

# X-RAY DIFFRACTION, ELECTRON DENSITIES AND CHEMICAL BONDING

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**ABSTRACT**— The «Chemical Deformation Density» (CDD) is defined as the minimal electron density difference between the molecule or crystal, and the optimally and uniquely positioned and oriented ground state atoms. The CDD offers a coherent picture of bond and lone pair deformations. Fluorine, oxygen, and nitrogen compounds do no longer exhibit exceptional features. Even carbon ground states may be strongly quadrupolar at asymmetric sites. Intermolecular interactions may strongly influence the conventional difference densities by changing the orientations of the atomic quadrupoles without changing the genuine CDD significantly.

## 1 — INTRODUCTION

Molecular electron densities are often examined in the form of difference densities (DDs) [1]. Conventionally they are defined with respect to the superimposed densities of the *spherically averaged* atoms. These DDs are denoted here as «Total Difference Densities» (TDDs). They are particularly useful for the discussion of the electrostatic fields created by the molecules in the space around them. However, only atoms with spatially nondegenerate ground states are of necessity spherical. Most atoms with open p and d shells are not, and consequently their TDDs are often dominated by *quadrupolar* density distributions [2], which

are the result of the *orientation of the undeformed atoms*. These orientational effects can be quite large and hide the genuine *atomic deformations* [3], which are associated with bond formation. Because of this superposition of atomic orientation as well as chemical deformation effects, it is intrinsically quite difficult to interpret TDDs and to compare them for different systems. Therefore, we shall *not* use the term «deformation densities» for them.

As a more appropriate quantity for the elucidation of the nature of chemical bonds, the «Chemical Deformation Density» (CDD) is defined here with respect to the reference density of a promolecule whose *unperturbed* atoms, in addition to

being positioned at their correct places in the molecule, also have their multipoles appropriately oriented [4]. The orientation is accomplished by choosing the atomic reference densities so as to minimize the norm of the DD. The approach has been applied to theoretical densities of a series of small molecules [5] in section 2, and to experimental X-ray scattering data of a series of organic molecular crystals [6], see section 3.

## 2 — THEORETICAL DENSITIES OF HF AND CH<sub>2</sub>

The TDD of the HF molecule (Fig. 1a) is dominated by a strong quadrupolar distribution around the F nucleus. It shows that the <sup>2</sup>P ground state of the F atom in HF should not be spherically averaged to  $(1/3 \ ^2P_x + 1/3 \ ^2P_y + 1/3 \ ^2P_z)$ . Instead, the referred to orientation procedure yields the non-spherical average  $(0.21 \ ^2P_x + 0.21 \ ^2P_y + 0.58 \ ^2P_z)$ , corresponding to the orbital population  $p_x^{1.79} p_y^{1.79} p_z^{1.42}$  as most appropriate for the CDD construction. It indicates a superposition of about 0.4 oriented F (<sup>2</sup>P<sub>z</sub>) and 0.6 spherical F, corresponding to a mixture of covalent Fp<sub>σ</sub>—Hs and ionic F<sup>-</sup>—H<sup>+</sup> bonding, respectively. The Mulliken charge of -0.53 on F is in reasonable agreement with this.

The CDD of HF in Fig. 1b shows three characteristic features:

1. the electron charge deficit «behind» the proton indicates the positive partial charge attributable to H in HF;

2. the «bond charge» with maximum CDD value of 0.6 e/Å<sup>3</sup> is typical for σ-covalencies;

3. the dipolar density shift around the F nucleus describes the lone pair formation on F.

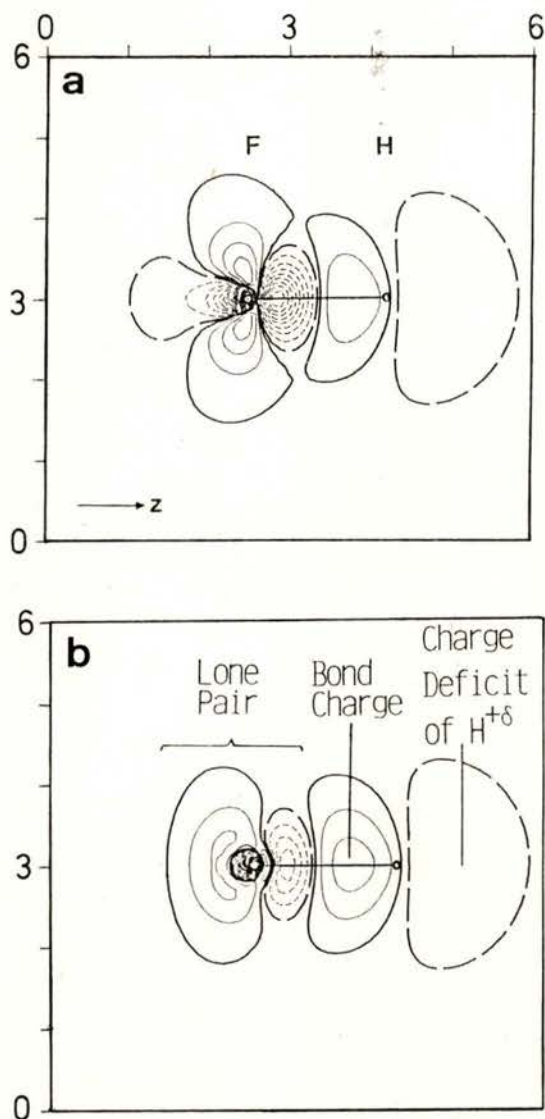


Fig. 1 — SCF difference density maps of HF [5]. a) TDD, molecular density minus sphericalized atoms. b) CDD, molecular density minus optimally oriented atomic ground states. Length scale in  $a_0$ . Density contour lines: 0.01, 0.04, 0.08, 0.12, ...  $e/a_0^3$ ; broken lines: negative values.

