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Crystal and Molecular Structures of Acetoacetanilide, and *o*- and *p*-Chloroacetoacetanilides: X-Ray Crystallographic and MO Study

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X-Ray structure analyses and MO calculations have been performed for acetoacetanilide (AAA), and *o*- and *p*-chloroacetoacetanilides (*o*-CAAA and *p*-CAAA) in order to elucidate the contribution of hydrogen bonding to crystal and molecular structures. The molecular conformations have been classified into two categories, planar for *o*-CAAA and nonplanar for AAA and *p*-CAAA. The molecular conformation of *o*-CAAA can be well-reproduced by the geometry optimization based on the AM1 (Austin Model 1) MO method, while those of AAA and *p*-CAAA are different from the optimized geometries. The deviation from the optimized structure can be explained on the basis of the formation of intermolecular hydrogen bonding and C–H···O=C interactions in the crystals. The hydrogen bonding of these compounds is discussed together with the infrared (IR) spectral data.

As an extension of the previous works on the crystal structures and hydrogen bonding of N-(aromatic substituted) amides,[1,2] AAA derivatives having an additional acetyl group on the side chain of acetanilide have been studied in order to examine the pattern of N–H···O=C hydrogen bonding and C–H···O=C interactions. The importance of the C–H···O=C interactions in crystals has recently been noted[3,4] and elucidated for a series of crystals.[5] The effect of the hydrogen bonding on the molecular structures is also expected, when the intramolecular hydrogen bonding is formed. The investigations of the molecular structures of Cl-substituted AAA, further, involve the interests in the effect of Cl substitution on molecular geometry, including the effect of the substituted position.

We have employed the semiempirical (AMl) and *ab initio* MO calculations in order to elucidate the primary factor contributing to the molecular conformation. Recently, a reasonable agreement has been shown between the geometries obtained by the X-ray structural analyses and those evaluated by the AMl method.[6,7]

Experimental

The samples (Nakarai Chemicals; GR for AAA, Tokyo Kasei; EP for *o*-CAAA and *p*-CAAA) were used without further purification. The crystals of AAA and those of *o*-CAAA and *p*-CAAA were obtained from an ethanol solution and benzene solutions, respectively, by slow evaporation.

X-Ray Structure Analysis. Experimental details and crystal data are listed in Table 1. The densities were measured by flotation in KI aqueous solutions.

AAA. The unit cell dimensions were determined from oscillation photographs; Ni filtered Cu *Kα* radiation (λ= 1.5418 Å) was used. The diffraction data were collected by the equi-inclination Weissenberg method at room temperature. The intensities were determined by visual comparison. Many trials to collect the data of better quality by a diffractometer were unsuccessful because of the high cleavage property along the {1 0 0} planes of the crystals. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by the Patterson method and refined by the block-diagonal least-squares method anisotropically for the non-H atoms and isotropically for the H atoms except for those attached to the benzene rings, which were fixed at the positions calculated by assuming an usual geometry. $\Sigma w(|F_o|-|F_c|)^2$ was minimized with $w=1.0$ for $0<F_o\leq 12.0$ and $w=12.0/|F_o|$ for $|F_o|>12.0$.

***o*-CAAA and *p*-CAAA.** The intensities were measured on a Rigaku AFC-5R diffractometer with graphite monochromated Mo *Kα* radiation (λ= 0.71073 Å, 40 kV, 200 mA, 295 K) at the X-Ray Laboratory of Okayama University. The unit

Table 1. Experimental Details and Crystal Data

	AAA	*o*-CAAA	*p*-CAAA
	$C_{10}H_{11}NO_2$	$C_{10}H_{10}NO_2Cl$	$C_{10}H_{10}NO_2Cl$
M_r	177.20	211.65	211.65
Morphology	Plate developed {1 0 0}	Prismatic *a*	Plate developed {0 1 0}
Size of specimen (l/mm)	0.30×0.40×0.41 0.08×0.38×1.68	0.35×0.25×0.28	0.30×0.30×0.10
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbc*2₁ (No. 29)	*P*2₁/*c* (No. 14)	*Pcab* (No. 61)
a/Å	11.136(5)	7.619(3)	9.491(1)
b/Å	19.28(1)	12.244(3)	26.264(7)
c/Å	8.707(4)	10.557(3)	8.412(2)

Table 1. (Continued)

