The influence of weak hydrogen bonds on the properties of 3-cyano-N-methylpyridinium chloride and iodide

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The iodide salt of 3-cyano-*N*-methylpyridinium cation crystallizes as yellow needles in the monoclinic space group $P2_1/n$ with a = 4.8726(5), b = 12.9380(15), c = 13.4629(15) Å, $\beta = 97.463(2)^\circ$, and Z = 4 (mp 196°C). The chloride salt forms colorless plates in the monoclinic space group $P2_1/m$ with a = 7.9488(8), b = 6.4023(7), c = 8.0844(8) Å, $\beta = 112.987(2)^\circ$, and Z = 2 (mp > 220°C). For ring hydrogens interacting with the anion, each salt has C-H···X distances and angles consistent with weak hydrogen bonds as described by recently published criteria (Brammer *et al. Cryst. Growth Design* 2001, *1*, 277; Steiner *Acta Crystallogr*, Sect B 1998, *54*, 456; *Crystallogr. Rev.* 1996, *6*, 1). The chloride salt has an additional interaction between H5 and the cyano nitrogen on an adjacent cation in the same layer, or a total of four coplanar hydrogen bonds from the ring and the cations are tilted relative to each other. There is an unusual hydrogen bond from a methyl hydrogen to a cyano nitrogen in the iodide. Roughly oval $(3.8 \times 5.7 \text{ Å})$ open channels bounded by H5 and iodides run along the *a* axis. Stabilization of these solids by hydrogen bonding is estimated to be at least 1.9 kcal/mole more for the chloride than for the iodide.

KEY WORDS: Weak hydrogen bond; 3-cyano-N-methylpyridinium chloride; iodide.

Introduction

While investigating 3-cyano-*N*-methylpyridinium chloride (CMPCl) as a possible analytical reagent for certain nucleophiles, we discovered that the iodide precursor readily formed long yellow needles from concentrated aqueous solutions. We used the crystals to help characterize this intermediate product by x-ray diffraction. Since we found that 3-cyano-*N*-methylpyridinium iodide (CMPI) melts at 196°C while CMPCl decomposes by charring at around 220°C, we suspected that the chloride was more ionically bound while the iodide, with a larger, softer anion, might exhibit more covalency. However, when we were able to grow and analyze crystals of the chloride for comparison with the iodide, we determined that hydrogen bonding also plays an important role in stabilizing both solids as well as influencing the details of their crystal structures.

Recent analyses of intermolecular interactions in a wide variety of compounds by Brammer, Bruton, and Sherwood,¹ and by Steiner ^{2,3} show persuasively that even H atoms bound to carbon can form weak hydrogen bonds not only with conventional hydrogen bond acceptors such as O, N,

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and F but also with halide ions. We give a detailed analysis of the extent to which the interactions in CMPI and CMPCl conform to the geometric preferences for hydrogen bonds established in these reviews. Cation distortions in the solids relative to a calculated gas-phase ion are also consistent with the hydrogen bonding interactions described herein.

Experimental

CMPI synthesis (see also ref. 4)

The synthesis of 3-cyano-N-methylpyridinium iodide (CMPI) was carried out by dissolving 10.5 g of 3-cyanopyridine in 20-mL benzene and 21.5 g of methyl iodide in 20-mL benzene. (Handle methyl iodide with extreme care-it is a vesiccant which causes blisters on contact with skin.) These solutions were mixed together in a round-bottom flask, closed with a glass stopper and stirred for at least 2 h. The resulting solution is orange yellow. This solution was then refluxed for 5-8 h. All work was performed in a fume hood. The resulting bright yellow slush was stored in a refrigerator overnight then suction filtered to collect the solid product which was subsequently dried in a desiccator. Typical yields were 30-45%. Melting point is 196°C (melt is blood red) in agreement with Pfleiderer et al.⁴

CMPCl synthesis (see also ref. 4)

The chloride is obtained from the iodide by anion exchange of an aqueous solution using Dowex $1 \times 8-400$ (strongly basic anion, 8% cross linking, 200–400 mesh) prepared according to the manufacturer's directions. (The ion exchange resin tends to turn yellow, probably because of an irreversible reaction with some of the hydrolyzed cation. It is only possible to use it once.) Eluent containing dissolved 3-cyano-Nmethylpyridinium chloride (CMPC1) is collected and rotovapped to remove excess water. When most of the solvent has been removed, an oily liquid remains in the bottom of the flask. Addition of absolute ethanol to this liquid causes CMPCl to precipitate as a white solid which can be collected and dried by suction filtration and desiccation. It decomposes by charring at about 220°C so that no melting point was determined. It is typical to obtain yields of no more than 50%.

