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Role of C—H···O hydrogen bonds in the ionic complexes of 1,8-bis(dimethylamino)naphthalene[†]

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ABSTRACT: On the basis of experimental charge density distributions in a series of ionic complexes of 1,8-bis(dimethylamino)naphthalene (**DMAN**) with four different acids, 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid), 4,5-dichlorophthalic acid, dicyanoimidazole and *o*-benzoic sulfimide dihydrate (saccharin), the role of minor C—H···O hydrogen bonds was analysed. We propose a multicentre model of hydrogen bonding in proton sponges $\{[Me_2N—H\cdots .NMe_2]^+ \cdots X^{\delta-}\}$. It appears that weak interactions of electronegative atoms with the nearest methyl hydrogen atoms can influence the location of the proton in the intramolecular $[N—H\cdots N]^+$ hydrogen bridge. In the case of C—H···O hydrogen bonds, the amount of electron density in the donor C—H bonds involved in hydrogen bonding is slightly larger than that in those C—H from the same methyl group which are not involved in hydrogen bonding. Numerical values of the Laplacian follow a reverse relation (they are smaller for the donor C—H bonds). Both of these critical point parameters (rho and Laplacian) are linearly dependent on the length of interaction line. An increase in the amount of electron density in the H···O hydrogen bonding is associated with an increase in electron density in the donor C(methyl)—H donor bond, which confirms the mainly ionic nature of such weak hydrogen bonds. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: proton sponges; experimental charge density distributions; hydrogen bonding

INTRODUCTION

According to literature data searches, more than 300 papers have been published on proton sponges and their complexes. The parent proton sponge—an aromatic diamine, 1,8-bis(dimethylamino)naphthalene (**DMAN**)—has been known since the early 1940s.[1] Its high basicity ($pK_a \approx 12$) was realised by Alder *et al.*[2] in the late 1960s. Proton sponges[3] have attracted significant interest owing to their very high proton affinity, low nucleophilicity, slow protonation/deprotonation and applications in modelling of enzymatic catalysis processes.[4] Many of their properties result from the strain induced by the proximity of the two amine substituents. With mineral or organic acids proton sponges form very stable ionic complexes containing low barrier intramolecular $[N\cdots H\cdots N]^+$ hydrogen bonding.[3] This H-bonding is asymmetric according to *ab initio* calculations,[5,6] numerous diffraction studies and isotope shift investigations.[7]

Research in the field of proton sponges has followed several main directions: (a) synthesis of new proton sponges and their complexes;[8–10] (b) mainly theoretical studies of factors responsible for enhanced basicity such as cationic H-bond energies,[11–13] lone pair–lone pair repulsion energies,[14,15] strain energies[5,6,16] and resonance (aromatic stabilization energies);[13,17] (c) experimental studies of structural and spectroscopic properties,[18,19] and (d) some applications in catalysis.[4]

DMAN itself and its complexes are very good model systems to study a number of interesting chemical phenomena such as unusual proton affinity, ionic $[N—H\cdots N]^+$ hydrogen bonding and its short- and long-range consequences, aromaticity and conjugation in the aromatic part and weak hydrogen bonding.

The whole series of compounds that we have studied consist of the ionic complexes of protonated **DMAN** with the anions (Scheme 1) of the following acids: 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid), 4,5-dichlorophthalic acid, dicyanoimidazole and *o*-benzoic sulfimide dihydrate (saccharin). The names of the complexes are hereafter abbreviated as **DMANH**$^+$**tCA**$^-$, **DMANH**$^+$ **dCldCA**$^-$, **DMANH**$^+$ **dCI**$^-$ and **DMANH**$^+$**SAC**$^-$. The labelling schemes of

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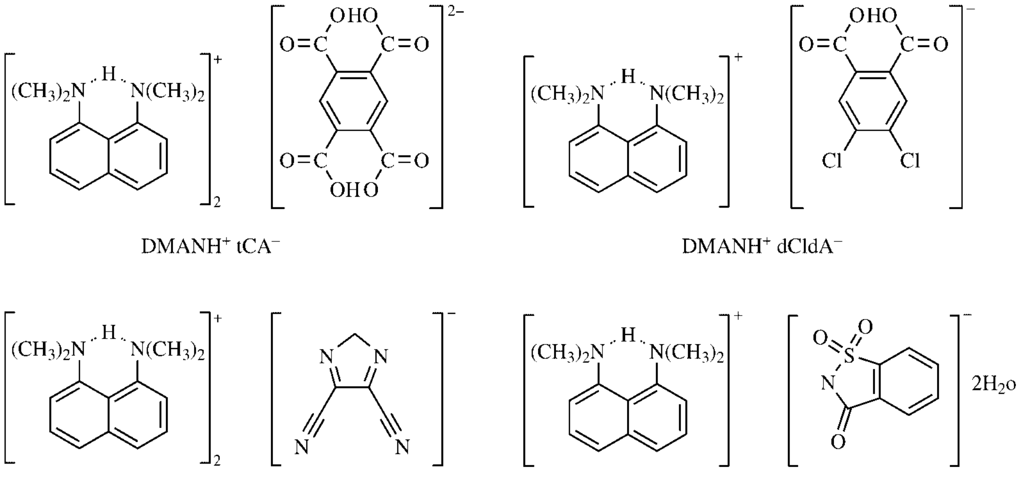


