

## Geometries of Donor–Acceptor Complexes: Crystal Structures of the Iodide, Chloride, and Picrate Salts of 1-Methylnicotinamide

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Three-dimensional X-ray diffraction data, collected with an automated diffractometer, were used to determine the crystal structures of the iodide, chloride, and picrate salts of 1-methylnicotinamide (3-carbamyl-1-methylpyridine; 1-MN). Crystals of 1-MN iodide ( $C_7H_9N_2O \cdot I$ ) are monoclinic, space group  $P2_1/c$ , with  $a=4.875$  (1),  $b=13.069$  (1),  $c=14.657$  (3) Å and  $\beta=104.66$  (2)°; crystals of 1-MN chloride ( $C_7H_9N_2O \cdot Cl$ ) are orthorhombic, space group  $Pbca$ , with  $a=15.501$  (5),  $b=13.937$  (4), and  $c=7.600$  (2) Å; and crystals of 1-MN picrate ( $C_7H_9N_2O \cdot C_6H_2N_3O_7$ ) are triclinic, space group  $P\bar{1}$ , with  $a=13.258$  (4),  $b=8.041$  (3),  $c=7.887$  (4) Å,  $\alpha=112.38$  (6),  $\beta=94.97$  (7), and  $\gamma=100.65$  (5)°. Trial structures, obtained by direct and heavy-atom methods, were refined by least-squares calculations to  $R$  values of 0.043, 0.030, and 0.069 for the iodide, chloride, and picrate salts, respectively. The iodide and chloride structures display exceptionally close contacts between halide anions and nicotinamide moieties. In both structures, the halide ions are in intimate contact with atom C(2) of the nicotinamide; the C(2)···I distance of 3.537 Å and the C(2)···Cl distance of 3.239 Å are about 0.3 Å shorter than normal van der Waals contacts. The bond lengths and angles for the 1-MN cations in the three crystal structures are in agreement. The conformation about C(3)–C(8), the bond between the pyridinium ring and the carboxamide moiety, is considerably different in the halide structures from that in the picrate structure. The results indicate that charge-transfer interactions, which are probably involved in the iodide salt but not in the chloride and picrate salts, exert little influence on the iodide contacts with 1-MN or on the geometry of the 1-MN cation.

### Introduction

During the past decade there has been considerable interest in the physical and structural properties of donor–acceptor (charge-transfer) complexes (Mulliken & Person, 1969; Hassel, 1970; Foster, 1969; Lippert, Hanna & Trotter, 1969; Dewar & Thompson, 1966; Prout & Wright, 1968). Despite numerous theoretical and experimental studies, several fundamental questions concerning the geometries of donor–acceptor complexes remain unanswered. In particular, little is known about the relative importance of coulombic factors, classical van der Waals interactions, and charge-transfer forces in controlling the overall configuration and donor–acceptor contacts in charge-transfer complexes. Neither is there a suitable method for predicting the effects that charge-transfer interactions exert on the internal geometries of the donor and acceptor moieties.

Of the many aromatic acceptors that have been investigated by spectroscopic methods, pyridinium cations have been studied especially extensively (Kosower, 1956; Verhoeven, Dirx & DeBoer, 1970; Mackay, Landolph & Poziomek, 1971; Kosower & Skorcz, 1960; Mackay & Poziomek, 1972; Cozzens & Gover, 1970; Kosower, 1955; Rembaum, Hadek & Yen, 1971; Bradshaw & Deranleau, 1970; Cilento & Tedeschi, 1961; Alivisatos, Ungar, Jibril & Mourkides, 1961; Robbins & Holmes, 1972; Deranleau & Schwyzer, 1970; Cilento & Zinner, 1968; Shifrin, 1965, 1969;

Kosower, 1960; Shifrin, 1968), usually as iodide charge-transfer complexes (Kosower, 1956; Verhoeven, Dirx & DeBoer, 1970; Mackay, Landolph & Poziomek, 1971; Kosower & Skorcz, 1960; Mackay & Poziomek, 1972; Cozzens & Gover, 1970; Kosower, 1955; Shifrin, 1969). Of the pyridinium cations, particular attention has been given to the acceptor properties of substituted nicotinamide derivatives (Bradshaw & Deranleau, 1970; Cilento & Tedeschi, 1961; Alivisatos, Ungar, Jibril & Mourkides, 1961; Robbins & Holmes, 1972; Deranleau & Schwyzer, 1970; Cilento & Zinner, 1968; Shifrin, 1965, 1969; Kosower, 1960; Shifrin, 1968), since the nicotinamide coenzymes of biological systems may mediate their activity through the formation of charge-transfer complexes (Cilento & Zinner, 1968; Shifrin, 1965, 1969; Kosower, 1960; Shifrin, 1968). The simplest of the substituted nicotinamides, 1-methylnicotinamide (3-carbamyl-1-methylpyridine; 1-MN, Fig. 1), forms donor–acceptor complexes with iodide ions (Kosower, 1960) and with indoles (Alivisatos, Ungar, Jibril & Mourkides, 1961; Robbins & Holmes, 1972; Deranleau & Schwyzer, 1970), but no structural studies of these complexes have been reported.

To investigate the structural factors involved in iodide interactions with pyridinium cations, we determined the crystal structure of the iodide salt of 1-MN. To compare the interactions and structural features in this iodide salt with that found in related systems where charge-transfer forces are expected to be of little or

no importance, we also determined the crystal structures of the chloride and picrate salts of 1-MN. In this paper we describe these three crystal structures, and discuss the effects that charge-transfer interactions appear to exert on iodide-pyridinium contacts and on the geometry of the 1-MN cation.

### Experimental

#### 1-Methylnicotinamide iodide

Large yellowish-green prisms of 1-MN iodide were obtained by slow evaporation of an aqueous solution of the salt. Weissenberg and oscillation photographs showed the crystals to be monoclinic; the space group  $P2_1/c$  was indicated by the absence of reflections  $0k0$  with  $k$  odd and  $h0l$  with  $l$  odd. A crystal with approximate dimensions of  $0.20 \times 0.20 \times 0.22$  mm was mounted on a Picker FACS-1 diffractometer with its  $a$  axis slightly inclined to the  $\varphi$  axis of the diffractometer. Unit-cell parameters were obtained by a least-squares refinement of  $2\theta$  values for 12 high-angle  $\text{Cu } K\alpha_1$  reflections ( $\lambda = 1.54051 \text{ \AA}$ ) measured with the diffractometer. Table 1 lists unit-cell parameters and other crystal data.

The intensities of 1501 independent reflections were measured with the diffractometer, by using a scintillation counter, nickel-filtered copper radiation and a  $\theta$ - $2\theta$  scanning technique to the limit of  $128^\circ$  in  $2\theta$ . Those reflections with scan counts below background levels were assigned intensity values of 0.00, and were retained in all subsequent calculations. The intensities were assigned variances,  $\sigma^2(I)$ , based on the counting statistics plus a correctional term  $(0.03S)^2$ ,  $S$  being the scan count. The intensities and their variances were corrected for Lorentz and polarization factors, and absorption corrections were applied by using the computer program *ORABS* (Wehe, Busing & Levy, 1962). The first derivatives of the transmission factors with respect to the absorption coefficient were computed for subsequent calculation of extinction correction factors. The data were scaled by means of a Wilson (1942) plot. A suitable trial structure was obtained by the heavy-atom method.

#### 1-Methylnicotinamide chloride

Clear, colorless prisms of 1-MN chloride were obtained by slowly evaporating an aqueous solution of the salt. Weissenberg and oscillation photographs showed that the crystals are orthorhombic. The space group is  $Pbca$  as indicated by the absence of reflections  $0kl$  with  $k$  odd,  $h0l$  with  $l$  odd, and  $hk0$  with  $h$  odd. A prism with approximate dimensions of  $0.21 \times 0.21 \times 0.22$  mm was mounted on the diffractometer with its  $c$  axis slightly inclined to the  $\varphi$  axis of the diffractometer. The  $2\theta$  values for ten high-angle  $\text{Cu } K\alpha_1$  reflections were measured, and the unit-cell parameters were obtained from a least-squares analysis of these measurements. Crystal data are listed in Table 1.