	AAA	*o*-CAAA	*p*-CAAA
$\beta/°$		99.64(2)	
$V/\text{Å}^3$	1869(2)	970.8(2)	2097(2)
$D_o/\text{Mg m}^{-3}$	1.25	1.45	1.31
$D_x/\text{Mg m}^{-3}$	1.260	1.448	1.341
Z	8	4	8
$F(0\,0\,0)$	752	440	880
μ/cm^{-1}	7.3	3.6	3.4
Radiation	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
$2\theta_{\text{max}}/°$	124	55	50
Range of h,k,l	$0\leq h\leq 12$	$0\leq h\leq 9$	$0\leq h\leq 11$
	$0\leq k\leq 22$	$0\leq k\leq 15$	$0\leq k\leq 31$
	$0\leq l\leq 10$	$-13\leq l\leq 13$	$-1\leq l\leq 10$
Fluctuation of standard reflections/%	—	0.85	0.80
R_{int}		0.014	0.028
Number of unique reflections used	1304	1723 $\lvert F_o\rvert>3\sigma(F_o)$	1092 $\lvert F_o\rvert>3\sigma(F_o)$
Number of parameters	324	168	168
R	0.091	0.043	0.062
wR	0.115	0.048	0.025
S	1.25	1.67	1.17
Constants for w			
p	—	−0.0313	0.0536
q	—	0.0027	−0.0004
$(\Delta/\sigma)_{\text{max}}$	0.31	0.84	0.69
$\Delta\rho_{\text{max}}/\text{eA}^{-3}$	0.36	0.24	0.22
$\Delta\rho_{\text{min}}/\text{eA}^{-3}$	−0.36	−0.25	−0.22

cell dimensions were determined from 25 reflections with 2θ range of 20 to 23°. The intensities were collected by the ω–2θ scan method with a scan width of $(1.68+0.30\tan\theta)°$ for *o*-CAAA and $(1.15+0.30\tan\theta)°$ for *p*-CAAA. The scan speed was $6°\,\text{min}^{-1}$ in ω for both cases. Three standard reflections were measured after every 97 reflections. The intensities were corrected for Lorentz and polarization effects. The structure of *o*-CAAA was solved by the Patterson method and that of *p*-CAAA by the direct method using MULTAN84.[8] The structures were refined by the block-diagonal least-squares method anisotropically for the non-H atoms and isotropically for the H atoms; $\Sigma w(|F_o|-|F_c|)^2$ was minimized with $w=[\sigma(F_o)^2+p|F_o|+q|F_o|^2]^{-1}$. The correction for secondary extinction effect was made for the strongest 8 reflections of *o*-CAAA by $I_{\text{corr}}=I_{\text{obsd}}(1+6.67\times 10^{-6}\,I_c)$.

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[9] The programs used: RSSFR-5,[10] HBLS-V and DAPH,[11] MOLCON[12] and ORTEP.[13] Calculations were carried out at the Okayama University Computer Center.

IR Measurement. IR spectra were measured with a JASCO FT/IR spectrometer at room temperature. The measurements in solution state were performed with chloroform as solvent, while those in solid state with powdered samples in KBr disks.

Theoretical Calculations. The geometry optimizations were carried out by the AM1 method in MOPAC Ver. 5.02 available from JCPE.[14–16] The geometries obtained by the X-ray structure analyses were adopted for the optimization. The calculations were performed at the Okayama University Computer Center. The Gaussian 88 program accessible at the Computer Center of Kyushu University was used for the *ab initio* calculations at STO-3G level.

Table 2. Fractional Atomic Coordinates and Equivalent Thermal Parameters B_{eq} with Their esd's in Parentheses