DMANH$^+$ dCl$^-$

DMANH$^+$ SAC$^-$

Scheme 1

the atoms and an ORTEP illustration of their thermal motions are shown in Fig. 1.

Modern high-resolution X-ray diffraction methods allow the characterization of the nature of chemical interactions.[20,21] We accomplished our studies by the construction of a mathematical model of charge density in a crystal and then by fitting the parameters of such a model to the experimental pattern of diffracted X-rays. We applied the so-called κ-formalism proposed by Hansen and Coppens.[22] In this model, electron density in a crystal is described by a sum of aspherical 'pseudoatoms' where the 'pseudoatom' density has the form

$$\rho_{\mathrm{at}}(r) = P_{\mathrm{c}}\rho_{\mathrm{core}}(r) + P_{\mathrm{v}}\kappa^3\rho_{\mathrm{val}}(\kappa r) + \sum_{l=0}^{l_{\max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\upsilon, \phi)$$

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 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 pseudo-atom density from sphericity. This is represented by deformation functions taking the shape of density normalized spherical harmonics $d_{lm\pm}$ of order l oriented with index m. The radial term for the deformation functions takes the form of a normalized Slater (or Gaussian) functions $R_l(\kappa' r)$ with an expansion contraction parameter κ'.

Once experimental electron density has been established, Bader's atoms-in-molecules approach,[23,24] i.e. topological analysis of electron density $\rho(\mathbf{r})$, provides an excellent tool for the interpretation of X-ray-determined charge densities. Any bonded pair of atoms has a bond path, i.e. a line of the highest electron density, linking them. The point on this line where the gradient of ρ, $\nabla\rho(\mathbf{r})$, is equal to zero, is termed the bond critical point (BCP) and the properties of the density at this point, ρ_{b}, give quantitative information on that bond's characteristics. A bond path between a pair of non-covalently bonded atoms is called an interaction line. Its length, which can be different from the length of the internuclear vector, will be denoted R_{ij}. In our opinion, R_{ij} better represents the influence of the local electronic environment on a given interaction.

The Laplacian of the density $[\nabla^2\rho(\mathbf{r})]$ contains a large amount of chemical information. Since this is the second derivative of the electron density, it indicates where the density is locally concentrated $[\nabla^2\rho(\mathbf{r}) < 0]$ and depleted $[\nabla^2\rho(\mathbf{r}) > 0]$, and hence graphically shows features such as bonds and lone pairs, which are not observable in $\rho(\mathbf{r})$ itself.

We have already devoted a full paper[25] to discuss Koch and Popelier's[26] hydrogen bond criteria. In that paper, we studied the variation of charge density and geometric properties and also local energy densities over all inter- and intramolecular interactions present in five complexes of **DMAN**. It appeared that all the interactions studied ($[\mathrm{O}\cdots\mathrm{H}\cdots\mathrm{O}]^-$, C—H···O, $[\mathrm{N—H}\cdots\mathrm{N}]^+$, O—H···O, C—H···N, C$\pi$···N$\pi$, C$\pi$···C$\pi$, C—H···Cl, N—H$^+$) follow exponential dependences of the electron density, local kinetic and potential energies at the bond critical points on the length of the interaction line. The local potential energy density at the bond critical points has a near-linear relationship to the electron density. There is also a Morse-like dependence of the Laplacian of rho on the length of interaction line, which allows a differentiation of ionic and covalent bond characters. The strength of the interactions studied varies systematically with the relative penetration of the critical points into the van der Waals spheres of the donor and acceptor atoms and also the interpenetration of the van der Waals spheres themselves.

