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Neutron Diffraction of a Complex of 1,8-Bis(dimethylamino)naphthalene with 1,2-Dichloromaleic Acid

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Abstract

A neutron study of the crystalline complex of 1,8-bis(dimethylamino)naphthalene (DMAN) with 1,2-dichloromaleic acid ($ClMH_2$) has been carried out at 100 K using the Laue time-of-flight technique. The moieties are planar. The neutron data indicate that both $[N—H\cdots N]^+$ and $[O—H\cdots O]^-$ hydrogen bonds in the complex are asymmetric. There are significant differences between the neutron and X-ray temperature factors, C—H, N—H and O—H bond lengths. There is a strong correlation between the neutron and X-ray temperature factors for non-H atoms and no correlation for H-atom temperature factors. According to the neutron data the involvement of a given H atom in a weak $C—H\cdots O$ hydrogen bond can be correlated with the ratio of equivalent temperature factors of the H and non-H atoms to which they are attached.

1. Introduction

Neutrons, having a wavelength comparable in magnitude to the spacing between atoms and a frequency comparable to the vibrational frequencies of the atoms, are an excellent probe for studying both the structure and dynamics of the condensed state (Willis, 1970; Windsor, 1981; Bacon, 1975). The coherent elastic scattering cross section gives a time-averaged view of the positions of atoms in an ordered structure (clearly showing the positions of hydrogens), whereas inelastic scattering gives rich information on the vibrational states of atoms or molecules.

The purpose of this work is to determine as precisely as possible, using neutron diffraction, the positions of atoms and their thermal parameters in 1,8-bis(dimethylamino)naphthalene 1,2-dichloromaleate [$DMANH^+.ClMH^-$]. Such information will be used later in experimental charge-density studies of strong and weak hydrogen bonds in this complex. According to the X-ray structure of this compound, a number of short $C—H\cdots X$ contacts exist which may be treated as weak hydrogen bonds. Reliable hydrogen positions obtained from neutron diffraction will allow a very detailed description of these hydrogen bonds.

$DMANH^+.ClMH^-$ is an ionic complex of the aromatic diamine 1,8-bis(dimethylamino)naphthalene (DMAN) with 1,2-dichloromaleic acid ($ClMH_2$, Fig. 1). DMAN belongs to the class of compounds with extremely high basicity constants and proton affinities, known as proton sponges (Staab & Saupe, 1988; Alder, 1989; Einspahr, Robert, Marsh & Roberts, 1973; Wozniak, He, Klinowski & Grech, 1995; Platts, Howard & Wozniak, 1994; Wozniak, He, Klinowski, Jones & Barr, 1996). These compounds have already attracted considerable attention. With mineral or organic acids, proton sponges form very stable ionic complexes containing asymmetric intramolecular $[N—H\cdots N]^+$ hydrogen bonds. On the other hand, the hydrogen maleate anion and its derivatives contain an asymmetric anionic $[O—H\cdots O]^-$ hydrogen bond.

The $DMANH^+.ClMH^-$ complex has already been studied by means of electron spectroscopy (ESCA) as well as low- and room-temperature solid-state NMR and X-ray diffraction (Wozniak, He, Klinowski, Jones & Barr, 1996). A significant influence of strong hydrogen bonds on the binding energies of the core electrons of atoms involved in hydrogen bonding was observed.

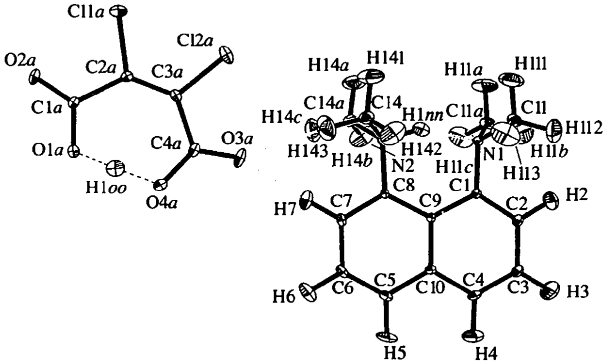

Fig. 1. Numbering scheme and atomic displacement parameters for the $DMANH^+$ and $ClMH^-$ ions at 100 K obtained from neutron data. The ellipsoids are drawn at the 50% probability level.

According to the X-ray structure there are two strong asymmetric hydrogen bonds, $[N—H\cdots N]^+$ and $[O—H\cdots P]^-$, in the cation and anion, respectively. Additionally, both the cation and the anion interact with each other in the crystal lattice through weak $C—H\cdots$acceptor hydrogen bonds.

