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Crystal Structures of Acrylamide Derivatives: *N*-*t*-Butylacrylamide, *N*-*t*-Butylmethacrylamide, Dimorphs of *N*-Phenylmethacrylamide, and *N*-*o*-Chlorophenylmethacrylamide

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The crystal structures of *N*-*t*-butylacrylamide, *N*-*t*-butylmethacrylamide, dimorphs of *N*-phenylmethacrylamide, and *N*-*o*-chlorophenylmethacrylamide have been determined by X-ray diffraction method. In all these crystals the molecules related by a glide plane are held together by an N–H···O hydrogen bond between the amide groups. The difference in the reactivity of the *N*-arylmethacrylamides in γ-ray induced solid-state polymerization is ascribed to the difference in an intermolecular steric effect for the molecular movement, but not to the difference in the hydrogen-bond type.

Acrylamide and methacrylamide have been reported to polymerize in the solid-state by irradiation with γ-rays.[1,2] *N*-*t*-Butylacrylamide and its complexes with metal halides have also been reported to polymerize in the solid-state.[3,4] However, there are no reports on the crystal structures of any derivatives of acrylamide or methacrylamide.

N-Arylmethacrylamides are less reactive than methacrylamide in the solid-state polymerization. Some *o*-substituted *N*-arylmethacrylamides show higher reactivity compared with the *m*- and *p*-isomers.[5] It has been suggested that the difference in the reactivity may be ascribed to the difference in the hydrogen-bond type in the solid-state.[5]

In the solid-state polymerization the reaction scheme and the structure of a polymer formed are expected to be influenced by the crystal structure of the monomer. In the present work, the structures of *N*-*t*-butylacrylamide (**1**), *N*-*t*-butylmethacrylamide (**2**), the dimorphs of *N*-phenylmethacrylamide [*Pbca* form (**3**); $Pca2_1$ form (**4**)], and *N*-*o*-chlorophenylmethacrylamide (**5**) have been studied in order to get structural information which is required to establish the relationship between the reaction scheme in the initial stage and the molecular arrangement in the solid-state.

Experimental

Crystal data and experimental details are listed in Table 1. The crystals of **1** were grown from a diethyl ether solution, and those of **2**—**4** were grown from ethanol solutions. The compound of **5** was prepared by the method described by James and Ciotti,[6] and the crystals were grown from a tetrahydrofuran solution, by slow evaporation at room temperature. D_m of the crystals of **1** was measured by flotation in water by adjusting the temperature to 295 K, and those of **2**—**5** were measured by flotation in aqueous KI solutions.

A crystal of **1** was mounted on a Rigaku AFC-3 four-circle diffractometer (graphite monochromated Mo $K\alpha$, $\lambda=0.71073$ Å, 40 kV, 20 mA). The crystals of **2**—**5** were mounted on Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (Ni-filtered Cu $K\alpha$, $\lambda=1.54178$ Å, 40 kV, 200 mA). The lattice parameters were determined with 25 reflections for **1** and 20 reflections for **2**—**5**. The intensity data were collected by ω–2θ scan method [scan speed in ω: 1° min^{-1} for **1** and 4° min^{-1} for **2**—**5**; scan range in ω: $(1.0+0.15\tan\theta)°$ for **1** and $(1.2+0.15\tan\theta)°$ for **2**—**5**]. Background was measured for 4 s on either side of the peak for **1**—**3** and **5**, and 3 s for **4**. Three standard reflections were recorded every 57 reflections for **1** and every 97 reflections for **2**—**5**. Corrections for Lorentz and polarization effects were applied, but no absorption correction was made.

The reflections used in the structure analyses and refinements were those with $|F_o|$ larger than $2\sigma(F_o)$ for **1**, and the non-zero unique reflections for **2**—**4**, and reflections with $|F_o|$ larger than $3\sigma(F_o)$ for **5**. The structures were solved by a direct method. The positions of the H atoms were determined from difference Fourier maps. The structures of **1** and **5** were refined by block-diagonal least-squares method with anisotropic thermal parameters for non-H atoms. The parameters of some H atoms were fixed. The structures were refined by block-diagonal least-squares method for **2**, and by full-matrix least-squares method for **3** and **4**, with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms. In **1**—**5** $\sum w(|F_o|-|F_c|)^2$ was minimized with $w=1.0/[\sigma(F_o)^2+p|F_o|+q|F_o|^2]$. The values of p and q are listed in Table 1. Correction for secondary extinction effect was made for **2** and **5** according to $I_{\text{corr}}=I_0(1+gI_c)$, where $g=7.20\times10^{-6}$ for **2** and 2.15×10^{-7} for **5**.