Crystal growth

CMPI grows long (1-2 cm) yellow needles from aqueous solutions (~0.2 g per mL) within a few hours. Crystals can also be grown from methanol, ethanol, or a 1:1 mixture of acetonitrile and ethanol (~0.02 g in 0.8 mL). CMPI crystals have been observed to be stable in air for more than a year. We have only been successful at growing small CMPCl crystals from a 1:1 mixture of acetonitrile and ethanol (~0.02 g in 0.8 mL) with one drop of 1 M HCl(aq). Left in a shallow pool in a tilted Petri dish, this mixture evaporates overnight to give colorless flat plates. CMPCl crystals degrade if exposed to air for more than a few days.

X-ray crystallography

Crystals of CMPI and CMPCl, obtained as described earlier, were cut to size and mounted on thin glass fibers with silicone grease. Full spheres of data were collected at 100 K on a Bruker Smart APEX CCD diffractometer by using narrow frames $(0.300^{\circ} \text{ scans in } \omega \text{ at } \phi = 0, 120,$ and 240°; detector swing angle = -28.00°) and converted to integrated intensities using standard procedures.⁵ Details specific to the present study are presented in Table 1. In both instances, the choice of space group was made with a combination of observed systematic absences and intensity statistics. An empirical absorption correction (SADABS⁵) was performed for CMPI. The location of the halide ion in each compound was obtained from a Patterson function and the remainder of the structure developed by successive cycles of full-matrix, least-squares refinement followed by

H-bonding in N-methylpyridinium halides

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CCD deposit no.	201734	201735
Compound	CMPI	CMPCl
Empirical formula	$C_7H_7IN_2$	$C_7H_7ClN_2$
Formula weight	246.05	154.6
Temperature, K	100(1)	100(1)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/m
Unit cell dimensions	$a = 4.8726(5) \text{ Å} \qquad \alpha = 90^{\circ}$	$a = 7.9488(8) \text{ Å} \alpha = 90^{\circ}$
	$b = 12.9380(15) \text{ Å} \beta = 97.463(2)^{\circ}$	$b = 6.4023(7) \text{ Å} \beta = 112.987(2)^{\circ}$
	$c = 13.4629(15) \text{ Å} \gamma = 90^{\circ}$	$c = 8.0844(8) \text{ Å} \gamma = 90^{\circ}$
Volume, Å ³	841.53(16)	378.75(7)
Ζ	4	2
Density (calculated), Mg/m ³	1.942	1.356
Absorption coefficient, mm ⁻¹	3.733	0.424
F(000)	464	160
Crystal size	$0.271.183 \times 0.083 \text{ mm}$	$0.285 \times 0.217 \times 0.12 \text{ mm}$
θ range for data collection	2.19–28.72°	2.74–28.26°
Index ranges	$-6 \le h \le 6, -16 \le k \le 17, \\ -17 \le l \le 17$	$-10 \le h \le 10, -8 \le k \le 8, \\ -10 \le l \le 10$
Reflections collected	7141	3495
Independent reflections	$2017 (R_{int} = 0.0161)$	999 ($R_{\rm int} = 0.0287$)
Completeness (to θ)	92.1% (28.72°)	97.3% (28.26°)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	2017/0/92	999/0/61
Goodness of fit on F^2	1.139	1.135
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0167, wR_2 = 0.0412$	$R_1 = 0.0288, wR_2 = 0.0752$
R indices (all data)	$R_1 = 0.0172, wR_2 = 0.0414$	$R_1 = 0.0301, wR_2 = 0.0758$
Extinction coefficient	0.0171(6)	None
Largest diff. peak and hole, eÅ ³	0.586 and -0.632	0.335 and -0.223

Table 1. Crystal Data and Structure Refinement

calculation of a difference map. In both instances, good positions for all of the hydrogen atoms could be obtained from difference maps calculated following completion of the refinement of the non-hydrogen atoms. These locations were used for the hydrogen atoms, which were allowed to ride on the attached carbon atoms with fixed isotropic displacement parameters 20% larger than those of the latter. All calculations were performed with the SHELXTL-PLUS⁶ program package.

Calculation of gas-phase CMP + properties

MacSpartan *Plus* software⁷ was used to calculate properties of the gas-phase cation. Within this software constellation, we ran the ABINITIO program, Release 1.1.9, using the Hartree–Fock approximation and 6-31G* basis set⁸ to optimize the cation geometry. All resultant bond lengths and angles are given in Tables 2 and 3.

