TOPOLOGICAL ANALYSIS OF ELECTRON DENSITIES GIVEN ON REGULAR 3D GRIDS

P. Rabiller[1] C. Katan[1] M. Souhassou[2] C. Lecomte[2] M. Guezo[1,3] V. Oison[1,4]
[1]groupe Matiere Condensee Et Materiaux Umr-Cnrs 6626 Universite Rennes 1 Campus De Baulieu Rennes 35042 France [2]lcm3b Umr-Cnrs-7036, Universite H. Poincare - Nancy 1, Bp239, 54506 Vandoeuvre Les Nancy, France [3]lps Insa Rennes, 20 Av. Buttes De Coesmes, 35043 Rennes, France [4]cea/Saclay Dmn/Srmp, Bat.52, 09191 Gif-Sur-Yvette, France

Results of topological analysis following Bader's approach of Atoms in Molecules and performed on electron densities given on regular 3D grids obtained from either experimental X-ray data or theoretical calculations will be presented. The software package uses tricubic interpolation to get the electron density, its gradient and Hessian matrix at any required position. It is not only found reliable but mostly contributes to short computing times for both critical point (CP) search and integration of atomic properties. Compounds such that NaCl and TTF-2,5Cl$_2$BQ have been studied. The survey will thus span over the different kinds of chemical bonds: ionic, covalent, hydrogen bonds, intermolecular contacts. Grid spacing of about 0.1 a.u. is in most cases sufficient to get converged results for both CP and integrated properties. Only very short covalent bonds (e.g. C=O) need fine grid spacing and very accurate input data. Treating the valence density apart from the total density enables one to calculate accurately atomic charges and volumes by integration over atomic basins. For example, the charge transfer in the molecular charge transfer crystal TTF-2,5Cl$_2$BQ, which is close to 0.5 electron (out of 192 electrons in the unit cell containing 26 atoms) is obtained within 0.02 electron precision in a few minutes per atom.

Keywords: ELECTRON DENSITY, CRITICAL POINTS, ATOMIC CHARGES

TOPOLOGICAL ANALYSIS OF 2,4,6,8-TETRAPHENYLBARBARALANE BASED ON A SYNCHROTRON/CCD AREA DETECTOR EXPERIMENT AT 110 K

S. Scheins[1] B. Dittrich[1] C. Paulmann[2] H. Quast[3] P. Luger[1]
[1]Freie Universitaet Berlin Institute of Chemistry / Crystallography Takustr.6 BERLIN 14195 GERMANY [2]Mineralogisch-Petrographisches Institut, Universitaet Hamburg, Grindelallee 48, D-20146, Hamburg, Germany [3]Institut fuer Organische Chemie der Universitaet Wuerzburg, Am Hubland, D-97074, Wuerzburg, Germany

Like bullvalene and semibullvalene barbaralane belongs to the class of cage compounds, which undergoes degenerate Cope rearrangement. To investigate the different C-C bond types the experimental charge density of 2,4,6,8-Tetraphenylbarbaralane was determined, based on a high-resolution synchrotron/charge coupled device (CCD) dataset at 110 K. The dataset was analyzed using the aspherical atom multipol formalism according to the method of Hansen and Coppens [1]. A topological analyses of the charge density, according to Bader`s AIM-theory [2], was performed. This topological analysis allows the derivation of electronic properties like the charge density (ρ), its second derivative (Δρ) and the ellipticity (ε) at the bond critical points of the different C-C bond types. The topological properties of the experimental charge distribution are compared to those obtained by theoretical methods from HF/6-311++G(d,p) and B3LYP/6-311G++G(d,p) calculations. All critical points of the electron density at the covalent bonds, as well as the ring and cage critical points, were located, confirming that the electron density is also given correctly far away from the atomic centers. The different C-C bond typs in the title compound were compared to related molecules like bullvalene and semibullvalene. This comparison gives a good agreement of the electronic properties of bonds in the same chemical environment.

