The Crystal and Molecular Structures of Pyrrolidinium *p*-Chlorobenzoate and Pyrrolidinium *p*-Toluate

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The crystal structures of pyrrolidinium *p*-chlorobenzoate (PYC) and pyrrolidinium *p*-toluate (PYT) have been determined from visually estimated Cu $K\alpha$ data. The crystals of PYC are orthorhombic, space group Pbca, $a=9.53(1)$, $b=27.28(3)$, $c=9.39(2)$ Å, and $Z=8$. Those of PYT are monoclinic, space group $P2_1/c$, $a=14.66(3)$, $b=9.00(2)$, $c=9.44(1)$ Å, $\beta=101.3(4)°$, and $Z=4$. The structures of PYC and PYT were refined by the block-diagonal least-squares method to R values of 0.073 and 0.089 for 855 and 1277 non-zero reflections, respectively. In both PYC and PYT, the pyrrolidinium and benzoate ions are linked together by two kinds of N–H···O hydrogen bonds to form a ribbon along the twofold screw axis. The shorter hydrogen bond [N···O 2.697(7) Å for PYC, 2.674(5) Å for PYT] lies nearly perpendicular to the twofold screw axis, and the longer bond [N···O 2.730(7) Å for PYC, 2.738(5) Å for PYT] makes an angle of about 20° with the axis. The O···N···O angle is near to the regular tetrahedral angle [105.4(2)° for PYC, 107.1(2)° for PYT]. The crystals of PYC are isomorphous with those of piperidinium *p*-chlorobenzoate, piperidinium *p*-bromobenzoate, piperidinium *p*-toluate and pyrrolidinium *p*-bromobenzoate, but PYT crystallizes in a subgroup of the space group of the others because of the cooperative effects of the bulkiness of the methyl group and the ring size of the base moiety. The pyrrolidine rings in PYC and PYT take an approximate C_s symmetry.

Previously, we have shown that the crystals of piperidinium *p*-chlorobenzoate (PIC), piperidinium *p*-bromobenzoate (PIB) and piperidinium *p*-toluate (PIT) are isomorphous.[1,2] The present investigation was undertaken in order to elucidate the effect of the ring size of the base moiety and the effect of the *para* substituent of the acid moiety on the crystal structure and on the geometry of hydrogen bond in the crystals. The conformation of the pyrrolidine ring in the solid state is of additional interest.

Experimental

The compounds were prepared by dissolving equimolar quantities of the acid and the base in dry benzene, in a similar manner described for piperidinium benzoates.[3] Crystallographic data for PYC, PYT and pyrrolidinium *p*-bromobenzoate (PYB) are listed in Table 1, and experimental details are in Table 2.

As the crystals of these compounds decomposed gradually, the specimens were sealed in glass capillaries. The intensity data were collected on the equi-inclination Weissenberg photographs using Cu $K\alpha$ radiation. Intensities were esti-

TABLE 1. CRYSTALLOGRAPHIC DATA

	Pyrrolidinium *p*-chlorobenzoate (PYC) $(C_4H_8NH_2)^+(ClC_6H_4CO_2)^-$	Pyrrolidinium *p*-bromobenzoate (PYB) $(C_4H_8NH_2)^+(BrC_6H_4CO_2)^-$	Pyrrolidinium *p*-toluate (PYT) $(C_4H_8NH_2)^+(CH_3C_6H_4CO_2)^-$
F.W.	227.7	272.2	207.3
Mp (°C)	127—129	123—124	133—134
Morphology	plates developed {010}	plates developed {010}	plates developed {100}
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pbca	Pbca	$P2_1/c$
a (Å)	9.53(1)	9.44(1)	14.66(3)
b	27.28(3)	27.49(3)	9.00(2)
c	9.39(2)	9.41(1)	9.44(1)
β (°)			101.3(4)
D_m (g cm^{-3})	1.24	1.48	1.12
		(Weld pycnometer and liquid paraffin)	
D_x	1.240	1.480	1.128
Z	8	8	4
$F(000)$	960	1104	448