Results and discussion

The crystallographic features of CMPI and CMPCl are summarized in Table 1 (see CIF files and Tables 3–9 for greater detail). As can be seen from this summary, exchange of chloride for iodide produces drastic differences in the properties of the CMP halide crystals even though these simple anions are very similar in that they have the same charge, come from the same chemical family, and differ by only about 20% in ionic radius. We might have reasonably expected the two salts to have essentially the same structure but with a somewhat smaller unit cell for the chloride. This proved not to be the case. The unit cell of CMPI

(°)	CMP ⁺	CMPI	CMPCl	(Å)	CMP^+	CMPI	CMPCl
Cyano group							
N2-C7-C3	179.8	177.7(2)	179.59(18)				
Methyl group							
H1a-C1-H1b	110	106	109	N1-C1	1.486	1.496(3)	1.481(2)
H1a-C1-H1c (or a')	111	118	113				
H1b-C1-H1c (or a')	110	107	109	C1-H1a	1.079	0.94	0.94
Average (SD)	110(1)	110(7)	110(2)	C1-H1b	1.077	1.05	1.00
N1-C1-H1a	109	109	108	C1-H1c		0.93	
N1-C1-H1b	109	107	109	C1-H1a'	1.079		0.94
N1-C1-H1c (or a')	109	110	108	avg (SD)	1.078(1)	0.97(7)	0.96(3)
Average (SD)	109(<1)	109(2)	108(1)				
Ring hydrogens							
H2-C2-C3	122	122	122	H2-C2	1.071	0.96	0.82
H2-C2-N1	117	118	118				
H4-C4-C5	121	124	120	H4-C4	1.074	1.02	0.86
H4-C4-C3	120	118	122				
H5-C5-C6	120	116	124	H5-C5	1.072	1.07	0.90
H5-C5-C4	121	124	116				
H6-C6-N1	116	120	115	H6-C6	1.072	1.02	0.98
H6-C6-C5	123	119	125				
Average (SD)	120(2)	120(3)	120(4)	avg (SD)	1.072(1)	1.02(5)	0.89(7)

 Table 2. A Comparison of Selected Experimental Bond Angles and Lengths for the Cation

Note: Significant differences with calculated gas-phase cation noted by boldface (at least 4° for angles including H atoms); such differences between the two salts are indicated in italic.

	CMP ⁺	CMPI	CMPCl
Bond lengths			
N(1) - C(2)	1.332	1.345(3)	1.341(2)
N(1) - C(6)	1.342	1.354(3)	1.344(2)
N(1) - C(1)	1.486	1.496(3)	1.481(2)
N(2)-C(7)	1.134	1.146(3)	1.145(2)
C(2)-C(3)	1.380	1.392(3)	1.379(2)
C(3) - C(4)	1.390	1.402(3)	1.390(2)
C(3)-C(7)	1.440	1.446(3)	1.443(2)
C(4) - C(5)	1.388	1.393(3)	1.388(2)
C(5) - C(6)	1.370	1.392(3)	1.379(2)
Bond angles			
C(2) = N(1) = C(6)	120.8	120.65(18)	121.68(15)
C(2) - N(1) - C(1)	120.4	119.50(17)	118.22(14)
C(6) = N(1) = C(1)	118.7	119.85(17)	120.11(14)
N(1)-C(2)-C(3)	120.8	120.24(18)	119.42(16)
C(2) - C(3) - C(4)	119.0	120.76(19)	120.77(15)
C(2) - C(3) - C(7)	119.3	117.92(18)	118.29(15)
C(4) - C(3) - C(7)	121.7	121.30(19)	120.94(15)
C(5) - C(4) - C(3)	119.1	117.31(19)	117.94(16)
C(6) - C(5) - C(4)	118.9	120.17(19)	119.79(16)
N(1) - C(6) - C(5)	121.3	120.84(19)	120.39(15)
N(2) - C(7) - C(3)	179.8	177.7(2)	179.59(18)

 Table 3. Bond Lengths (Å) and Angles (°) for the Cation (Calculated Gas-Phase for CMP⁺)

consists of four ion pairs having the cation rings tilted relative to one another and oriented with H5 pointed in toward an open oval channel bounded by anions about 5.7 Å apart on the major axis and H5 ring hydrogens about 3.8 Å apart on the minor axis (see Fig. 1). The cations spiral along the *a* axis of the crystal alternating with the io-

Table 4. Atomic Coordinates (10^4) and Equivalent IsotropicDisplacement Parameters (10^3 Å^2) for CMPI

	x	у	z	U _{eq}
I	54(1)	8454(1)	1505(1)	15(1)
N(1)	7016(3)	5991(1)	2413(1)	16(1)
N(2)	4616(4)	8818(2)	4382(2)	27(1)
C(1)	5834(5)	5602(2)	1401(2)	22(1)
C(2)	5901(4)	6830(2)	2794(2)	16(1)
C(3)	6927(4)	7185(2)	3746(2)	16(1)
C(4)	9174(4)	6693(2)	4311(2)	18(1)
C(5)	10309(4)	5840(2)	3883(2)	19(1)
C(6)	9183(4)	5494(2)	2938(2)	18(1)
C(7)	5651(4)	8091(2)	4119(2)	20(1)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table 5. Anisotropic Displacement Parameters (10³ Å²) for CMPI