Features 2, and especially 3, are covered up in the TDD by the large fluorine quadrupole. The norm of the TDD (0.026 a. u.) is nearly twice as large as the value for the CDD (0.015 a. u.).

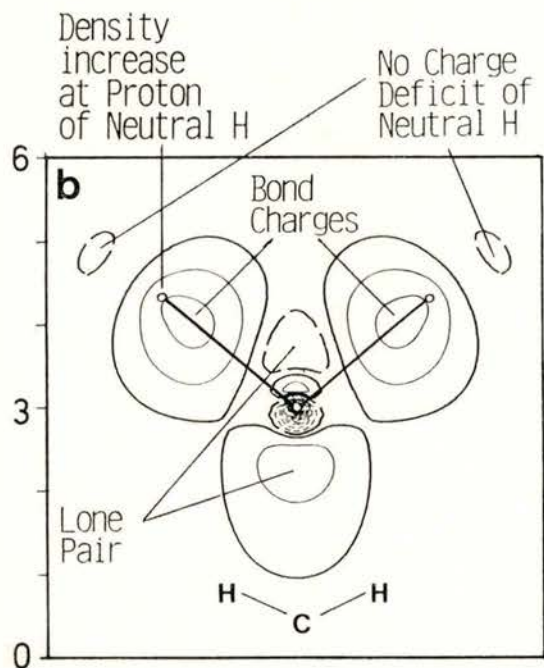
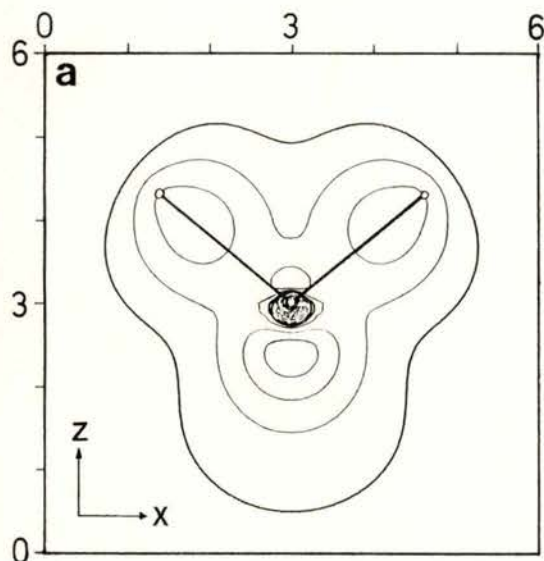


Fig. 2 — SCF difference density maps of  ${}^1\text{CH}_2$ .  
a) TDD. b) CDD. See caption of Fig. 1.

While the open shell  $p^2\ ^3\text{P}$  ground state of carbon atoms is evenly populated in aliphatic compounds, this is not always so for asymmetrically coordinated C-atoms. The simplest example, singlet methylene  ${}^1\text{CH}_2$ , is shown in Fig. 2. The large positive TDD values in the whole molecular plane demonstrate that the  $\text{C}p_x$  and  $\text{C}p_z$  AOs have a higher population than according to the spherical average of the  ${}^3\text{P}$  state. Optimal orientation reduces the norm from 0.055 a. u. for the TDD down to 0.021 a. u. for the CDD, corresponding to a  $(0.06\ ^3\text{P}_x + 0.94\ ^3\text{P}_y)$  reference density on C with orbital population  $p_x^{0.94}\ p_y^{0.06}\ p_z^{1.00}$ . The CDD (Fig. 2b) exhibits various density features, which are covered up in the TDD (Fig. 2a). Further examples are given in Refs. [5, 8].

### 3 — EXPERIMENTAL DENSITIES OF 9-t-BUTYL-ANTHRACENE AND 1,2,3-TRIAZINE

Miller et al. [6] have analyzed the X-ray scattering data of Angermund et al. [7] on butyl-anthracene (BA) and triazine. The predominantly positive TDD of BA (Fig. 3a) again indicates uneven population of the C2p-shells. The optimized populations of the p-orbitals are rather similar for all ring-C-atoms:  $p_{\pi}^{0.1}\ p_{\text{rad}}^{1.0}\ p_{\text{tang}}^{0.9}$ . The CDD bond charges in Fig. 3b (maxima of  $0.50 \pm 0.05\ \text{e}/\text{\AA}^3$ ) scatter less than the TDD ones (maxima of  $0.66 \pm 0.12\ \text{e}/\text{\AA}^3$ ).

