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Structural Change by Chemical Substitution. Crystal Structures of Acid Salts of *p*-Nitrobenzoic Acid and Cyclic Secondary Amines

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The crystal structures of pyrrolidinium hydrogen bis(*p*-nitrobenzoate) (I), piperidinium hydrogen bis(*p*-nitrobenzoate) (II), and perhydroazepinium hydrogen bis(*p*-nitrobenzoate) (III) have been determined by an X-ray diffraction method in order to study an effect of the ring size of the cyclic secondary amines on the crystal structures. There is a close similarity among the crystal structures of I – III, because the schemes of the O–H···O and N–H···O hydrogen bonds are similar in these crystals. It has been found that the space group $P2_1/c$ of I descends to its subgroup $P\bar{1}$ with an occurrence of two formula units in II and ascends to its supergroup $C2/c$ with an occurrence of disorder in III. Such a supergroup-subgroup relationship would make it possible to assume the structure after a transformation caused by chemical substitution.

In the crystals of acid salts of *p*-substituted benzoic acids and cyclic secondary amines, the cations and the hydrogen bis(benzoate) anions are held together by two N–H···O hydrogen bonds, and two benzoate residues in the anions are linked by short O–H···O hydrogen bonds.[1–4] An effect of the crystallographic environments on the symmetry and O···O distance of the short O–H···O hydrogen bond has been studied using a series of pyrrolidinium hydrogen bis(*p*-methylbenzoate), piperidinium hydrogen bis(*p*-methylbenzoate) and perhydroazepinium hydrogen bis(*p*-methylbenzoate).[1,3] During the course of this study, it was found that crystals of the pyrrolidinium and piperidinium compounds belong to the same space group, *Pcan* (No. 60), with $Z = 4$, and that the structures are disordered around a twofold axis. It was proposed that eliminating the twofold axis may result in two possible types of N–H···O hydrogen-bond systems: a glide type and a centrosymmetric type.[1] A centrosymmetric hydrogen-bonded ring composed of two formula units has been found in the crystal of the perhydroazepinium compound in accordance with a previous proposal.[3] The crystal of the perhydroazepinium compound is not disordered and belongs to the space group $P2_1/n$ ($Z = 4$), a *translationengleiche* subgroup[5] of *Pcan*. Thus, a structural change through a supergroup-subgroup relationship has been found for a series of acid salts of *p*-methylbenzoic acid and the cyclic secondary amines. Typical examples of such types of structural change can be given for a series of aromatic compounds:[6] e. g., between benzene (*Pbca*, $Z = 4$) and naphthalene ($P2_1/a$, $Z = 2$) or anthracene ($P2_1/a$, $Z = 2$) and tetracene ($P\bar{1}$, $Z = 2$). However, such a supergroup-subgroup relationship has not been extensively studied.

The present study on a series of pyrrolidinium hydrogen bis(*p*-nitrobenzoate) (I), piperidinium hydrogen bis(*p*-nitrobenzoate) (II), and perhydroazepinium hydrogen bis(*p*-nitrobenzoate) (III) was undertaken in order to ascertain whether a structural change through the supergroup-subgroup relationship is merely a special phenomenon for the acid salts of *p*-methylbenzoic acid or, rather, is a general one for the acid salts of *p*-substituted benzoic acids. The acid salts of *p*-nitrobenzoic acid were chosen because the geometric size and electronic properties of the nitro group are fairly different from those of the methyl group, and it is considered that the *p*-nitro analogues are appropriate to investigate the generality of the relationship.

Experimental

Crystals of I, II and III were obtained as colorless prisms by slow evaporation from ethanol solutions of *p*-nitrobenzoic acid and the respective cyclic amines, with molar ratios of 2:1.

X-ray Structure Analysis.

For I, II and III, a single crystal was mounted on a glass fiber. The intensities and lattice parameters were measured on a Rigaku AFC-5R automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 298 K. The intensities were corrected for Lorentz and polarization effects. The experimental details and crystallographic data are listed in Table 1.