$$B_{\text{eq}}=(4/3)\sum_i\sum_j\beta_{ij}/a_ia_j$$

Atom	x	y	z	$B_{\text{eq}}/\text{Å}^2$	Atom	x	y	z	$B_{\text{eq}}/\text{Å}^2$
AAA					*o*-CAAA				
Molecule A					Cl(1)	0.44290(6)	0.52697(4)	0.72814(4)	3.86(2)
O(1)	0.0199(6)	0.5315(3)	0.3987(9)	5.0(3)	O(1)	0.0640(2)	0.4756(1)	0.2757(1)	4.58(6)
O(2)	−0.1952(6)	0.4443(4)	0.2436(7)	5.3(3)	O(2)	0.2890(2)	0.28035(9)	0.5886(1)	4.17(6)
N(1)	0.0937(6)	0.4241(3)	0.3683(8)	3.3(3)	N(1)	0.2265(2)	0.4789(1)	0.4771(1)	3.02(6)
C(1)	0.2060(7)	0.4411(3)	0.304(1)	2.7(3)	C(1)	0.2517(2)	0.5909(1)	0.5002(1)	2.68(6)
C(2)	0.2743(8)	0.4972(4)	0.356(1)	4.1(4)	C(2)	0.3510(2)	0.6241(1)	0.6170(1)	2.86(7)
C(3)	0.3854(9)	0.5087(4)	0.294(1)	4.6(4)	C(3)	0.3790(2)	0.7337(1)	0.6473(2)	3.47(7)
C(4)	0.4314(9)	0.4661(5)	0.178(1)	4.9(5)	C(4)	0.3072(2)	0.8119(1)	0.5608(2)	4.03(8)
C(5)	0.364(1)	0.4117(5)	0.125(1)	5.4(5)	C(5)	0.2089(2)	0.7811(1)	0.4441(2)	3.84(8)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/ Å^2	Atom	x	y	z	B_{eq}/ Å^2
C(6)	0.2519(8)	0.3987(4)	0.190(1)	3.9(4)	C(6)	0.1807(2)	0.6724(1)	0.4139(1)	3.37(7)
C(7)	0.0098(7)	0.4693(3)	0.4132(9)	3.1(3)	C(7)	0.1390(2)	0.4287(1)	0.3708(1)	3.03(7)
C(8)	−0.0999(9)	0.4366(4)	0.490(1)	4.0(4)	C(8)	0.1401(2)	0.3049(1)	0.3715(1)	3.26(7)
C(9)	−0.2025(7)	0.4250(4)	0.3744(8)	3.2(3)	C(9)	0.2186(2)	0.2391(1)	0.4886(1)	3.23(7)
C(10)	−0.311(1)	0.3866(6)	0.434(1)	6.2(6)	C(10)	0.2053(3)	0.1175(1)	0.4745(2)	4.7(1)
Molecule B					*p*-CAAA				
O(1)	0.0262(5)	0.2791(3)	0.4012(9)	4.8(3)	Cl(1)	0.3181(2)	0.00087(6)	0.2722(2)	9.7(1)
O(2)	−0.2164(7)	0.2012(4)	0.2811(9)	6.4(4)	O(1)	0.2031(2)	0.2464(1)	0.4756(4)	6.3(2)
N(1)	0.0831(6)	0.1678(3)	0.3737(9)	3.4(3)	O(2)	0.3703(4)	0.3349(1)	0.3076(3)	7.7(2)
C(1)	0.1993(7)	0.1765(3)	0.3091(9)	2.7(3)	N(1)	0.4221(3)	0.2128(1)	0.4712(4)	4.0(2)
C(2)	0.2696(7)	0.2323(4)	0.344(1)	3.7(4)	C(1)	0.3925(4)	0.1627(1)	0.4210(4)	3.7(2)
C(3)	0.3868(7)	0.2359(4)	0.277(1)	4.5(4)	C(2)	0.4894(4)	0.1250(2)	0.4580(5)	4.7(2)
C(4)	0.4274(8)	0.1848(5)	0.184(1)	4.4(4)	C(3)	0.4663(5)	0.0755(2)	0.4130(6)	5.4(2)
C(5)	0.3569(9)	0.1294(5)	0.151(1)	4.6(4)	C(4)	0.3460(5)	0.0631(2)	0.3291(5)	5.7(2)
C(6)	0.2404(8)	0.1248(4)	0.212(1)	3.8(4)	C(5)	0.2523(4)	0.1005(2)	0.2907(6)	5.9(3)
C(7)	0.0074(8)	0.2181(4)	0.426(1)	3.5(3)	C(6)	0.2743(4)	0.1500(2)	0.3345(5)	5.0(2)
C(8)	−0.0999(8)	0.1920(4)	0.509(1)	3.4(3)	C(7)	0.3298(4)	0.2509(2)	0.4998(4)	4.2(2)
C(9)	−0.2137(7)	0.1923(4)	0.418(1)	3.4(3)	C(8)	0.3912(4)	0.2990(2)	0.5642(5)	4.3(2)
C(10)	−0.3249(8)	0.1812(5)	0.508(1)	4.5(4)	C(9)	0.3881(4)	0.3418(2)	0.4469(5)	5.0(2)
					C(10)	0.4120(6)	0.3936(2)	0.5111(7)	8.0(3)