2. Experimental

2.1. *Synthesis*

DMANH$^+$.ClMH$^-$ was prepared by mixing maleic acid with DMAN in acetonitrile. The product was then recrystallized from methanol. Crystals of DMANH$^+$.ClMH$^-$ suitable for the neutron work were grown from acetonitrile by slow evaporation.

2.2. *Laue time-of-flight technique*

Neutron measurements were made using the time-of-flight Laue diffraction (TOFLD) technique. This method accesses a large volume of reciprocal space, sorted in both time and space, in a single measurement which is termed a histogram or frame. Collection of a complete structure-factor set in this diffraction geometry consists of the collection of a series of such frames, each collected with a stationary crystal and position-sensitive detector (PSD) arrangement.*

The crystal, of dimensions $4 \times 2 \times 1$ mm, was mounted on a two-circle orienter (φ, χ) in a Displex closed-cycle refrigerator (CCR) helium cryostat, on the single crystal diffractometer SXD at the ISIS spallation neutron source (Wilson, 1990). The data were collected at a temperature of 100 ± 2 K, the computer-controlled temperature being measured by a Rh–Fe thermocouple sited around 10 mm from the sample at the CCR head.

In the present experiment two PSD's, each of 192×192 mm^3 active area, in 3×3 mm pixels, were used. These were situated with their centres at $2\theta = 55°$, ~190 mm from the sample (low-angle detector) and $2\theta = 125°$, ~160 mm from the sample (high-angle detector). There is thus a very large angle subtended at the sample by both detectors.

Data were collected in 47 frames from each detector, at a series of (φ, χ) angles to give good coverage of reciprocal space. The wavelength range used was 0.5–5 Å. The nature of the data collection is such that different $\sin\theta/\lambda$ values are reached in different parts of the detector. Typical frame exposure times were around 3-4 h, resulting in several hundred observed reflections in each detector. This data collection method, and the large degree of overlap between frames collected at different time, leads to a large overdetermination of equivalent reflections in the data set. It was clear from the normalization and merging procedure that there was no measurable change in the diffracting power of the crystal during the data collection.

Reflection intensities were extracted using standard SXD procedures and normalized to the incident beam using the incoherent scattering from a polycrystalline vanadium sample. Semi-empirical absorption corrections were also applied at this stage, using the vanadium and sample scattering. It should be noted that reflections for which the intensity extraction procedure fails to produce an observed value are excluded from the data set, thus resulting in a somewhat reduced occurrence of very weak or 'unobserved' reflections in the final data set. It should also be noted that the nature of the data collection method allows some reflections at very high $\sin\theta/\lambda$ values to be observed, even when no real attempt has been made to access all data to this resolution. The resulting intensities were reduced to structure factors, giving data sets of 15 750 and 10 670 reflections from the high- and low-angle detectors, respectively. These data were used in the CCSL (Brown & Matthewman, 1993) least-squares refinement program *SFLSQ*, to apply a variable-wavelength extinction correction based on the Becker–Coppens formalism (Becker & Coppens, 1974*a*,*b*) using a Gaussian model with one variable parameter, the mosaic spread.

The resulting corrected structure factors were merged, subject to initial refinements in the *GSAS* program (Larsen & von Dreele, 1986) before final refinement proceeded in *SHELX* as described below. The total set of 26 420 observed data resulted in 3005 unique, merged reflections ($R_{\rm int} = 0.06$) to be used in the final refinements, emphasizing the overdetermination in the set collected here. The data were refined using *SHELXL*93 (Sheldrick, 1996). The starting parameters for the atoms were taken from an earlier low-temperature X-ray diffraction study (Wozniak, He, Klinowski, Jones & Barr, 1996). The scattering lengths ($b_{\rm C} = 6.646$, $b_{\rm H} = -3.739$, $b_{\rm Cl} = 9.577$, $b_{\rm O} = 5.803$ and $b_{\rm N} = 9.360$ fm) were taken from *International Tables for Crystallography* (1992, Vol. C).

Weighted *R* factors, *wR*, and all goodness-of-fit *S* values are based on F^2. Conventional *R* factors are based on *F* with *F* set to zero for negative F^2. The criterion $F_o^2 > 2\sigma(F_o^2)$ was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. *R* factors based on F^2 are approximately twice as large as those based on *F* and *R* factors based on all data are even larger.