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I	13(1)	15(1)	17(1)	1(1)	1(1)	0(1)
N(1)	15(1)	15(1)	17(1)	1(1)	2(1)	-1(1)
N(2)	33(1)	23(1)	26(1)	-2(1)	5(1)	4(1)
C(1)	27(1)	22(1)	17(1)	-4(1)	1(1)	1(1)
C(2)	14(1)	15(1)	18(1)	3(1)	2(1)	-1(1)
C(3)	16(1)	13(1)	19(1)	1(1)	5(1)	-1(1)
C(4)	15(1)	20(1)	18(1)	2(1)	1(1)	-3(1)
C(5)	14(1)	18(1)	23(1)	5(1)	1(1)	1(1)
C(6)	15(1)	15(1)	23(1)	3(1)	5(1)	0(1)
C(7)	21(1)	19(1)	18(1)	2(1)	1(1)	1(1)

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

dide ions. The cyano and methyl groups follow each other in a head-to-tail fashion and are not disordered. In contrast, the chloride salt crystallizes in a layer structure with a unit cell of less than half the volume observed for CMPI. The result is that the cations in the chloride salt have crystallographically imposed mirror symmetry and the anions are coplanar with them (see Fig. 2). Successive layers are rotated by 180° with respect to one another allowing the anion in one plane to lie roughly between cations in the adjacent planes. ORTEP drawings of the ion pairs of CMPC1 and CMPI are given, respectively, in Figures 3 and 4.

By carefully examining the interatomic distances and angles found in the crystal structures of CMPI and CMPCl, we show herein that the chloride possesses four hydrogen bonds per CMP⁺, three from ring hydrogens to chloride and one with a cyano nitrogen, while the iodide compound has similar interactions between the cation and the

Table 6. Hydrogen Coordinates (10^4) and Isotropic Displacement Parameters (10^3 Å^2) for CMPI

	x	у	z	$U_{\rm eq}$
H(1A)	5292	4835	1534	21
H(1B)	4028	6038	1190	21
H(1C)	7480	5617	971	21
H(2)	4452	7184	2378	16
H(4)	9886	6986	5001	22
H(5)	12006	5403	4248	40
H(6)	9960	4847	2653	19

 Table 7. Atomic Coordinates (10⁴) and Equivalent Isotropic

 Displacement Parameters (10³ Å²) for CMPCl

	x	У	z	$U_{\rm eq}$
Cl	9045(1)	7500	6794(1)	18(1)
N(1)	9316(2)	2500	7748(2)	17(1)
N(2)	5521(2)	2500	1525(2)	32(1)
C(1)	11327(2)	2500	8729(2)	23(1)
C(2)	8639(2)	2500	5946(2)	18(1)
C(3)	6773(2)	2500	4999(2)	18(1)
C(4)	5589(2)	2500	5890(2)	20(1)
C(5)	6347(2)	2500	7755(2)	22(1)
C(6)	8220(2)	2500	8661(2)	20(1)
C(7)	6081(2)	2500	3062(2)	22(1)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

anion but lacks the ring-hydrogen–cyano-nitrogen (H5–N2) bond. Apparently the smaller ionic radius and higher electronegativity of the chloride ion allow, or promote, the formation of this additional coplanar hydrogen bond. These hydrogen bonds may be responsible for holding the CMPCl cations in flat sheets with the chloride anions while the iodide arranges itself very differently.

Table 10. summarizes the important bond lengths and angles for our samples and compares them to results from Brammer *et al.*¹ and Steiner.² Steiner's analysis included separating out chemically different types of bonds, adjusting C–H distances to 1.083 Å (common practice^{1,2,10} to correct for asphericity by using neutron diffraction measurements¹¹), recalculating associated

Table 8. Anisotropic Displacement Parameters (10³ Å²) for CMPCl

	U^{11}	U^{22}	<i>U</i> ³³	U^{23}	U^{13}	U^{12}
Cl N(1) N(2) C(1) C(2) C(3) C(4) C(5) C(6)	18(1) 18(1) 26(1) 17(1) 22(1) 23(1) 17(1) 24(1) 24(1)	$18(1) \\ 15(1) \\ 48(1) \\ 26(1) \\ 16(1) \\ 16(1) \\ 20(1) \\ 25(1) \\ 19(1)$	$16(1) \\ 16(1) \\ 19(1) \\ 24(1) \\ 18(1) \\ 14(1) \\ 21(1) \\ 21(1) \\ 16(1)$	0 0 0 0 0 0 0 0 0 0	$6(1) \\ 4(1) \\ 6(1) \\ 5(1) \\ 10(1) \\ 5(1) \\ 4(1) \\ 12(1) \\ 7(1)$	0 0 0 0 0 0 0 0 0 0
C(7)	21(1)	26(1)	20(1)	0	8(1)	0

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \cdots + 2hka^* b^* U^{12}].$

