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Charge Density Studies of Weak Interactions in Organic Solids

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Proton sponges, such as 1,8-bis(dimethylamino)naphthalene (DMAN), are aromatic diamines characterized by exceptional basicity. For these compounds protonation causes substantial redistribution of electron density which may be traced by observing the changes in structural parameters and in the properties of electron density at bond critical points. On protonation electron density in DMAN goes from the terminal atoms towards the centre of the molecule. This redistribution can also be confirmed by good quality neutron structural data.

Keywords: proton sponges; DMAN; 1,8-bis(dimethylamino)-naphthalene; charge density; Laplacian; protonation

INTRODUCTION

Modern crystallography can supply not only the geometrical details of structure of molecules and crystals but also the distribution of electronic charge in their atoms and bonds. This is done by construction of a mathematical model of charge density in a crystal and then by fitting the parameters of such a model to experimental pattern of diffracted X-rays. One of the most popular models of charge density is based on, so called, κ- formalism proposed by Hansen&Coppens [1]. In this model the electron density is described

by a sum of aspherical "pseudoatoms" where the "pseudoatom" density has the form:

where the first term describes the core density (P_c stands for the core populations and ρ_{core} is the spherically-averaged Hartree-Fock core

$$\rho_{at}(r) = P_c\rho_{core}(r) + P_v\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}}\kappa'^3 R_l(\kappa' r)\sum_{m=0}^{l} P_{lmt} d_{lmt}(\vartheta,\phi)$$

density for the atom). The second term describes the spherical part of the valence density. κ is an expansion/contraction coefficient which allows the radial density to become more or less diffuse. P_v stands for the valence population. The third term describes the deviation of pseudoatom density from sphericity. This is represented by deformation functions taking the shape of density normalised spherical harmonics $d_{lm\pm}$ of order l oriented with index m. The radial term for the deformation functions takes the form of a normalised Slater (or Gaussian) functions $R_l(\kappa' r)$ with an expansion-contraction parameter κ'.

Usually, the expansion in the multipole refinement [2] is truncated at the octapole level for carbon and nitrogen atoms and at the dipole level for all hydrogens except those particularly interesting (for example strongly H-bonded). Coordinates and temperature factors for H-atoms are fixed at the values obtained from neutron diffraction.

Once electron density has been established a number of different properties can be obtained, for example: moments of a charge distribution (monopoles, dipoles, quadrupoles, etc.), critical points and their properties, electrostatic potential, electric field, electric field gradient, gradient of charge density, Hessian, Laplacian, diamagnetic shielding tensor, diamagnetic current density, gradient of

field gradient, electrostatic energies, core and valence properties, etc. Many of these properties can independently be verified using different experimental techniques.

The topology of charge distribution is well characterised by its properties at critical points (i.e.: those points where the first derivative of ρ disappears - $\nabla\rho=0$) which has been shown by Bader [3]. In such a case the second derivatives of ρ characterise the curvatures of the charge density at its critical point (CP). In fact, the diagonal version of the matrix of the second derivatives of ρ with respect to x,y,z is analysed. It can have up to three non-zero terms which can have different signs. According to the number of the non-zero terms of the diagonal Hessian matrix of ρ (rank) and the sum of their signs (signiture), critical points of ρ can be divided into different classes. When at a given critical point all three curvatures of ρ are negative [(3,-3) critical point], there is a local maximum of ρ at this CP. This is the case for nuclear positions. When two curvatures of ρ are negative and one curvature is positive, this is (3,-1) CP - so called bond critical point. For two positive curvatures (local minimum of ρ) and one curvature negative (local maximum of ρ) one has a ring (3,+1) critical point and finally for all three curvatures positive (local minimum of ρ in all three directions), one has a (3,+3) CP called cage critical point. This means that the chemical structure of molecules can be extracted from an analysis of the topology of ρ.

The trace of the Hessian matrix is termed the Laplacian of rho and it represents local concentrations (Laplacian < 0) and depletions (Laplacian>0) of charge density. The Laplacian distribution recovers the electronic shell structure of atoms and its maxima correspond to

the localised pairs of electrons assumed in the Lewis and VSEPR models of electron pairs [4].

All above properties can be used to characterise the strength and nature of interactions as properties of the charge distribution. This is why charge density studies are so important for physical chemists.

In this contribution we will present some selected results obtained for the parental proton sponge DMAN and one of its salts.

DMAN and its complexes

Diamines with a rigid structure - called 'proton sponges' - have strong basicity observed both in the gas phase [5] and in solution [6,7-10]. A good example illustrating this phenomenon is provided by 1,8-bis(dimethylamino)naphthalene (DMAN), synthesised by Alder in 1968 [11] (see Fig. 1).