A preliminary examination showed that the triclinic lattice of II would be transformed to a centered monoclinic lattice by

$$\begin{pmatrix}\mathbf{a}'\\ \mathbf{b}'\\ \mathbf{c}'\end{pmatrix} = \begin{pmatrix}3/2 & 1/2 & 0\\ 1/2 & -1/2 & 0\\ 0 & 0 & -1\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix}, \qquad (1)$$

where the lattice translation vectors (**a**, **b** and **c**) refer to a triclinic lattice, and **a′**, **b′** and **c′** to a monoclinic lattice. The lattice con-

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[#] On leave from MITSUI CHEMICAL ANALYSIS & CONSULTING SERVICE INC., Waki 6-1-2, Waki-cho, Kuga-gun, Yamaguchi 740-0061 stants obtained by the transformation have similar dimensions to those of I and Ⅲ: $a' = 21.402(5)$, $b' = 10.931(3)$, $c' = 9.045(3)$ Å, $\alpha' = 89.67(2)$, $\beta' = 112.55(2)$, $\gamma' = 90.21(2)°$. However, Weissenberg photographs of Ⅱ showed additional reflections which should not be observed for a monoclinic lattice, and the intensity distribution showed no Laue symmetry of $2/m$. Thus, a data collection and a structure determination of Ⅱ were carried out based on the triclinic lattice.

The structures of I, Ⅱ and Ⅲ were solved by a direct method, *SIR*92,[7] using the teXsan crystallographic software package.[8] All H atoms were found from difference Fourier maps. Refinements were carried out by the full-matrix least-squares method on F^2 of all unique reflections using SHELXL-97.[9] For I and Ⅱ, all non-hydrogen atoms were refined anisotropically. The cation in Ⅲ was disordered around a twofold axis, and the non-hydrogen atoms of the cation were refined isotropically by restraining the C–C distance to be 1.52 Å and that of C–N to be 1.49 Å. For I, Ⅱ and Ⅲ, the positional and isotropic displacement parameters of hydrogen atoms bonded to the O atoms were refined, and the positional parameters of the other hydrogen atoms were fixed to the ideal values; further, their isotropic displacement parameters were fixed at 1.2-times the equivalent displacement parameters of the parent atoms. The atomic scattering factors were taken from International Tables for Crystallography (Vol. C).[10] The CIF data are deposited as Document No. 75024 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 179399–179401.

Results and Discussion

The thermal ellipsoids of the molecules are shown in Fig's. 1–3 along with the atomic numbering of the asymmetric units. Selected bond distances and angles are listed in Table 2. The geometries of the hydrogen bonds are summarized in Table 3.

In I the O1 and O5 atoms of the hydrogen bis(*p*-nitrobenzoate) anion are linked together by the O5–H9···O1 hydrogen bond. The O6 atom does not concern any hydrogen bonds. The pyrrolidinium cations and the anions form a ribbon via