Table 3. Bond Lengths and Angles for *o*-CAAA and *p*-CAAA

	o-CAAA	*p*-CAAA		*o*-CAAA	*p*-CAAA
	l/Å	l/Å		ϕ/°	ϕ/°
C(1)-C(2)	1.395(3)	1.387(6)	C(1)-C(2)-C(3)	121.7(2)	120.6(4)
C(2)-C(3)	1.388(3)	1.372(6)	C(2)-C(3)-C(4)	119.5(2)	119.8(5)
C(3)-C(4)	1.372(3)	1.381(7)	C(3)-C(4)-C(5)	119.9(2)	119.4(5)
C(4)-C(5)	1.383(3)	1.364(7)	C(4)-C(5)-C(6)	120.7(2)	121.4(5)
C(5)-C(6)	1.377(3)	1.367(7)	C(5)-C(6)-C(1)	120.7(2)	119.8(5)
C(6)-C(1)	1.398(3)	1.378(6)	C(6)-C(1)-C(2)	117.5(2)	119.1(4)
C(2)-Cl(1)	1.734(2)	—	C(1)-C(2)-Cl(1)	119.7(2)	—
C(4)-Cl(1)	—	1.724(5)	C(3)-C(4)-Cl(1)	—	119.5(4)
N(1)-C(1)	1.400(2)	1.410(5)	C(2)-C(1)-N(1)	118.5(2)	117.8(4)
N(1)-C(7)	1.353(2)	1.352(5)	C(1)-N(1)-C(7)	128.6(1)	128.0(3)
C(7)-O(1)	1.213(2)	1.225(5)	N(1)-C(7)-O(1)	124.7(2)	122.4(4)
C(7)-C(8)	1.516(3)	1.493(6)	N(1)-C(7)-C(8)	116.7(2)	116.0(3)
C(8)-C(9)	1.512(3)	1.496(6)	C(7)-C(8)-C(9)	122.5(2)	112.9(4)
C(9)-O(2)	1.211(2)	1.198(6)	C(8)-C(9)-O(2)	123.2(2)	122.3(5)
C(9)-C(10)	1.498(3)	1.481(8)	C(8)-C(9)-C(10)	115.9(2)	116.5(4)

Table 4. Torsion Angles of Side Chains in AAA, *o*-AAA, and *p*-CAAA Obtained from X-Ray Structural Analyses and by AM1 Method[a]

	τ/°	τ/°	τ/°	τ/°
X-Ray data				
	AAA(A)	AAA(B)	*o*-CAAA	*p*-CAAA
τ_1[C(1)-N(1)-C(7)-O(1)]	−2(1)	−11(2)	−0.9(3)	−4.2(6)
τ_2[C(1)-N(1)-C(7)-C(8)]	175.9(8)	171.0(8)	177.6(2)	175.4(4)
τ_3[N(1)-C(7)-C(8)-C(9)]	95.4(9)	102.1(9)	5.8(3)	109.9(4)
τ_4[C(7)-C(8)-C(9)-O(2)]	4(1)	−12(1)	−1.6(3)	−16.7(6)
τ_5[C(7)-C(8)-C(9)-C(10)]	−174.3(7)	167.2(8)	178.6(2)	164.8(4)
AM1 method				
τ_1[C(1)-N(1)-C(7)-O(1)]	7.1		−0.5	2.3
τ_2[C(1)-N(1)-C(7)-C(8)]	−175.6		178.5	179.3
τ_3[N(1)-C(7)-C(8)-C(9)]	54.4		8.4	61.1
τ_4[C(7)-C(8)-C(9)-O(2)]	−59.8		4.7	−56.2
τ_5[C(7)-C(8)-C(9)-C(10)]	121.4		−176.1	124.9

a) Torsion angles for AAA(A) and AAA(B) refer to the enantiomers of the molecules constructed from the atoms in Table 2 for the convenience of comparison with *p*-CAAA.

Results

The final atomic parameters are listed in Table 2.[17] The thermal ellipsoids of the molecules are shown in Fig. 1 with atomic numbering. The bond lengths and angles are listed in Table 3. The selected torsion angles are listed in Table 4 along with those calculated by the AM1 method. Geometries of N–H···O=C hydrogen bonds and C–H···O=C interactions are summarized in Table 5. The crystal structures are shown in Fig. 2.