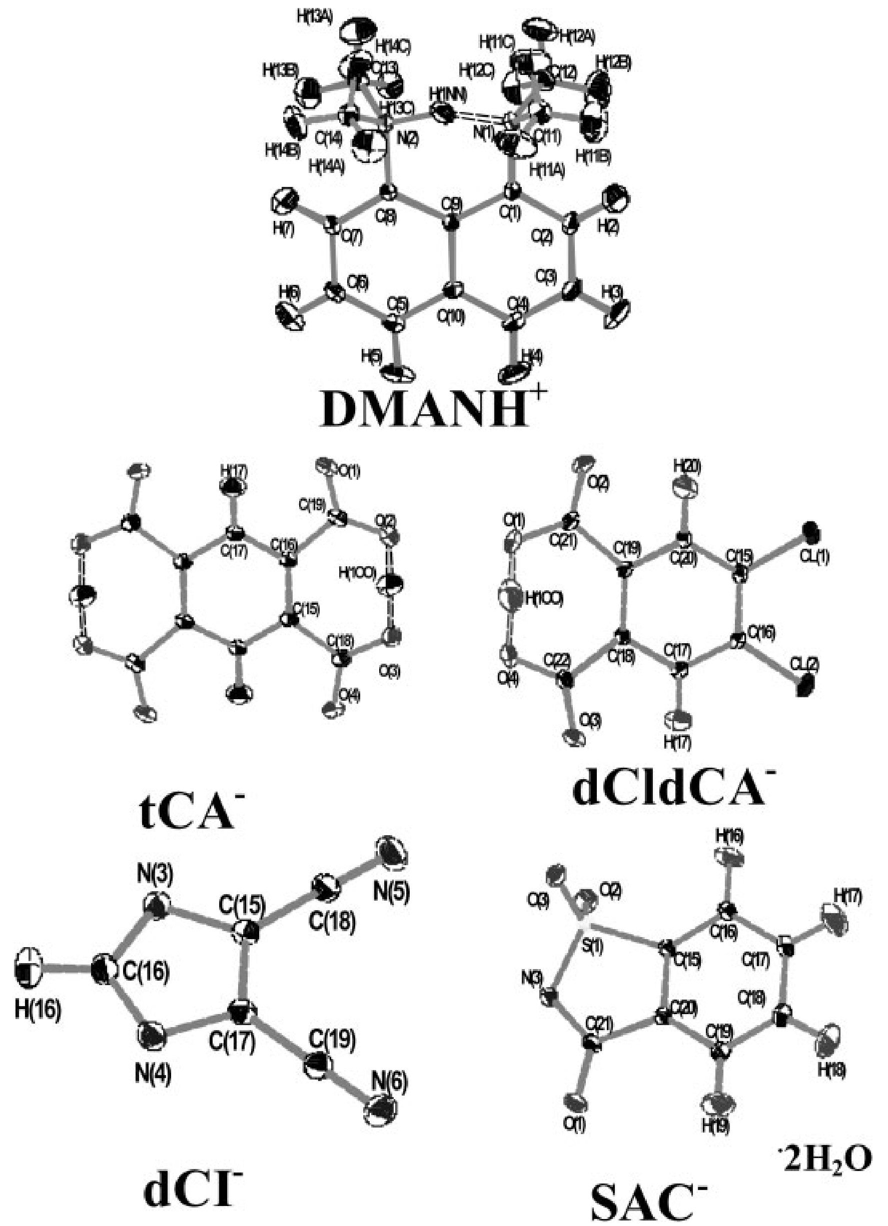


Figure 1. Numbering schemes and atomic displacement parameters (ADPs) for the ionic complexes of **DMANH**$^+$ cation with **tCA**$^-$, **dCldCA**$^-$, **dCI**$^-$ and **SAC**$^-$ from neutron data at 100 K. The ellipsoids are drawn at the 50% probability level

In this work, however, we used the same experimental charge density data to discuss the nature of weak C—H$\cdots$O hydrogen bonds. Let us concentrate on a slightly larger fragment of the cation than just the three atoms [N—H$\cdots$N]$^+$ participating in the H-bond. In fact, periamino derivatives of naphthalene do not have proton sponge properties unless the nitrogen atoms are fully substituted. This means that the alkyl groups attached to the nitrogen atoms play a very important role. If this is so, one should look at the arrangement and structural parameters of a wider group of H bonds, present in the [Me$_2$N—H$\cdots$NMe$_2$]$^+\cdots$X$^{\delta-}$ region, where X$^{\delta-}$ is the nearest electronegative atom. In most cases of **DMAN** complexes this is oxygen. Then, we will call the strong H-bond in [Me$_2$N—H$\cdots$NMe$_2$]$^+$ the major component and the weak H-bonds between the methyl groups and $\cdots$X$^{\delta-}$ the minor component of the [Me$_2$N—H$\cdots$NMe$_2$]$^+\cdots$X$^{\delta-}$ H-bonding. We want to examine the role of a minor secondary [Me$_2$N—H$\cdots$NMe$_2$]$^+\cdots$X$^{\delta-}$ interaction of the [Me$_2$N—H$\cdots$NMe$_2$]$^+$ fragment with the nearest electronegative atom (X$^{\delta-}$) in the crystal.