3. Results and discussion

The crystal data and a summary of the data collection and refinement parameters for DMANH$^+$.ClMH$^-$ are shown in Table 1. The final atomic coordinates and the anisotropic atomic displacement parameters for the H and non-H atoms are displayed in Tables 2 and 3. The

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* A list of structure factors has been deposited with the IUCr (Reference: AN0523). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data and summary of the data collection and refinement*

Identification code	DMANH$^+$.ClMH$^-$
Chemical formula	$C_{18}H_{20}Cl_2N_2O_4$
Chemical formula weight	399.10
Temperature (K)	100 (2)
Colour	Transparent
Cell setting	Orthorhombic
Space group	*Pnma*
a (Å)	18.086 (1)
b (Å)	6.983 (1)
c (Å)	14.363 (1)
V (Å^3)	1814.0 (3)
Z	4
D_x (Mg m^{-3})	1.461
μ (mm^{-1}) for $\lambda = 1.80$ Å	0.898
Crystal size (mm^3)	4 × 2 × 1
Index ranges	$0 \le h \le 51, 0 \le k \le 19,$ $0 \le l \le 42$
Total no. of reflections collected	26 420
No. of reflections measured with the high-angle detector	15 750
No. of reflections measured with the low-angle detector	10 670
No. of independent reflections	3005 ($R_{\rm int} = 0.06$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2990/0/253
Goodness-of-fit on F^2	1.067
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0703$, $wR_2 = 0.1428$
All data	$R_1 = 0.0718$, $wR_2 = 0.1509$

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
N1	0.26735 (8)	1/4	0.8538 (1)	0.0086 (2)
N2	0.15237 (8)	1/4	0.9675 (1)	0.0087 (2)
C1	0.2166 (1)	1/4	0.7757 (2)	0.0077 (2)
C2	0.2428 (1)	1/4	0.6856 (2)	0.0136 (4)
C3	0.1949 (1)	1/4	0.6087 (2)	0.0154 (4)
C4	0.1202 (1)	1/4	0.6231 (2)	0.0121 (4)
C5	0.0129 (1)	1/4	0.7281 (2)	0.0135 (4)
C6	−0.0163 (1)	1/4	0.8160 (2)	0.0165 (4)
C7	0.0301 (1)	1/4	0.8945 (2)	0.0147 (4)
C8	0.1054 (1)	1/4	0.8835 (1)	0.0075 (3)
C9	0.1392 (1)	1/4	0.7934 (1)	0.0064 (3)
C10	0.0907 (1)	1/4	0.7147 (2)	0.0084 (3)
C11	0.3134 (1)	0.0761 (3)	0.8564 (1)	0.0151 (3)
C14	0.1420 (1)	0.0751 (3)	1.0257 (1)	0.0139 (3)
Cl1*a*	−0.0409 (1)	1/4	1.4491 (2)	0.0336 (6)
Cl2*a*	0.0446 (1)	1/4	1.2693 (2)	0.0191 (3)
O1*a*	−0.2168 (2)	1/4	1.2933 (2)	0.0180 (5)
O2*a*	−0.1941 (2)	1/4	1.4438 (2)	0.0218 (6)
O3*a*	−0.0336 (2)	1/4	1.1018 (2)	0.0255 (7)
O4*a*	−0.1488 (2)	1/4	1.1511 (2)	0.0168 (5)
C1*a*	−0.1731 (1)	1/4	1.3637 (2)	0.0116 (4)
C2*a*	−0.0893 (1)	1/4	1.3459 (2)	0.0114 (4)
C3*a*	−0.0507 (1)	1/4	1.2649 (2)	0.0098 (3)
C4*a*	−0.0790 (1)	1/4	1.1644 (2)	0.0124 (4)
H1*nn*	0.2090 (3)	1/4	0.9383 (4)	0.0206 (9)
H1*oo*	−0.1848 (3)	1/4	1.2242 (4)	0.0258 (11)
H141	0.1837 (3)	0.0796 (8)	1.0809 (3)	0.0342 (10)
H142	0.1492 (3)	−0.0511 (7)	0.9812 (3)	0.0359 (10)
H143	0.0864 (3)	0.0782 (9)	1.0550 (4)	0.0372 (11)
H111	0.3460 (3)	0.0782 (8)	0.9197 (3)	0.0366 (10)
H112	0.3502 (3)	0.0664 (10)	0.7962 (4)	0.0418 (12)
H113	0.2773 (3)	−0.0490 (7)	0.8570 (5)	0.0401 (11)
H2	0.3021 (3)	1/4	0.6748 (5)	0.0328 (14)
H3	0.2172 (4)	1/4	0.5385 (4)	0.0410 (18)
H4	0.0814 (4)	1/4	0.5641 (4)	0.0314 (13)
H5	−0.0231 (3)	1/4	0.6664 (4)	0.0330 (14)
H6	−0.0759 (3)	1/4	0.8254 (5)	0.0404 (18)
H7	0.0060 (4)	1/4	0.9639 (4)	0.0343 (15)