TABLE 2. EXPERIMENTAL DETAILS

	PYC	PYT
μ (cm^{-1}) for Cu $K\alpha$	32.2	6.5
Dimensions of crystals used (mm)	0.60×0.16×0.22 0.20×0.20×0.95	0.18×1.1×0.22 0.30×0.30×1.1
Layers photographed	$0kl$ to $5kl$ $hk0$ to $hk5$	$h0l$ to $h6l$ $hk0$ to $hk6$

	PYC	PYT
No. of observed reflections	855	1277
Percent to accessible	31	45
B (Å^2) from Wilson's plot	6.8	6.6

TABLE 3. ATOMIC PARAMETERS

(a) Final atomic parameters for the non-hydrogen atoms ($\times 10^4$) with their e.s.d.'s in parentheses. The β_{ij}'s are defined by $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pyrrolidinium *p*-chlorobenzoate (PYC)									
C(1)	3810(7)	1285(2)	8577(6)	145(9)	16.9(1.0)	148(9)	5(5)	−16(17)	−5(5)
C(2)	3367(7)	1639(2)	9552(7)	200(11)	18.1(1.0)	155(9)	11(6)	40(19)	4(5)
C(3)	3886(8)	2120(3)	9468(8)	208(13)	23.0(1.3)	173(11)	16(7)	−24(21)	−4(6)
C(4)	4797(8)	2237(3)	8367(8)	162(11)	21.3(1.2)	197(11)	−13(6)	−80(20)	8(6)
C(5)	5201(9)	1892(3)	7395(9)	198(12)	25.2(1.3)	170(10)	−3(7)	71(20)	17(7)
C(6)	4738(8)	1416(2)	7489(8)	168(10)	18.7(1.0)	160(8)	−1(6)	10(18)	4(6)
C(7)	3247(7)	766(2)	8660(6)	157(10)	18.5(1.0)	129(8)	12(5)	−48(17)	2(5)
O(8)	2460(5)	669(2)	9718(6)	201(8)	23.3(0.9)	228(8)	−11(4)	131(15)	−4(4)
O(9)	3635(6)	456(2)	7758(5)	259(9)	20.0(0.7)	134(7)	−0(4)	3(13)	−10(4)
Cl(10)	5420(3)	2839(1)	8233(5)	363(5)	21.4(0.3)	268(4)	−56(2)	−119(8)	16(2)
N(11)	2945(5)	306(2)	4970(5)	139(7)	17.8(0.8)	130(7)	4(4)	28(12)	1(4)
C(12)	1631(7)	588(3)	4800(9)	144(10)	25.1(1.3)	241(13)	34(6)	27(22)	−14(7)
C(13)	2037(10)	1034(4)	4037(14)	221(16)	33.4(2.2)	614(35)	53(9)	17(39)	104(14)
C(14)	3347(11)	964(4)	3369(10)	339(20)	32.5(2.0)	286(18)	−17(10)	17(32)	97(9)
C(15)	3992(8)	489(3)	3883(8)	177(12)	24.5(1.3)	180(11)	−10(6)	34(20)	11(6)
Pyrrolidinium *p*-toluate (PYT)									
C(1)	7555(3)	8818(4)	7260(4)	56(2)	119(5)	164(6)	16(5)	39(6)	58(10)
C(2)	8174(3)	9775(5)	8148(5)	61(2)	161(7)	205(7)	−8(7)	17(7)	−21(11)
C(3)	9103(3)	9821(5)	8021(6)	60(3)	175(7)	310(10)	−5(7)	−4(8)	−22(15)
C(4)	9447(3)	8960(6)	7025(7)	52(2)	199(8)	357(11)	22(7)	73(8)	45(16)
C(5)	8819(3)	8018(6)	6159(6)	67(3)	196(8)	296(10)	30(8)	89(8)	−49(15)
C(6)	7896(3)	7929(5)	6282(5)	60(2)	152(6)	211(7)	26(6)	43(7)	−20(12)
C(7)	6539(3)	8799(5)	7361(4)	64(2)	146(6)	165(6)	6(6)	52(6)	56(10)
O(8)	6264(2)	9800(4)	8106(4)	68(2)	291(7)	268(6)	−18(6)	107(6)	−187(11)
O(9)	6015(2)	7833(3)	6659(3)	63(2)	155(4)	246(5)	−34(5)	39(5)	16(8)
C(10)	10475(4)	9034(8)	6916(10)	60(3)	301(13)	650(23)	−3(11)	160(14)	−39(29)
N(11)	5587(2)	4964(4)	7214(4)	57(2)	139(5)	167(5)	0(5)	49(5)	5(8)
C(12)	6087(3)	4712(6)	8762(5)	78(3)	259(9)	137(6)	−22(9)	32(6)	−31(13)
C(13)	7006(4)	4020(8)	8616(6)	83(4)	440(16)	196(8)	126(13)	−18(8)	−91(20)
C(14)	6948(4)	3553(7)	7130(6)	78(3)	299(11)	225(9)	115(10)	34(8)	−19(17)
C(15)	5970(3)	3852(6)	6334(5)	74(3)	224(8)	147(6)	21(8)	55(6)	−39(12)