This weak interaction is the reason for small structural changes of the **DMANH**$^+$ cation. By variation of the anions we will generate variations of minor components in the hydrogen bonding in **DMANH**$^+$ complexes. Ideally, this will be reflected in details of the electron density distributions which we hope to demonstrate in this paper.

EXPERIMENTAL

Crystals of the compounds studied are well defined, colorless prisms, grown by slow evaporation from acetonitrile. All details of high-resolution X-ray and neutron data collections, structure and multipole refinements are described in Ref. 25.

RESULTS AND DISCUSSION

All structural and crystallographic details for all four structures can be found in Ref. 25. It also contains details of experimental electron density distributions and a discussion of networks of interactions of varying strength, which exist in these structures. The interactions are classified into nine types. When these are taken together with previously published results for the complex of **DMAN** with dichloromaleic acid, a total of 63 interactions can be identified. It appears that the lengths of the interaction lines can be correlated with topological properties, local kinetic and potential energy densities, interpenetrations of van der Waals spheres and interpenetrations of CPs with van der Waals spheres. When the full range of interactions including the N—H$^+$ covalent bonds is considered, the variation of the Laplacian of ρ at BCPs reveals a continuous transition from the weak hydrogen bonding to the covalent bonding situation. It appears that quantitative relationships or unifying dependences exist, derived from charge density distributions, linking weak $\pi\cdots\pi$ electron interactions, weak and strong hydrogen bonds and covalent bonds. These general relationships open up a new field which can be termed ‘quantitative crystal engineering.’ We found that the hydrogen atoms in the N(2)—H(1NN)···N(1) hydrogen bond carry a positive charge in the range 0.31–0.39e, whereas the aromatic and aliphatic hydrogen charges are close to zero within the level of errors. The methyl carbons, in all except the saccharide complex, carry a significant positive charge (ca 0.4e). The charges of the donor and acceptor nitrogen atoms are in the range −0.18(2)e to −0.41(2)e.

Among those 63 above-mentioned interactions there is a subset of C—H···O weak hydrogen bonds, where the donor C—H comes from a methyl group and an acceptor oxygen atom from the closest counterion in the crystal lattice. In this contribution we want to analyse the role of minor secondary $[Me_2N—H\cdots NMe_2]^+\cdots X^{\delta-}$ hydrogen bonds.

The crystal structures of the complexes of **DMANH$^+$A$^-$** are built up either from layers of pairs of stacked cations and anions which form molecular planes or from a single **DMANH$^+$** cation (anion) interacting with six anions (cations) in the closest 3D neighbourhood. This resembles the type of close packing characteristic of ionic inorganic compounds. In the first case, two cations and two anions are placed in an antiparallel manner owing to strong dipole–dipole interactions and other kinds of weak interactions. As a result of strong electrostatic interactions and the weak interactions (mentioned above), some relatively short intermolecular contacts occur. The shortest of them can be considered as weak C—H···acceptor (usually oxygen) hydrogen bonds.

The structures of ionic **DMANH$^+$X$^-$** complexes may be used to find possible relationships between the major and minor components of $[Me_2N—H\cdots NMe_2]^+\cdots X^{\delta-}$ H-bonding. A good illustration of such and other weak interactions in the four subject structures is shown in Fig. 2.

First, it appears that the nearest electronegative atom is located more or less at the central position in front of four hydrogens which protrude from the methyl groups of the **DMANH$^+$** cation. In fact, the electronegative atom, e.g. oxygen, is almost always slightly closer to the nitrogen donor atom {N(2) in the $[Me_2N(2)—H\cdots N(1)Me_2]^+$ bridge}, i.e. the N(2)···O distance is shorter than N(1)···O. This means, that the N(2)—H(1NN)···O angle is larger than the N(1)···H(1NN)···O angle. The nearest oxygen atom is much closer to the methyl hydrogen atoms than it is to the acidic proton. Hence the hydrogen bonding involving methyl hydrogens is more significant than the $[N—H\cdots N]^+\cdots O^{\delta-}$ interaction.

In general, the **DMAN** methyl groups can interact with more than one electronegative atom independently, and such electrostatic interactions can induce localization of the acidic proton at one or other of the nitrogen atoms. Also, order or disorder of the hydrogen atom position in the hydrogen bonding seems to be dependent on the number and location of the electronegative atoms in the neighbourhood. The next important factor influencing the situation of the proton is the charge associated with the hydrogen and the 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 for the complexes of **DMANH$^+$** obtained from the present charge density studies gives charges in the range +0.31 to +0.39 for the acidic proton, and charges about two times smaller for the methyl hydrogen atoms. This suggests that a delicate balance exists between the electrostatic interactions of the methyl hydrogens on the left- and right-hand sites of the **DMANH$^+$** cation and electronegative atoms of the counter-moiety. This may be illustrated by the ρ_b and $\nabla^2\rho_b$ values for the donor C—H bond lengths and H···O hydrogen bond distances. They are listed in Table 1.

