Crystal Structure of Lutidinium Chloranilates

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The crystal structure of four lutidinium chloranilates, $(CH_3)_2C_6H_3NH^+ \cdot C_6HO_4Cl_2^-$, was determined by single crystal X-ray diffraction at room temperature. 2,4-lutidinium chloranilate (I): triclinic, $P\bar{1}$ (#2), $Z = 2$, $a = 11.401(2)$, $b = 11.639(2)$, $c = 5.1588(8)$ Å, $\alpha = 91.899(15)°$, $\beta = 90.104(14)°$, and $\gamma = 83.355(16)°$, 2,5-lutidinium chloranilate (II): monoclinic, $P2_1/c$ (#14), $Z = 4$, $a = 7.709(2)$, $b = 11.294(2)$, $c = 15.572(3)$ Å, and $\beta = 95.54(2)°$, 2,6-lutidinium chloranilate (III): triclinic, $P\bar{1}$ (#2), $Z = 2$, $a = 9.1312(17)$, $b = 9.127(2)$, $c = 9.1108(13)$ Å, $\alpha = 93.027(17)°$, $\beta = 110.766(13)°$, and $\gamma = 105.206(17)°$, 3,4-lutidinium chloranilate (IV): monoclinic, $P2_1/c$ (#14), $Z = 4$, $a = 10.6356(15)$, $b = 5.1896(5)$, $c = 24.528(3)$ Å, and $\beta = 95.807(10)°$. In these salts, the hydrogen chloranilate monoanions are present as a hydrogen-bonded dimer which has an inversion center. The lutidinium ions are linked on both sides of the dimer via N-H...O hydrogen bonds. Hydrogen bonding patterns in the chloranilic acid-amine (1:1) systems are discussed based on the present crystallographic data and those retrieved mainly from CSD. The patterns can be classified into three types depending on the shape of the amine molecules. Molecular orbital calculations at HF/6-311+G(d,p), MP2/6-311+G(d,p), and B3LYP/6-311+G(d,p) levels of theory were carried out to compare the molecular structure of chloranilic acid with those of its monoanion and dianion.

Key words: Crystal Structure; X-ray Diffraction; Hydrogen Bond; HF.

1. Introduction

Proton transfer through intermolecular hydrogen-bonds enabling charge and energy transfers in solid and biological systems has been the subject of detailed experimental and theoretical studies [1 - 4]. Several hydrogen-bonded complexes of the chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, abbreviated to CLA)-amine (1:1) system have been studied by Issa et al. [5] and Habeeb et al. [6], using IR, NMR, and UV techniques. Habeeb et al. reported that, in the solid state, the hydrogen bonds formed between CLA and amines vary from an O-H...N to an O^-...H-N^+ type with increasing pKa values of the amines, and that the critical (inversion) point at 50% proton transfer exists in the complex of 2,4-lutidine (2,4-dimethylpyridine). They measured the IR spectra and evaluated the center of gravity of the broad protonic absorption band, ν_{cg}. The plot of ν_{cg} vs. pKa of amines showed a deep minimum around the pKa value of 2,4-lutidine, which they assigned to the critical point. From these results, CLA-2,4-lutidine and CLA-amines with pKa similar to 2,4-lutidine seem to be an interesting candidate for a model compound to investigate the proton transfer in hydrogen-bonded systems. However, there is not yet any crystallographic evidence supporting the above findings. In the present study we took 2,4-lutidine as well as other lutidines (2,5-, 2,6-, and 3,4-lutidines) as counter bases for CLA and determined the crystal structures to clarify whether a critical point exists in the crystals. We also discussed the hydrogen-bonding patterns in CLA-amine (1:1) from the present crystallographic data, together with the data mainly retrieved from the Cambridge Structural Database [7], because the CLA-amine system appears attractive from a crystal engineering point of view [8 - 11]; CLA, a strong dibasic acid endowed with hydrogen-bond donor as well as acceptor groups, is expected to be a template for generating tightly bound self-assemblies with polarizable bases. In addition, we carried out molecular orbital calculations at HF/6-311+G(d,p), MP2/6-311+G(d,p), and B3LYP/6-311+G(d,p) levels in order to compare the structure of chloranilic acid with those of hydrogen chloranilate monoanion (CLA^-) and chloranilate dianion (CLA^{2-}) in gas phase.