Table 1. Crystallographic Data and Experimental Details

	I	Ⅱ	Ⅲ
Formula	$C_{18}H_{19}N_3O_8$	$C_{19}H_{21}N_3O_8$	$C_{20}H_{23}N_3O_8$
F. M.	405.36	419.39	433.41
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$
a/Å	20.750 (6)	12.035 (4)	21.441 (7)
b/Å	10.936 (2)	19.551 (5)	11.537 (3)
c/Å	9.075 (3)	9.045 (5)	9.144 (4)
α/deg		101.85 (3)	
β/deg	112.85 (2)	110.06 (3)	113.96 (3)
γ/deg		84.02 (2)	
V/Å^3	1897.7 (9)	1955.2 (14)	2067.1 (12)
Z	4	4	4
D_x/Mg cm^{-1}	1.419	1.425	1.393
F (000)	848	880	912
μ/mm^{-1}	0.113	0.113	0.109
Cryst size/mm	0.40×0.30×0.20	0.35×0.20×0.20	0.50×0.40×0.20
Cell dimensions			
2θ range/°	21–23	21–23	21–23
No. of refs.	25	25	25
Scan mode	2θ–ω	2θ–ω	2θ–ω
Scan speed ω/°mm^{-1}	4	6	6
Scan width $\Delta\omega$/°	$1.63 + 0.30\tan\theta$	$1.78 + 0.30\tan\theta$	$1.63 + 0.30\tan\theta$
$2\theta_{\max}$/°	54	52	56
Reflections (hkl) limits	$0 \leqq h \leqq 26$	$0 \leqq h \leqq 14$	$0 \leqq h \leqq 28$
	$0 \leqq k \leqq 13$	$-23 \leqq k \leqq 24$	$-1 \leqq k \leqq 15$
	$-11 \leqq l \leqq 10$	$-11 \leqq l \leqq 10$	$-12 \leqq l \leqq 11$
Standard refs.	3 (every 97 refls.)	3 (every 97 refls.)	3 (every 97 refls.)
Decay/%	4.25	6.33	1.15
Unique reflections	4132	7673	2495
No. of reflections [$> 2\sigma$(I)]	1789	3256	958
Rint	0.027	0.035	0.035
Extinction coef.	0.027	0.024	0.015
No. of parameters	267	550	142
R [$I > 2\sigma(I)$]	0.070	0.067	0.083
Rw [$I > 2\sigma(I)$]	0.168	0.160	0.214
Goodness of fit	1.035	0.904	1.033
$(\Delta/\sigma)_{\max}$	0.003	0.001	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$	0.22, −0.20	0.20, −0.20	0.37, −0.28

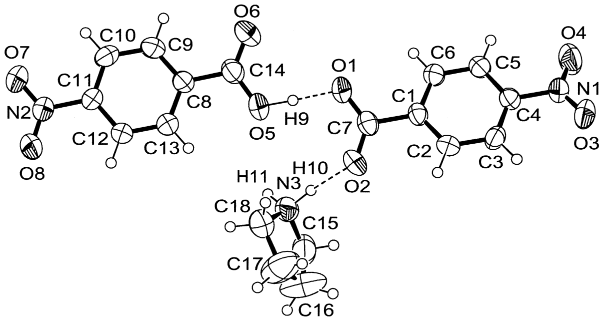

Fig. 1. Thermal displacement ellipsoids with 50% probability of the molecules in **I** and the atomic numbering of the asymmetric unit. Hydrogen bonds are indicated by dashed lines.

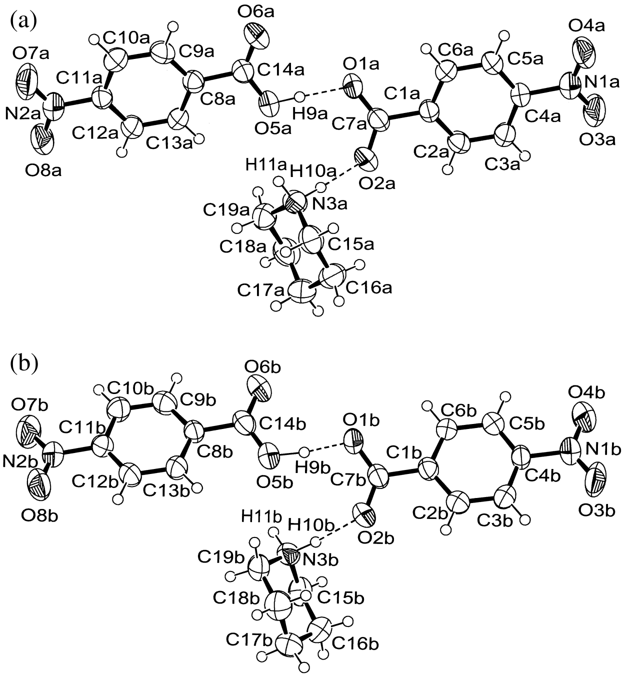

Fig. 2. Thermal displacement ellipsoids with 50% probability of the molecules in **II** and the atomic numbering of the asymmetric unit. Hydrogen bonds are indicated by dashed lines. (a) Formula unit **A**, (b) Formula unit **B**.