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Table 9. Hydrogen Coordinates (10^4) and Isotropic Displacement Parameters (10^3 Å^2) for CMPCl

	x	У	Z	$U_{\rm eq}$
H(1A)	11793	1280	8427	27
H(1B)	11623	2500	10052	27
H(2)	9360	2500	5453	19
H(4)	4427	2500	5328	22
H(5)	5684	2500	8435	25
H(6)	8859	2500	9966	23

 $H \cdots X$ distances, then averaging interactions where $H \cdots X$ was not more than 3.0 Å (3.2 for $H \cdots I$) and the $C-H \cdots X$ angle was not less than 140°. Similarly recalculated distances and angles

for our data are given in Table 10 for comparison. Steiner found the mean $H \cdots Cl$ distance for hydrogens bound to C2 or C6 in pyridine rings to be 2.64 ± 0.02 Å (the uncertainty given here is two standard deviations representing the 95% confidence interval). For the same group of atoms, he found the C \cdots Cl distance to average 3.66 ± 0.02 Å. The three ring hydrogens H2, H4, and H6 in CMPCl easily fit Steiner's hydrogen bond criteria since all the H \cdots Cl distances are shorter than 2.64 Å by at least 0.24 Å and the C \cdots Cl distances are all shorter than 3.66 by at least 0.19 Å.

For iodides, Steiner found the average $H\cdots I$ distance to be 2.99 ± 0.04 Å and $C\cdots I$ to be



Fig. 1. Packing diagram emphasizing the open channel outlined by $H4 \cdots I$ and $H6 \cdots I$ close contacts in CMPI. Looking down the *a* axis, asymmetric unit labeled. Iodide ions are stacked along *a* axis separated by 4.91 Å.



Fig. 2. Layer of CMPCl showing four different hydrogen bonds, three $C-H\cdots Cl$ and one C5H5 \cdots N2. Looking along the *b* axis. Distance between layers is 3.35 Å.

 4.00 ± 0.04 Å (uncertainty as 95% confidence interval). Again, our CMPI data for H2…I, C2…I, and C4…I are easily within their respective ranges. The H4…I distance of 3.03 Å just matches the upper end of the 95% confidence interval so this interaction must be considered to be a marginal case. H6…I is clearly too long since the recalculated distance of 3.08 Å exceeds even the 95% confidence limit of the distribution. Note that the H…I interactions for both H6 and H4 would not have been considered at all by Steiner since the C-H…I angles are less than 140°.

To map out the geometric preferences for halogens as weak hydrogen bond acceptors, Brammer *et al.*¹ used a normalization procedure from Lommerse *et al.*⁹ whereby each close contact of interest in the crystal is divided by the sum of the van der Waals radii for the two atoms in contact, or $R_{\text{HX}} = d(H \cdots X)/(r_{\text{H}} + r_{\text{X}})$. Here $d(H \cdots X)$ is also recalculated after the C–H bond length has been extended along the experimental vector to 1.08 Å.¹ Unlike Steiner, these authors did not distinguish between chemically different types of bonds. They have determined that the mean value of $R_{\rm HX}$ for weak hydrogen bonds between C-H donors and halide ion acceptors is 0.960 for chloride and 0.982 for iodide by considering just cases where $R_{\rm HX} <\sim 1.05$ with C-H...X angles of $\geq 110^{\circ}$. These investigators also found that, for both halides, the C-H...X angle in hydrogen bonds tends to be close to 180° especially for shorter H...X distances.

Because the H····Cl distances for the ring hydrogens H2, H4, and H6 in CMPCl all result in $R_{\rm HX}$ values of about 0.8 (<1 and near 0.960) with angles $\geq 165^{\circ}$, we can conclude that all three of these interactions are described appropriately as hydrogen bonds. We also reach the same conclusion for the iodide case because all of the $R_{\rm HX}$ and angular parameters for the ring hydrogens fit into the distributions determined by Brammer and coworkers (see distribution maps on p. 279 of ref. 1). The H2···I interaction qualifies as a hydrogen bond with $R_{\rm HX} = 0.858$ and a C2-H2···I angle of 168° . H4···I can be classified as a hydrogen bond since $R_{\rm HX} = 0.959$ is

		Bond lengths (Å)					
	$C\cdots X$	Experimental $H \cdots X$	$\begin{array}{c} Recalculated \\ H \cdots X \end{array}$	Recalculated C-H-X (°)	R _{HX}		
CMPCl	3.66(1)		2.64(1)		0.960		
C2H2Cl	3.388(1)	2.59	2.33	165	0.790		
C4H4Cl	3.469(1)	2.62	2.40	172	0.814		
C6H6Cl	3.463(1)	2.50	2.39	170	0.810		
C1H1bCl ^a	3.745(1)	2.80	2.73	157	0.925		
	na		na		na		
C5H5N2	3.359(2)	2.55	2.40	148	0.857		
C1H1bN2 ^a	3.216(2)	2.85	2.84	142	1.014		
CMPI	4.00(2)		2.99(2)		0.982		
C2H2I	3.776(2)	2.83	2.71	168	0.858		
C4H4I	3.843(2)	3.07	3.03	132	0.959		
C6H6I	3.856(2)	3.13	3.08	130	0.978		
	na		na		na		
C1H1cN2	3.556(3)	2.60	2.58	151	0.921		