(b) Positional($\times 10^3$) and isotropic thermal parameters for the hydrogen atoms.

	x	y	z	B/Å^2	x	y	z	B/Å^2	Bonded to
	PYC				PYT				
H(16)	269(7)	157(2)	1047(7)	5.1(1.6)	791(4)	1036(7)	888(6)	7.9(1.6)	C(2)
H(17)	346(7)	237(3)	1008(10)	8.2(2.3)	948(4)	1052(6)	869(5)	6.6(1.3)	C(3)
H(18)	567(7)	199(3)	672(8)	6.1(1.9)	896(4)	749(6)	536(6)	7.9(1.5)	C(5)
H(19)	503(7)	114(2)	690(7)	4.8(1.6)	749(3)	735(5)	561(5)	5.8(1.2)	C(6)
H(20)	309(6)	32(2)	588(6)	3.1(1.4)	569(3)	590(5)	706(5)	4.7(1.1)	N(11)
H(21)	272(7)	−8(2)	486(7)	4.7(1.6)	486(3)	488(5)	722(4)	4.1(1.0)	N(11)
H(22)	116	66	584	6.8	618(4)	559(6)	925(6)	6.8(1.4)	C(12)
H(23)	89	39	412	6.8	574(3)	403(5)	915(5)	5.8(1.2)	C(12)
H(24)	218	134	490	6.8	761(6)	484(11)	896(9)	16.6(3.3)	C(13)
H(25)	122	117	335	6.8	723(6)	346(10)	927(8)	14.2(2.5)	C(13)
H(26)	403	128	353	6.8	755(6)	389(10)	670(8)	14.4(2.7)	C(14)
H(27)	315	94	221	6.8	716(4)	253(7)	694(6)	8.6(1.6)	C(14)
H(28)	499	57	442	6.8	594(3)	416(6)	534(5)	5.7(1.2)	C(15)
H(29)	409	23	302	6.8	550(4)	291(7)	628(6)	8.2(1.5)	C(15)
H(30)					1095(6)	834(12)	779(9)	17.6(3.1)	C(10)
H(31)					1066(5)	1006(8)	695(7)	10.7(2.1)	C(10)
H(32)					1057(6)	850(10)	601(8)	14.2(2.6)	C(10)

mated visually and corrected for Lorentz and polarization factors and spot shape.