Intensity data for the 1361 independent reflections with  $2\theta \leq 128^\circ$  were collected with the diffractometer. The experimental conditions and treatment of the data were the same as described for 1-MN iodide. A suitable trial structure was obtained by the heavy-atom method.

#### 1-Methylnicotinamide picrate

The picrate salt of 1-MN was crystallized as yellow prisms by slowly cooling a hot, saturated aqueous solution containing approximately equimolar quantities of 1-MN iodide and of picric acid. Weissenberg and oscillation photographs showed that the crystals are triclinic, with space group  $P1$  or  $P\bar{1}$ . A crystal fragment, with approximate dimensions of  $0.08 \times 0.18 \times 0.20$  mm, was cut from a large prism and mounted on the diffractometer with its  $c$  axis slightly inclined to the  $\varphi$  axis

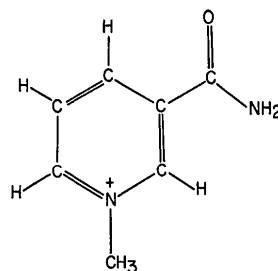


Fig. 1. Structural formula of 1-MN.

Table 1. *Crystal data*

	1-Methylnicotinamide iodide	1-Methylnicotinamide chloride	1-Methylnicotinamide picrate
Stoichiometry	$\text{C}_7\text{H}_9\text{N}_2\text{O} \cdot \text{I}$	$\text{C}_7\text{H}_9\text{N}_2\text{O} \cdot \text{Cl}$	$\text{C}_7\text{H}_9\text{N}_2\text{O} \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_7$
$Z$	4	8	2
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$
$a$	4.875 (1) $\text{\AA}$	15.501 (5) $\text{\AA}$	13.258 (4) $\text{\AA}$
$b$	13.069 (1)	13.937 (4)	8.041 (3)
$c$	14.657 (3)	7.600 (2)	7.887 (4)
$\alpha$	—	—	112.38 (6) $^\circ$
$\beta$	104.66 (2) $^\circ$	—	94.97 (7)
$\gamma$	—	—	100.65 (5)
Cell volume	903.479 $\text{\AA}^3$	1642.004 $\text{\AA}^3$	752.624 $\text{\AA}^3$
$\rho$ (calculated)	1.941 $\text{g cm}^{-3}$	1.396 $\text{g cm}^{-3}$	1.612 $\text{g cm}^{-3}$
$\rho$ (observed)	1.95 $\text{g cm}^{-3}$	1.42 $\text{g cm}^{-3}$	1.60 $\text{g cm}^{-3}$
$\mu$ ( $\text{Cu } K\alpha$ )	280.0 $\text{cm}^{-1}$	36.7 $\text{cm}^{-1}$	12.0 $\text{cm}^{-1}$

of the diffractometer. The  $2\theta$  values for 12 high-angle  $\text{Cu } K\alpha_1$  reflections were measured, and the unit-cell parameters were obtained from a least-squares analysis of these measurements. Table 1 lists unit-cell parameters and other crystal data.

Intensity data for the 2498 independent reflections with  $2\theta \leq 127.5^\circ$  were collected with the diffractometer. The experimental conditions and treatment of the data duplicate those described for 1-MN iodide.

The statistical distribution of normalized structure factor magnitudes ( $|E|$ 's) indicated that the crystal structure is centrosymmetric, and the experimental density indicated that the unit cell contains two formula units of 1-MN picrate. Consequently, we as-

sumed that the space group is  $P\bar{1}$ ; this assumption was corroborated by the final structure analysis. A trial structure was obtained by direct methods with the use of Long's (1965) computer program which determines signs by reiterative application of Sayre's (1952) relationship.

### Refinement of the trial structures

The trial structures were refined by use of a modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962; Busing, 1971). The quantity minimized was  $\sum w(F_o^2 - F_c^2/k^2)^2$ , where  $k$  is a scale factor and the weight  $w$  is equal to  $1/\sigma^2(F_o^2)$ .