 Table 10. Close Contacts and Angles Compared to Criteria Characteristic of Weak Hydrogen Bonds from Refs. 1 and 2 (Given in Boldface (SD))

Note: $R_{\text{HX}} = d(H \cdots X)/(r_H + r_X)$ where $r_H = 1.20$, $r_{\text{Cl}} = 1.75$, $r_{\text{I}} = 1.96$, and $r_{\text{N}} = 1.60$ Å from Ref. 9. Criteria for comparison with CH \cdots N not available (na).

^a These interactions not counted in stabilization estimate.

less than 1 and close to 0.982 with a C4—H4…I angle of 132°. H6…I also qualifies with $R_{\text{HX}} =$ 0.978 \approx 0.982 and a C6—H6…I angle of 130°. So using the broader criteria from Brammer *et al.*, we arrive at the same count of three ring H…Cl hydrogen bonds per mole of CMPCl, but we find three ring H…I interactions per mole of CMPI to



Fig. 3. ORTEP perspective of CMPCl (50% probability).

be hydrogen bonds. By Steiner's more restrictive criteria, we identified only two of these interactions as hydrogen bonds in CMPI.

As can be seen in Table 10 and Figs. 1 and 2, there is an additional important close contact in CMPCl that does not exist in CMPI. Here H5 on one cation ring is only 2.40 Å (when the C5-H5 distance is adjusted to 1.08 Å) away from the cyano nitrogen, N2, on the nearest cation in CMPCl. The corresponding $C5-H5\cdots N2$ angle is 148°. We were unable to locate an analysis of a large set of CH ···· N hydrogen bonding interactions so the best comparison available is with a large data set of $CO \cdots H$ bonds.^{12,13} The average distance found for terminal CO · · · H was 2.62 Å, so CMPCl has a contact that is 0.22 Å shorter. Typical angles are around 140° while CMPCl has an even larger, more nearly linear angle of about 148°. It is also true that Reddy et al.¹⁴ reported the synthesis of a 1:1 molecular complex between 1,3,5-tricyanobenzene and hexamethylbenzene where the tricyanobenzene layers show linear CH · · · N hydrogen bonds. The distance between the ring carbon and the cyano nitrogen in



Fig. 4. ORTEP perspective of CMPI (50% probability).

Reddy's compound is either 3.47 or 3.52 Å so that the H \cdots N distance is no more than 2.6 Å. Therefore, we conclude that CMPCl has a fourth hydrogen bond between cations. Apparently this type of bond is weak relative to other packing forces in the iodide so that interactions between ring hydrogens and cyano nitrogens do not exist in these CMPI crystals. Figure 1 shows that all H5 sites are far away from all cyano groups in the iodide salt.

However, CMPI shows evidence of a very unusual weak hydrogen bond between a methyl hydrogen and the cyano nitrogen of an adjacent cation. As we noted when describing the overall crystal structures, the cyano and methyl groups follow each other in a head-to-tail fashion and are not disordered. H1c is always closest to the nearest N2 at 2.58 Å with a C1-H1c ··· N2 angle of 151°. As this distance is less than the sum of the van der Waals radii (1.60 Å for N and 1.20 Å for H = 2.80 Å⁹) and less than the CO···H distance of 2.62 Å discussed in the preceding paragraph, and the $CH \cdots N$ angle is greater than 140°, it warrants consideration even though methyl hydrogens are not generally considered to be acidic enough to form hydrogen bonds. A similar interaction is noted by Thalladi et al.¹⁵ between a methyl hydrogen and an oxygen atom in trimethylisocyanurate as part of the 1:1 molecular complex formed between this compound and 1,3,5-trinitrobenzene. As discussed by Steiner and Desiraju¹⁶, $CH \cdots O/N$ interactions are the archetypes for weak hydrogen bonds in organic and organometallic systems. These authors also point out that even methyl group hydrogens can be activated, or acidified, by attachment to electron-withdrawing groups or atoms (e.g. nitrogen atoms in pyridine or isocyanurate rings). Further evidence for the existence of this hydrogen bond is given in our analysis of cation geometries (*vide infra*).

We might wonder whether a similar methylcyano hydrogen bond exists in CMPC1. It is true that H1b is closer than H1a or H1a' to the nearest N2 by about 0.25 Å at a C-H-N angle of 142°. However, the H-N distance of 2.84 Å slightly exceeds the van der Waals contact of 2.80 Å. We choose not to call this interaction a hydrogen bond until a better basis for judging CH · · · N bonds is available.