The low  $p_{\pi}$ -population deserves an explanation. Since the X-ray scattering from the 2s density is nearly identical to that from the average 2p density, experimental density determinations from X-rays cannot detect  $2s \rightarrow 2p$  promotion. The C2s<sup>2</sup> density of the promolecule simulates some

of the  $C2p_x 2p_y 2p_z$  density so that a correspondingly reduced p-population is calculated.

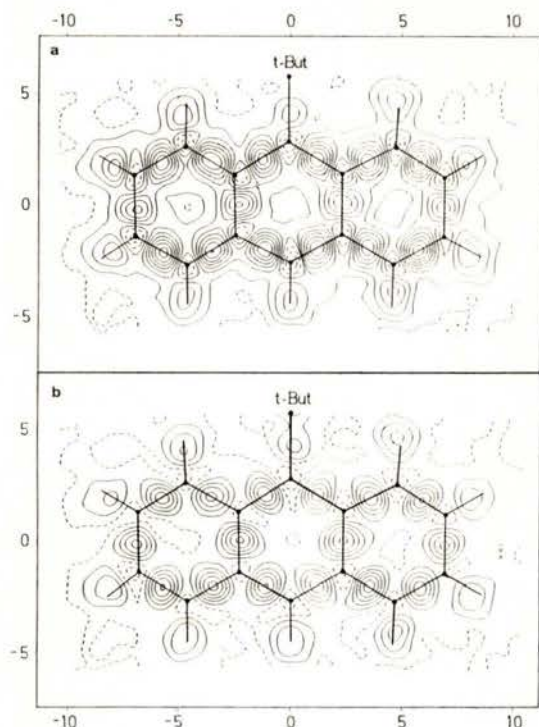


Fig. 3—Projection of the experimental static difference densities in the C-ring planes of 9-t-butyl-anthracene [6] onto a common plane. (Due to the bulky t-butyl group, the molecule obtains a distorted butterfly structure). a) TDD. b) CDD. Length scale in  $a_0$ . Density contour lines: 0.1, 0.2, 0.3, ...  $e/\text{\AA}^3$ ; broken lines: negative values.

Due to strong intermolecular interactions in the crystal, the TDD of triazine (Fig. 4a) does not reflect the nearly perfect symmetry of the molecule. The same problem will also show up, if density derivatives (the Laplacian, [9]) are preferred instead of total density differences.

The optimized p-shell populations of similar atoms are rather similar ( $p_{\pi}^{0.2} p_{\text{rad}}^{0.7} p_{\text{tang}}^{1.1}$  for C,  $p_{\pi}^{0.55} p_{\text{rad}}^{1.4} p_{\text{tang}}^{1.05}$  for N). The corresponding CDD (Fig. 4b) reflects the molecular symmetry and the order of bond strengths,  $C-C > C-N > N-N$ . The intermolecular interactions, however, change the orientation of the tangential and radial  $p_{\sigma}$ -AOs significantly, and that of the  $p_{\pi}$ -AOs still by up to  $10^\circ$ .

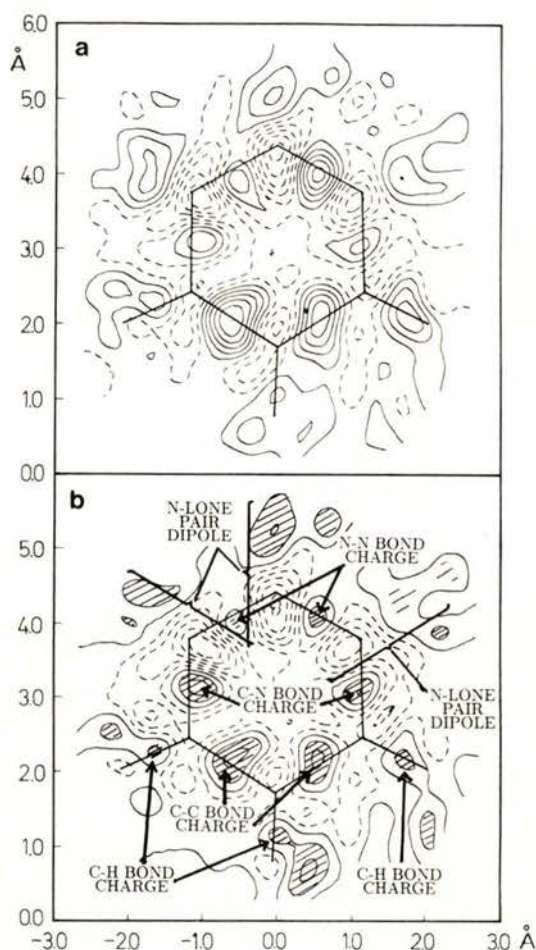


Fig. 4—Experimental static difference densities of 1,2,3-triazine [6]. a) TDD. b) CDD (promolecule from orientated  $C-3^2/P/D$  and  $N-5^4/D$  states). Length scale in  $\text{\AA}$ . Density lines as in Fig. 3.

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