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Table 1. Crystal data and experimental details for 2,4-lutidinium, 2,5-lutidinium, 2,6-lutidinium, and 3,4-lutidinium chloranilates.

	2,4-lutidinium (I)	2,5-lutidinium (II)	2,6-lutidinium (III)	3,4-lutidinium (IV)
Crystal Data				
Crystal System	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)	$P\bar{1}$ (# 2)	$P\,2_1/c$ (# 14)
a / Å	11.401(2)	7.709(2)	9.1312(17)	10.6356(15)
b / Å	11.639(2)	11.294(2)	9.127(2)	5.1896(5)
c / Å	5.1588(8)	15.572(3)	9.1108(13)	24.528(3)
α / °	91.899(15)		93.027(17)	
β / °	90.104(14)	95.54(2)	110.766(13)	95.807(10)
γ / °	83.355(16)		105.206(17)	
V / Å^3	679.6(2)	1349.5(5)	676.1(2)	1346.9(3)
Z	2	4	2	4
D_x / Mg m^{-3}	1.545	1.556	1.553	1.559
μ(Mo Kα) / mm^{-1}	0.488	0.492	0.491	0.493
F (000)	324	648	324	648
T / K	297	297	298	297
Data Collection				
$\theta_{\min}$, $\theta_{\max}$ / °	1.8, 27.5	2.2, 27.5	2.4, 27.5	2.4, 27.5
h	0→14	–1→10	0→11	–1→13
k	–15→15	0→14	–11→11	0→6
l	–6→ 6	–20→20	–11→11	–31→31
No. of measured reflections	3292	3770	3308	3596
No. of independent reflections	3134	3087	3110	3103
[reflections with $I > 2\sigma(I)$]	2047	1942	2178	1994
R_{int}	0.021	0.018	0.014	0.037
Refinement				
Refinement on	F^2	F^2	F^2	F^2
No. of reflections and	3132	3087	3109	3103
parameters used in refinement	226	204	226	204
Absorption correction	ψ scans [16]	ψ scans	ψ scans	ψ scans
$T_{\min}$, $T_{\max}$	0.786, 0.907	0.809, 0.908	0.830, 0.863	0.773, 0.908
Extiction method	Zachariasen [17]	SHELXL97	Zachariasen	SHELXL97
Extinction coefficient	$8.3(5)\times10^{-6}$	0.0072(11)	$9.3(6)\times10^{-6}$	0.0054(12)
R [$F^2 > 2\sigma(F^2)$]	0.053	0.041	0.047	0.043
wR [F^2]	0.102	0.103	0.091	0.132
S	1.19	1.02	1.19	1.07
Weighting scheme	(a)	(b)	(c)	(d)
$(\Delta/\sigma)_{\max}$	0.01	0.01	0.01	0.01
$\Delta/\rho_{\min}$ / e Å^{-3}	–0.37	–0.21	–0.32	–0.36
$\Delta/\rho_{\max}$ / e Å^{-3}	0.38	0.28	0.38	0.30

(a) $w = 1 / [\sigma^2(F_O) + 0.00038|F_O|^2]$; (b) $w = 1 / [\sigma^2(F_O{}^2) + (0.0327P)^2 + 0.1948P]$, $P = (F_O{}^2 + 2F_C{}^2) / 3$; (c) $w = 1 / [\sigma^2(F_O) + 0.00032|F_O|^2]$; (d) $w = 1 / [\sigma^2(F_O{}^2) + 1.6605P]$, $P = (F_O{}^2 + 2F_C{}^2) / 3$.

2. Experimental

The lutidinium chloranilates were prepared by mixing chloranilic acid with the corresponding lutidine (molar ratio 1:1) in acetonitrile. Single crystals were grown by slow evaporation of the solutions at room temperature. Brown prismatic crystals of 2,4-lutidinium chloranilate (I), 2,5-lutidinium chloranilate (II), 2,6-lutidinium chloranilate (III), and 3,4-lutidinium chloranilate (IV) with a size of 0.20 × 0.40 × 0.45, 0.20 × 0.40 × 0.45, 0.30 × 0.30 × 0.40, and 0.20 × 0.30 × 0.55 mm, respectively, were sealed in glass capillaries for the X-ray measurements. The diffraction data were collected using the ω-2θ scan technique on a Rigaku AFC-5R diffractometer [12] with Mo $K\alpha$ radiation (λ = 0.71073 Å) at the X-ray Laboratory of