N3–H10···O2 and N3–H11···O1 hydrogen bonds along a *c*-glide plane. The ribbons related by the inversion centers at (0, 1, 0) and (1/2, 1/2, 1) and those related by a translation along *b* are hexagonally packed by van der Waals interactions to complete the structure, as shown in Fig. 4.

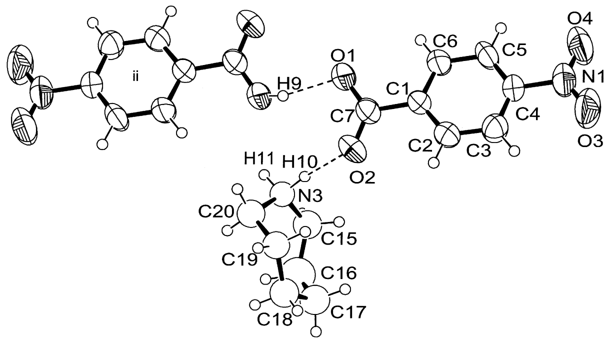

Fig. 3. Thermal displacement ellipsoids with 50% probability of the formula unit in **III** and the atomic numbering of the asymmetric unit. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (ii) $-x+1$, $-y+1$, $-z+1$].

Table 2. Selected Bond Distances (Å) and Angeles (deg)

	I	**II**		**III**
		(a)	(b)	
C1–C7	1.497(5)	1.507(6)	1.503(6)	1.496(5)
C7–O1	1.273(4)	1.265(5)	1.273(5)	1.268(5)
C7–O2	1.242(4)	1.240(5)	1.227(5)	1.206(5)
C4–N1	1.470(4)	1.475(5)	1.472(5)	1.479(5)
N1–O3	1.220(4)	1.197(5)	1.195(5)	1.211(5)
N1–O4	1.206(4)	1.212(5)	1.221(5)	1.211(5)
C8–C14	1.486(5)	1.500(6)	1.497(6)	
C14–O5	1.301(5)	1.306(5)	1.307(5)	
C14–O6	1.211(5)	1.199(5)	1.208(5)	
O5–H9	1.04(6)	0.92(6)	1.06(7)	0.73(9)
C11–N2	1.476(5)	1.474(5)	1.476(5)	
N2–O7	1.209(4)	1.202(5)	1.207(5)	
N2–O8	1.205(4)	1.215(5)	1.214(5)	
C2–C1–C7	120.4(3)	120.8(4)	120.2(4)	120.1(4)
C6–C1–C7	120.4(3)	120.5(4)	121.5(4)	121.3(4)
C1–C7–O1	116.7(3)	117.1(4)	116.4(4)	116.2(4)
C1–C7–O2	118.2(4)	117.3(4)	118.2(4)	120.5(4)
C1–C7–O2	125.0(3)	125.6(4)	125.4(4)	123.3(4)
C3–C4–N1	119.5(3)	119.6(4)	118.5(4)	119.0(4)
C5–C4–N1	118.4(3)	117.9(4)	119.1(4)	118.6(4)
C4–N1–O3	117.9(3)	118.4(4)	119.5(4)	118.5(4)
C4–N1–O4	118.5(3)	118.3(4)	117.9(4)	118.3(4)
O3–N1–O4	123.6(3)	123.3(4)	122.6(4)	123.2(4)
C9–C8–C14	119.5(4)	118.9(4)	119.5(4)	
C13–C8–C14	121.6(4)	122.1(4)	120.9(4)	
C8–C14–O5	113.9(4)	113.2(4)	113.7(4)	
C8–C14–O6	122.8(4)	122.2(4)	121.8(5)	
O5–C14–O6	123.3(4)	124.6(4)	124.5(4)	
C14–O5–H9	115(3)	113(3)	115(3)	128(8)
C10–C11–N2	119.9(3)	119.0(4)	119.2(4)	
C12–C11–N2	118.3(3)	118.4(4)	118.1(4)	
C11–N2–O7	118.7(3)	118.8(4)	118.8(4)	
C11–N2–O8	118.7(3)	118.4(4)	117.8(4)	
O7–N2–O8	122.6(4)	122.8(4)	123.4(4)	