It appears that the values of ρ_b for the C—H bonds involved in C—H···O hydrogen bonding are slightly increased (usually less than 0.1e Å^{-3}) compared with those from the same methyl groups, not being hydrogen bonded (Scheme 2).

There is also a small decrease of the $\nabla^2\rho_b$ values (usually less than 3e Å^{-5}) for such C—H bonds (also

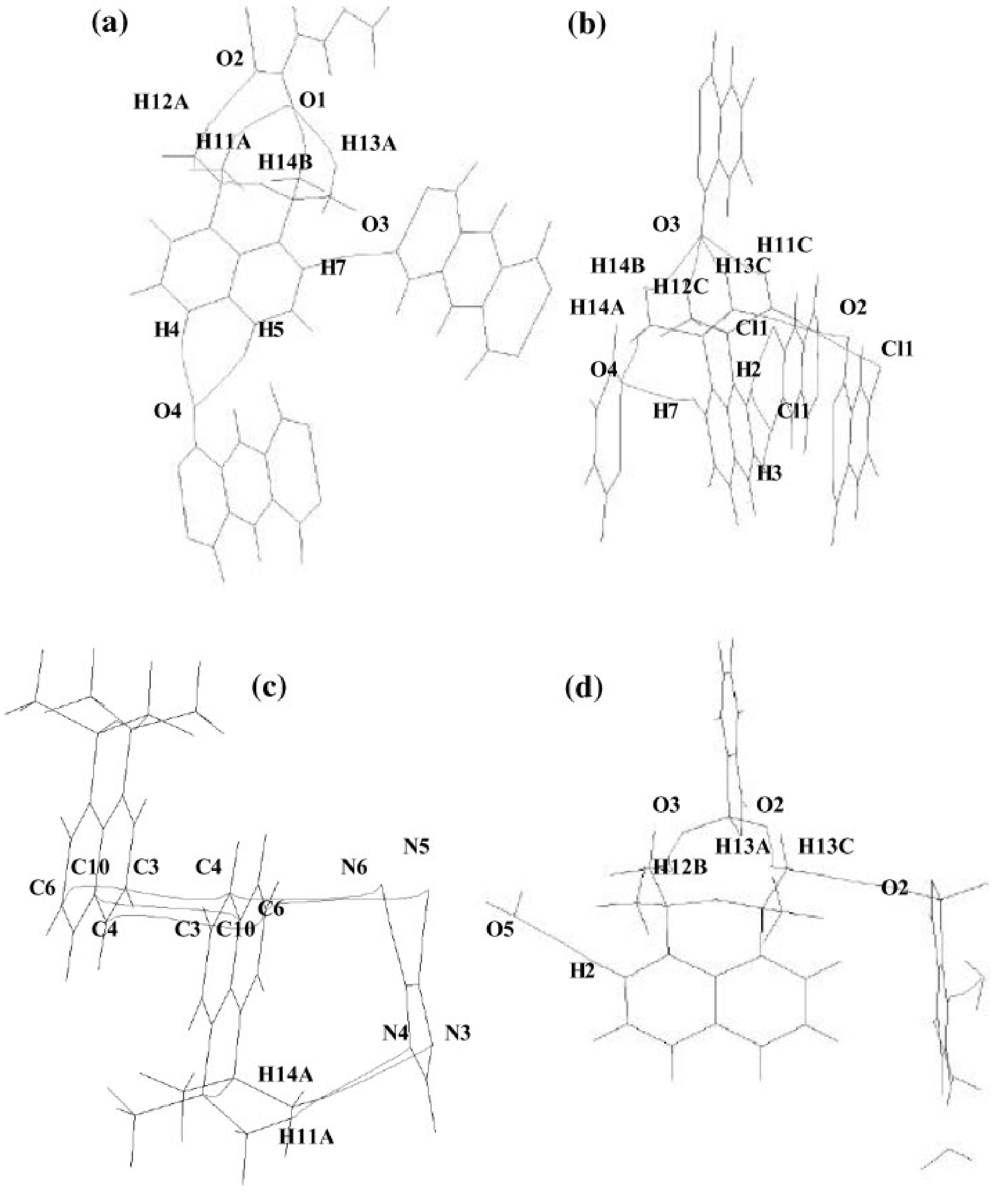


Figure 2. Interaction lines for weak interactions in complexes of the **DMANH$^+$** cation with (a) **tCA$^-$**, (b) **dCldCA$^-$**, (c) **dCl$^-$** and (d) **SAC$^-$**

compared with the non-bonding situation). For both properties there is only one exception, which is illustrated in Fig. 3. This one data point [for C(12)—H(12A) in **DMANH$^+$tCA$^-$**] deviates because its parent methyl group strongly interacts with three oxygen atoms in the close neighbourhood. In such a case all three interactions can influence the CP properties, thus changing them more than may be expected in the simplest case of the methyl hydrogens interacting with only one oxygen atom. There also seems to be a trend: the stronger the C—H bond the larger is the difference between the ρ_b values for the C—H bonds involved and not involved in H-bonds [Fig. 3(b)].