most significant vibrations of atoms take place in the direction perpendicular to the plane of the molecule (U_{22} is larger than the other components of the U_{ij} tensor). The DMANH$^+$.ClMH$^-$ complex crystallizes in the orthorhombic *Pnma* space group with four molecules in the unit cell. The asymmetric unit of the DMANH$^+$.ClMH$^-$ complex consists of the coplanar DMANH$^+$ cation and the ClMH$^-$ anion (Fig. 1) located at the *m* symmetry plane. As a result, only two methyl groups of DMANH$^+$ are independent. Due to the planar geometry and strong electrostatic interactions, the crystal structure of the complex is built up from layers of molecules. The crystal packing of DMANH$^+$.ClMH$^-$ drawn with the neutron data is shown in Fig. 2.

The geometry of the cation closely resembles the *ab initio* calculated geometry of the symmetric DMANH$^+$ cation (Platts, Howard & Wozniak, 1994) with the largest deviations of 0.017 and 0.016 Å for C1—C2 and N1—C1 bond lengths, respectively. In the case of the bond angles the largest differences are between C1—C2—C3, C1—N1—C11 and C5—C10—C4 angles (1.3, 1.4 and 1.1°, respectively). All other differences are less than 1°. The values reflect the expected differences in structural parameters when the symmetric [N· · ·H· · ·N]$^+$ hydrogen bond in the cation used for the *ab initio* calculations is compared with the asymmetric [N—H· · ·N]$^+$ hydrogen bond in the real DMANH$^+$.ClMH$^-$. structure. The geometry of the anion deviates more from the results of the *ab initio* calculations for the ClMH$^-$ anion (George, Bock & Trachtman, 1983; Hodoscek & Hadzi, 1990). The largest deviations are 0.029 Å for the O1—H1*oo* and C1—C2 bond lengths and 1.8 and 1.3° for O3—C4—O4 and O1—C1—O2 angles. These differences are likely to be due to the fact that *ab initio* calculations do not take into account intermolecular interactions, whereas the anion in the DMANH$^+$.ClMH$^-$ complex is very sensitive to them.

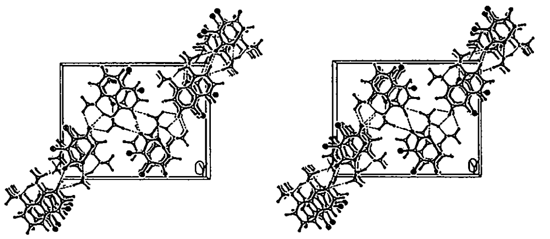

Fig. 2. Crystal packing of the DMANH$^+$.ClMH$^-$ molecules in the crystal lattice drawn from the neutron data.

The detailed description of this structure at 293 and 120 K can be found elsewhere (Wozniak, He, Klinowski, Jones & Barr, 1996) and hence we would like to concentrate here on the differences between the neutron and X-ray results. For both temperatures at

Table 3. *Atomic displacement parameters ($Å^2 \times 10^4$) from the refinement of the neutron data*