Table 2. Final heavy-atom parameters and their standard deviations

The values have been multiplied by  $10^5$ . Temperature factors are in the form

$$T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl).$$

ATOM	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
<b>1-METHYLNICOTINAMIDE IODIDE</b>									
I	12072(8)	13815(3)	16608(3)	3840(31)	418(4)	340(3)	-100(5)	484(6)	-2(2)
N(1)	54287(119)	36001(33)	28823(39)	4289(257)	284(27)	342(28)	-22(60)	480(69)	9(20)
C(2)	67823(122)	27220(43)	32152(40)	3948(264)	334(31)	291(28)	63(74)	379(71)	-14(23)
C(3)	67333(117)	23604(39)	40886(37)	3908(250)	283(27)	263(27)	-40(72)	264(67)	-20(23)
C(4)	52288(135)	29015(45)	46170(42)	4918(299)	379(33)	304(30)	-85(83)	453(77)	13(26)
C(5)	38808(167)	37984(52)	42607(52)	5581(371)	469(36)	396(37)	283(97)	597(97)	-35(29)
C(6)	39980(132)	41410(52)	33960(45)	4558(316)	352(35)	474(39)	204(83)	422(89)	-40(28)
C(7)	54457(207)	39439(62)	19205(52)	7607(493)	421(41)	346(36)	-192(120)	510(109)	79(30)
C(8)	82151(149)	13770(41)	44733(47)	4634(313)	372(35)	325(33)	44(78)	482(81)	21(25)
N(8)	99709(143)	09704(55)	40374(51)	5672(333)	564(41)	494(37)	703(99)	880(92)	214(32)
O(8)	76489(136)	09979(40)	51737(37)	9281(384)	481(30)	480(29)	1047(93)	1254(87)	186(25)
<b>1-METHYLNICOTINAMIDE CHLORIDE</b>									
Cl	25123(2)	39224(3)	44995(6)	334(2)	508(3)	1725(11)	100(2)	71(3)	97(4)
N(1)	43108(9)	56729(9)	29219(17)	345(6)	303(6)	1276(25)	-10(5)	-43(10)	32(11)
C(2)	40055(10)	48898(10)	21055(21)	296(7)	330(8)	1313(30)	-20(6)	-46(11)	68(12)
C(3)	45505(10)	41532(10)	16304(20)	308(7)	323(8)	1113(28)	-16(6)	14(11)	96(11)
C(4)	54242(11)	42491(12)	19740(23)	295(7)	411(9)	1531(34)	12(6)	44(12)	83(14)
C(5)	57245(11)	50628(12)	28170(24)	279(7)	527(10)	1632(35)	-69(6)	-66(12)	113(15)
C(6)	51580(11)	57647(12)	32949(22)	399(8)	389(9)	1372(31)	-89(7)	-101(13)	67(14)
C(7)	37011(16)	64434(15)	34141(36)	510(11)	421(10)	2236(48)	108(8)	-122(19)	-227(19)
C(8)	42310(11)	32674(12)	07021(20)	344(7)	320(8)	1246(30)	9(6)	-33(12)	86(12)
N(8)	34172(10)	30258(12)	09998(24)	363(7)	440(9)	1837(34)	-82(6)	43(13)	-278(14)
O(8)	47231(8)	28229(8)	-02740(17)	426(6)	389(7)	1578(25)	49(5)	113(9)	-78(10)
<b>1-METHYLNICOTINAMIDE PICRATE</b>									
<b>1-METHYLNICOTINAMIDE CATION</b>									
N(1)	62118(16)	32682(28)	88583(29)	373(13)	1100(41)	1430(46)	63(18)	11(19)	507(35)
C(2)	57413(20)	14813(34)	84053(35)	443(17)	1059(48)	1362(54)	119(23)	122(24)	533(42)
C(3)	47693(18)	07120(32)	73212(34)	410(16)	1105(48)	1218(50)	137(22)	190(23)	447(40)
C(4)	42849(20)	18026(35)	66808(37)	367(17)	1258(51)	1548(59)	125(23)	127(25)	551(44)
C(5)	47833(20)	36310(36)	71622(39)	434(18)	1220(51)	1916(65)	240(24)	148(26)	795(48)
C(6)	57416(20)	43407(36)	82514(38)	426(17)	1091(50)	7138(60)	112(23)	156(25)	664(45)
C(7)	72549(26)	40552(47)	100233(57)	478(21)	1475(63)	2540(87)	-108(28)	-395(34)	795(61)
C(8)	43083(20)	-12952(34)	69182(37)	460(18)	1139(49)	1580(58)	123(24)	115(25)	586(44)
N(8)	34148(18)	-21215(33)	57451(36)	423(15)	981(46)	2200(61)	19(22)	-20(24)	557(43)
O(8)	47821(16)	-20886(26)	76585(31)	729(16)	1282(40)	2630(56)	26(20)	-314(24)	997(40)
<b>PICRATE ANION</b>									
C(1)	13255(19)	-03932(33)	33673(34)	409(17)	1036(48)	1325(54)	97(22)	29(23)	483(41)
C(2)	10774(19)	11753(32)	30993(34)	393(16)	970(46)	1301(53)	9(21)	67(23)	449(40)
C(3)	01230(20)	12876(35)	24372(36)	493(18)	958(47)	1468(57)	168(24)	88(25)	538(44)
C(4)	-07225(18)	-01876(32)	20969(34)	358(15)	1067(47)	1302(52)	122(21)	43(22)	496(41)
C(5)	-05824(21)	-17171(34)	23806(37)	414(17)	1006(49)	1602(59)	24(23)	59(25)	489(44)
C(6)	03934(19)	-18247(32)	29785(36)	424(17)	867(45)	1619(57)	118(22)	21(24)	561(41)
O(1)	22374(14)	-04897(25)	37847(28)	370(12)	1397(39)	2336(50)	110(17)	-89(19)	859(37)
N(2)	19494(18)	27739(30)	35471(35)	455(15)	1017(42)	2067(60)	70(20)	106(25)	595(42)
O(2)	20960(19)	33559(32)	23518(35)	929(20)	2101(53)	2642(61)	-276(25)	475(27)	1224(48)
O'(2)	24672(19)	34752(30)	50885(35)	864(19)	1695(48)	2743(64)	-452(24)	-670(28)	908(46)
N(4)	-17523(17)	-01140(30)	14302(31)	417(15)	1397(47)	1597(52)	231(21)	52(21)	585(40)
O(4)	-24998(14)	-13024(28)	13877(30)	348(12)	1884(47)	2444(53)	88(20)	143(20)	837(41)
O'(4)	-18450(16)	11054(31)	-09078(34)	618(16)	2229(52)	3248(64)	424(23)	70(24)	1791(49)
N(6)	04607(19)	-35196(31)	31860(38)	512(17)	1125(47)	2854(70)	87(23)	-71(27)	1029(48)
O(6)	-02337(21)	-48809(32)	23353(51)	957(23)	1258(49)	7289(130)	-297(27)	-1147(43)	2097(66)
O'(6)	11780(18)	-34994(31)	42710(39)	656(17)	2131(53)	4412(82)	206(24)	-269(29)	2144(57)

Scattering factors for chlorine, oxygen, nitrogen, and carbon atoms were from *International Tables for X-ray Crystallography* (1962). Scattering factors for the iodide ion were from Cromer & Waber (1965). The scattering factors that were used for iodine were those for a monovalent iodide anion; all other scattering factors, including those that were used for chlorine, were for the un-ionized states of the atoms. Anomalous dispersion correction factors from *International Tables for X-ray Crystallography* (1962) were applied to the scattering factors for oxygen, chlorine and iodide. Hydrogen atom scattering factors were from Stewart, Davidson & Simpson (1965). All hydrogen atoms were located in difference Fourier maps that were calculated during the latter stages of refinement. Final cycles of refinement included positional parameters for all atoms, anisotropic temperature factors for the non-hydrogen atoms, isotropic temperature factors for the hydrogen atoms, and Zachariasen's (1963) isotropic extinction parameter  $g$  (as formulated by Coppens & Hamilton, 1970). During the last cycles of refinement, no parameter shifted more than one-fifth of its estimated standard deviation. Difference Fourier maps that were calculated after the refinements showed residual fluctuations ranging from  $-0.3$  to  $0.4 \text{ e}\text{\AA}^{-3}$  in the picrate structure, and from  $-0.1$  to  $0.2 \text{ e}\text{\AA}^{-3}$  in the chloride structure; a final difference Fourier map for the iodide structure showed several large peaks and troughs with magnitudes of about  $1 \text{ e}\text{\AA}^{-3}$  in the immediate vicinity of the iodide ion, but no other fluctuations with magnitudes in excess of  $0.5 \text{ e}\text{\AA}^{-3}$ . The final  $R$  index ( $= \sum |F_o| - |F_c| / \sum |F_o|$ ) is 0.043 for 1-MN iodide, 0.030 for 1-MN chloride and 0.069 for 1-MN picrate. The final goodness-of-fit  $\{[\sum w(F_o^2 - F_c^2/k^2)^2 / (m-s)]^{1/2}$ , where  $m$  is the number of reflections used and  $s$  is the number of parameters refined} is 1.97 for 1-MN iodide, 2.04 for 1-MN chloride and 2.42 for 1-MN picrate.

## Results

Tables 2 and 3 list final parameters and estimated standard deviations for nonhydrogen atoms and for hydrogen atoms, respectively. The estimated errors in positional coordinates are as follows: in the iodide structure,  $0.0004 \text{ \AA}$  for the iodide ion,  $0.007 \text{ \AA}$  for the carbon, nitrogen, and oxygen atoms, and  $0.15 \text{ \AA}$  for the hydrogen atoms; in the chloride structure,  $0.0003 \text{ \AA}$  for the chloride ion,  $0.002 \text{ \AA}$  for the carbon, nitrogen, and oxygen atoms, and  $0.03 \text{ \AA}$  for the hydrogen atoms; and in the picrate structure,  $0.003 \text{ \AA}$  for the carbon, nitrogen, and oxygen atoms, and  $0.04 \text{ \AA}$  for the hydrogen atoms. Observed and calculated structure factors for 1-MN iodide, 1-MN chloride, and 1-MN picrate are listed in Tables 4, 5, and 6, respectively.