Atomic scattering factors were taken from "International Tables for X-Ray Crystallography".[7] Programs used were MULTAN84,[8] HBLS-V, FMLS and DAPH,[9] MOLCON,[10] and ORTEP.[11] Computations were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Results and Discussion

The final atomic parameters are listed in Table 2.[12] Thermal ellipsoids of the molecules are shown in Fig. 1 with atomic numbering, where the same numbering scheme is used for the C atoms of the C=C double bond of the molecules in the crystals **1**—**5**. Bond lengths and bond angles are listed in Table 3, and selected torsion angles in Table 4. Projections of the crystal structures

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Table 1. Experimental Details and Crystal Data

	$C_7H_{13}NO$ (**1**)	$C_8H_{15}NO$ (**2**)	$C_{10}H_{11}NO$ (**3**)	$C_{10}H_{11}NO$ (**4**)	$C_{10}H_{10}NOCl$ (**5**)
M_r	127.19	141.21	161.20	161.20	195.65
Mp/K	399.4—401.0	324.0—325.5	355.9—357.8	358.1—358.5	328.0—329.1
Morphology	Prismatic	Prismatic	Prismatic	Plate	Prismatic
Size of specimen (l/mm)	0.28×0.23×0.63	0.55×0.38×0.38	0.39×0.08×0.44	0.51×0.28×0.25	0.20×0.10×0.38
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Cc* (No.9)	$P2_1/c$ (No.14)	*Pbca* (No.61)	$Pca2_1$ (No.29)	$P2_1/c$ (No.14)
a/Å	13.258(5)	5.8339(6)	12.954(1)	10.214(1)	14.229(2)
b/Å	7.803(2)	15.887(1)	15.543(1)	9.409(2)	7.7558(6)
c/Å	9.452(4)	10.0918(7)	9.1374(8)	9.750(1)	9.183(1)
β/°	120.32(2)	102.246(6)			105.48(1)
V/Å^3	844.1(4)	914.1(1)	1839.7(3)	936.9(2)	976.6(1)
Z	4	4	8	4	4
D_m/g cm^{-3}	0.998	1.03	1.16	1.14	1.30
D_x/g cm^{-3}	1.001	1.026	1.164	1.143	1.331
F (000)	280	312	688	344	408
μ (Radiation)/mm^{-1}	0.07 (Mo $K\alpha$)	0.54 (Cu $K\alpha$)	0.61 (Cu $K\alpha$)	0.60 (Cu $K\alpha$)	3.13 (Cu $K\alpha$)
$2\theta_{max}$/°	50	120	125	125	125
Range of h	$-14\leqq h\leqq 14$	$-6\leqq h\leqq 6$	$0\leqq h\leqq 14$	$0\leqq h\leqq 11$	$-16\leqq h\leqq 16$
k	$0\leqq k\leqq 9$	$0\leqq k\leqq 17$	$0\leqq k\leqq 17$	$0\leqq k\leqq 10$	$0\leqq k\leqq 8$
l	$0\leqq l\leqq 11$	$0\leqq l\leqq 11$	$0\leqq l\leqq 10$	$0\leqq l\leqq 11$	$0\leqq l\leqq 10$
Fluctuation of standard reflections/%	2	2	1	1	3
Number of reflections used	602	1359	1367	762	1266
Number of parameters	87	152	154	154	159
R	0.058	0.062	0.080	0.046	0.075
wR	0.051	0.077	0.055	0.038	0.068
Constants for w; p	−0.119	0.014	0.0	−0.064	−0.829
q	0.009	0.000	0.0	0.005	0.070
S	2.53	1.11	0.63	1.43	2.53
$\Delta\rho_{max}(\Delta\rho_{min})/e$Å^{-3}	0.16 (−0.17)	0.17 (−0.14)	0.17 (−0.22)	0.10 (−0.10)	0.41 (−0.48)
$(\Delta/\sigma)_{max}$	0.39	0.10	0.80	0.55	0.61

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters $B_{eq}=(4/3)\sum_i \beta_{ii}/\boldsymbol{a}_i^{*2}$.