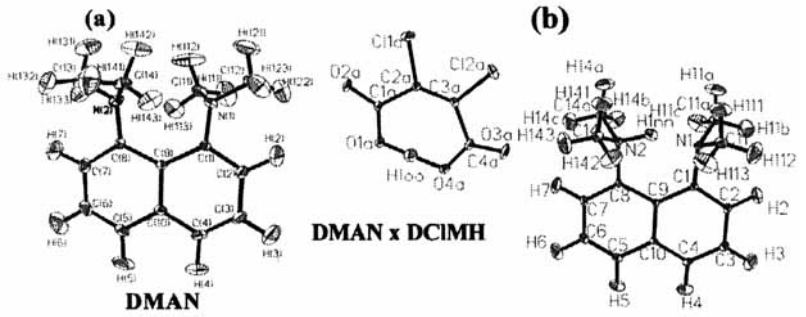

FIGURE 1. (a) 1,8-bis(dimethylamino)naphthalene (DMAN) and (b) DMAN complex with 1,2-dichloromaleic acid (DClMH).

The *ab initio* calculations have shown that DMAN has C_2 symmetry in the gas phase and a markedly nonplanar $N(C_{10}H_6)N$ fragment [12]. A high value of the C1-C9-C8 bond angle (125.9° in DMAN as compared with 122° in naphthalene) shows that there exists

strong repulsion between the NMe_2 groups. On protonation the $N(C_{10}H_6)N$ moiety becomes more planar. An intramolecular asymmetric cationic $[N\text{-}H...N]^+$ hydrogen bond is formed in DMAN with an energy barrier for proton jump equal to 22 kJ/mol. According to model calculations [9,13,14-16] for the isolated molecule, the formation of an intramolecular cationic hydrogen bonding increases the proton affinity (PA) value of a single amine group by ca. 100 kJ/mol. The strain energy in DMAN was estimated to be relatively small (ca. 20 kJ/mol) [16] suggesting that the high basicity of DMAN is mainly due to the ionic $[N\text{-}H...N]^+$ H-bond.

RESULTS AND DISCUSSION

The application of Bader's Atoms-In-Molecules theory [3] to the neutral and protonated forms of DMAN confirmed the structural changes found by *ab initio* calculations and showed the changes in the electron density distribution on protonation [12]. Such changes can be discussed in terms of the charge density ρ topology and its laplacian ($-\nabla^2\rho$) [3]. For a series of some smaller diamines (ammonia, $MeNH_2$, Me_2NH, Me_3N, $C_6H_5NMe_2$, etc) and DMAN, the PA shows a linear trend with the N-lone pair $-\nabla^2\rho$. The larger values of ρ and $-\nabla^2\rho$ at bond critical points (CPs) support the idea of partial delocalization of the N-lone electron pairs to the aromatic rings [12]. The bond critical point ρ values (and the $-\nabla^2\rho$) for the ring bonds are closer in $DMANH^+$ to the equivalent parameters in naphthalene, thus suggesting an increase in aromaticity of the naphthalene fragment on protonation. This supports the idea that the nitrogens are sp^2 hybridized in the free base whereas in $DMANH^+$ the N-lone electron

pair density is only slightly delocalized and the nitrogens have a very weak sp^2 character. Since the first paper on ab-initio calculations for proton sponges [12] many additional results have been published [13,14-16]. Peräkylä [13], for example, suggests four main contributions to the gas-phase PA: (i) the proton affinity of a single amine group, (ii) the relief of strain and a decrease in the lone pair repulsion on protonation, (iii) the formation of an intramolecular cationic hydrogen bond, (iv) the change in zero-point or thermal energy on protonation. According to Platts, Howard and Peräkylä [13,14-16], factor (iv) appears to be quite constant for a range of diamine proton sponges (ca. 38±7 kJ/mol at 0 K). (i) always dominates the PA (ca. 950 kJ/mol for a group such as $R(Me)_2N$, (iii) can be ca. 100 kJ/mol or more according to model gas calculations [13,14-16].

Structural consequences of protonation of DMAN in the solid state

According to X-ray and neutron studies [17,18], DMAN crystallizes in a general position of the orthorhombic $P2_12_12_1$ space group with one molecule in the asymmetric unit. That means that this possibly symmetric molecule is embedded in an asymmetric structural environment. And although the asymmetry of crystal forces has not been sufficient to destroy the nearly twofold symmetry of the molecule, the lack of symmetry can easily be detected by carbon magic angle spinning (^{13}C MAS) solid-state NMR [19, 20] with cross-polarization (CP) and other spectroscopic methods [21].