This same methyl-group hydrogen (H1b) makes a 2.73 Å contact with a chloride ion. Criteria specific to methyl group $C-H\cdots$ Cl interactions are not available but this distance is just outside the range of 2.64 ± 0.02 Å for Steiner's criterion for (NC)Csp²-H. In addition, the C \cdots Cl distance (3.745 Å) is longer than Steiner's criterion of 3.66 ± 0.02 Å. However, the C-H-Cl angle of 157° and the $R_{\rm HX}$ value of 0.925 are consistent with broader criteria from Brammer *et al.*

Along with comparisons of bond distances and angles with published criteria, cation distortions relative to non-hydrogen-bonded CMP⁺ might offer further evidence for the existence of these weak hydrogen bonds. The only other published example of a crystal structure containing CMP⁺ is that of 3-cyano-N-methylpyridinium tetraphenylborate.¹⁷ The structure of this compound is dominated by the large anion and affords no opportunities for hydrogen bonding between the cations. However, the methyl and cyano groups of the cation are found to occupy similar spaces in the anion framework such that the whole cation is disordered in the crystal. Because of the disorder, the estimated standard deviations (esd's) associated with bond distances and angles for the cation are too large to allow useful comparisons with our data. Ultimately we chose

to compare cation geometries in the crystals (see Figs. 3 and 4) to that calculated for a gas-phase cation. MacSpartan software was used to perform a Hartree–Fock calculation for this purpose $(6-31G^*$ basis set, geometry optimization).^{7,8}

Perhaps the most interesting outcome of this analysis is that it convincingly supports the existence of the H1c \cdots N2 hydrogen bond, between the methyl group on one cation and the cyano group on another, in CMPI. Useful data for CMPI, CMPCl, and gas-phase CMP⁺ (calculated) are given in Table 2. Note that the bond from the pyridine nitrogen to the methyl carbon, N1-C1, is significantly longer in CMPI than in either CMPCl or CMP⁺ since the respective 99% confidence intervals of this bond length in CMPI and CMPCl just meet at their limits, 1.496 - 3(0.003) = 1.487 =1.481 + 3(0.002). This distance is essentially the same in both CMP⁺ and CMPCl. In addition, the almost perfectly linear trio of atoms N2-C7-C3 is bent by about 2° at C7 in CMPI. This angle also differs significantly (99% confidence level) since $177.7 + 3(0.2) = 178.3^{\circ} <$ $179.05^{\circ} = 179.59 - 3(0.18)$. It is easy to envision these clearly complementary distortions with one cation bending slightly at C7 while a neighboring cation elongates somewhat at N1-C1, thereby allowing N2 on one cation and H1c on another to be closer together in order to facilitate an attractive force between them (see Fig. 1).

Table 2 also summarizes the experimentally determined bond angles and lengths for the methyl group and ring hydrogens found in CMPI, CMPCl, and gas-phase CMP⁺ (calculated). Because the hydrogen atom positions were not refined, no derived esd's are available. However, esd's for the C-C-H ring angles can be estimated to be approximately six to eight times those for the C-C-C angles, or $1.2-1.6^{\circ}$. Thus one needs angular differences of $> 3.2^{\circ}$ to be significant at the 95% confidence level. This crude estimate suggests that differences of 4° may be meaningful so we have indicated discrepancies of at least that size between gas-phase CMP⁺ and either crystal with boldface while such differences between the two crystals are shown in italic.

H-bonding in N-methylpyridinium halides

One might notice that H1a-C1-H1c in CMPI is the only methyl group angle showing meaningful differences with the other two cation types. Indeed, 118° is by far the largest methyl group angle for any of the three cation types with almost all of the angles very close to the sp^3 theoretical value of 109.5°. This observation fits with the discussion in the previous paragraph since it is H1c that hydrogen bonds with N2 on another cation.

The largest distortion in this data for the ring hydrogens relative to the calculated gas-phase result is the H5-C5 vector tilted toward C4 by 5° in CMPCl; the two crystals also differ from each other by 8° in the orientation of this vector. This comparison supports the idea that the H5...N2 interaction is an important, structuredetermining force for CMPCl. It was apparently this type of interaction that created sheets of 1,3,5-tricyanobenzene molecules in Reddy's complex.¹⁴ Differences between the two solids of at least 4° for the angles about C4 and C6 are consistent with assignments to ring $H \cdots X$ hydrogen bonds based on reviews as discussed previously. However, neither salt has angles appreciably different from those about C2 in the gas-phase ion, or from each other, even though both structures clearly exhibit hydrogen bonding from this ring position. Interestingly, CMPCl has the greatest variance for ring hydrogen angles (standard deviation of 4°) even though the CMPCl structure generally has lower esd's for the refined atoms. It should be noted that all of the interior ring angles, observed as well as calculated, are $120 \pm 2^{\circ}$ with the exception of C5-C4-C3 that is calculated to be 119° but observed to be 117° in CMPI and 118° in CMPCl (see Table 3 for complete list).