Atom	x	y	z	B_{eq}/Å^2
N-*t*-Butylacrylamide (**1**)				
O(1)	0.5019(2)	0.4343(3)	−0.1384(2)	6.4(1)
N(1)	0.5536(2)	0.4142(3)	0.1267(3)	5.4(1)
C(1)	0.3542(4)	0.7131(6)	−0.1714(4)	7.8(3)
C(2)	0.4212(3)	0.6360(5)	−0.0323(4)	6.3(2)
C(3)	0.4958(3)	0.4852(4)	−0.0205(4)	4.8(1)
C(5)	0.6296(3)	0.2612(4)	0.1737(4)	6.0(2)
C(6)	0.5557(4)	0.1085(5)	0.0845(5)	8.8(3)
C(7)	0.7252(4)	0.2885(6)	0.1343(5)	9.5(3)
C(8)	0.6853(5)	0.2428(6)	0.3544(5)	8.9(3)
N-*t*-Butylmethacrylamide (**2**)				
O(1)	0.3019(3)	0.7445(1)	0.3366(2)	6.53(8)
N(1)	0.4191(3)	0.7274(1)	0.1387(2)	5.17(8)
C(1)	0.2801(6)	0.8983(2)	0.0753(3)	7.6(1)
C(2)	0.2003(4)	0.8523(1)	0.1719(2)	5.5(1)
C(3)	0.3106(4)	0.7697(1)	0.2223(2)	4.9(2)
C(4)	0.0160(6)	0.8815(2)	0.2332(4)	9.9(1)
C(5)	0.5386(4)	0.6455(1)	0.1689(2)	5.3(1)
C(6)	0.7257(5)	0.6507(2)	0.2992(3)	6.6(1)
C(7)	0.3595(5)	0.5772(2)	0.1807(3)	7.0(1)
C(8)	0.6572(6)	0.6269(2)	0.0515(3)	8.5(2)
N-Phenylmethacrylamide *Pbca* form (**3**)				
O(1)	0.0946(2)	0.1761(1)	0.8607(2)	7.56(9)
N(1)	0.1380(1)	0.2501(1)	0.6551(2)	5.60(9)
C(1)	0.0247(3)	0.1275(2)	0.4912(3)	10.1(1)
C(2)	0.0134(2)	0.1344(2)	0.6403(3)	6.2(1)
C(3)	0.0854(2)	0.1884(2)	0.7278(3)	5.8(1)
C(4)	−0.0650(2)	0.0891(2)	0.7169(3)	8.9(2)
C(5)	0.2106(2)	0.3082(2)	0.7158(3)	5.5(1)
C(6)	0.2772(2)	0.2835(2)	0.8277(3)	7.3(2)
C(7)	0.3453(2)	0.3442(3)	0.8828(3)	9.6(2)
C(8)	0.3483(2)	0.4257(3)	0.8308(4)	10.5(2)
C(9)	0.2843(2)	0.4489(2)	0.7168(4)	8.7(2)
C(10)	0.2150(2)	0.3902(2)	0.6594(3)	6.6(2)
N-Phenylmethacrylamide $Pca2_1$ form (**4**)				
O(1)	0.2714(2)	0.2724(2)	0.0517(2)	8.27(9)
N(1)	0.1813(2)	0.2710(2)	0.2625(2)	5.86(8)
C(1)	0.3804(3)	0.4807(4)	0.3229(4)	9.6(2)
C(2)	0.3934(2)	0.3771(3)	0.2318(3)	7.2(1)
C(3)	0.2767(3)	0.3022(3)	0.1747(2)	6.3(1)
C(4)	0.5217(3)	0.3299(5)	0.1749(4)	11.7(2)
C(5)	0.0601(2)	0.2032(2)	0.2313(3)	5.6(1)
C(6)	−0.0050(3)	0.2265(3)	0.1094(3)	6.8(1)
C(7)	−0.1259(2)	0.1616(3)	0.0868(3)	7.9(2)
C(8)	−0.1800(3)	0.0760(3)	0.1845(3)	8.3(2)
C(9)	−0.1144(2)	0.0528(3)	0.3060(3)	8.1(2)
C(10)	0.0052(3)	0.1161(3)	0.3299(3)	6.7(1)
N-*o*-Chlorophenylmethacrylamide (**5**)				
Cl(1)	0.39543(7)	0.8675(1)	0.5588(1)	4.95(5)
O(1)	0.1677(2)	0.8549(3)	0.4862(3)	4.3(1)
N(1)	0.2271(2)	0.7583(4)	0.2969(3)	3.3(1)
C(1)	0.1339(3)	1.0487(5)	0.1277(5)	5.4(2)
C(2)	0.1085(2)	0.9887(5)	0.2485(4)	3.6(2)
C(3)	0.1699(2)	0.8619(4)	0.3532(4)	3.1(1)
C(4)	0.0216(3)	1.0499(6)	0.2917(6)	6.6(3)
C(5)	0.2834(2)	0.6233(4)	0.3818(4)	3.2(1)
C(6)	0.3598(2)	0.6573(4)	0.5083(4)	3.5(2)
C(7)	0.4099(3)	0.5250(5)	0.5964(5)	4.5(2)
C(8)	0.3890(3)	0.3561(5)	0.5503(5)	5.3(2)
C(9)	0.3177(3)	0.3205(4)	0.4215(5)	5.1(2)
C(10)	0.2643(3)	0.4535(5)	0.3376(4)	4.1(2)