Structure Determination and Refinement

The structures were solved from sharpened Patterson maps, and refined by block-diagonal least-squares calculations. For PYC an extinction correction was applied at the stage of $R=0.089$, for the four strongest reflections according to the formula $I_{corr}=I_{obsd}/(1-1.3\times 10^{-4} I_{obsd})$. In the subsequent refinements, the parameters of the H atoms attached to the C atoms of pyrrolidine ring were fixed. The weighting scheme used was $w=1.0$ for $0<|F_o|\leq F_{max}$, and $w=(F_{max}/|F_o|)^2$ for $|F_o|>F_{max}$, where F_{max} was 18.0. The final R value was 0.073 for 855 non-zero reflections.

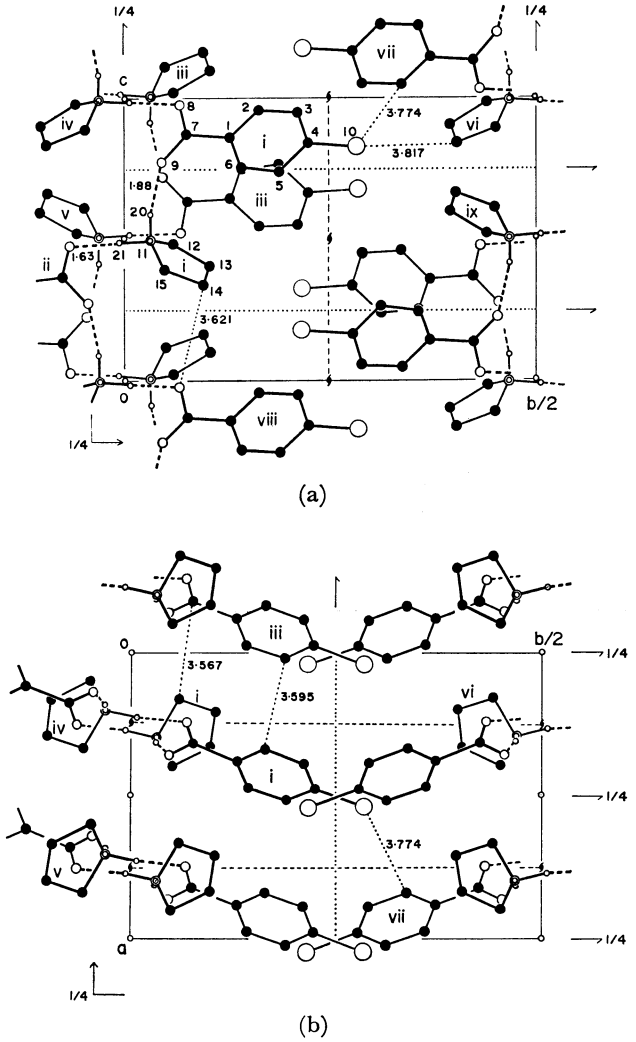

Fig. 1. Projections of the crystal structure of PYC along the a axis (a), and the c axis (b).
Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.
Symmetry code: i x, y, z; ii $1/2-x, -y, -1/2+z$; iii $-1/2+x, y, 3/2-z$; iv $1/2-x, -y, 1/2+z$; v $1-x, -y, 1-z$; vi $x, 1/2-y, 1/2+z$; vii $1/2+x, 1/2-y, 2-z$; viii $x, y, -1+z$; ix $1/2+x, 1/2-y, 1-z$.

For PYT a difference Fourier map revealed all the H atoms at the stage of $R=0.104$. Further refinements gave a final R value of 0.089 for 1277 non-zero reflections. The same weighting scheme as that for PYC was used with $F_{max}=10.0$.

The final atomic parameters are listed in Table 3.[4]

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[5] The computations were carried out on a NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were HBLS-5 and DAPH.[6]

Results and Discussion

The projections of the crystal structure of PYC viewed along a and c axes are shown in Fig. 1, and those of PYT along c and b axes in Fig. 2. Some intermolecular distances are summarized in Table 4. Bond lengths and angles are listed in Table 5.