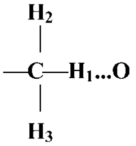
Further interesting trends are found for the relation between $\nabla^2\rho_b$ and ρ_b for the donor C(methyl)—H bonds [Fig. 4(a)], and for H$\cdots$O hydrogen bonds [Fig. 4(b)].

It appears that the smallest negative values of $\nabla^2\rho_b$ are associated with the strongest C—H bonds (with the largest ρ_b). The slope of such a relation is negative for the donor C—H groups. There is no similar relation for the average values of $\nabla^2\rho_b$ and ρ_b of the non-interacting

Table 1. CP properties characterising C(methyl)—H···O hydrogen bonds

DMANH$^+$ complex with	Hydrogen bonding	ρ_b C—H (e Å^{-3})	$<\rho_b>$ C—H (e Å^{-3})	$\Delta\rho_b$ C—H (e Å^{-3})	$\nabla^2\rho_b$ C—H (e Å^{-5})	$<\nabla^2\rho_b>$ C—H (e Å^{-5})	$\Delta\nabla^2\rho_b$ C—H (e Å^{-5})	ρ_b H···O (e Å^{-3})	$\nabla^2\rho_b$ H···O (e Å^{-5})
TCA$^-$	C11—H11A···O1(1 + x,y,z)	1.91(3)	1.86	0.05	−20.9(1)	−20.4	−0.5	0.066	0.8
TCA$^-$	C12—H12A···O2(1 + x,y,z)	1.90(3)	1.79	0.11	−21.1(1)	−17.7	−3.4	0.097	0.7
TCA$^-$	C13—H13A···O1(1 + x,y,z)	1.89(4)	1.85	0.04	−20.4(1)	−19.6	−3.4	0.037	0.5
TCA$^-$	C14—H14B···O1(1 + x,y,z)	1.96(3)	1.89	0.07	−23.4(1)	21.7	−1.7	0.086	0.9
dCldCA$^-$	C11—H11A···O1(1−z,1−y,−z)	1.78(3)	1.87	−0.11	−14.6(1)	−16.2	+1.6	0.056	0.8
dCldCA$^-$	C11—H11C···O3(1−z,1−y,−z)	1.88(3)	1.87	0.01	−17.4(1)	−16.2	−1.2	0.057	0.9
dCldCA$^-$	C12—H12C···O3(1−z,1−y,−z)	1.81(3)	1.83	−0.02	−15.9(1)	−16.0	+0.1	0.063	0.9
dCldCA$^-$	C13—H13C···O3(1−z,1−y,−z)	1.89(3)	1.83	0.06	−17.8(1)	−15.8	−2.0	0.065	1.0
dCldCA$^-$	C13—H13B···O2(1−x,1−y,−z)	1.85(3)	1.83	0.02	−16.6(1)	−15.8	−0.8	0.068	1.1
dCldCA$^-$	C14—H14A···O4(1 + x,y−1,1 + z)	1.88(3)	1.86	0.02	−17.3(1)	−17.3	0.0	0.041	0.7
dCldCA$^-$	C14—H14B···O3(1−x,1−y,−z)	1.89(3)	1.86	0.03	−17.7(1)	−17.3	−0.4	0.054	0.9
dCldCA$^-$	C13—H13A···O2(x,y−1,z)	1.86(3)	1.84	0.02	−18.2(1)	−16.6	−1.2	0.047	0.8
SAC$^-$	C13—H13B···O1(x,y−1,z)	1.90(3)	1.84	0.06	−18.7(1)	−16.6	−2.1	0.060	0.9
SAC$^-$	C13—H13C···O2	1.83(3)	1.84	−0.01	−16.8(1)	−16.6	−0.2	0.058	0.8
SAC$^-$	C12—H12B···O3(x,y−1,z)	1.84(3)	1.86	−0.02	−17.6(1)	−16.3	−1.1	0.031	0.5

[a] ρ_b is the electron density at the CP of the donor C—H bond; $<\rho_b>$ is the average electron density at the CPs of the C—H bonds not involved in H-bonding, in the same methyl group; $\Delta\rho_b$ is the difference $\rho_b - <\rho_b>$. The same nomenclature applies to the Laplacian values. The final two columns contain ρ_b and $\nabla^2\rho_b$ for the hydrogen bonds formed.