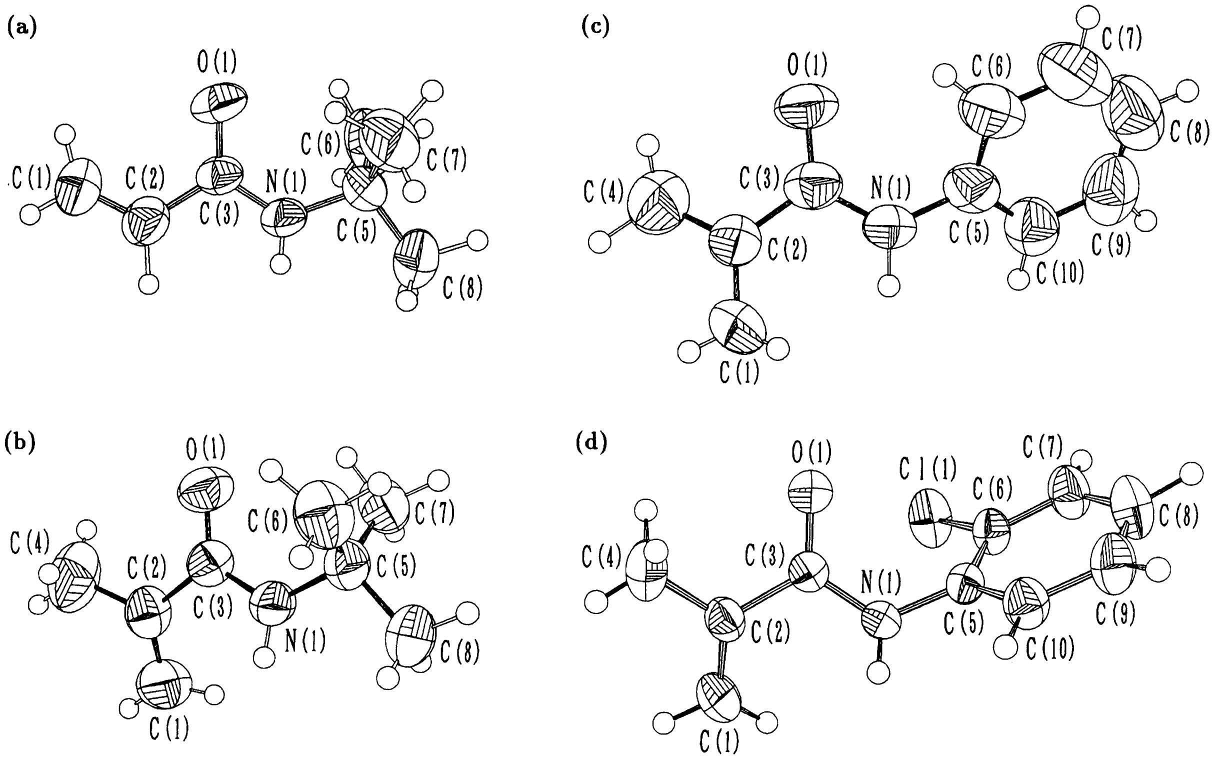

Fig. 1. The thermal ellipsoids of the molecules in the crystals of **1** (a), **2** (b), **3** (c) and **5** (d) with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to B=1.0 Å^2. For the molecule in the crystal of **4** the thermal ellipsoids are abbreviated. The atomic numbering is the same as that in (c).

and the symmetry codes are shown in Fig. 2.

Molecular Structures. For all these molecules the amide groups are planar as seen from the torsion angle τ_1 in Table 4. τ_2's show that the C=C double bond of **1** takes a cis conformation to the carbonyl group, while that of **2** takes a trans conformation. In **2** the steric hindrance would arise between H(N) and the methyl group in a cis conformation. For **1** and **2** the *t*-butyl groups take a staggered conformation to the C(3)–N(1) bond (τ_3, τ_4, and τ_5). For **3**—**5** the conformation of the C=C double bonds around the C(2)–C(3) bond is a trans to each carbonyl group as seen from τ_2. τ_3 in **3** and **4** are close to 31.6° estimated for the most stable conformation of aromatic amides.[13,14] τ_3 in **5** is −65.2(5)° because of the steric hindrance between O(1) and Cl(1).