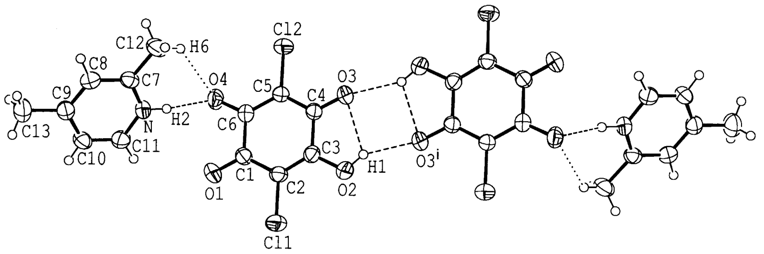

Fig. 1. ORTEP-3 [22] drawing of 2,4-lutidinium chloranilate (I) showing the atomic labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level, and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (symmetry codes are as in Table 3).

Table 2. Selected bond lengths (Å) determined for 2,4-lutidinium, 2,5-lutidinium, 2,6-lutidinium, and 3,4-lutidinium chloranilates.

	2,4-lutidinium (I)	2,5-lutidinium (II)	2,6-lutidinium (III)	3,4-lutidinium (IV)
Cl1-C2	1.729(2)	1.726(2)	1.720(2)	1.726(3)
Cl2-C5	1.730(2)	1.733(2)	1.7350(19)	1.733(3)
O1-C1	1.214(3)	1.227(3)	1.216(2)	1.222(3)
O2-C3	1.326(3)	1.316(3)	1.331(2)	1.321(4)
O3-C4	1.238(3)	1.246(3)	1.240(2)	1.240(3)
O4-C6	1.250(3)	1.230(3)	1.251(2)	1.249(4)
C1-C2	1.446(3)	1.440(3)	1.454(3)	1.439(4)
C2-C3	1.343(3)	1.349(3)	1.339(3)	1.354(4)
C3-C4	1.512(3)	1.517(3)	1.512(3)	1.512(4)
C4-C5	1.404(3)	1.391(3)	1.406(3)	1.400(4)
C5-C6	1.388(3)	1.396(3)	1.392(3)	1.400(4)
C6-C1	1.546(3)	1.549(3)	1.539(3)	1.531(4)
N-C7	1.342(3)	1.343(3)	1.354(2)	1.319(5)
N-C11	1.341(3)	1.344(3)	1.348(3)	1.327(6)
C7-C8	1.376(3)	1.385(4)	1.371(3)	1.376(5)
C8-C9	1.384(3)	1.367(4)	1.381(3)	1.395(4)
C9-C10	1.391(4)	1.393(4)	1.375(3)	1.373(5)
C10-C11	1.355(4)	1.369(3)	1.371(3)	1.363(5)
C7-C12	1.492(3)	1.493(4)	1.486(3)	
C9-C13	1.497(4)			
C10-C13		1.504(4)		
C11-C13			1.490(3)	
C8-C12				1.496(5)
C9-C13				1.509(4)