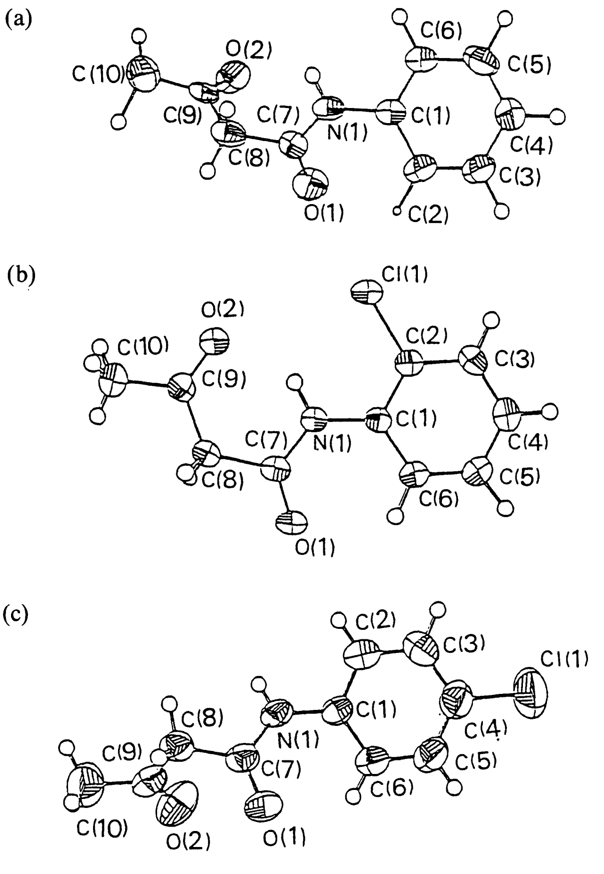

Fig. 1. The thermal ellipsoids and atomic numbering for non-H atoms for (a) AAA(A), (b) *o*-CAAA, and (c) *p*-CAAA. The thermal ellipsoids of 50% probability are used for non-H atoms. The H atoms are represented as spheres equivalent to B=1.0 Å^2.

Although the precision of the atomic parameters of AAA is low, it has been possible to describe the molecular arrangement and conformations.

Description of the Structures. (1) AAA. In the crystal there are crystallographically independent molecules, A and B. In both molecules τ_1 [C(1)–N(1)–C(7)–O(1)] and τ_4 [C(7)–C(8)–C(9)–O(2)] are close to 0° and τ_3 [N(1)–C(7)–C(8)–C(9)] around 90° (Table 4). The carbamoyl groups of A and B, which are arranged in nearly parallel, are linked by an N–H···O=C hydrogen bond to form a hydrogen-bonded unit (A···B). The units related by a *b* glide plane are linked through the other N–H···O=C hydrogen bond to form a molecular chain ···A···B···A′···B′···A···B··· along the *b* axis, where (A···B) and (A′···B′) are related by the glide plane. In the chain there exist C–H···O=C interactions between the methylene and carbamoyl groups (Table 5). The chains related by a *c* glide plane and thus by a 2_1 axis are stacked along the *c* axis to form a sheet parallel to (1 0 0) plane. In the sheet the acetyl groups of both A and B participate in the C–H···O=C interactions (Table 5). The sheets are stacked along the *a* axis by weak van der Waals interactions which cause the high cleavage property of the crystals.

(2) *o*-CAAA. The non-hydrogen atoms of the molecule of *o*-CAAA lie in a plane with the maximum deviation of 0.118(1) Å at O(2), and the torsion angles τ_1, τ_3, and τ_4 being close to 0° (Table 4). An intramolecular N–H···O=C hydrogen bond is formed between the carbamoyl N–H and acetyl C=O (Table 5). The other intramolecular short contacts are also found [H(N1)···Cl(1), 2.48(2) Å; H(6)···O(1), 2.28(2) Å]. The C(7)–(C8)–C(9) angle, 122.5(2)°, is larger than the value expected for the sp^3 angle.