Crystal Structures. The crystals of PYC are isostructural with those of piperidinium compounds *i.e.* PIC, PIB, and PIT, and also with PYB, judging from the space group, the cell dimensions, and the intensity distribution.

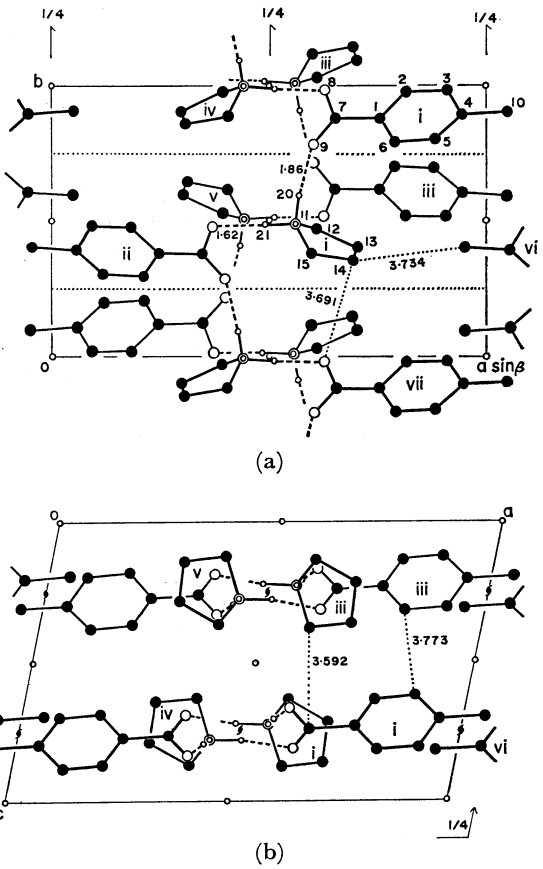

Fig. 2. Projections of the crystal structure of PYT along the c axis (a), and the b axis (b).
Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.
Symmetry code: i x, y, z; ii $1-x, -1/2+y, 3/2-z$; iii $x, 3/2-y, -1/2+z$; iv $1-x, 1/2+y, 3/2-z$; v $1-x, 1-y, 1-z$; vi $2-x, -1/2+y, 3/2-z$; vii $x, -1+y, z$; viii $x, 3/2-y, 1/2+z$.

TABLE 4. INTERMOLECULAR DISTANCES (Å) FROM THE MOLECULE (i) WITH THEIR e.s.d.'s IN PARENTHESES
Symmetry code is given in the legend of Figs. 1 and 2.

PYC					
C(7)	H(20^{i})	2.89(6)	H(21)	H(28^{v})	2.65
C(2)	C(5^{iii})	3.595(11)	Cl(10)	H(26^{vi})	2.77
C(12)	C(7^{iii})	3.567(11)	Cl(10)	C(14^{vi})	3.817(11)
H(22)	C(1^{iii})	2.86	Cl(10)	H(16^{vii})	2.97
H(22)	C(6^{iii})	2.92	Cl(10)	C(2^{vii})	3.774(8)
H(22)	C(7^{iii})	2.83	H(27)	O(8^{viii})	2.54
C(7)	H(21^{iv})	2.38(7)	H(27)	H(16^{viii})	2.41
O(9)	H(21^{iv})	2.57(7)	C(14)	O(8^{viii})	3.621(12)
O(9)	H(23^{iv})	2.67	Cl(10)	H(25^{ix})	3.18
O(9)	H(29^{v})	2.95			
PYT					
C(7)	H(20^{i})	2.88(5)	C(7)	H(21^{iv})	2.37(4)
C(5)	C(2^{iii})	3.773(8)	O(9)	H(21^{iv})	2.59(4)
H(18)	C(2^{iii})	2.98(6)	H(21)	H(28^{v})	2.61(7)
H(28)	O(8^{iii})	2.44(5)	C(14)	C(10^{vi})	3.734(12)
C(7)	C(12^{iii})	3.592(7)	H(26)	C(10^{vi})	2.94(9)
C(7)	H(22^{iii})	2.93(6)	H(26)	H(30^{vi})	2.22(14)
O(9)	H(22^{iii})	2.73(6)	H(27)	C(2^{vii})	3.00(6)
C(6)	H(24^{iii})	2.94(10)	C(14)	O(8^{vii})	3.691(7)