Table 3. Hydrogen-Bonding geometry for 2,4-lutidinium, 2,5-lutidinium, 2,6-lutidinium, and 3,4-lutidinium chloranilates.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
2,4-lutidinium (I)				
O2-H1···O3	0.83(3)	2.19(3)	2.645(2)	114(3)
O2-H1···O3^{i}	0.83(3)	1.97(3)	2.733(2)	152(3)
N-H2···O4	0.84(2)	1.86(2)	2.698(3)	170(2)
C10-H4···O1^{ii}	0.88(2)	2.46(2)	3.291(3)	157.4(19)
C12-H6···O4	0.98(3)	2.56(3)	3.336(4)	137(3)
2,5-lutidinium (II)				
O2-H1···O3	0.79(3)	2.19(3)	2.635(3)	116(3)
O2-H1···O3^{iii}	0.79(3)	2.05(4)	2.726(2)	143(3)
N-H2···O1	0.87(3)	2.14(3)	2.961(3)	157(2)
N-H2···O4	0.87(3)	2.33(3)	2.930(3)	126(2)
C8-H3···Cl2^{iv}	0.93(3)	2.81(3)	3.595(3)	143(2)
C11-H5···O4	0.94(3)	2.31(3)	2.934(3)	123(2)
C12-H6···Cl2^{v}	0.96	2.78	3.723(3)	166
2,6-lutidinium (III)				
O2-H1···O3	0.90(3)	2.17(3)	2.649(2)	112(2)
O2-H1···O3^{vi}	0.90(3)	1.94(3)	2.743(2)	147(3)
N-H2···O4	0.835(19)	1.845(19)	2.670(2)	169.3(17)
C12-H8···O1	0.94(3)	2.59(3)	3.350(3)	138(2)
C13-H11···Cl1^{vii}	0.87(4)	2.81(4)	3.476(3)	135(3)
3,4-lutidinium (IV)				
O2-H1···O3	0.80(5)	2.14(5)	2.636(3)	120(5)
O2-H1···O3^{viii}	0.80(5)	2.05(5)	2.744(3)	145(5)
N-H2···O1	0.97(5)	2.42(5)	2.934(4)	113(4)
N-H2···O4	0.97(5)	1.85(5)	2.763(4)	156(5)
C7-H3···O1^{ix}	0.93(3)	2.43(4)	3.054(5)	125(3)
C10-H4···O4^{x}	0.98(4)	2.36(4)	3.210(5)	144(3)

Symmetry codes: ^{i} $2-x, -y, 2-z$; ^{ii} $1-x, 1-y, -z$; ^{iii} $-1-x, 1-y, 1-z$; ^{iv} $1+x, 1/2-y, -1/2+z$; ^{v} $x, 1/2-y, -1/2+z$; ^{vi} $-x, -y, -z$; ^{vii} $1-x, 1-y, -z$; ^{viii} $-x, 2-y, 1-z$; ^{ix} $x, -1+y, z$; ^{x} $1-x, 1/2+y, 1/2-z$.

Okayama University. The crystal lattice parameters were determined from 25 reflections in the 2θ range of 20-25°. The structures were solved by SIR92 [13]. The structure refinement was carried out by LS in TEXSAN [14] for (I) and (III), and by SHELXL97 [15] for (II) and (IV). All H atoms in (I) and (III) were refined isotropically. The refined distances are C-H = 0.87(4) - 0.98(3), N-H = 0.85(2), and O-H = 0.83(3) Å for (I); C-H = 0.85(4) - 0.95(3), N-H = 0.84(2), and O-H = 0.91(3) Å for (III). For (II) and (IV), H atoms in methyl groups were treated as riding atoms with C-H = 0.96 Å and U_{iso}(methyl H) = 1.5 U_{eq}(methyl C), while other H atoms were refined isotropically. The refined distances are C-H = 0.93(3) - 0.94(3), N-H = 0.87(3), and O-H = 0.79(3) Å for (II); C-H = 0.89(4) - 0.98(4), N-H = 0.97(5), and O-H = 0.81(5) Å. Crystal data and experimental details are given in Table 1[*].

Molecular orbital calculations were performed with the Gaussian 98 [18] package. The *ab ini-*

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[*] Crystal data of (I) - (IV) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementator publication No. CCDC 190140, CCDC 190141, CCDC 190142, and CCDC 190143, respectively.

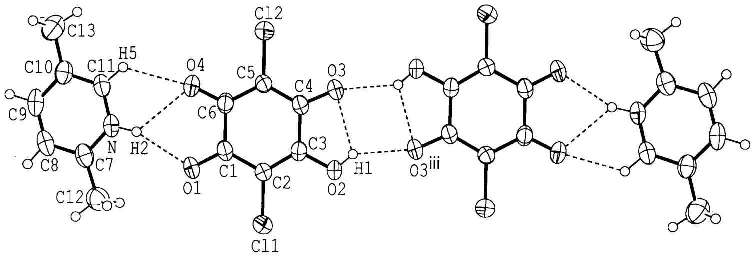

Fig. 2. ORTEP-3 drawing of 2,5-l. (II) showing the atomic labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (symmetry codes are as in Table 3).