Scheme 2

C—H groups. However, for the C(methyl)—H···O H-bonds the slope of such an obvious trend is positive with the scatter of data points resulting from the complexity of H-bond interactions.

The plots characterizing C—H···O H-bonds, such as that in Fig. 4(a), might alternatively be formulated so as to show the differences on the donor site between the electron density (or Laplacian) in the H-bonded C(methyl)—H donor bonds minus the amount of electron density (Laplacian) at the BCPs of the C—H groups coming from the same methyl group and not being involved in any hydrogen bonding. The differences are in fact comparable to the values of the CP parameters for the C(methyl)—H···O hydrogen bonds (Fig. 5).

The first dependence describes the consequences of formation of C(methyl)—H···O hydrogen bonds on the relation between ρ_b and $\nabla^2\rho_b$ for the donor C—H bonds. Because of the reference to the C—H groups not involved in H-bonding but coming from the same methyl substituent, one can say that it describes quantitatively consequences of the C—H···O hydrogen bonding on the electron and Laplacian distributions on the donor site. The stronger is the C—H bond, the more negative are the Laplacian values at the BCPs.

Figure 5(b) links the changes in ρ_b for the donor and acceptor groups. It appears that the stronger is the H(methyl)···O hydrogen bonding the more electron density is associated with the C(methyl)—H BCPs.

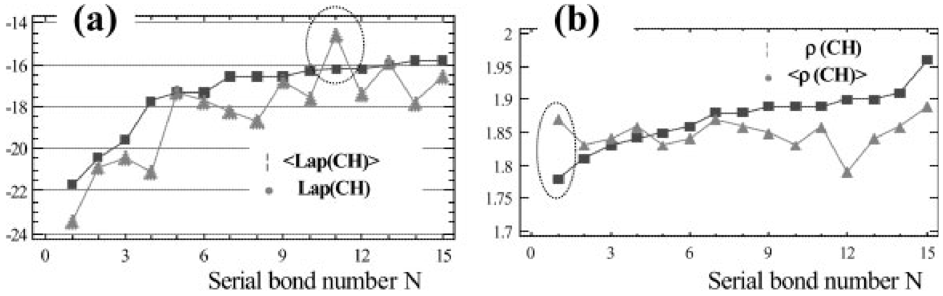


Figure 3. Illustration of BCP parameters for the methyl C—H bonds involved and not involved in weak C—H···O hydrogen bonds: (a) comparison of the Laplacian values at BCP for the C—H bonds participating in C—H···O hydrogen bonds (triangles) and the average values of 0.$\nabla^2\rho_b$ (e Å^{-5}) for the C—H bonds not participating in any H-bond and coming from the same methyl group (squares) as a function of the serial bond number; (b) comparison of the ρ_b (e Å^{-3}) values for the C—H bonds participating in C—H···O hydrogen bonds (squares) and the average values of ρ_b for the C—H bonds not participating in any H-bond and coming from the same methyl group (triangles) as a function of the serial bond number. The deviating point is shown in the ellipsoid

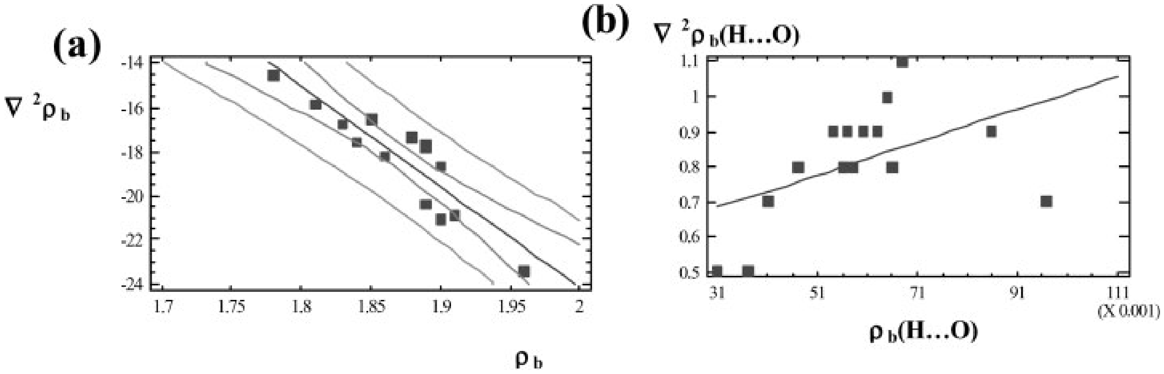


Figure 4. (a) Dependence of $\nabla^2\rho_b$ (e Å^{-5}) and ρ_b (e Å^{-3}) for C(methyl)—H bonds involved in hydrogen bonding on the proton donor site [$\nabla^2\rho_b = 67(12) - 45(6)\rho_b$, $R = -0.89$ for $N = 15$ data points], and (b) dependence of $\nabla^2\rho_b$ and ρ_b for C(methyl)—H$\cdots$O H-bonds on the proton accepting site [$\nabla^2\rho_b$ (H$\cdots$O) $= 0.5(1) + 5(2)\rho_b$(H$\cdots$O), $R = 0.5$ for $N = 15$ data points]