In **II** an asymmetric unit is composed of two formula units, **A** and **B**, as shown in Fig. 2. In the formula unit **A**, the O1a and O5a atoms are linked by O–H···O hydrogen bonds, and the N3a and O2a atoms are linked by N–H···O hydrogen bonds. Similar O–H···O and N–H···O hydrogen bonds are formed in the formula unit **B**. The formula units **A** and **B** are linked by N3a–H11a···O1b and N3b–H11b···O1a hydrogen bonds along a pseudo glide plane along *c* to form a ribbon in a similar manner to that found in **I**. The ribbons related by the inversion centers at (1/2, 0, 1/2) and (1/2, 1/2, 1/2) and those related by a translation along *a* are hexagonally packed in a similar arrangement to that in **I**, as shown in Fig. 5. Thus, the space group of **II** descends from $P2_1/c$ of **I** to its *translationengleiche*

Table 3. Geometry of Hydrogen Bonds, Distances (Å) and Angeles (deg)

D–H···A	D–H	H···A	D···A	D–H···A
I				
O5–H9···O1	1.04(6)	1.49(5)	2.513(3)	170(7)
N3–H10···O2	0.95	1.82	2.740(5)	162
N3–H11···O1^{ii}	0.95	1.93	2.858(5)	163
II				
O5B–H9B···O1B	1.06(7)	1.49(6)	2.522(4)	166(8)
O5A–H9A···O1A	0.92(6)	1.61(5)	2.535(4)	178(6)
N3A–H10A···O2A	0.95	1.80	2.746(5)	176
N3B–H10B···O2B	0.95	1.83	2.773(5)	173
N3B–H11B···O1A	0.95	1.96	2.899(5)	168
N3A–H11A···O1B^{viii}	0.95	1.99	2.926(5)	167
III				
O1–H9···O1^{ii}	0.73(9)	1.84(6)	2.521(6)	156(11)
N3–H10···O2	0.95	1.89	2.835(10)	172
N3–H11···O1^{iv}	0.95	2.17	3.026(8)	149

Symmetry codes: (ii) $x, -y + 3/2, z - 1/2$ for **I**; (viii) $x, y, z - 1$ for **II**; (ii) $-x + 1, -y + 1, -z + 1$, (iv) $x, -y + 1, z - 1/2$ for **III**.

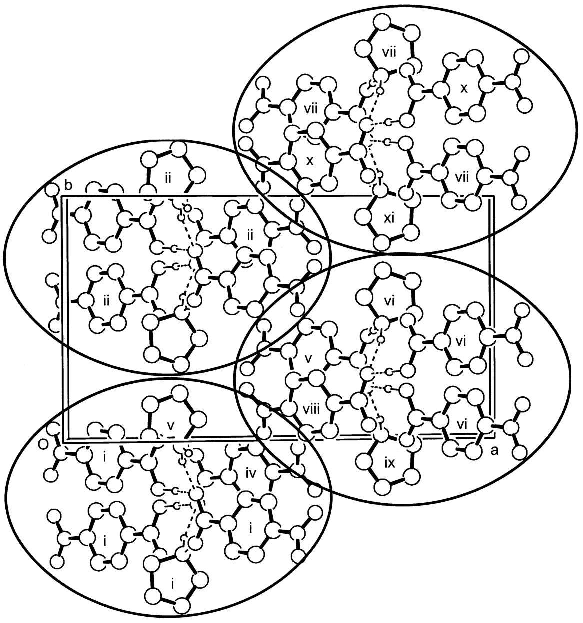

Fig. 4. Packing of the hydrogen-bonded ribbons circled by ellipses in I. The H atoms attached to C atoms are omitted. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $x, y - 1, z$; (ii) $x, -y + 3/2, z - 1/2$; (iii) $x, -y + 3/2, z + 1/2$; (iv) $x, -y + 1/2, z - 1/2$; (v) $x, -y + 1/2, z + 1/2$; (vi) $-x + 1, -y + 1, -z + 2$; (vii) $-x + 1, -y + 2, -z + 2$; (viii) $-x + 1, y - 1/2, -z + 5/2$; (ix) $-x + 1, y - 1/2, -z + 3/2$; (x) $-x + 1, y + 1/2, -z + 5/2$; (xi) $-x + 1, y + 1/2, -z + 3/2$].