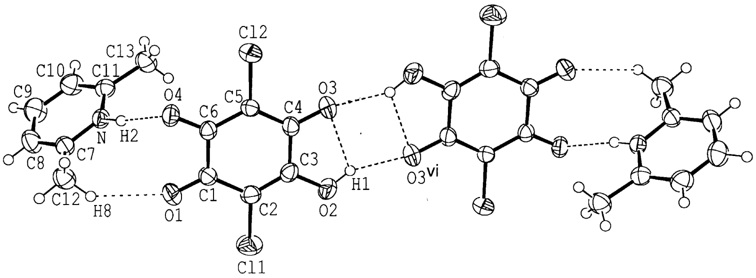

Fig. 3. ORTEP-3 drawing of 2,6-l. (III) showing the atomic labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (symmetry codes are as in Table 3).

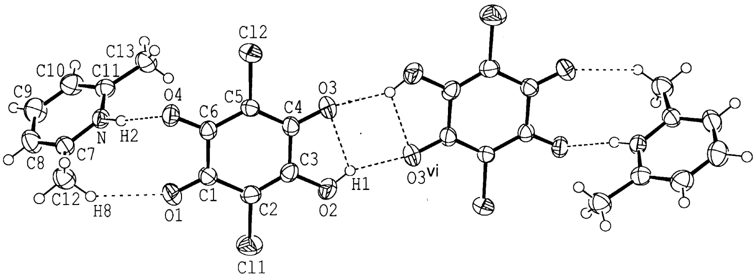

Fig. 4. ORTEP-3 drawing of 3,4-l. (IV) showing the atomic labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (symmetry codes are as in Table 3).

tio Hartree-Fock (HF), second-order Møller-Plesset (MP2) [19] and Becke's three parameter hybrid DFT-HF [20] with the Lee-Yange-Parr correlation functional (B3LYP) [21] with the 6-311+G(d,p) basis set were used for geometry optimization and vibrational frequency calculations. The stable structures were confirmed by the vibrational analysis which showed real frequencies for the optimized structures.

3. Results and Discussion

The molecular structures of (I), (II), (III), and (IV) are shown in Figs. 1, 2, 3, and 4, respectively. Selected bond lengths and hydrogen bonding geometries are given in Tables 2 and 3, respectively. In all compounds, the asymmetric unit is composed of $(CH_3)_2C_6H_3NH^+\cdot C_6HO_4Cl_2^-$ and an acid-base interaction involving a proton transfer is observed between lutidine and chloranilic acid. The existence of the hydrogen chloranilate monoanion is also confirmed by comparing the structure with that calculated by MO calculations as mentioned below. The critical point, as reported by Habeeb et al., is not found in the present study.

As shown in Figs. 1 - 4, two chloranilate ions, related by an inversion center, are connected by O-H...O hydrogen bonds and form a dimeric unit. The H1 atom is also involved in an intramolecular hydrogen bond with O3. The lutidinium ions are linked on both sides of the dimer via N-H2...O4 hydrogen bonds [(II) and (IV)] or via bifurcated hydrogen bonds N-H2...O4 and N-H2...O1 [(I) and (III)], forming 2:2 complexes of lutidine and chloranilic acid. Besides the strong intermolecular interactions, such as O-H...O and N-H...O hydrogen bonds, there are some important C-H...O and C-H...Cl hydrogen bonds within the 2:2 complexes and between the complexes (Table 3). Especially, the C11-H5...O4 hydrogen bond within the complex (II) is quite short (H5...O4 2.31 Å). This bond may contribute the almost flat structure of the 2:2 complex of (II), where the dihedral angle between the pyridine ring and the C1-C6 plane of the chloranilate ion is 12.16(11)°. In the 2:2 complexes of (I) and (III), the pyridine ring twists out largely from the

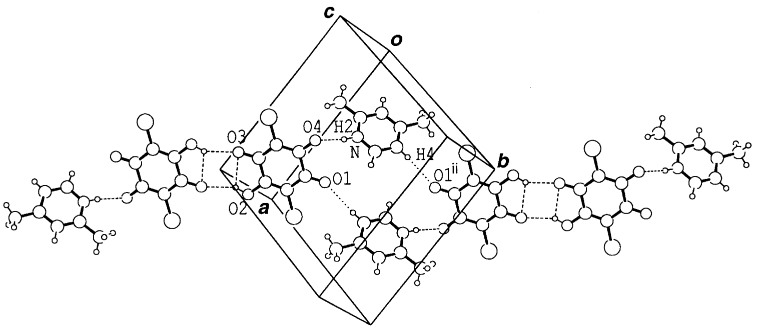

Fig. 5. Part of the crystal structure of 2,4-l. (I), showing the zigzag molecular tape running parallel to the [1 $\bar{1}$ 2] direction. N-H...O and O-H...O hydrogen bonds are shownated by dashed lines, and C-H...O hydrogen bonds by dotted lines.