The pyrrolidinium and *p*-chlorobenzoate ions are linked together by two kinds of hydrogen bonds [N(11)–H(21)···O(8^{ii}) and N(11)–H(20)···O(9)] to form a ribbon along the twofold screw axis parallel to ***c***. The ribbons related by an a-glide plane are held together side by side by van der Waals interactions to form a sheet parallel to (010). The sheets related by a c-glide plane are stacked along ***b*** to complete a whole crystal.

In the crystals of PYT, similar hydrogen bonds to those in PYC effect a ribbon around the twofold screw axis at $x=1/2$. The ribbons related by a c-glide plane are held together to form a sheet parallel to (100). The sheets are stacked along ***a***. The axes ***a*** sin β, ***b***, and ***c*** of PYT correspond to the axes ***b***/2, ***c***, and ***a*** of PYC, respectively.

In both PYC and PYT six close contacts between the

TABLE 5. BOND LENGTHS (Å) AND ANGLES (°) WITH THEIR e.s.d.'s IN PARENTHESES

	PYC (X=Cl)	PYT (X=C)
C(1)–C(2)	1.395(10)	1.404(6)
C(2)–C(3)	1.405(11)	1.391(8)
C(3)–C(4)	1.388(11)	1.387(9)
C(4)–C(5)	1.364(11)	1.393(9)
C(5)–C(6)	1.376(11)	1.383(8)
C(6)–C(1)	1.397(10)	1.387(6)
C(1)–C(7)	1.516(9)	1.511(6)
C(7)–O(8)	1.272(8)	1.257(6)
C(7)–O(9)	1.254(8)	1.259(5)
C(4)–X(10)	1.753(8)	1.533(12)
N(11)–C(12)	1.479(10)	1.495(6)
N(11)–C(15)	1.512(9)	1.496(6)
C(12)–C(13)	1.464(16)	1.515(9)
C(13)–C(14)	1.410(17)	1.451(10)
C(14)–C(15)	1.514(13)	1.507(8)
N(11)–H(20)	0.86(6)	0.88(5)
N(11)–H(21)	1.08(7)	1.06(4)
C(1)–C(2)–C(3)	120.2(7)	119.8(5)
C(2)–C(3)–C(4)	118.4(7)	122.3(5)
C(3)–C(4)–C(5)	121.1(7)	116.9(6)
C(4)–C(5)–C(6)	121.1(7)	122.1(5)
C(5)–C(6)–C(1)	119.4(7)	120.6(5)
C(6)–C(1)–C(2)	119.6(6)	118.5(4)
C(3)–C(4)–X(10)	118.7(6)	121.0(6)
C(5)–C(4)–X(10)	120.1(6)	122.2(6)
C(2)–C(1)–C(7)	120.3(6)	120.0(4)
C(6)–C(1)–C(7)	120.0(6)	121.6(4)
C(1)–C(7)–O(8)	116.3(6)	117.1(4)
C(1)–C(7)–O(9)	119.5(6)	118.8(4)
N(11)–C(12)–C(13)	105.1(8)	104.6(5)
C(12)–C(13)–C(14)	109.9(10)	108.8(6)
C(13)–C(14)–C(15)	109.4(9)	107.5(5)
C(14)–C(15)–N(11)	103.3(6)	105.1(4)
C(15)–N(11)–C(12)	108.3(5)	106.3(4)
H(20)–N(11)–C(12)	103(4)	105(3)
H(21)–N(11)–C(12)	109(4)	108(2)
H(20)–N(11)–C(15)	123(4)	115(3)
H(21)–N(11)–C(15)	113(4)	115(2)

TABLE 6. GEOMETRY OF HYDROGEN BONDS
Lengths in Å and angles in degree.