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hk\,a^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H1*nn*	158 (18)	261 (23)	198 (20)	0	−34 (16)	0
H1*oo*	215 (23)	365 (29)	194 (21)	0	−21 (18)	0
H141	377 (22)	410 (24)	238 (17)	90 (17)	−142 (16)	−35 (20)
H142	561 (30)	221 (17)	294 (20)	−21 (15)	−9 (20)	12 (19)
H143	233 (17)	468 (27)	415 (24)	160 (22)	93 (16)	−26 (18)
H111	350 (22)	433 (25)	315 (20)	−26 (19)	−191 (17)	121 (19)
H112	378 (24)	553 (31)	323 (21)	−49 (22)	89 (18)	224 (24)
H113	401 (25)	232 (21)	570 (31)	20 (20)	−114 (24)	−26 (17)
H2	134 (20)	603 (44)	246 (25)	0	55 (18)	0
H3	337 (31)	756 (56)	148 (23)	0	45 (21)	0
H4	273 (27)	479 (37)	189 (23)	0	−114 (20)	0
H5	186 (22)	576 (42)	228 (23)	0	−147 (19)	0
H6	104 (20)	760 (55)	347 (32)	0	1 (21)	0
H7	229 (24)	634 (45)	166 (21)	0	94 (18)	0
N1	69 (5)	120 (6)	69 (5)	0	−2 (4)	0
N2	79 (5)	126 (6)	55 (5)	0	7 (4)	0
C1	70 (7)	101 (7)	61 (7)	0	6 (6)	0
C2	101 (9)	236 (11)	71 (7)	0	19 (6)	0
C3	133 (9)	263 (8)	63 (8)	0	16 (7)	0
C4	133 (9)	173 (9)	58 (7)	0	−26 (6)	0
C5	82 (8)	191 (10)	132 (9)	0	−36 (7)	0
C6	59 (8)	282 (13)	154 (10)	0	−13 (7)	0
C7	71 (8)	253 (12)	116 (9)	0	23 (7)	0
C8	52 (7)	107 (7)	67 (7)	0	15 (5)	0
C9	57 (6)	79 (7)	57 (6)	0	2 (5)	0
C10	79 (7)	108 (7)	65 (7)	0	−14 (5)	0
C11	129 (6)	166 (6)	159 (6)	−17 (5)	−45 (5)	56 (5)
C14	152 (6)	159 (6)	106 (5)	32 (5)	−13 (5)	−1 (5)
Cl1*a*	165 (8)	719 (18)	124 (7)	0	−58 (6)	0
Cl2*a*	88 (6)	208 (8)	278 (9)	0	34 (6)	0
O1*a*	96 (10)	335 (16)	110 (10)	0	14 (8)	0
O2*a*	154 (12)	409 (19)	92 (10)	0	58 (9)	0
O3*a*	241 (16)	400 (20)	123 (11)	0	102 (11)	0
O4*a*	141 (10)	278 (14)	85 (9)	0	−8 (8)	0
C1*a*	104 (8)	173 (9)	72 (8)	0	13 (6)	0
C2*a*	103 (9)	165 (9)	74 (8)	0	−5 (6)	0
C3*a*	72 (7)	99 (8)	124 (8)	0	7 (6)	0
C4*a*	142 (9)	136 (9)	92 (8)	0	32 (7)	0

Table 4. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D···H	H—A	D···A	D—H···A
N2—H1*nn*···N1	1.106 (5)	1.608 (6)	2.644 (2)	153.3 (5)
O1*a*—H1*oo*···O4*a*	1.149 (7)	1.235 (7)	2.383 (4)	178.5 (6)
C11—H111···O2a^{i}	1.084 (4)	2.410 (6)	3.118 (3)	121.6 (4)
C14—H141···O2a^{i}	1.095 (4)	2.535 (6)	3.235 (3)	120.8 (3)
N2—H1*nn*···O2a^{i}	1.106 (5)	2.437 (6)	3.055 (3)	113.7 (4)
C7—H7···O3*a*	1.087 (6)	2.107 (7)	3.193 (4)	176.1 (6)
C14—H142···O4a^{ii}	1.096 (5)	2.353 (5)	3.408 (3)	160.9 (4)
C14—H141···O1a^{i}	1.095 (4)	2.815 (5)	3.844 (3)	156.6 (4)
C14—H142···O3a^{ii}	1.096 (5)	2.778 (7)	3.514 (4)	124.2 (4)
C14—H143···O3*a*	1.091 (5)	2.570 (6)	3.575 (4)	152.8 (4)
C11—H111···Cl1a^{i}	1.084 (4)	3.029 (5)	4.028 (3)	153.5 (5)
C11—H112···Cl2a^{iii}	1.084 (5)	2.941 (5)	3.654 (2)	123.0 (4)
C11—H113···O4a^{ii}	1.090 (6)	2.718 (6)	3.749 (3)	157.7 (4)
C11—H113···O1a^{ii}	1.090 (6)	2.797 (6)	3.586 (3)	129.1 (5)
C4—H4···Cl1a^{iv}	1.099 (6)	2.760 (6)	3.838 (3)	166.4 (5)
C5—H5···Cl1a^{iv}	1.100 (6)	3.137 (7)	4.123 (3)	149.6 (5)