References
[1] N. K. Hansen, P. Coppens, Acta Cryst. A34, 909 (1978)
[2] R. F. W. Bader, Atoms in Molecules : A Quantum Theory, Oxford University Press Inc., New York, 2nd ed., 1994

Keywords: TOPOLOGICAL ANALYSIS, CHARGE DENSITY, BARBARALANE

ELECTRON DELOCALIZATION IN LITHIUM ALKYLS: NEGATIVE HYPERCONJUGATION AND AGOSTIC BONDING

P. Sirsch[1] W. Scherer[1] M. Gardiner[2] S. A. Mason[3] G. S. McGrady[4]
[1]Technische Universitaet Muenchen Anorganisch-Chemisches Institut Lichtenbergstr. 4 GARCHING B. MUENCHEN D-85747 GERMANY [2]School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart TAS 7001 (Australia) [3]Institut Laue-Langevin, BP156, 38042 Grenoble cedex 9 (France) [4]Department of Chemistry, King's College London, Strand, WC2R 2LS (UK)

Alkyllithium complexes are of central importance in both organic and organometallic synthesis, and their structures display a remarkable range of bonding modes, which have challenged established chemical bonding theories since their discovery. In the compound [{2-(Me$_3$Si)$_2$CLiC$_5$H$_4$N}$_2$] 1 featuring a formal lithium coordination number of only 2, secondary interactions including so-called Li...H-C 'agostic' interactions are crucial in understanding not just the structure, but also the reactivity of the species. Agostic interactions are ubiquitous in organotransition-metal chemistry, and have central relevance to important processes like C-H activation and Ziegler-Natta catalysis. The neutron structure of 1 obtained at 20 K displays short Li...H-C(γ) contacts of 2.320(6) Å accompanied by a remarkably acute Li-C(α)-Si(β) angle of 88.8(2)°; however, no significant C-H activation is evident. The origin of this unusual deformation of the alkyl group is revealed by a topological analysis of the experimental and theoretical charge density, using the 'Atoms in Molecules' method of Bader: The distortion of the Li-C(α)-Si(β)-C(γ)-H moiety is thus shown to arise from negative hyperconjugation, with delocalization of the Li-C(α) bonding electrons over the entire alkyl fragment, depletion of the metal-directed charge concentrations at C(α), and characteristic ellipticity profiles for the bonds involved in this hyperconjugative delocalization. Close Li...H-C contacts are a consequence rather than a cause of this delocalization and further secondary interactions, with Li...H-C agostic interactions playing only a minor role in stabilizing the structure.

Keywords: CHARGE DENSITY ANALYSIS NEGATIVE HYPERCONJUGATION AGOSTIC INTERACTIONS

CHARGE DENSITY OF A FULLERENE DERIVATIVE BASED ON A HIGH RESOLUTION SYNCHROTRON RADIATION EXPERIMENT

A. Wagner[1] R. Flaig[1] D. Zobel[1] B. Dittrich[1] H. G. Krane[2] T. Koritsanszky[3] P. Luger[1]
[1]FU Berlin Institut Für Chemie - Kristallographie Takustr. 6 BERLIN 14195 GERMANY [2]Institut für MIneralogie und Petrologie, Universität Bonn, Germany [3]Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

The experimental charge density of a highly substituted fullerene derivative, the T_h-symmetrical dodekakis-ethoxycarbonyl-C$_{60}$-fullerene cocrystallized with difluorobenzene, was determined based on a high-resolution single crystal synchrotron/CCD data set of more than 300 000 reflections. A full topological analysis according to Bader's AIM theory was performed. Experimental bond critical point (BCP) properties obtained by three multipole models were compared to each other and to those derived by theoretical methods from HF/6-31G** and B3LYP/6-31G** calculations. ρ(r_BCP) vs bond distance relationships were investigated for the different experimental and theoretical models. Based on the linear fits obtained for the experimental model densities, ρ(r_BCP) values of further C-C bonds can be predicted. Due to the substitution this C$_{60}$ derivative has 6 chemically different C-C bonds. A statistical analysis of the BCP properties for these bonds was executed to give information about the reproducibility of the different topological descriptors. The results support earlier observations that among theses descriptors ρ(r_BCP) is the most, whereas λ3, the curvature in bond direction, is the least reproducible quantity.

Keywords: FULLERENE CHARGE DENSITY SYNCHROTRON