Table 5. Geometries of N–H···O=C Hydrogen Bonds and C–H···O=C Interactions

Donor(D)	Acceptor(A)	D···A l/Å	H···A l/Å	D–H···A ϕ/°	H···O=C ϕ/°
AAA					
N(1B^{ii})	O(1A^{i})	2.88(1)	1.9(1)	169(9)	153(3)
N(1A^{i})	O(1B^{i})	2.91(1)	2.0(1)	170(9)	174(3)
C(8B^{ii})	O(1A^{i})	3.36(1)	2.3(1)	151(7)	146(3)
C(8A^{i})	O(1B^{i})	3.43(1)	2.6(1)	139(7)	130(2)
C(8B^{i})	O(2B^{iii})	3.40(1)	2.4(1)	163(8)	136(3)
C(10B^{i})	O(2A^{iii})	3.48(1)	2.3(1)	160(7)	110(3)
o-CAAA					
N(1^{i})	O(2^{i})	2.708(1)	1.93(2)	145(2)	99.6(6)
C(8^{ii})	O(2^{i})	3.526(2)	2.52(2)	167(2)	120.2(5)
p-CAAA					
N(1^{i})	O(1^{ii})	2.874(4)	2.09(3)	161(3)	146.8(9)
C(8^{i})	O(1^{ii})	3.227(5)	2.50(4)	137(3)	141(1)
C(8^{i})	O(2^{iii})	3.353(6)	2.46(4)	160(3)	133(1)

Symmetry codes: For AAA, (i) x, y, z, (ii) $-x$, $1/2+y$, z, (iii) x, $1/2-y$, $1/2+z$; for *o*-CAAA, (i) x, y, z, (ii) x, $1/2-y$, $1/2+z$; for *p*-CAAA, (i) x, y, z, (ii) $1/2+x$, $1/2-y$, z, (iii) $1/2-x$, y, $1/2+z$.