Symmetry codes: (i) $\frac{1}{2}+x, y, \frac{5}{2}-z$; (ii) $-x, -y, 2-z$; (iii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (iv) $x, y, z-1$.

which the X-ray data were collected there is a linear dependence between the equivalent temperature factors of non-H atoms from X-ray and neutron diffraction, whereas such a dependence does not exist for the hydrogens. The dependence for non-H atoms may be described by the equation

$$U_{eq}(\mathrm{X},\ 120\,\mathrm{K}) = 1.00\ (2)\ U_{eq}(\mathrm{N},\ 100\,\mathrm{K}) + 0.0095\ (3)$$

for the X-ray data acquired at 120 K; X and N denote the X-ray and neutron data. The correlation coefficient $R = 0.997$ for 24 data points. A similar dependence for 293 K is described by the equation

$$U_{eq}(\mathrm{X},\ 293\,\mathrm{K}) = 2.68\ (8)\ U_{eq}(\mathrm{N},\ 100\,\mathrm{K}) = 0.022\ (1).$$

This dependence has a correlation coefficient $R = 0.991$ for 24 data points. The slopes of both these regression lines are close to the ratios of the measurement temperatures: however, they are not equivalent. There is an approximate constant difference of *ca* 0.2 between the slopes and the ratios of temperatures. Part of this difference is likely to be accounted for by the different data collection techniques used in both low-temperature units used during X-ray and neutron data collections. It is worth mentioning that the X-ray value of U_{eq} of the H atom involved in the ionic $[\mathrm{O—H\cdots O}]^-$ hydrogen bond deviates furthest from its neutron value. A similar picture is obtained for the e.s.d. values of the equivalent temperature factors. All the e.s.d. values of U_{eq}'s at room temperature are higher than those of the equivalent U_{eq}'s at 120 K. The differences between the e.s.d.'s are particularly large for H atoms.

As expected (Taylor & Kennard, 1983; Allen, 1986), there is a systematic shift of hydrogen positions between the neutron and X-ray data. Hence, all the neutron hydrogen-bond parameters are different from the X-ray parameters. In particular, the neutron C—H distances are longer than the X-ray values, the neutron H···*X* distances are shorter than the corresponding X-ray values and the neutron C—H···*X* angles are slightly smaller than the equivalent X-ray angles. This is due to the fact that X-rays tend to underestimate these bond lengths, because they are diffracted by the electron-density maximation which, in *X*—H bonds, is shifted towards the non-H atoms. There is no such relation for the bonds between non-H atoms. It is also noteworthy that the neutron C—H, N—H and O—H bonds also have significantly smaller e.s.d.'s than the e.s.d.'s obtained from X-ray diffraction and are thus more precisely determined in the neutron experiment.

3.1. *Hydrogen bonds in $DMANH^{+}.ClMH^{-}$*

There are two strong ionic $[\mathrm{N—H\cdots N}]^+$ and $[\mathrm{O—H\cdots O}]^-$ hydrogen bonds in the cation and anion, respectively, and a number of short C—H···*X* contacts, *X* = O, N or Cl, which may be treated as weak C—H···*X* hydrogen bonds. The geometry of all these bonds is given in Table 4. The geometries of the $[\mathrm{N—H\cdots N}]^+$ and $[\mathrm{O—H\cdots O}]^-$ hydrogen bonds are close to those reported for the other DMAN salts (Truter & Vickery, 1972; Pyzalska, Pysalski & Borowiak, 1983; Glowiak, Malarski, Sobczyk & Grech, 1987; Wozniak, Krygowski, Kariuki, Jones &

Table 5. *Selected geometric parameters* (Å, °)