### Molecular structures

Fig. 2 shows the conformations and the heavy-atom thermal ellipsoids (Johnson, 1965). The three nicotina-

Table 3. *Hydrogen-atom parameters and their standard deviations*

The positional parameters have been multiplied by  $10^3$

	$x$	$y$	$z$	$B (\text{\AA}^2)$
1-Methylnicotinamide iodide				
H(C2)	761 (12)	242 (5)	278 (4)	2.4 (1.2)
H(C4)	520 (10)	265 (4)	530 (4)	1.3 (0.9)
H(C5)	295 (13)	425 (5)	470 (5)	2.8 (1.3)
H(C6)	294 (16)	479 (7)	312 (5)	4.4 (1.6)
H(C7)	396 (26)	359 (7)	154 (9)	6.3 (2.7)
H'(C7)	714 (33)	354 (9)	165 (9)	8.5 (3.6)
H''(C7)	586 (19)	453 (9)	191 (7)	5.9 (2.3)
H(N8)	1047 (16)	117 (6)	360 (6)	3.1 (1.6)
H'(N8)	1072 (17)	049 (7)	424 (6)	4.5 (1.9)
1-Methylnicotinamide chloride				
H(C2)	341 (1)	489 (1)	177 (2)	3.1 (0.4)
H(C4)	580 (1)	378 (1)	158 (2)	3.3 (0.4)
H(C5)	630 (1)	512 (1)	314 (2)	3.9 (0.4)
H(C6)	533 (1)	636 (1)	387 (3)	3.8 (0.4)
H(C7)	328 (2)	618 (2)	414 (4)	8.2 (0.9)
H'(C7)	398 (2)	691 (2)	420 (3)	7.3 (0.7)
H''(C7)	356 (2)	676 (2)	249 (5)	9.2 (0.9)
H(N8)	310 (1)	325 (2)	186 (3)	5.1 (0.5)
H'(N8)	321 (1)	251 (2)	055 (3)	4.6 (0.5)
1-Methylnicotinamide picrate				
1-Methylnicotinamide cation				
H(C2)	613 (2)	078 (4)	889 (4)	3.2 (0.6)
H(C4)	360 (2)	132 (4)	600 (4)	3.5 (0.6)
H(C5)	447 (2)	440 (4)	678 (4)	3.2 (0.6)
H(C6)	616 (2)	558 (4)	863 (4)	3.4 (0.6)
H(C7)	744 (4)	534 (8)	1032 (7)	10.3 (1.4)
H'(C7)	781 (4)	366 (8)	940 (8)	11.9 (1.7)
H''(C7)	725 (3)	366 (6)	1094 (6)	8.1 (1.2)
H(N8)	303 (3)	-153 (5)	532 (4)	4.9 (0.8)
H'(N8)	316 (2)	-327 (5)	556 (4)	4.3 (0.7)
Picrate anion				
H(C3)	002 (2)	230 (4)	228 (4)	3.5 (0.6)
H(C5)	114 (2)	274 (4)	783 (4)	4.4 (0.7)

midium cations assume different conformations about C(3)-C(8), the bond between the pyridinium ring and the carboxamide group. The torsion angle  $\tau[\text{C}(2)-\text{C}(3)-\text{C}(8)-\text{O}(8)]$  is  $166^\circ$  in the iodide structure,  $152^\circ$  in the chloride structure and  $5^\circ$  in the picrate structure. A theoretical calculation (Coubeils, Pullman & Courri re, 1971) of the conformation of nicotinamide predicts that the most stable conformation would be one in which  $\tau = 150^\circ$ , and that a second energy minimum occurs in the regions where  $\tau = 35^\circ$ ; thus the iodide and chloride structures are consistent with the conformation predicted for nicotinamide, and the picrate structure displays a conformation that is only  $30^\circ$  displaced from the second energy minimum predicted for nicotinamide. The 1-MN cations in the halide structures assume the same conformation found in the crystal structure of nicotinamide (Wright & King, 1954) where  $\tau = 156^\circ$ . The conformation of 1-MN in the picrate structure is similar to that found for the 1-MN cation in the crystal structure of 1-methylnicotinamide aden-9-ylacetate (Voet, 1973), where  $\tau = 3^\circ$ .

Deviations from least-squares planes through the nicotinamide cations and through the picrate anion are given in Table 7. As expected, the pyridinium rings

are planar within experimental error. However, in all three structures the methyl groups are displaced significantly (0.01–0.07 Å) from the pyridinium plane, and, in the picrate structure, atom C(8) is about 0.02 Å out of the plane. The benzene ring of the picrate anion is slightly nonplanar, with deviations of up to 0.026 Å from the least-squares plane through the ring. The substituents atoms O(1), N(2), N(4), and N(6) are displaced from the benzene plane by 0.13, 0.09, 0.02, and 0.02 Å, respectively; the N(2), N(4), and N(6) nitro groups are tilted out of the benzene plane by 53, 6, and 22°, respectively.

The bond lengths and angles involving nonhydrogen atoms of the 1-MN cations are listed in Tables 8 and 9, respectively. Bond lengths and angles for the picrate anion are given in Table 10. Those bond lengths and angles involving hydrogen atoms in the three structures are given in Table 11. There is little difference in the dimensions of the 1-MN cations in these structures. The largest differences in bond angles occur around atom C(3), and these differences can be attributed to variations in the conformation about the C(3)–C(8) bond. The largest bond-length difference is in the

C(8)–N(8) bond, which is only 0.02 Å ( $2\sigma$ ) shorter in 1-MN iodide than in the chloride and picrate structures.

### Crystal packing

The crystal packing schemes for the iodide, chloride, and picrate structures are shown in Figs. 3, 4, and 5, respectively. Possible hydrogen-bonded contacts are described in Table 6. In all three structures, the amino groups are hydrogen bonded to halide anions and/or oxygen atoms. The picrate and iodide structures display short C–H...O contacts that may be considered as weak hydrogen bonds. In addition to the interactions listed in Table 12, there are several other C...O, and N...O contacts that fall in the range 2.9–3.2 Å. However, none of these apparently correspond to N–H...O or C–H...O contacts that can be attributed to hydrogen bonding, since the H...O distances are within the range expected for van der Waals contacts. In the 1-MN picrate structure, the picrate and 1-MN cations do not overlap, and, except for hydrogen-bonded interactions, there are no unusually short intermolecular contacts.

Table 4. Observed and calculated structure factors for 1-MN iodide

From left to right columns contain values of  $I$ ,  $10F_o$ , and  $10F_c$ .

$h$	$k$	$l$	$I$	$10F_o$	$10F_c$
0	0	0	100	100	100
0	0	1	100	100	100
0	0	2	100	100	100
0	0	3	100	100	100
0	0	4	100	100	100
0	0	5	100	100	100
0	0	6	100	100	100
0	0	7	100	100	100
0	0	8	100	100	100
0	0	9	100	100	100
0	0	10	100	100	100
0	0	11	100	100	100
0	0	12	100	100	100
0	0	13	100	100	100
0	0	14	100	100	100
0	0	15	100	100	100
0	0	16	100	100	100
0	0	17	100	100	100
0	0	18	100	100	100
0	0	19	100	100	100
0	0	20	100	100	100
0	0	21	100	100	100
0	0	22	100	100	100
0	0	23	100	100	100
0	0	24	100	100	100
0	0	25	100	100	100
0	0	26	100	100	100
0	0	27	100	100	100
0	0	28	100	100	100
0	0	29	100	100	100
0	0	30	100	100	100
0	0	31	100	100	100
0	0	32	100	100	100
0	0	33	100	100	100
0	0	34	100	100	100
0	0	35	100	100	100
0	0	36	100	100	100
0	0	37	100	100	100
0	0	38	100	100	100
0	0	39	100	100	100
0	0	40	100	100	100
0	0	41	100	100	100
0	0	42	100	100	100
0	0	43	100	100	100
0	0	44	100	100	100
0	0	45	100	100	100
0	0	46	100	100	100
0	0	47	100	100	100
0	0	48	100	100	100
0	0	49	100	100	100
0	0	50	100	100	100
0	0	51	100	100	100
0	0	52	100	100	100
0	0	53	100	100	100
0	0	54	100	100	100
0	0	55	100	100	100
0	0	56	100	100	100
0	0	57	100	100	100
0	0	58	100	100	100
0	0	59	100	100	100
0	0	60	100	100	100
0	0	61	100	100	100
0	0	62	100	100	100
0	0	63	100	100	100
0	0	64	100	100	100
0	0	65	100	100	100
0	0	66	100	100	100
0	0	67	100	100	100
0	0	68	100	100	100
0	0	69	100	100	100
0	0	70	100	100	100
0	0	71	100	100	100
0	0	72	100	100	100
0	0	73	100	100	100
0	0	74	100	100	100
0	0	75	100	100	100
0	0	76	100	100	100
0	0	77	100	100	100
0	0	78	100	100	100
0	0	79	100	100	100
0	0	80	100	100	100
0	0	81	100	100	100
0	0	82	100	100	100
0	0	83	100	100	100
0	0	84	100	100	100
0	0	85	100	100	100
0	0	86	100	100	100
0	0	87	100	100	100
0	0	88	100	100	100
0	0	89	100	100	100
0	0	90	100	100	100
0	0	91	100	100	100
0	0	92	100	100	100
0	0	93	100	100	100
0	0	94	100	100	100
0	0	95	100	100	100
0	0	96	100	100	100
0	0	97	100	100	100
0	0	98	100	100	100
0	0	99	100	100	100
0	0	100	100	100	100