Combining the high resolution X-ray data with bond lengths and temperature factors from neutron diffraction allows one also to obtain experimental charge density distributions in crystals (multipole

refinement) [1,2]. It is then possible to get reliable atomic charges and determine the critical points of the electron density.

The possible asymmetry of DMAN cannot be seen either in the monopole charges at atoms or in the ρ values at the bond critical points [18]. The most sensitive parameter appears to be Laplacian of ρ at the bond critical points. For this parameter there are some small differences between the values for possibly symmetrical bonds, for example, -15.9(2) and -13.3(1) $eÅ^{-5}$, for N1C1 and N2C8, respectively, or -21.2(1) and -18.7 $eÅ^{-5}$ for C3C4 and C5C6, respectively [18]. Bond paths and ρ at bond critical points for DMAN molecule are illustrated in FIGURE 2. The amount of charge density for the left hand site ring and the and right hand site one are almost the same. This means that a number of the weakest interactions can not be observed either at the structural level or at the level of charge distribution and it is the Laplacian of the charge density which is required to confirm their presence.

The most significant structural consequences of protonation based on neutron structures [18, 22] are summarised in FIGURE 3. It compares of the neutron bond lengths in DMAN and $DMANH^+$. The most evident consequence at the structural level is a lengthening of the CN bonds nearest to the protonation site (from 1.438 Å in DMAN up to 1.476 Å for the cation). This reflects the breaking - on protonation - of the conjugation between the nitrogen lone pairs and the aromatic electron density.

It is interesting to note that the aromatic C-H bonds also exhibit a clear trend - they are shorter in DMAN and longer in $DMANH^+$ (on average 1.073 Å and 1.091 Å for DMAN and the cation, respectively). Even C-H bonds far from the acidic proton are

weakened by formation of the cationic $[N\text{-}H...N]^+$ hydrogen bond. This can be attributed to redistribution of electron density from the outer part of the moiety toward its center which also causes an increase of the double bond character of the aromatic CC bonds in $DMANH^+$ and their effective shortening (on average 1.402 Å and 1.412 Å for $DMANH^+$ and DMAN, respectively).

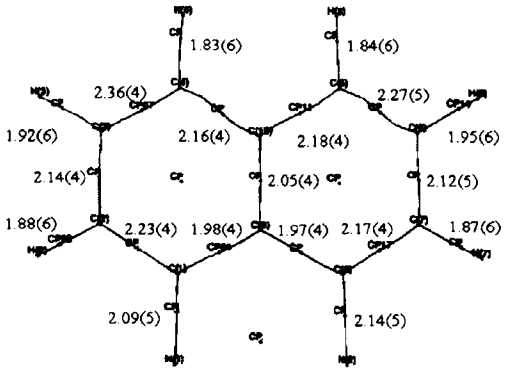

FIGURE 2. Bond paths and ρ at bond critical points for DMAN.

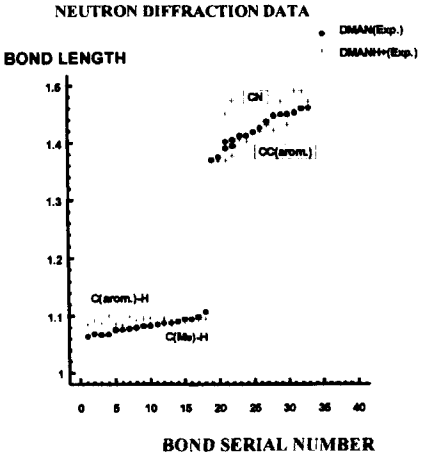

FIGURE 3. Protonation of DMAN - structural consequencies.

It appears that the asymmetric hydrogen bonding in the cation causes far stronger differences in CP properties of electron density than weak, asymmetric, intermolecular interactions in the DMAN molecule. This is clearly seen in the values of ρ and $\nabla^2\rho$ obtained for the two nearly symmetric halves of the cation [22], the values of $\nabla^2\rho$ at the C4C10 and C5C10 bond critical points (and also for CN bonds) in $DMANH^+$ are significantly different. Far less sensitive to protonation is the charge density distribution at the bond critical points in DMAN. Only for the CN bonds some significant differences (2.22 $e\text{Å}^{-3}$ and 2.01 $e\text{Å}^{-3}$ for C1N1 and C8N8, respectively) can be found.