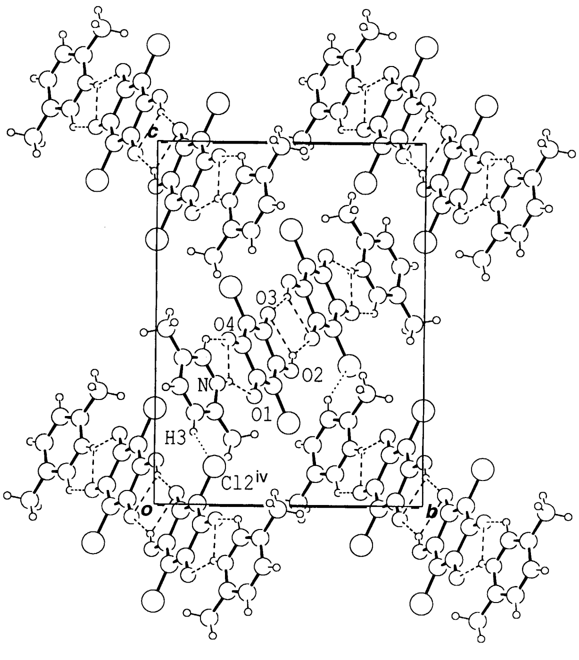

Fig. 6. Packing diagram of 2,5-l. (II) viewed down the *a* axis. N-H...O, O-H...O, and C-H...O hydrogen bonds are shown by dashed lines, and C-H...Cl hydrogen bonds by dotted lines.

C1-C6 plane to avoid the steric repulsion between the methyl group and the O atoms of the chloranilate ion; the dihedral angles are 56.73(10)° and 77.54(10)° for (I) and (III), respectively. On the other hand, despite the absence of a methyl group at the 2 or 6 position, the pyridine ring in (IV) is nearly perpendicular to the C1-C6 plane; the dihedral angle is 87.72(17)°. This may be due to the intermolecular C-H...O hydrogen bonds (C7-H3...O1$^{\text{ix}}$), as mentioned below.

The crystal structures of (I) - (IV) are shown in Figs. 5 - 8, respectively. In (I), the 2:2 complexes are linked together by C-H...O hydrogen bonds (C10-H4...O1$^{\text{ii}}$: Table 3) to afford a zigzag molecular tape running parallel to the [1 $\bar{1}$ 2] direction. The complexes in (III) are linked together by C-H...Cl interactions (C13-H11...Cl1$^{\text{vii}}$) forming a similar tape to (I) along the [1 1 0] direction. On the other hand, the 2:2 complexes in (II) and (IV) are stacked in columns along the *a* and *b* axes, respectively. In (II), there are C-H...Cl interactions in the column (C12-H6...Cl2$^{\text{v}}$) and between the columns (C8-H3...Cl2$^{\text{iv}}$). In (IV), C-H...O hydrogen bonds connect the units of the 2:2 complex in the column (C7-H3...O1$^{\text{ix}}$) and between the columns (C10-H4...O4$^{\text{x}}$).

The bond lengths calculated for CLA, CLA$^-$, and CLA^{2-} at HF/6-311+G(d,p), MP2/6-311+G(d,p), and B3LYP/6-311+G(d,p) levels are given in Table 4. The atomic numbering in the table is the same as that used in Figs. 1 - 4. The deprotonation of CLA causes the Cl-C bond to become longer; the bond lengths of Cl1-C2 and Cl2-C5 increase in order of CLA < CLA$^-$ < CLA^{2-}. The C3-C4 bond length also increases in the same order. On the other hand, the C1-C2, C5-C6, and C6-C1 bonds take a maximum value in CLA$^-$, while C2-C3 and C4-C5 a minimum value. This results in the characteristic structure of CLA$^-$ distorted from the centrosymmetric structure of CLA, that is, C3-C4 < C6-C1, C4-C5 < C1-C2, C2-C3 < C5-C6, Cl1-C2 < Cl2-C5, and the long O2-C3 bond. This feature coincides with the results in the present X-ray diffraction, indicating that the present compounds are clearly salts accompanied with a charge and proton transfer.