Halide contacts with 1-MN cations

Table 13 lists those contacts between halide ions and nicotinamide moieties that are shorter than normal (Pauling, 1960) van der Waals contacts. Fig. 6 depicts the positions of the halide ions with respect to the 1-MN cations and the distances for the halide contacts with N(1) and C(2). The halide ions are positioned above the 1-MN plane, near the N(1)-C(2) bond. The shortest iodide-nicotinamide contact (3.537 Å), which occurs at atom C(2), is considerably shorter than a normal van der Waals contact (Pauling, 1960). Similarly, in the 1-MN chloride structure the chloride ion forms an unusually close contact of 3.239 Å with atom C(2) of the pyridinium ring. In both the iodide and the chloride structures, there are several short H...halide contacts, but except for those given in Table 12, none of these appears to be attributable to hydrogen bonding.

Discussion

It has been shown that halide 1-MN forms an iodide donor-acceptor complex in solution (Kosower, 1960). Charge-transfer interactions may also be of importance in the crystal structure of 1-MN iodide, and may be respon-

sible for the yellowish-green color of the crystals. As shown in Fig. 6(a), the iodide ion is situated about 3.42 Å above the plane through the pyridinium ring, and is in close contact with atom C(2). The C(2)···I distance of 3.537 Å is more than 0.3 Å shorter than the sum of the van der Waals radii for carbon and iodide (Pauling, 1960), thus indicating an unusually strong interaction at this site. Crystal structures of several other charge-transfer complexes involving iodide donors and aromatic acceptors have been determined (Sakanoue, Yasuoka, Kasai & Kakudo, 1970; Nakamura, Yasuoka, Kasai & Mikawa, 1970; Russell & Wallwork, 1972), but, to our knowledge, the C···I contact in the 1-MN iodide complex is the shortest that has been reported.

As shown in Fig. 6(a), the iodide ion is also in contact with atom N(1) of the pyridinium ring, but the N···I distance is actually longer than would be expected for a normal van der Waals contact. Thus the major iodide-pyridinium interaction does not occur at N(1), the expected (Mulliken & Person, 1966, p. 206) locus of positive charge. Although coulombic factors would dictate that the iodide ion be as close as possible to the N(1) position, charge-transfer interactions should

Table 5. Observed and calculated structure factors for 1-MN chloride

From left to right columns contain values of h, 10F<sub>o</sub>, and 10F<sub>c</sub>.

Table with columns for h, 10F0, and 10Fc, containing a grid of numerical data for various h values. The table is organized into multiple columns and rows, representing different h values and their corresponding structure factor values.

be most favorable when the iodide ion is in close contact with either atom C(2) or atom C(6) (Mulliken & Person, 1966, pp. 207-208). Therefore, the geometry

of the 1-MN iodide complex appears to be the one that is suitable for charge-transfer interactions. Despite appreciable differences in the crystal-pack-

Table 6. Observed and calculated structure factors for 1-MN picrate  
From left to right, the columns contain values of  $h$ ,  $10F_o$ , and  $10F_c$ .

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

Table 7. Deviations (Å) from least-squares planes

	1-Methylnicotinamide picrate	1-Methylnicotinamide chloride	1-Methylnicotinamide iodide
Pyridinium ring			
N(1)	-0.001	0.004	-0.003
C(2)	-0.003	0.006	-0.003
C(3)	0.004	-0.010	0.008
C(4)	-0.002	0.006	-0.006
C(5)	-0.001	0.004	0.000
C(6)	0.003	-0.008	0.005
*C(7)	-0.009	0.015	-0.065
*C(8)	0.019	0.001	-0.000
*O(8)	0.109	0.491	-0.244
*N(8)	-0.093	-0.524	0.226
*H(C2)	-0.01	0.10	-0.05
*H(C4)	0.06	0.06	0.02
*H(C5)	0.02	-0.05	0.10
*H(C6)	-0.02	0.01	-0.03
Amide group			
C(3)	-0.002	0.001	-0.002
C(8)	0.007	-0.003	0.006
O(8)	-0.002	0.001	-0.002
N(8)	-0.002	0.001	-0.002
Picrate anion			
Benzene ring			
C(1)	-0.018	*O(1) -0.126	*O'(4) -0.245
C(2)	0.026	*N(2) 0.089	*N(6) -0.019
C(3)	-0.015	*O(2) -0.752	*O(6) -0.416
C(4)	-0.005	*O'(2) 0.986	*O'(6) 0.425
C(5)	0.011	*N(4) -0.020	*H(C3) 0.00
C(6)	-0.000	*O(4) 0.176	*H(C5) 0.03

## Equations for least-squares planes

Pyridinium ring (picrate)	$-7.576x + 0.369y + 6.463z = 1.140 \text{ \AA}$
Pyridinium ring (chloride)	$2.156x + 6.156y - 6.736z = 2.450$
Pyridinium ring (iodide)	$3.638x + 6.790y + 3.135z = 5.326$
Amide group (picrate)	$-8.490x + 0.692y + 6.054z = 0.434$
Amide group (chloride)	$-4.521x + 7.833y - 5.883z = 0.236$
Amide group (iodide)	$3.022x + 6.821y + 6.009z = 6.104$

## Picrate ring

$$1\text{-Methylnicotinamide picrate } -4.260x + 0.783y + 6.893z = 1.743$$

\* Atoms given zero weight in least-squares calculation.

Table 8. Bond lengths (Å) involving only nonhydrogen atoms for the 1-methylnicotinamide cation in the three crystal structures

	1-Methyl- nicotinamide picrate	1-Methyl- nicotinamide chloride	1-Methyl- nicotinamide iodide
N(1)-C(2)	1.349 (3)	1.342 (2)	1.352 (7)
N(1)-C(6)	1.350 (4)	1.350 (2)	1.349 (9)
N(1)-C(7)	1.473 (4)	1.479 (3)	1.482 (10)
C(2)-C(3)	1.373 (3)	1.378 (2)	1.370 (8)
C(3)-C(4)	1.388 (4)	1.386 (2)	1.388 (9)
C(3)-C(8)	1.514 (4)	1.506 (2)	1.512 (8)
C(4)-C(5)	1.384 (4)	1.383 (2)	1.380 (9)
C(5)-C(6)	1.359 (3)	1.364 (2)	1.359 (10)
C(8)-O(8)	1.229 (4)	1.231 (2)	1.232 (9)
C(8)-N(8)	1.324 (3)	1.325 (2)	1.304 (11)

Standard deviations ( $\times 10^3$ ) are given in parentheses.