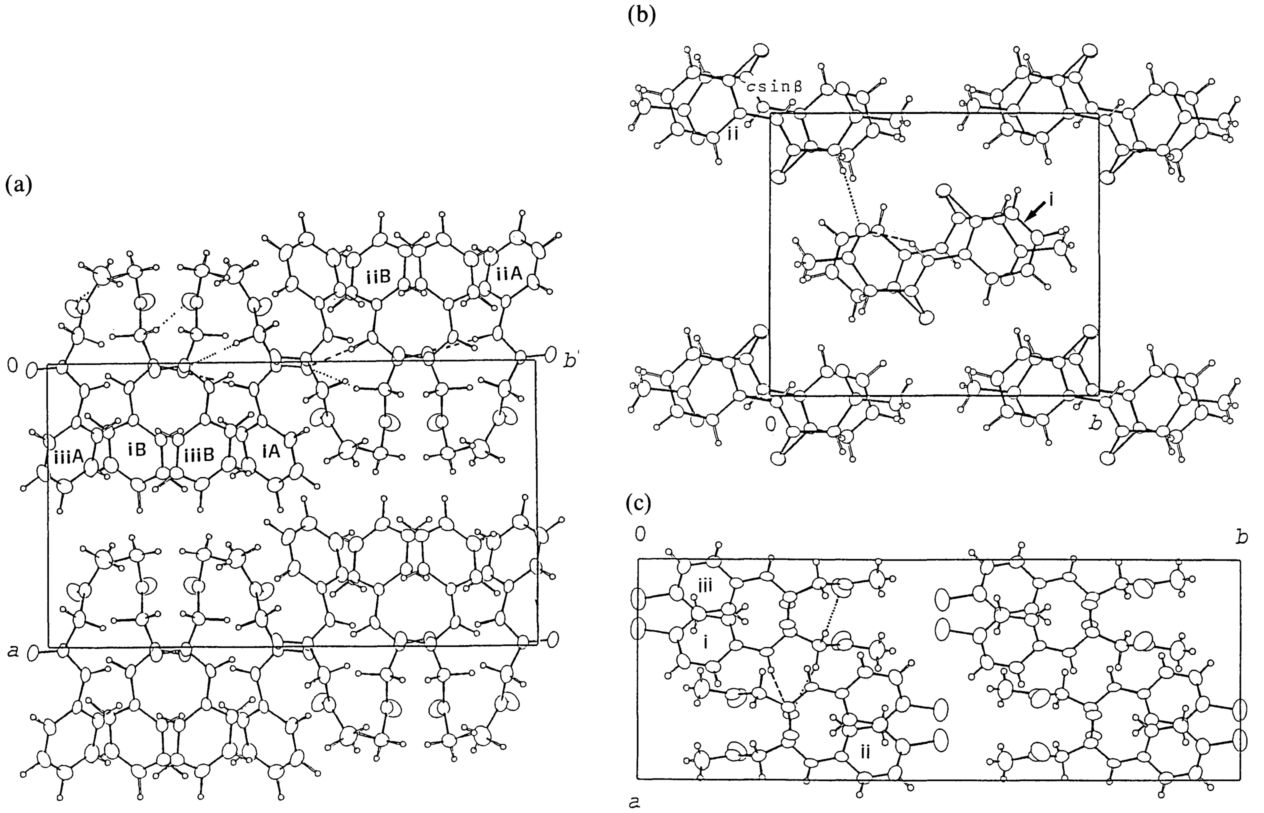

Fig. 2. Projections of the crystal structures. (a) AAA viewed along the *c* axis, (b) *o*-CAAA viewed along the *a* axis, and (c) *p*-CAAA viewed along the *c* axis. Broken lines show N–H···O=C hydrogen bonds and dotted lines C–H···O=C interactions for the molecules with the symmetry codes given in Table 5.

The molecules related by $\bar{1}$ at (0, 1/2, 1/2) and (1/2, 1/2, 1/2) are stacked along the *a* axis, the interplanar distances beng 3.438(2) and 3.569(2) Å, respectively, for the molecular planes through the non-hydrogen atoms. The benzene moieties are overlapped with the polar side-chains in antiparallel to form a column. The columns are hexagonally packed in the crystal. An C–H···O=C interaction is found between the methylene and acetyl groups of the molecules related by a *c* glide plane, but no intermolecular hydrogen bond is found.

(3) *p*-CAAA. The molecule takes a similar conformation to those of AAA (Table 4). The molecules related by an *a* glide plane are linked through an N–H···O=C hydrogen bond between the carbamoyl groups to form a molecular chain. In the chain an intermolecular C–H···O=C interaction is formed between the methylene and carbamoyl groups. The chains related by a *c* glide plane are stacked along the *c* axis to form a sheet parallel to (0 1 0) plane. In the sheet there is a C–H···O=C interaction between the other H atom of the methylene group and an acetyl oxygen (Table 5). The sheets are stacked along the *b* axis by weak van der Waals interactions to complete the whole structure.

Discussion

Molecular Conformations. The resultant conformations of the side chains of the acetoacetanilides can be classified into two types only by the difference in τ_3. The first type is that found in *o*-CAAA and the second is that in AAA and *p*-CAAA.

In *o*-CAAA the C(9)=O(2) bond is orientated toward the H(1)–N(1) bond to form an intramolecular N–H···O=C hydrogen bond. In AAA and *p*-CAAA, no intramolecular hydrogen bond is formed, but their C(7)=O(1) bonds participate in the intermolecular hydrogen bonds.

For *o*-CAAA the optimization well reproduces the experimental torsion angles (Table 4). This result shows that the intramolecular hydrogen bond and the attractive interactions H(N1)···Cl(1) and H(6)···O(1) make the molecule to stabilize in planar conformation in both isolated and crystalline states. In this stable conformation the molecular width is larger than those of AAA and *p*-CAAA, so that in the crystal of *o*-CAAA the planar molecules are stacked in antiparallel way which is consistent with the most stable interactions between the dipole and induced dipole.[18]

For AAA and *p*-CAAA the optimized values for τ_1 are in good agreement with the experimental values, but the optimized τ_3 and τ_4, both of these corresponding to the *gauche* conformation, exhibit a disagreement with the experimental values. The optimized conformations would make possible to form an intramolecular N–

H···O=C hydrogen bond [H(N1)···O(2), 2.22 Å for AAA; 2.25 Å for *p*-CAAA]. Thus, the AM1 calculations show that the most important factor for the stabilization in energy is the intramolecular hydrogen bonding for the isolated molecules of AAA and *p*-CAAA as well as *o*-CAAA. On the other hand, in the crystalline state of AAA and *p*-CAAA the intermolecular C–H···O=C interactions in addition to the intermolecular hydrogen bonding play an important role for the stabilization, because the τ_3 and τ_4 observed for the molecules in different crystallographic environments are consistent with the respective intermolecular C–H···O=C interaction (Table 5).

