.293
N1-C3	1.3282	1.3253	1.3282	1.3255	1.3274	1.324
N2-C6	1.407	1.4074	1.4069	1.4075	1.4086	1.404
C-C-Phenyl	1.396	1.394	1.397	1.394	1.394	1.379

Fig. S1: Graphical representation of the differences between optimized geometries and geometry from the X-ray structure analysis of **2**.



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