	PYC	PYT	PIC	PIB	PIT
N(11)···O(8^{ii})	2.697(7)	2.674(5)	2.674(10)	2.687(8)	2.698(5)
N(11)–H(21)···O(8^{ii})	174(6)	170(4)			175(4)
C(12)–N(11)···O(8^{ii})	112.5(4)	113.8(3)	108	109	108.7(4)
C(15)–N(11)···O(8^{ii})	111.2(4)	112.2(3)	106	108	108.1(4)
C(7^{ii})–O(8^{ii})···N(11)	111.0(4)	113.6(3)	112	111	110.2(3)
N(11)···O(9)	2.730(7)	2.738(5)	2.722(11)	2.762(9)	2.766(6)
N(11)–H(20)···O(9)	168(5)	175(4)			161(4)
C(12)–N(11)···O(9)	103.2(4)	104.3(3)	102	101	101.0(4)
C(15)–N(11)···O(9)	116.0(4)	112.9(3)	124	123	122.2(4)
O(8^{ii})···N(11)···O(9)	105.4(2)	107.1(2)	107	105	105.2(3)
Angle between N(11)···O(9) bond and the 2_1 axis along which the bond extends	16	19	22	21	21
Angles between the plane perpendicular to the 2_1 axis and					
N(11)···O(8^{ii}) bond, δ_1	5	−3	3	2	2
C(7)···X(10) axis, δ_2	4	−2	3	4	4
carboxylate group plane, δ_3	56	53	56	55	55
benzene ring plane, δ_4	54	44	48	48	47

ribbons are concerned with the atoms in the pyrrolidine ring as seen from Table 4. However, the contacts around C(13) in the ring are rather loose; the closest being C(13)···C(1^{iii}) 3.866(15) Å in PYC, and C(13)···C(6^{viii}) 3.780(9) Å in PYT.

Geometry of the Hydrogen Bonds. The geometry in PYC and PYT is summarized in Table 6, along with that in the piperidinium compounds. In all these crystals the hydrogen bond N(11)···O(8^{ii}) lies nearly perpendicular to the twofold screw axis along which the ribbon extends, as seen in δ_1, and the bond N(11)···O(9) makes a constant angle of about 20° with the twofold screw axis. Thus the angle O(8^{ii})···N(11)···O(9) is near to the regular tetrahedral angle. The N(11)···O(8^{ii}) bond is shorter and hence stronger than the N(11)···O(9) bond. The former associates with the nearly tetrahedral C–N···O and C–O···N angles, and with linear N–H···O angle. Dihedral angle, δ_3, between the carboxylate group and the plane perpendicular to the twofold screw axis remains almost constant throughout the compounds, and the long axis of the acid anion lies nearly on the plane as seen from δ_2 in Table 6.

Morphotropism. In the structures of PYC, PYT and the piperidinium compounds many contacts between the ribbons are concerned with the atoms of the base moiety. Thus the effect of ring size of the bases is reflected in the thickness of the ribbons, hence in the cell dimension along ***a*** for PYC and ***c*** for PYT. The values for the pyrrolidinium compounds are smaller than those for the piperidinium compounds. Furthermore, the angle of the long axis of the acid anion with (010) in PYC, 70°, is widened from 64—61° in the piperidinium compounds. This is also the case for the corresponding angle with (100) in PYT, the angle here being 75°.

It has been shown[2] that in the piperidinium compounds the contacts around the *p*-substituents are rather loose and hence the crystal structures are little affected by the bulkiness of the substituents. On the other hand, in PYC the contacts become close as an effect of the ring size mentioned above: Cl···H(26^{vi}) 2.77 Å, Cl···H(16^{vii}) 2.97 Å. Therefore, a mode of stacking of the sheets seems to be more largely affected by the bulkiness of the substituents in the pyrrolidinium compounds than in the piperidinium compounds. The reason why PYT crystallizes in a subgroup of the space group Pbca is the disappearance of the c-glide plane by the cooperative effects of the bulkiness of the methyl group and the thickness of the ribbon.