Electronic Properties. The total energies for structures optimized by the AM1 method are −2279.47 eV for AAA and −2639.58 eV for *p*-CAAA. On the other hand, the energies estimated by the AM1 method with the experimental geometries are −2278.48 eV for AAA and −2638.83 eV for *p*-CAAA, only the geometries of the H atoms being optimized in this calculation. Consequently, the molecular geometries obtained by the X-ray structure analyses are higher in energy than those optimized by the AM1 method for both AAA and *p*-CAAA. This unstabilization could be supplemented by the stabilization due to the intermolecular interactions in the crystalline state. The experimental geometry for *o*-CAAA is higher in energy by 0.50 eV than the optimized: the energies are −2639.48 eV for the optimized geometry and −2638.98 eV for the experimental. The total energy of *o*-CAAA is similar to that of *p*-CAAA irrespective of the positions of Cl substitution. In fact, the interactions between Cl atom and the side chain are small in these molecules.

The net atomic charges, q's, on atoms were estimated for AAA, *o*-CAAA, and *p*-CAAA molecules; hereafter the $q(\mathrm{A})$ and $q(\mathrm{G})$ refer to the q estimated by the AM1 and the *ab initio* method, respectively. For *o*-CAAA, strong electrostatic attraction is operative between the positive charge on H(N1) [$q(\mathrm{A})=0.2682$, $q(\mathrm{G})=0.2744$] and the negative charge on O(2) [$q(\mathrm{A})=-0.2943$, $q(\mathrm{G})=-0.2288$]. In *o*-CAAA the interaction between Cl(1) [$q(\mathrm{A})=-0.0202$, $q(\mathrm{G})=-0.1427$] and H(N1) is weak attractive. For all the acetoacetanilides the atomic charge on O(1) [$q(\mathrm{A})=-0.3496$, $q(\mathrm{G})=-0.2823$ for AAA; $q(\mathrm{A})=-0.3651$, $q(\mathrm{G})=-0.2796$ for *o*-CAAA; $q(\mathrm{A})=-0.3456$, $q(\mathrm{G})=-0.2710$ for *p*-CAAA] is large negative in comparison with that on O(2) [$q(\mathrm{A})=-0.3016$, $q(\mathrm{G})=-0.2337$ for AAA; $q(\mathrm{A})=-0.3008$, $q(\mathrm{G})=-0.2213$ for *p*-CAAA].

Table 6. Infrared Stretching Vibrations of N–H and C=O and Bond Orders P_{NH} between N and H in AAA, *o*-CAAA, and *p*-CAAA

	N(1)–H(N1) ν/cm^{-1}	C(7)=O(1) ν/cm^{-1}	C(9)=O(2) ν/cm^{-1}	P_{NH}
Solution				
AAA	3306	1682	1715	0.8852
o-CAAA	3248	1688	1720	0.8673
p-CAAA	3298	1684	1713	0.8844
Solid				
AAA	3256	1663	1710	
o-CAAA	3208	1680	1711	
p-CAAA	3254	1659	1715	

IR Vibration Frequency Shifts. IR vibration frequencies of N(1)–H(N1), C(7)=O(1), and C(9)=O(2) in AAA, *o*-CAAA, and *p*-CAAA are collected in Table 6, along with the bond orders, P_{NH}'s of their N(1)–H(N1) bonds evaluated for the optimized geometries by the AM1 method. The N(1)–H(N1) stretching vibrations in the solid state decrease by ca. 40—50 cm^{-1} compared with those in the solution state for all the compounds. The result implies an increase in the strength of hydrogen bonding in the solid state[19,20] compared with the solution state. The N(1)–H(N1) stretching vibration for *o*-CAAA is observed at lower frequencies by ca. 50 cm^{-1} than those for AAA and *p*-CAAA in consistent with the values of P_{NH} (Table 6).

The C(7)=O(1) vibration frequencies of AAA and *p*-CAAA in the solid state shift to lower frequencies by ca. 20 cm^{-1} than those in the solution state. This result is reasonably explained by assuming that the molecular structures in the solution state take the AM1-optimized geometry, because the C(7)=O(1) bonds participate in the intermolecular hydrogen bonds in the solid state, but no hydrogen bonding involving these bonds would be formed in the solution state. The shift for the C(7)=O(1) bond of *o*-CAAA is small, because the bond is free from any hydrogen bonding in both states.

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