With respect to C—H bond length distortions for the cation in the solids, all of the ring C—H bonds for the gas-phase ion are calculated to be about 1.07 Å while the observed distances from x-ray diffraction data are about 1.02 Å in CMPI and 0.89 Å for CMPCl (see Table 2). Lower values in the solids are probably primarily due to typical bond length shortening for hydrogen locations determined with x-rays attributable to asphericity as described by Allen.¹¹ It is perhaps sufficient to note that CMPCl exhibits greater variance than CMPI in these bond lengths, as well as for the bond angles as mentioned previously, even though esd's for the refined atoms in the chloride structure are smaller. Wider variation in these parameters could be an indication of more extensive, probably stronger, hydrogen bonding in CMPCl. All of the methyl C-H bonds are calculated to be about 1.08 Å while the salts each exhibit two bonds at about 0.94 Å and one longer bond (1.05 Å in CMPI, 1.00 Å in CMPCI). We note slightly greater variance in C-H lengths for the CMPI methyl group in agreement with the notion that it participates in hydrogen bonding with N2 while the methyl group in the CMPCl cation probably does not.

As mentioned previously, the cation in 3cyano-N-methylpyridinium tetraphenylborate is disordered because of its location on a site of crystallographic mm2 symmetry. It is noteworthy that such disorder is not found in CMPI or CMPCI. This contrast with the tetraphenylborate is one more testament to the influence of the hydrogen bonds on the structures of the halide compounds because those forces are clearly absent, or at least unable to develop, in the tetraphenylborate.

While it is beyond our expertise to construct an adequate overall theoretical model for these crystals, we can make a crude attempt at assigning energies for the special interactions identified previously to estimate and compare the amount of stabilization they confer upon these compounds. An appropriate estimate for the minimum difference in stabilization between CMPCl and CMPI can be obtained by assigning a reasonable energy to each of the hydrogen bonds discussed previously, summing these energies for each salt, then subtracting the answers. To obtain a minimum difference, questionable assignments are included for CMPI (C6H6 \cdots I) but excluded for CMPCl (C1H1b \cdots Cl, C1H1b \cdots N2). Following Desiraju and Steiner (Ref. 16, p. 110), the cation-cation interactions can be assigned. This approach gives H5...N2 in CMPCl a value of 2 kcal/mol by analogy with $C-H \cdots O$ hydrogen bonds with acidic donors, and H1c ··· N2 in CMPI a value of 1 kcal/mole since H1c is part of an activated methyl group. We did not find the energy of stabilization for $H \cdots X$ interactions with halide ions to be clearly described in any reference. So we assign $H \cdots I$ a value of 0.5 kcal/mole since we expect this bond to be stronger than $H_3CH \cdots FCH_3$ at 0.2 kcal/mole¹⁸ but probably weaker than $-NH_2 \cdots I$ -Ir- at about 1.3 kcal/mole.¹⁹ In addition, we count $H \cdots Cl$ bonds as about 1.6 times as strong as analogous $H \cdots I$ bonds on the basis of the work of Peris et al.¹⁹ Combining all of this reasoning leads to $3(H \cdots I) + (H1c \cdots N2) = 3(0.5) +$ 1 = 2.5 kcal/mole in CMPI and 3 (H···Cl) + $(H5 \cdots N2) = 3(1.6)(0.5) + 2 = 4.4$ kcal/mole in CMPCl, or an additional 1.9 kcal/mole stabilization in the chloride salt. This greater stabilization for the chloride salt is consistent with the observed lower melting point of CMPI. Indeed, the fact that CMPCl chars at about 220°C rather than changing phase implies that the energy required to decompose the cation is less than that needed to dissociate intermolecular forces in the solid.

Summary

Four hydrogen bonds are present per cation in CMPCl, three between ring hydrogens H2, H4, H6, and chloride ions, and one between H5 and a cyano nitrogen on another cation. Similar hydrogen bonds exist in CMPI between ring hydrogens and iodide ions. There is also a hydrogen bond between a methyl group hydrogen and the cyano nitrogen in an adjacent cation in CMPI. While $H5 \cdots N2$ appears to be the strongest of all of these interactions based on the work of other investigators, this type of bond is missing in CMPI suggesting that other kinds of opposing packing forces dominate. Since four coplanar interactions are observed in CMPCl, either the opposing packing forces are weaker than the hydrogen bonds or the other packing forces are synergistic with the hydrogen bonds, e.g., chloride is small enough to allow closer anion–anion packing than iodide so the hydrogen bonding partners can get close enough to find one another. In any case, hydrogen bonds have a marked effect on the crystal structures and properties of these two compounds.

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