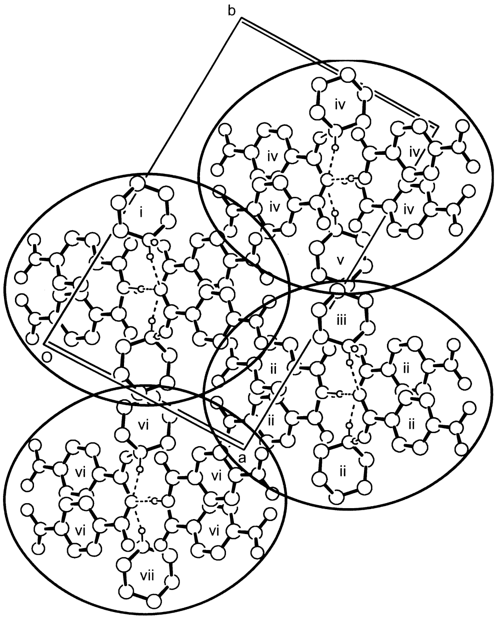

Fig. 5. Packing of the hydrogen-bonded ribbons circled by ellipses in **II**. The H atoms attached to C atoms are omitted. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $x, y, z + 1$; (ii) $x + 1, y, z$; (iii) $x + 1, y, z + 1$; (iv) $-x + 1, -y + 1, -z + 2$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + 1, -y, -z$].

subgroup, $P\bar{1}$.

In **III** a perhydroazepinium cation is disordered around a twofold axis and a hydrogen atom involved in an O–H···O hydrogen bond in the anion is disordered around an inversion center. The H atom may be locally ordered, because the O2···O2^{ii} distance [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$] is rather long and close to those found in non-disordered crystals, I and **II**, as can be seen from Table 3. The disordered structure of **III** can be split into two types of fundamental structures of $P2_1/c$ and Cc by eliminating the twofold axis. The space groups $P2_1/c$ and Cc are a *klassengleiche* subgroup[5] and a *translationengleiche* subgroup of $C2/c$, respectively. The scheme of the hydrogen bonds in these fundamental structures