Molecular Structures. (*a*) *Benzoate Ions*: The benzene rings are planar within 0.015 Å, as shown in Table 7. The dihedral angle between the ring and the carboxylate group is 1.9° for PYC, while is 9.7° for PYT. This difference is mainly due to the difference in δ_4 in Table 6. The inner angle at C(4) for PYT is smaller than the sp^2 angle as found in PIT and in many methyl substituted benzene derivatives.[7,8]

(*b*) *Pyrrolidinium Ions*: The torsion angles, χ_i (mod. 5), of the five bonds of the pyrrolidine rings are listed in Table 8. The χ_i in PYC corresponds to χ_{i-1} in PYT, being close to 0° for $i=3$. Hence, in PYC C(12) deviates from the plane through the other non-hydrogen atoms in the ring, while N(11) deviates in PYT, as seen from Table 7. Thus, the pyrrolidine ring in PYC and PYT take an approximate C_s (envelope) symmetry, the mirror plane passing through C(12) in PYC and N(11) in PYT.

In both PYC and PYT the C–C–C angles in the rings are slightly larger than the C–C–N angles. The C–N–C angles are close to the sp^3 angle. The C(13)–C(14) bonds are shortened by the unusually large vibrational motions of C(13) in the direction perpendicular to the ring planes, as found in prolyl residues of some oligopeptides.[9]

Table 7. The least-squares planes and displacements (Å) of the atoms from the planes $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

(I) Benzene ring

PYC: $-0.7747X+0.2375Y-0.5860Z+6.6943=0$

PYT: $0.0851X-0.7246Y+0.6839Z+0.3216=0$

	PYC	PYT
C(1)[a]	−0.0054	−0.0047
C(2)[a]	0.0147	−0.0027
C(3)[a]	−0.0112	0.0047
C(4)[a]	−0.0019	−0.0058
C(5)[a]	0.0112	−0.0047
C(6)[a]	−0.0073	0.0146
C(7)	0.0278	−0.0558
O(8)	−0.0358	−0.2831
O(9)	0.0378	0.0749
X(10)	0.0020	0.0068

(II) Carboxylate group

PYC: $-0.7904X+0.2492Y-0.5596Z+6.4968=0$

PYT: $-0.0449X+0.6035Y-0.7961Z+1.0003=0$

C(1)[a]	−0.0060		0.0032
C(7)[a]	0.0221		−0.0146
O(8)[a]	−0.0076		0.0046
O(9)[a]	−0.0075		0.0072

(III) Pyrrolidine ring

PYC: $-0.4617X-0.5114Y-0.7247Z+5.0955=0$

PYT: $-0.3593X-0.8980Y+0.2539Z+4.3613=0$

	PYC		PYT
N(11)[a]	−0.0088	N(11)	−0.4110
C(12)	0.2914	C(12)[a]	−0.0119
C(13)[a]	0.0098	C(13)[a]	0.0191
C(14)[a]	−0.0148	C(14)[a]	−0.0202
C(15)[a]	0.0138	C(15)[a]	0.0132

a) Atoms used for the calculation of the planes.

Table 8. The torsion angles (°) in the pyrrolidine rings

	PYC	PYT
χ_0: C(15)–N(11)–C(12)–C(13)	−19.9	26.0
χ_1: N(11)–C(12)–C(13)–C(14)	18.5	−13.7
χ_2: C(12)–C(13)–C(14)–C(15)	−9.9	−3.6
χ_3: C(13)–C(14)–C(15)–N(11)	−2.6	19.5
χ_4: C(14)–C(15)–N(11)–C(12)	14.0	−28.5

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