From the crystallographic data of the present salts and those mainly retrieved from the Cambridge Structural Database, the hydrogen-bond patterns in the chloranilic acid-amine (1:1) system can be classified into 3 types as shown in Figure 9. Type 1 is found in the complexes composed of imidazole [11], pyrazine [8], and dipyridyl-type molecules [9, 10, 23]. The amine and chloranilic acid are alternately arranged via O-H...N or N-H...O hydrogen bonds to form a

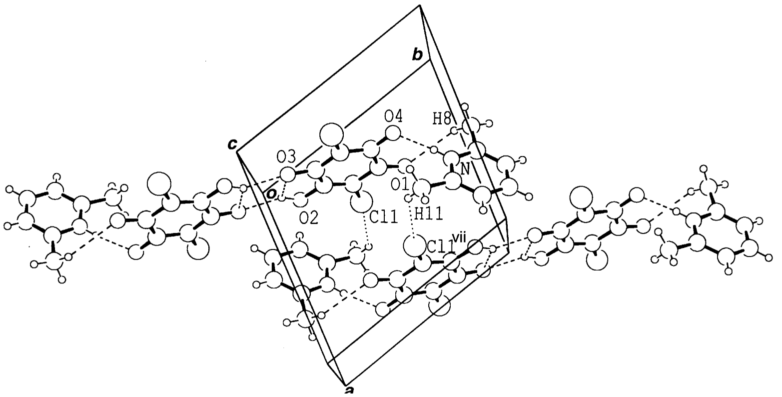

Fig. 7. Part of the crystal structure of 2,6-l. (III), showing the zigzag molecular tape running parallel to the [1 1 0] direction. N-H...O and O-H...O hydrogen bonds are shown by dashed lines, and C-H...Cl hydrogen bonds by dotted lines.

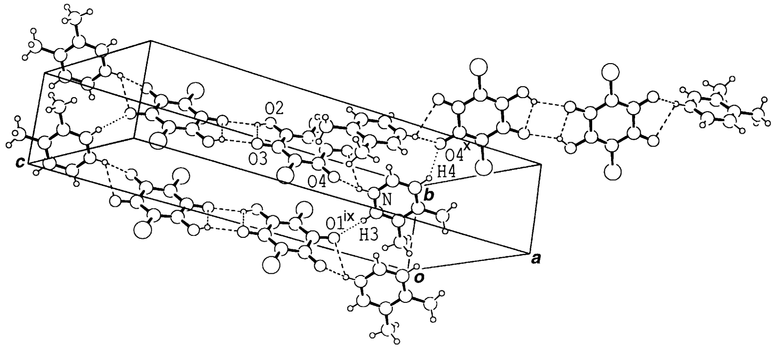

Fig. 8. Part of the crystal structure of 3,4-l. (IV), showing the stack in column along the b axis. N-H...O and O-H...O hydrogen bonds are shown by dashed lines, and C-H...O hydrogen bonds indicated by dotted lines.