Table 9. Bond angles ( $^\circ$ ) involving only nonhydrogen atoms for the 1-methylnicotinamide cation in the three crystal structures

	1-Methyl- nicotinamide picrate	1-Methyl- nicotinamide chloride	1-Methyl- nicotinamide iodide
C(2)-N(1)-C(6)	120.9 (2)	121.2 (1)	121.2 (6)
C(2)-N(1)-C(7)	119.5 (3)	118.8 (2)	118.8 (6)
C(6)-N(1)-C(7)	119.6 (2)	120.0 (1)	120.0 (5)
N(1)-C(2)-C(3)	120.7 (3)	120.7 (1)	120.5 (6)
C(2)-C(3)-C(4)	118.7 (2)	118.6 (1)	118.8 (5)
C(2)-C(3)-C(8)	116.3 (3)	122.1 (1)	121.5 (6)
C(4)-C(3)-C(8)	125.0 (2)	119.3 (1)	119.7 (5)
C(5)-C(4)-C(3)	119.5 (2)	119.7 (2)	119.3 (6)
C(6)-C(5)-C(4)	119.8 (3)	119.7 (2)	120.3 (7)
N(1)-C(6)-C(5)	120.3 (2)	120.2 (2)	119.8 (6)
O(8)-C(8)-N(8)	123.2 (3)	124.4 (2)	123.9 (6)
O(8)-C(8)-C(3)	119.1 (2)	119.4 (1)	117.8 (6)
N(8)-C(8)-C(3)	117.7 (3)	116.2 (1)	118.3 (6)

Standard deviations ( $\times 10$ ) are given in parentheses.



Table 10. Bond lengths and angles involving nonhydrogen atoms of the picrate anion in the crystal structure of 1-MN picrate

Standard deviations for the last digit are given in parentheses.

## (a) Bond distances

C(1)–C(2)	1.445 (4) Å	C(5)–C(6)	1.368 (4) Å
C(1)–C(6)	1.444 (3)	C(6)–N(6)	1.451 (4)
C(1)–O(1)	1.250 (3)	N(2)–O(2)	1.217 (4)
C(2)–C(3)	1.359 (4)	N(2)–O'(2)	1.207 (3)
C(2)–N(2)	1.466 (3)	N(4)–O(4)	1.231 (3)
C(3)–C(4)	1.396 (3)	N(4)–O'(4)	1.221 (4)
C(4)–C(5)	1.373 (4)	N(6)–O(6)	1.207 (3)
C(4)–N(4)	1.440 (4)	N(6)–O'(6)	1.216 (4)

## (b) Bond angles

O(1)–C(1)–C(6)	126.1 (3)°	C(5)–C(6)–C(1)	124.1 (3)°
O(1)–C(1)–C(2)	123.0 (2)	C(5)–C(6)–N(6)	115.9 (2)
C(6)–C(1)–C(2)	110.7 (2)	C(1)–C(6)–N(6)	120.0 (2)
C(3)–C(2)–C(1)	126.3 (2)	O'(2)–N(2)–O(2)	123.3 (2)
C(3)–C(2)–N(2)	117.4 (3)	O'(2)–N(2)–C(2)	118.7 (3)
C(1)–C(2)–N(2)	116.4 (2)	O(2)–N(2)–C(2)	117.9 (2)
C(2)–C(3)–C(4)	117.8 (3)	O'(4)–N(4)–O(4)	122.9 (2)
C(5)–C(4)–C(3)	120.7 (2)	O'(4)–N(4)–C(4)	118.6 (2)
C(5)–C(4)–N(4)	119.5 (2)	O(4)–N(4)–C(4)	118.4 (3)
C(3)–C(4)–N(4)	119.8 (3)	O'(6)–N(6)–O(6)	122.5 (3)
C(6)–C(5)–C(4)	120.2 (2)	O'(6)–N(6)–C(6)	119.4 (2)
		O(6)–N(6)–C(6)	118.1 (3)

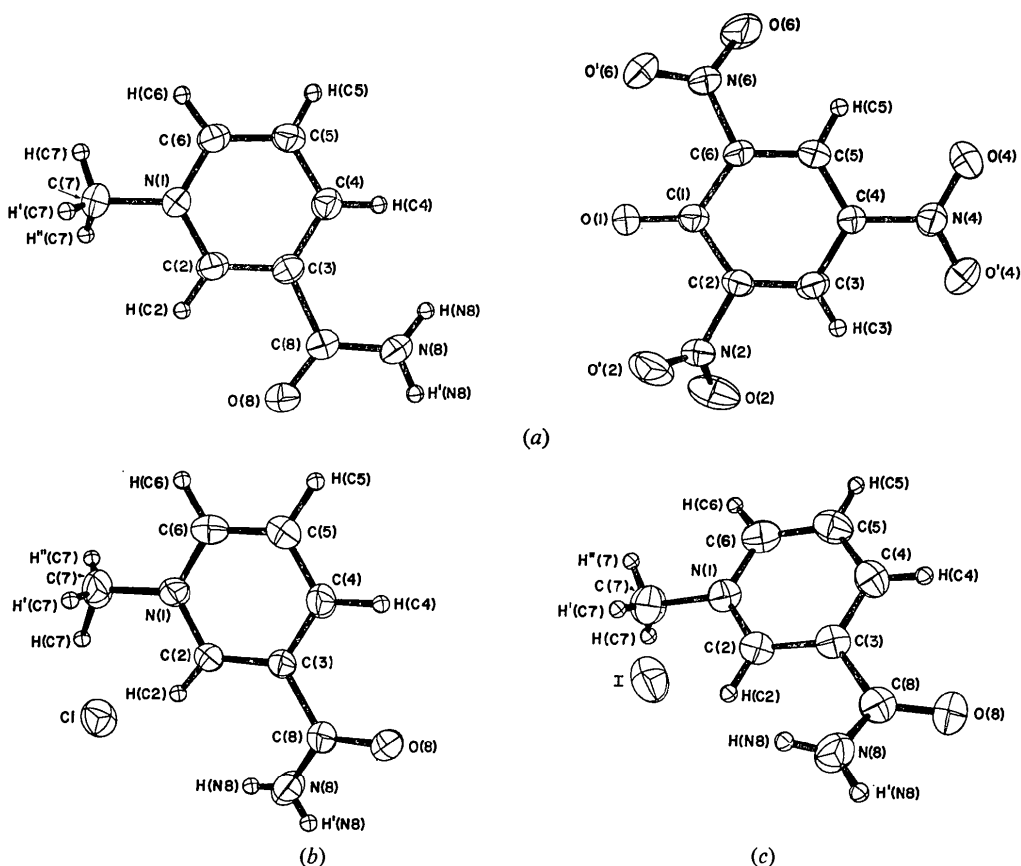


Fig. 2. Conformations and thermal ellipsoids in the crystal structures of (a) 1-MN picrate, (b) 1-MN chloride, and (c) 1-MN iodide. Nonhydrogen atoms are represented by thermal ellipsoids that are defined by the principal axes of thermal vibration and scaled to include 50% probability. Hydrogen atoms are represented by spheres of 0.1 Å radius. [This drawing and those in Figs. 3–5 were prepared by using the computer program *ORTEP* (Johnson, 1965)].

ing schemes of 1-MN chloride and 1-MN iodide, the two structures exhibit similar halide-pyridinium interactions. In both structures the major contacts occur at the C(2) position. As shown in Fig. 6(b), the chloride ion is positioned 2.52 Å above the plane of the pyridinium ring, and is extremely close to atom C(2). The C(2)···Cl distance of 3.239 Å is about 0.25 Å shorter than a normal van der Waals contact (Pauling, 1960), but as in the iodide structure, the N(1)···Cl distance is longer than that expected for a van der Waals contact. We were somewhat surprised to find this strong chloride-pyridinium interaction. The electronegative

chloride ion should be a poor donor, and the lack of color in the 1-MN chloride crystals suggests that charge-transfer interactions are probably of little importance in crystals of 1-MN chloride.

In crystal structures of some strong donor-acceptor complexes, it is found that charge-transfer bonding produces alterations in bond lengths and angles within the donor and acceptor moieties (Mulliken & Person, 1969, chap. 5; Bent, 1968; Hassel, 1970). To examine the possibility that the iodide interactions might significantly alter the bond lengths, bond angles, and conformation of 1-MN, we also determined the crystal

Table 11. Bond lengths and angles involving hydrogen atoms

Standard deviations for the last digit are given in parentheses.