As in the case of weak C-H...O hydrogen bonds [22], there are relations [18] between ρ and $\nabla^2\rho$ at CP for aromatic CC bonds (FIGURE 4), between Laplacian and the length of the aromatic CC bond (FIGURE 5). The largest difference in slopes is for the Laplacian vs the CC bond length dependence. This shows that $\nabla^2\rho$ is the most sensitive parameter for CPs. The experimental data show that on protonation of DMAN there occurs a decrease in the slope of the relation between ρ and $\nabla^2\rho$ (from -0.056 in DMAN to -0.042 in $DMANH^+$ [18,22]). A similar relation can be obtained for the laplacian vs the aromatic CC bond length. In this case the difference in slopes is the largest (58 for DMAN and 90 for $DMANH^+$). The relation between ρ and aromatic CC bond length is slightly less significant (the slopes are equal to -4.0 and -4.6 for DMAN and $DMANH^+$, respectively).

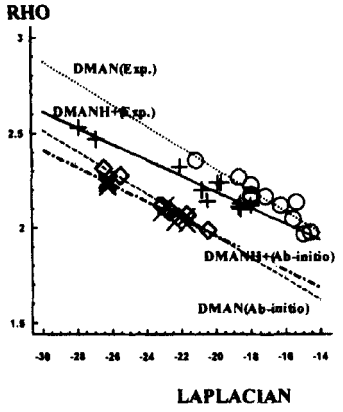

FIGURE 4. Relation [18] between ρ and $\nabla^2\rho$ at CPs for aromatic CC bonds.

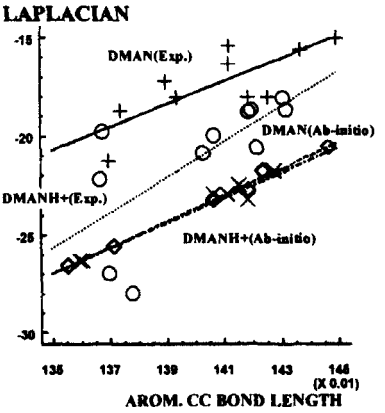

FIGURE 5. Laplacian vs.the length of the aromatic CC bond [18].

FIGURES 4 and 5 also illustrate a systematic difference between the experimental [18] and *ab-initio* [12] data. In the case of the relation between ρ and $\nabla^2\rho$ at the bond critical points, the values of slopes based on *ab-initio* data are close to those obtained from

multipole refinement although there is a systematic shift between the straight lines. Worse correlations are obtained from the *ab-initio* methods for Laplacian vs the CC bond length. In this case the slopes are also different and the *ab-initio* results are not sensitive to protonation.

Protonation of DMAN to $DMANH^+$ causes the deshielding of outer carbons as a result of charge migration toward the positive proton.

Another important factor influencing the localization of the proton are the charges at the hydrogen and electronegative atoms. A formal positive charge (+1) associated with the acidic proton is smeared over the whole cation which increases the charges also at the methyl hydrogen atoms. An estimation of atomic charges obtained for the complex of DMAN with dichloromaleic acid obtained from charge density studies [18] gives ca. +0.45 for the acidic proton and the values of charges ca. 2 times smaller for the methyl hydrogen atoms. This means that the final situation in the $[Me_2N\text{-}H....NMe_2]^+...O$ hydrogen bonding results from a delicate balance between the electrostatic and steric factors. Unfortunately, because the X-ray hydrogen positions suffer from obvious systematic errors (shortening of X-H bonds) it is difficult to quantify the role of a weaker component of hydrogen bonding in proton sponges without good quality neutron data.

In conclusion, we would like to emphasise that the intramolecular hydrogen bond formed in bifunctional ligands with rigid or flexible conformations strongly affects the thermodynamic parameters of simple proton transfer reactions. Proton affinities of these compounds are far higher than those of monofunctional compounds.

On the basis of neutron structural data it can be concluded that on protonation of DMAN all the bond lengths (including the aromatic C-H bonds) change. This results from redistribution of electron density toward the central part of DMAN. Such a redistribution is best illustrated in the experimental values of the Laplacian of ρ and confirmed by both *ab-initio* calculations as well as CP/MAS solid state NMR and NQR studies.

A strong ionic intramolecular $[N–H\cdots N]^{+}$ hydrogen bonding in proton sponge complexes of DMAN has in fact a multicentre character: $[Me_2N\text{-}H....NMe_2]^{+}...X(O)$. This is due to electrostatic interactions with the nearest electronegative atoms in the crystal lattice. Such interactions seem to affect localization of the proton in the $[N–H\cdots N]^{+}$ hydrogen bridge.

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