N1—C1	1.451 (3)	C8—C9	1.432 (3)
N1—C11	1.473 (2)	C9—C10	1.431 (3)
N2—C8	1.474 (3)	C11—H111	1.084 (4)
N2—C14	1.492 (2)	C11—H112	1.094 (5)
N2—H1*nn*	1.106 (5)	C11—H113	1.090 (6)
C1—C2	1.378 (3)	C14—H141	1.095 (4)
C1—C9	1.422 (3)	C14—H142	1.096 (5)
C2—C3	1.403 (4)	C14—H143	1.091 (5)
C2—H2	1.085 (6)	Cl1*a*—C2*a*	1.722 (3)
C3—C4	1.367 (4)	Cl2*a*—C3*a*	1.724 (3)
C3—H3	1.087 (7)	O1*a*—C1*a*	1.284 (4)
C4—C10	1.420 (3)	O1*a*—H1*oo*	1.149 (7)
C4—H4	1.099 (6)	O2*a*—C1*a*	1.212 (4)
C5—C6	1.368 (4)	O3*a*—C4*a*	1.217 (4)
C5—C10	1.419 (3)	O4*a*—C4*a*	1.276 (4)
C5—H5	1.100 (6)	O4*a*—H1*oo*	1.235 (7)
C6—C7	1.407 (4)	C1*a*—C2*a*	1.537 (3)
C6—H6	1.086 (7)	C2*a*—C3*a*	1.356 (3)
C7—C8	1.370 (3)	C3*a*—C4*a*	1.531 (3)
C7—H7	1.087 (6)		
C1—N1—C11	112.2 (1)	C5—C6—H6	119.9 (5)
C11—N1—C11$^{\rm i}$	111.1 (2)	C7—C6—H6	119.5 (5)
C1—N1—H1*nn*	99.7 (2)	C8—C7—C6	120.0 (2)
C11—N1—H1*nn*	110.6 (1)	C8—C7—H7	120.3 (4)
C4*a*—O4*a*—H1*oo*	113.2 (4)	C6—C7—H7	119.6 (4)
O2*a*—C1*a*—O1*a*	123.7 (3)	C7—C8—C9	121.9 (2)
C2*a*—C3*a*—C4*a*	129.5 (2)	C7—C8—N2	118.6 (2)
C2*a*—C3*a*—Cl2*a*	118.9 (2)	C9—C8—N2	119.5 (2)
C4*a*—C3*a*—Cl2*a*	111.6 (2)	C1—C9—C10	117.5 (2)
O3*a*—C4*a*—O4*a*	123.8 (3)	C1—C9—C8	125.6 (2)
O3*a*—C4*a*—C3*a*	118.1 (3)	C10—C9—C8	116.9 (2)
O4*a*—C4*a*—C3*a*	118.2 (2)	C5—C10—C4	119.8 (2)
C8—N2—C14	112.7 (1)	C5—C10—C9	120.1 (2)
C14$^{\rm i}$—N2—C14	109.9 (2)	C4—C10—C9	120.1 (2)
C8—N2—H1*nn*	102.9 (3)	N1—C11—H111	108.5 (3)
C14—N2—H1*nn*	109.2 (2)	N1—C11—H112	112.1 (4)
C2—C1—C9	120.4 (2)	H111—C11—H112	109.3 (5)
C2—C1—N1	120.6 (2)	N1—C11—H113	108.9 (3)
C9—C1—N1	119.0 (2)	H111—C11—H113	109.3 (5)
C1—C2—C3	121.8 (2)	H112—C11—H113	108.7 (5)
C1—C2—H2	118.3 (4)	N2—C14—H141	107.2 (3)
C3—C2—H2	119.9 (4)	N2—C14—H142	108.4 (3)
C4—C3—C2	119.4 (2)	H141—C14—H142	111.3 (5)
C4—C3—H3	120.5 (5)	N2—C14—H143	108.4 (3)
C2—C3—H3	120.1 (5)	H141—C14—H143	110.8 (4)
C3—C4—C10	120.8 (2)	H142—C14—H143	110.5 (5)
C3—C4—H4	120.9 (4)	C1*a*—O1*a*—H1*oo*	111.8 (4)
C10—C4—H4	118.3 (4)	O2*a*—C1*a*—C2*a*	117.9 (2)
C6—C5—C10	120.5 (2)	O1*a*—C1*a*—C2*a*	118.4 (2)
C6—C5—H5	121.0 (4)	C3*a*—C2*a*—C1*a*	130.5 (2)
C10—C5—H5	118.5 (4)	C3*a*—C2*a*—Cl1*a*	118.5 (2)
C5—C6—C7	120.6 (2)	C1*a*—C2*a*—Cl1*a*	111.0 (2)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Grech, 1990; Bartoszak, Jaskólski, Grech, Gustafsson & Olovsson, 1994; Miller, Abney, Rappe, Anderson & Strauss, 1988; Brown, Clegg, Colquhoun, Daniels, Stephenson & Wade, 1987; Kanters, Schouten, Kroon & Grech, 1991; Malarski, Lis, Grech, Nowicka-Scheibe & Majewska, 1990; Kellett, Anderson, Strauss & Abney, 1989; Wozniak, He, Klinowski, Jones & Grech, 1994; Bartoszak, Dega-Szafran, Grunwald-Wyspianska, Jaskólski & Szafran, 1993) and maleate complexes (James & Williams, 1974*a*,*b*,*c*; Ellison & Levy, 1965; Parvez, 1990; Hsu & Schlemper, 1980; James & Matsushima, 1976; Drobez, Golic & Leban, 1985; Golic, Leban, Detoni, Orel & Hadzi, 1985; Gupta, Van Alsenoy & Lenstra, 1984). The donor–acceptor distance (O2*a*· · ·O4*a*) in the anion is found to be the shortest O· · ·O distance in known hydrogen maleate salts. The formation of the intramolecular $[\mathrm{O{-}H\cdots O}]^-$ hydrogen bond is also accompanied by the deformation of C—C—C bond angles in the anion.