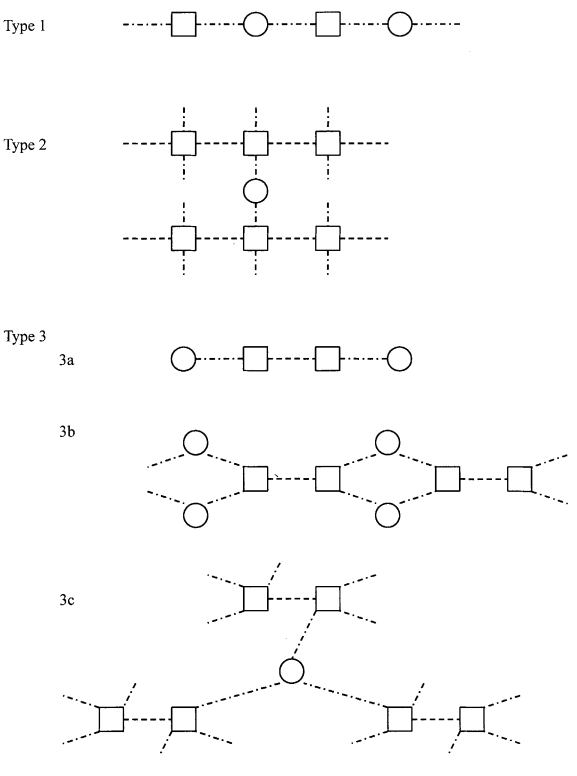

Fig. 9. Hydrogen bonding patterns in chloranilic acid-amine 1:1 system. CLA or CLA^- is drawn as □ and amine as ∘. N-H...O/N...H-O and O-H...O hydrogen bonds are indicated by dashed-and-dotted and dashed lines, respectively.

molecular chain or tape. Type 2 is found in morpholinium chloranilate [8], where a chain of chloranilate ions is formed through O-H...O hydrogen bonds, and morpholinium ions link the two chains through the N-H...O hydrogen bonds. Type 3 is found in the compounds composed of pyridine-type molecules such as lutidine in the present study and in compounds of primary and secondary amines. In this type, the chloranilic acids form a centrosymmetric dimer through O-H...O hydrogen bonds. The dimer is linked by N-H...O hydrogen bonds with amines to afford three different types of aggregates (Type 3a - 3c). In Type 3a, the dimer is linked by two amines to form 2:2 complexes in the case of the present salts. Pyridinium chloranilate monohydrate [24] can also be classified into this type, where the chloranilic acids form a dimer through the water molecule. Type 3b is a chain, where two diethylammonium ions, related by an inversion center, link the two dimers of CLA^- by N-H...O hydrogen bonds [25]. Type 3c is a three-dimensional hydrogen-bond network found in ethylammo-

Table 4. Bond lengths (Å) of chloranilic acid (CLA), hydrogen chloranilate ion (CLA^-), and chloranilate ion (CLA^{2-}), optimized by HF/6-311+G(d,p), MP2/6-311+G(d,p), and B3LYP/6-311+G(d,p).

		CLA			CLA^-			CLA^{2-}	
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
Cl1-C2	1.719	1.710	1.729	1.739	1.732	1.758	1.777	1.765	1.802
Cl2-C5	1.719	1.710	1.729	1.748	1.737	1.762	1.777	1.765	1.802
O1-C1	1.187	1.230	1.220	1.185	1.225	1.214	1.212	1.249	1.240
O2-C3	1.309	1.329	1.322	1.313	1.331	1.326	1.212	1.249	1.240
O3-C4	1.187	1.230	1.220	1.224	1.265	1.257	1.212	1.249	1.240
O4-C6	1.309	1.329	1.322	1.197	1.236	1.225	1.212	1.249	1.240
C1-C2	1.466	1.459	1.454	1.470	1.464	1.460	1.412	1.421	1.416
C2-C3	1.330	1.361	1.354	1.329	1.358	1.351	1.412	1.421	1.416
C3-C4	1.516	1.507	1.520	1.529	1.514	1.525	1.567	1.561	1.582
C4-C5	1.466	1.459	1.454	1.385	1.396	1.391	1.412	1.421	1.416
C5-C6	1.330	1.361	1.354	1.424	1.431	1.429	1.412	1.421	1.416
C6-C1	1.516	1.507	1.520	1.565	1.567	1.585	1.567	1.561	1.582
O2-H1	0.949	0.977	0.980	0.957	0.999	1.000			
O4-H2	0.949	0.977	0.980						

Atomic numbering is the same as that used in Figs. 1 - 4.

nium chloranilate [25] and propylammonium chloranilate [26].

The present study reveals that a critical point does not exist in the lutidine - chloranilic acid system, although Habeeb et al. reported its existence from the IR spectra. This shows that in the case where O-H...O and N-H...O/O-H...N hydrogen bonds coexist in the crystal it is difficult to assign the critical point only from IR spectral data. It is required to analyze the spectra carefully on the basis of the crystal structure. The critical point in a CLA-amine system of Type 3a may exist in a compound with an amine having a much lower pKa than lutidine. Moreover, the shapes of the proton donor and acceptor molecules may be as important as the pKa in determining the proton transfer in crystals. Further experimental studies are in progress in order to search the existence of the critical point.

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