Experimental report

12/06/2017

Proposal:	**5-12-321**	**Council:**	4/2016

Title: Exact determination of hydrogen positions in tris(3,5-di-tert-butyl phenyl)methane could reveal the shortest intermolecular CH...HC contact

Research area: Chemistry

This proposal is a new proposal

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Samples: tris(3,5-di-tert-butyl phenyl)methane

Instrument	Requested days	Allocated days	From	To
D19	6	4	08/11/2016	15/11/2016

Abstract:

Very short non-bonded CH...HC contacts thus far have only been found within cyclic molecules. The claimed record holder has an R(H...H) of 1.58 Å estimated from computations on an X-ray diffraction (XRD) structure. In the XRD structure of tris(3,5-di-tert-butylphenyl)methane a very short intramolecular CH...HC contact of 1.85 Å was found, which gives an estimated real R(H...H) of 1.55 Å, potentially a new record, if this distance can be confirmed by accurate determination of the hydrogen position through neutron diffraction. This would also underscore the very strong London dispersion forces within this arrangement and supports our research to quantify dispersion interactions in molecular structures.

London Dispersion Enables the Shortest Intermolecular Hydrocarbon H•••H Contact

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Introduction:

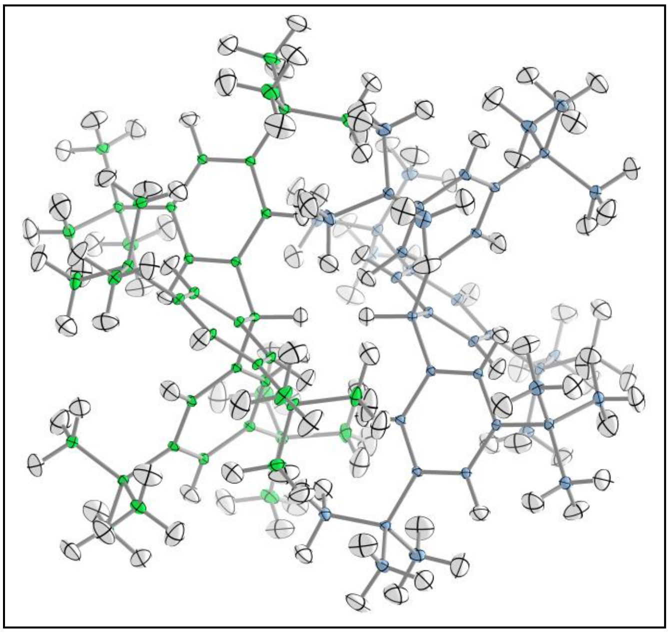
Intermolecular interactions are described by Morse potentials and feature a steep raise in energy for closed shells interaction, namely Pauli repulsion. While rather steep at the repulsive end, there is space for contacts closer than the sum of the vdW-radii. The shortest published record holder for H···H contacts determined indirectly from an X-ray crystal structure (XRD) in conjunction with density functional theory (DFT) computations a Si–H···H–Si distance of ~1.57 Å, underscoring the former record[1] by –0.05 Å and the sum of the vdW-radii by –35%.[2]

We found the hydrocarbon tri(3,5-di-*tert*-butylphenyl)methane **1** to crystallize as a dimer in an unusual head-to-head fashion $\mathbf{1}_2$ as determined by X-ray diffraction with a C−H···H−C distance of 1.77(7) Å. To precisely determine the hydrogen positions, a Neutron diffraction (NRD) experiment at the institute Laue-Langevin in Grenoble was performed.[3]

Experimental details:

Several large crystals (ca. 8–64 mm^3) of **1** were grown by isothermal evaporation of saturated solutions. While in all cases large crystals were gained suffered crystals grown from evaporation of Et_2O from surface defects originating from depleted inclusions towards the vessel walls or solvent levels below the crystal size. A solvent mixture of 3:1 Et_2O/EtOH ensured a coverage of the crystals at all time and reduced the mentioned surface defects. Two different crystals were mounted to onto the displex system on the monochromatic neutron thermal diffractometer at Beamline D19. A wavelength of 1.1708 Å was used and reflection intensities were collected by using 0.07° omega scan steps.[4] ILL program Multi Detector Acquisition Software was applied for data collection. DIRAX (unit cell determination), RETREAT and RAFD19 (processing of the data and refinement of the unit cell) were used for unit cell determination and processing of the raw data[5] and ILL program D19abs for absorption correction.[6] SHELXT[7] and full matrix least squares refinement on $|F^2|$ using SHELXL-2016/6[8] as implemented in the Olex2- program[9] was used for structure solvation and refinement.

While both were single crystals, one showed significant larger diffraction angles. The more suitable single crystal (32 mm^3) was first cooled to 100 K and could be solved in the space group *Pa*-3. A subsequent measurement at 20 K revealed a different space group, $P2_13$ (see figure on the right). Finally data collection at 200 K again was most likely solved in *Pa*-3. In every case, all atoms were refined with anisotropic displacement parameters. While at 20 K all the atoms showed reasonable thermal ellipsoids revealed the measurements at 100 K and 200 K enlarged thermal ellipsoids for one of the *tert*-butyl group. Weather lowering the symmetry to $P2_13$ nor the application of a disordering model reduced the enlarged thermal ellipsoids. While the overall R-value could be reduced by increasingly hard restrains upon refinement, no chemically reasonable structure was obtained. Therefore seemed the initial model the best. The structures were placed in the CCDC with the numbers 1529953 (20 K), 1529951 (100 K) and 1529952 (200 K).



Subsequent publication:

As these measurements revealed a very short H···H contact of 1.566(5) Å – the shortest experimental H···H contact determined to date – we decided to investigate its origin and published our results in the Journal of the American Chemical Society.[10] In summary is the remarkable short H···H contact of 1.567(1) Å the first example of such close intermolecular contacts and is enabled by the surrounding ^{t}Bu groups acting as "dispersion energy donors".[11]

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