Over the last 10 years or so there has been a considerable concentration of effort to study weaker and weaker intermolecular interactions (Green, 1974; Jeffrey & Saenger, 1991; Hobza & Zahradnik, 1980). Structural properties of weak C—H· · ·O hydrogen bonds have been described in a number of papers (Hobza & Zahradnik, 1980; Taylor & Kennard, 1982; Desiraju, 1991; Steiner & Saenger, 1992*a*,*b*, 1993).

It is interesting to see whether there is any influence of these weak C—H· · ·*X* hydrogen bonds on the thermal parameters of the atoms involved. If a given H atom is significantly involved in hydrogen bonding it should have reduced thermal motions (Steiner, 1994; Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995). On the other hand, the increase of the *D*—H distance should increase the amplitude of vibration of the hydrogen. H atoms are, however, only light atoms and their vibrations are associated with the vibrations of the C atoms they are attached to, hence one would expect a positive correlation between the ratio

$$U_{\rm eq}({\rm N,\ H})/U_{\rm eq}({\rm N,\ C})$$

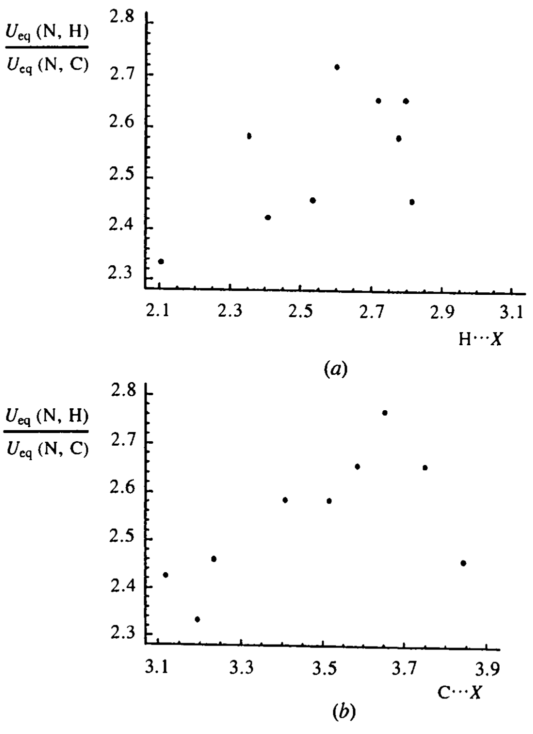

Fig. 3. Relationships between: (*a*) $U_{\rm eq}$(N, H)/$U_{\rm eq}$(N, C) and H· · ·*X* distance, where *X* is an acceptor atom, $U_{\rm eq}$(N, H) is an equivalent temperature factor for a H atom and $U_{\rm eq}$(N, C) is an equivalent temperature factor for the C atom to which the given H atom is attached; (*b*) $U_{\rm eq}$(N, H)/$U_{\rm eq}$(N,C) and C· · ·*X* distance. Interatomic distances in Å.

and the parameters of the C—H···X hydrogen bonds such as H···X or C···X. Such relationships for DMANH$^+$.ClMH$^-$ are displayed in Fig. 3. Both these trends confirm that the presence of weak C—H···C hydrogen bonds does in fact influence the thermal factors of hydrogens involved in hydrogens bonds. There is, however, no correlation between the ratio of U_{22}(N, H)/U_{22}(N, C) [where U_{22} indicates the largest components of the U tensors describing the vibrations of atoms in the direction perpendicular to the plane of the molecule (xz plane)] and any parameters of the C—H···X hydrogen bonds.

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