	1-Methylnicotinamide picrate	1-Methylnicotinamide chloride	1-Methylnicotinamide iodide
H(C2)—C(2)	0.99 (3) Å	0.96 (2) Å	0.93 (7) Å
H(C4)—C(4)	0.94 (3)	0.92 (2)	1.05 (6)
H(C5)—C(5)	0.92 (4)	0.93 (2)	1.05 (8)
H(C6)—C(6)	0.97 (3)	0.98 (2)	1.02 (8)
H(C7)—C(7)	0.95 (6)	0.93 (3)	0.92 (11)
H'(C7)—C(7)	0.96 (6)	0.99 (3)	1.14 (16)
H''(C7)—C(7)	0.89 (6)	0.86 (4)	0.80 (12)
H(N8)—N(8)	0.89 (4)	0.87 (2)	0.78 (10)
H'(N8)—N(8)	0.88 (4)	0.86 (2)	
H(C2)—C(2)—N(1)	116 (1)°	118 (1)°	112 (4)°
H(C2)—C(2)—C(3)	123 (1)	121 (1)	127 (4)
H(C4)—C(4)—C(5)	120 (2)	122 (1)	121 (3)
H(C4)—C(4)—C(3)	120 (2)	119 (1)	120 (3)
H(C5)—C(5)—C(6)	119 (1)	119 (1)	121 (4)
H(C5)—C(5)—C(4)	121 (1)	121 (1)	119 (4)
H(C6)—C(6)—N(1)	113 (2)	116 (1)	120 (5)
H(C6)—C(6)—C(5)	126 (2)	124 (1)	120 (5)
H'(C7)—C(7)—H(C7)	120 (4)	121 (3)	129 (9)
H''(C7)—C(7)—H'(C7)	106 (5)	105 (3)	104 (10)
H'(C7)—C(7)—H(C7)	101 (5)	102 (2)	95 (10)
H''(C7)—C(7)—N(1)	107 (3)	109 (2)	112 (7)
H'(C7)—C(7)—N(1)	115 (3)	111 (2)	112 (6)
H(C7)—C(7)—N(1)	108 (3)	108 (2)	103 (8)
H'(N8)—N(8)—H(N8)	119 (3)	113 (2)	113 (9)
H'(N8)—N(8)—C(8)	116 (2)	120 (1)	117 (7)
H(N8)—N(8)—C(8)	124 (2)	125 (1)	130 (6)
Picrate anion			
H(C3)—C(3)	0.90 (4) Å	H(C5)—C(5)	0.95 (3) Å
H(C3)—C(3)—C(2)	122 (2)°	H(C5)—C(5)—C(6)	117 (2)°
H(C3)—C(3)—C(4)	120 (2)	H(C5)—C(5)—C(4)	123 (2)

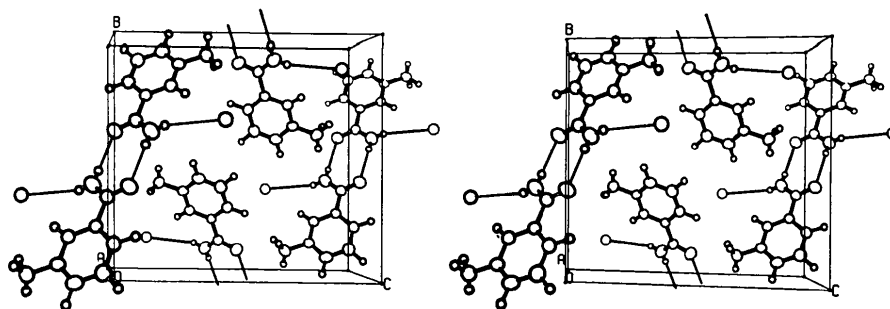


Fig. 3. Stereo drawing showing the crystal packing of 1-MN iodide. Covalent and hydrogen bonds are represented, respectively, by heavy and light lines.

structure of the picrate salt of 1-MN. The picrate ion is itself a strong electron acceptor (Briegleb & Delle, 1960; Kross & Fassel, 1957), so we expected that charge-transfer interactions would be especially un-

likely in the crystal structure of 1-MN picrate. The only major difference between the structure of 1-MN in the picrate and halide salts is the difference in the torsion angle around the C(3)–C(8) bonds. In both the

Table 12. Distances and angles for possible hydrogen bonds

	Donor	Acceptor	<i>D</i> – <i>A</i>	<i>H</i> ··· <i>A</i>	<i>D</i> – <i>H</i> ··· <i>A</i> Angle
1-MN picrate	N(8)–H(N8)	O(1) <i>e</i>	2.904 Å	2.03 Å	167°
	N(8)–H'(N8)	O'(2) <i>a</i>	3.351	2.48	178
	C(4)–H(C4)	O(1) <i>e</i>	3.139	2.23	161
	C(3)–H(C3)	O(6) <i>f</i>	3.232	2.34	172
1-MN iodide	N(8)–H'(N8)	O(8) <i>c</i>	2.936	2.19	173
	N(8)–H(N8)	I <i>d</i>	3.721	2.97	161
	C(7)–H'(C7)	O(8) <i>b</i>	3.018	2.31	118
1-MN chloride	N(8)–H(N8)	Cl <i>e</i>	3.256	2.40	168
	N(8)–H'(N8)	Cl <i>b</i>	3.262	2.41	174

Symmetry codes:

(a)	$x - 1.0 + y$	$z$	(d)	$1.0 + x$	$y$	$z$	
(b)	$x$	$0.5 - y - 0.5 + z$	(e)	$x$	$y$	$z$	
(c)	$2.0 - x$	$-y$	$1.0 - z$	(f)	$x$	$1 + y$	$z$

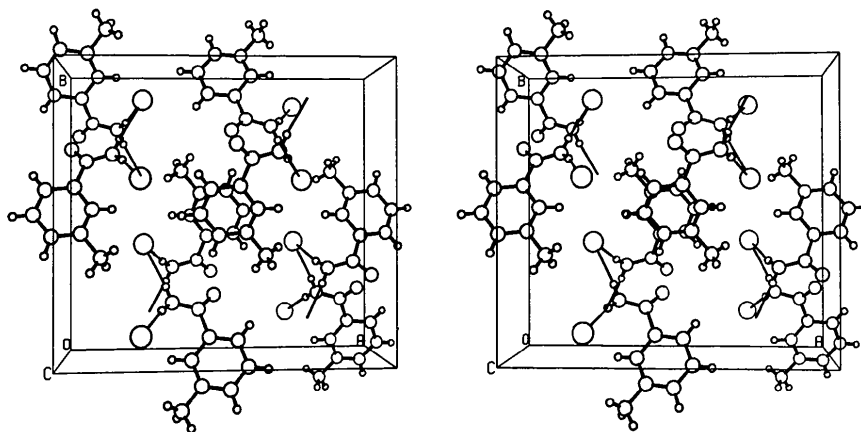


Fig. 4. Stereo drawing showing the crystal packing of 1-MN chloride. Covalent and hydrogen bonds are represented, respectively, by heavy and light lines.

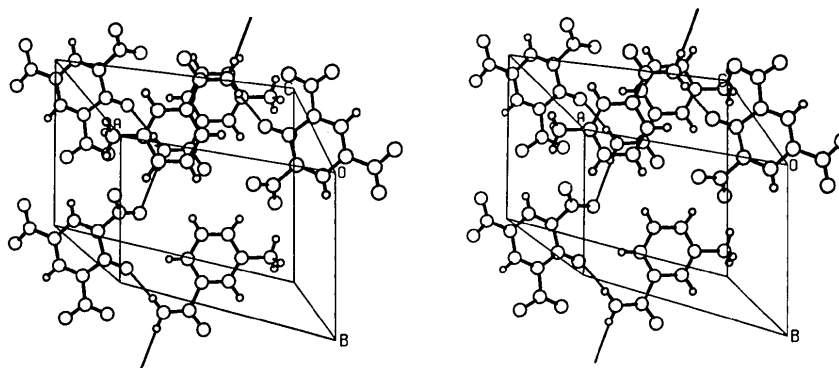


Fig. 5. Stereo drawing showing the crystal packing of 1-MN picrate. Covalent and hydrogen bonds are represented, respectively, by heavy and light lines. Only those hydrogen bonds involving the amino group of 1-MN are shown; in addition there are two short C–H···O contacts that are probably hydrogen bonds (see Table 6).