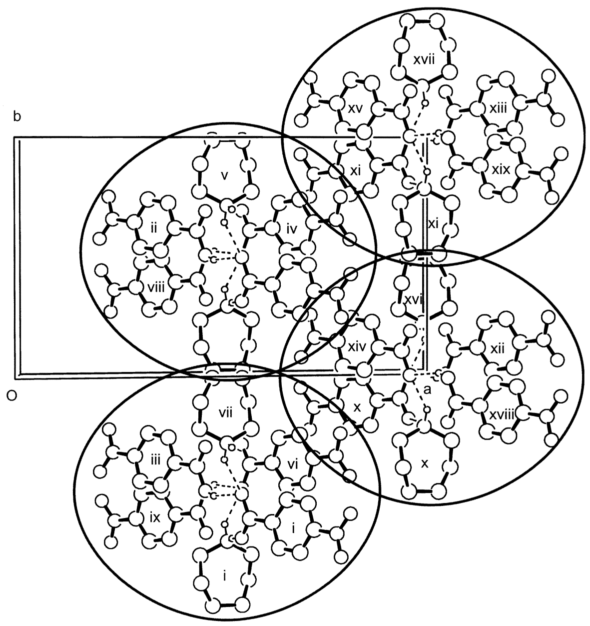

Fig. 6. Packing of the hydrogen-bonded ribbons circled by ellipses in **III** based on the fundamental structure $P2_1/c$. Counterparts of the disordered perhydroazepinium cations related by the twofold axis, the disordered H atoms of the anions, and the H atoms attached to C atoms are omitted. Hydrogen bonds are indicated by dashed lines. [Symmetry codes based on $C2/c$ of the disordered structure: (i) x, $y - 1$, z; (ii) $-x + 1$, $-y + 1$, $-z + 1$; (iii) $-x + 1$, $-y$, $-z + 1$; (iv) x, $-y + 1$, $z - 1/2$; (v) x, $-y + 1$, $z + 1/2$; (vi) x, $-y$, $z - 1/2$; (vii) x, $-y$, $z + 1/2$; (viii) $-x + 1$, y, $-z + 1/2$; (ix) $-x + 1$, $y - 1$, $-z + 1/2$; (x) $-x + 3/2$, $y - 1/2$, $-z + 3/2$; (xi) $-x + 3/2$, $y + 1/2$, $-z + 3/2$; (xii) $x + 1/2$, $-y + 1/2$, $z + 1/2$; (xiii) $x + 1/2$, $-y + 3/2$, $z + 1/2$; (xiv) $-x + 3/2$, $-y + 1/2$, $-z + 2$; (xv) $-x + 3/2$, $-y + 3/2$, $-z + 2$; (xvi) $-x + 3/2$, $-y + 1/2$, $-z + 1$; (xvii) $-x + 3/2$, $-y + 3/2$, $-z + 1$; (xviii) $x + 1/2$, $y - 1/2$, $z + 1$; (xix) $x + 1/2$, $y + 1/2$, $z + 1$].

is the same as that in I. The packing of the hydrogen-bonded ribbons in the $P2_1/c$ structure is shown in Fig. 6. The ribbons related by inversion centers and translations along *b* are packed as in I. In the fundamental structure of *Cc*, the ribbons related by *c*-centering translations are packed with a similar arrangement as in the $P2_1/c$ structure. That is, in the *Cc* structure, the arrangement of the anions is the same as in $P2_1/c$, when the disorder of the H atom involved in the O–H···O hydrogen bond is taken into account. The cation in the *Cc* structure is replaced by a counterpart related by the twofold axis in the disordered structure. The shortest distance is $O4^{xiv}\cdots H16$ 2.71 Å in both fundamental structures [symmetry code based on the disordered structure $C2/c$: (xiv) $-x + 3/2$, $-y + 1/2$, $-z + 2$]. This replacement results in no change in the numbers and the kinds of short contacts between the ribbons.

Through the structures of I – **III**, the O–H···O hydrogen bonds are formed with the same scheme. The scheme of the N–H···O hydrogen bonds is modified from the glide type in I to the pseudo glide type in **II**. The glide type is also recognized in the fundamental structures of $P2_1/c$ and *Cc* in **III**. The arrangements of the hydrogen-bonded ribbons in the crystals of I – **III** are similar to each other, although the differences in the symmetry operations between the ribbons are partly different, as described above. The space group $P2_1/c$ of I descends to its subgroup $P\bar{1}$ with the occurrence of two formula units in **II**, and ascends to its supergroup $C2/c$ along with the occurrence of disorder in **III**. In the structural transformation from I to **III**, an increase in the lattice energy caused by a slightly unfavorable packing should be compensated by an increase in the entropy accompanied by the disordering.

In the series of acid salts of *p*-nitrobenzoic acid the perhydroazepinium ring is disordered, while in the series of acid salts of *p*-methylbenzoic acid the pyrrolidinium and piperidinium rings are disordered. This fact indicates that these cyclic amines have a tendency to undergo disordering around a twofold axis in these series of acid salts. The most important fact observed in these series of acid salts is a phenomenon that the space group descends to one of its maximal non-isomorphic subgroups accompanying a loss of disorder, or the introduction of two formula units in one asymmetric unit. The supergroup-subgroup relationship proposes a possible way of structural change which can be realized by a steric perturbation on intermolecular interactions in organic crystals. In view of crystal engineering,[11] the space-group relationship should be studied more intensively for various kinds of molecular crystals, because it can be used to assume a possible structure after chemical substitution.

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