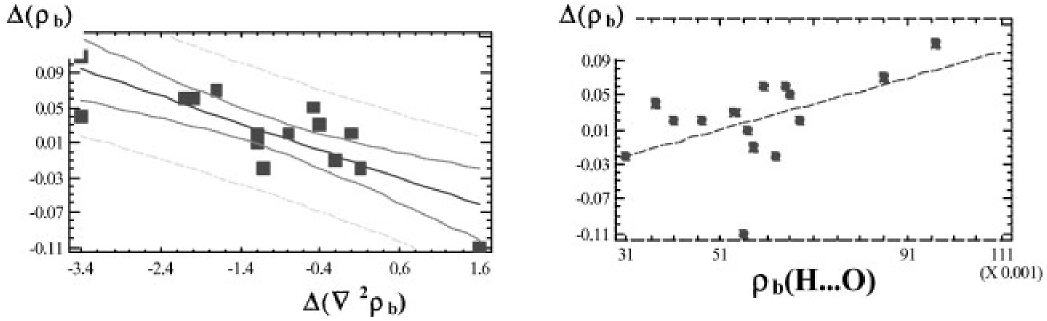


Figure 5. Results of fitting a linear model to describe the relationship between the difference Δ in ρ_b values for the C—H bonds involved in C—H$\cdots$O H-bonds (H_1 in Scheme 2) minus the average ρ_b for the C—H bonds not involved in any H-bonding (H_2 and H_3 in Scheme 2) but coming from the same methyl groups vs (a) the difference in the Laplacian values for the same bonds [Δ (ρ_b) $= -0.01(1) - 0.031(6)\Delta(\nabla^2\rho_b)$, for $N = 15$ datapoints, correlation coefficient $R = -0.81$, confidence interval for the slope and tolerance interval at the significance level $\alpha = 0.05$]; and (b) ρ_b for the H$\cdots$O hydrogen bonds [$H_1\cdots$O in Scheme 2, $\Delta(\rho_b) = -0.05(3) + 1.4(4)\rho_b$(H$\cdots$O) for $N = 14$ datapoints, $R = 0.67$]. The deviation of one point results from the multicentre character of weak interactions of the C(12)—H(3) methyl group in **DMANH$^+$tCA$^-$**]

This kind of relation clearly confirms the electrostatic nature of the C(methyl)—H$\cdots$O hydrogen bonds. We believe that these are some examples of new applications of the Laplacian function. Its numerical values seem to have quantitative significance and they can be applied in studies of such sophisticated problems as the weakest intermolecular interactions.

CONCLUSIONS

The strong, charge-supported intramolecular [N—H$\cdots$N]$^+$ hydrogen bond has a multicentre character which can be represented by the formula {[Me_2N—H$\cdots$$NMe_2$]$^+\cdots X^{\delta-}$}, where X is the nearest electronegative atom in the crystal lattice. Such interactions of the methyl hydrogens seem to affect the location of the proton in the [N—H$\cdots$N]$^+$ bridge. The proton is more likely to be found at the nitrogen which is closer to the atom X.

In the case of the C(methyl)—H$\cdots$O hydrogen bonds, we estimate changes in the values of CP parameters for C(methyl)—H bonds involved in H-bonding relative to those C—H from the same methyl groups which are not involved in any H-bonding. It appears that there are a number of relationships between CP parameters linking variation of ρ and Laplacian of ρ for the donor C(methyl)—H bonds with changes of the CP parameters in the H(methyl)$\cdots$O hydrogen bonds. Among others, there is slightly more electron density in the donor C—H bonds involved in hydrogen bonding than in those C—H from the same methyl groups which are not involved in hydrogen bonding. Numerical values of the Laplacian follow a reverse relation (they are smaller for the donor C—H bonds). Both of these critical point parameters (rho and Laplacian) are linearly dependent on the length of interaction line. An increase in the amount of electron density in the H$\cdots$O hydrogen bonding is associated with an increase in electron density in the donor C(methyl)—H donor bond. These relations stress the ionic nature of the C(methyl)—H$\cdots$O hydrogen bonds.

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