Table 13. *Contacts between halide ions and nicotinamide moieties which are shorter than normal van der Waals distances*

From Pauling (1966), normal van der Waals contacts are:  $I \cdots C = 3.8 \text{ \AA}$ ,  $I \cdots N = 3.7 \text{ \AA}$ ,  $I \cdots H = 3.4 \text{ \AA}$ ,  $Cl \cdots C = 3.5 \text{ \AA}$ ,  $Cl \cdots N = 3.3 \text{ \AA}$ ,  $Cl \cdots H = 3.0 \text{ \AA}$ .

$I \cdots C(2)$	<i>a</i>	3.537 $\text{\AA}$	$Cl \cdots C(2)$	<i>a</i>	3.238 $\text{\AA}$
$I \cdots C(4)$	<i>b</i>	3.732	$Cl \cdots N(8)$	<i>a</i>	3.256
$I \cdots C(6)$	<i>d</i>	3.761	$Cl \cdots N(8)$	<i>g</i>	3.262
$I \cdots H(N8)$	<i>f</i>	2.97	$Cl \cdots C(4)$	<i>h</i>	3.455
$I \cdots H(C6)$	<i>e</i>	2.97	$Cl \cdots C(2)$	<i>i</i>	3.493
$I \cdots H(C2)$	<i>f</i>	3.01	$Cl \cdots H(N8)$	<i>a</i>	2.40
$I \cdots H(C7)$	<i>a</i>	3.21	$Cl \cdots H'(N8)$	<i>g</i>	2.41
$I \cdots H''(C7)$	<i>d</i>	3.28	$Cl \cdots H(C2)$	<i>i</i>	2.79
$I \cdots H(C5)$	<i>c</i>	3.30	$Cl \cdots H(C4)$	<i>h</i>	2.79
$I \cdots H(C4)$	<i>b</i>	3.35	$Cl \cdots H(C2)$	<i>a</i>	2.84
$I \cdots H(C4)$	<i>c</i>	3.37	$Cl \cdots H(C5)$	<i>j</i>	2.89
			$Cl \cdots H'(C7)$	<i>i</i>	2.98

Symmetry codes:

(a)	$x$	$y$	$z$	(f)	$-1+x$	$y$	$z$
(b)	$-1+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	(g)	$x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(c)	$x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	(h)	$-\frac{1}{2}+x$	$y$	$\frac{1}{2}-z$
(d)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	(i)	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
(e)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	(j)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1+z$

iodide and the chloride complexes, the conformation is such that the C(8)–O(8) bond of the carboxamide group is nearly parallel to C(2)–C(3), but in the picrate salt the carboxamide group is rotated about  $180^\circ$  to an orientation in which C(8)–N(8) is parallel to C(2)–C(3). However, the conformations of 1-MN iodide and 1-MN chloride are nearly the same as that predicted and observed for nicotinamide, and the conformation of 1-MN picrate is similar to that of 1-MN aden-9-ylacetate. Therefore, it is likely that the 1-MN cation has considerable conformational freedom, and that little significance should be attached to the differences in conformation that are found in the iodide, chloride, and picrate structures. Theoretical calculations (Coubeils, Pullman & Courrière, 1971) indicate that the conformation found in the 1-MN halide complexes is only about 2 kcal mole<sup>-1</sup> more stable than that in the picrate structure, so it is likely that the conformational differences are merely a consequence of crystal-packing forces. As shown in Tables 8 and 9, the bond lengths and angles for 1-MN in the iodide structure are not significantly different from the corresponding values in the chloride and picrate structures, except in the C(2)–C(3)–C(8) and C(4)–C(3)–C(8) angles, which are affected by the differences in conformation about the C(3)–C(8) bond. Therefore, within the precision of these crystallographic results, the iodide interactions exert no obvious effects on the internal geometry of the 1-MN cation.

No spectroscopic studies of 1-MN iodide crystals have been reported, and, without direct evidence of charge-transfer absorption bands, it is not possible to state unequivocally that 1-MN iodide is a donor-acceptor complex. However, there are several reasons why one might believe that charge-transfer interactions occur in crystals of 1-MN iodide: (1) in solution,

many pyridinium iodides, including 1-MN iodide, give new absorption bands which can be attributed to charge-transfer from the iodide ion to the pyridinium cation; (2) the yellowish-green color of the 1-MN iodide crystals suggests a charge-transfer interaction, since, separately, both 1-MN and iodide are colorless; (3) the geometry of the 1-MN iodide complex (Fig. 6) is consistent with that predicted for the equilibrium configuration of the charge-transfer state for pyridinium iodides (Mulliken & Person, 1969, pp. 207–208); (4) the iodide ion forms exceptionally close contacts with the nicotinamide moiety.

Assuming that charge-transfer interactions do occur in crystals of 1-MN iodide, it is important to ascertain what effects charge-transfer forces exert on the iodide interactions with 1-MN cations, and on the geometry of the 1-MN moiety. As shown in Fig. 6, the halide-nicotinamide interactions are similar in the crystal structures of 1-MN iodide and 1-MN chloride, with unusually short halide–C(2) contacts involved in both cases. Also, the geometry of 1-MN in the iodide salt is essentially identical with that in the chloride salt. To account for these similarities, we could either conclude that both the iodide and the chloride salts involve charge-transfer interactions, or that charge-transfer forces contribute little to the geometrical arrangements in the two crystal structures. Since the chloride ion should be a rather poor donor, we feel that the latter possibility is the more plausible. Even if charge-transfer interactions do occur in both the iodide and chloride salts, the interactions are not pronounced enough to cause significant changes in the bond lengths and angles within the 1-MN cation, as evidenced by comparison with 1-MN picrate (Tables 8 and 9). Although charge-transfer interactions may occur in crystals of 1-MN iodide, it is likely that the observed geometrical arrangement is dictated primarily by classical coulombic and van der Waals forces. This interpretation is consistent with various studies which

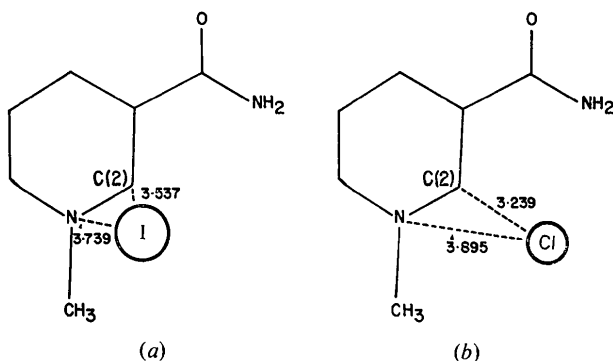


Fig. 6. Interaction of halide ions with the pyridinium rings in (a) 1-MN iodide and (b) 1-MN chloride, as viewed perpendicular to the plane of the pyridinium ring. The N(1)···halide and C(2)···halide contacts are shown. The halide ions are 3.42  $\text{\AA}$  and 2.52  $\text{\AA}$  above the pyridinium plane in (a) and (b), respectively.

suggest that van der Waals interactions are of predominant importance in controlling the ground-state stabilities and geometries of many donor-acceptor complexes (Mulliken & Person, 1969, pp. 301-312).

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