In **1**—**4** the angles C(3)–N(1)–C(5) are larger than those of O(1)–C(3)–N(1) as found in some *N*-aromatic amides[15] irrespective of the difference in the *N*-substituents. In **5** the corresponding C–N–C angle is smaller than those in **3** and **4** because of larger τ_3 in **5**.

Crystal Structures. In the crystals of **1**—**5** the molecules related by a glide plane are linked together by an N–H···O hydrogen bond between the amide groups to form a chain. The geometry of the hydrogen bonds are summarized in Table 5.

In the crystals of **1**, **4**, and **5** the hydrogen-bonded chains are held together by van der Waals interactions in a diagonal manner as shown in Fig. 2(a), (e) and (f). In the crystals of **2** and **3** the chains are held together by van der Waals interactions to form a sheet parallel to (0 4 0) [Fig. 2(c) and (d)]. The symmetry operation between the chains in the sheet is an *a* translation in **2** and an *a* glide plane in **3**. The sheets related by a 2_1 axis are packed along the *b* axis in **2**, while those related by a *b* glide plane are packed along the *b* axis in **3**, corresponding to the space group $P2_1/c$ for **2** and *Pbca* for **3**. Three glide operations perpendicular to each other are used in **3** to complete the whole crystal structure, while two glide operations perpendicular to each other are used in **4**. It is noted that the space group $Pca2_1$ for **4** is a maximal subgroup of *Pbca* for **3**. The densities and the melting points of **3** and **4** are very close to each other (Table 1). In the crystals of **5** the dimension of *b* is close to a half of that of **3**. The hydrogen-bonded chains related by a *b* glide plane are arranged along the *b* axis in **3**, while the chains related by a *b* translation are arranged along the *b* axis in **5**.

The Possibility of the Solid-State Reaction. The present discussion is restricted to the molecules containing one C=C double bond per molecule. For such molecules the polymerization may start between the C=C bonds related by a 2_1 axis, a glide plane or a translation.

The crystals of **1** are reported to polymerize in the

Table 3. Bond Lengths (l) and Angles (ϕ) with esd's in Parentheses

	1	**2**	**3**	**4**	**5**
	l/Å	l/Å	l/Å	l/Å	l/Å
Cl(1)–C(6)					1.734(4)
O(1)–C(3)	1.224(5)	1.232(3)	1.235(4)	1.233(4)	1.231(4)
N(1)–C(3)	1.324(5)	1.338(3)	1.351(4)	1.330(4)	1.342(4)
N(1)–C(5)	1.479(5)	1.477(3)	1.417(3)	1.425(3)	1.419(4)
C(1)–C(2)	1.304(6)	1.376(4)	1.374(5)	1.325(5)	1.339(6)
C(2)–C(3)	1.505(6)	1.502(3)	1.488(4)	1.492(4)	1.486(5)
C(2)–C(4)		1.427(4)	1.420(4)	1.491(5)	1.474(6)
C(5)–C(6)	1.502(7)	1.523(4)	1.392(4)	1.379(4)	1.388(5)
C(5)–C(7)	1.506(7)	1.528(4)			
C(5)–C(8)	1.486(7)	1.522(4)			
C(5)–C(10)			1.376(4)	1.382(4)	1.384(5)
C(6)–C(7)			1.386(5)	1.395(4)	1.382(6)
C(7)–C(8)			1.353(6)	1.364(4)	1.385(6)
C(8)–C(9)			1.379(5)	1.378(4)	1.365(7)
C(9)–C(10)			1.383(4)	1.379(4)	1.387(6)
	ϕ/°	ϕ/°	ϕ/°	ϕ/°	ϕ/°
C(3)–N(1)–C(5)	126.8(3)	125.3(2)	126.5(2)	126.7(2)	122.8(3)
C(1)–C(2)–C(3)	121.6(4)	121.3(2)	120.7(3)	121.1(3)	121.6(4)
C(1)–C(2)–C(4)		122.3(2)	121.7(3)	123.8(3)	122.8(4)
C(3)–C(2)–C(4)		116.4(3)	117.6(3)	115.0(3)	115.5(4)
O(1)–C(3)–N(1)	123.5(4)	123.1(2)	123.0(3)	122.9(3)	122.3(3)
O(1)–C(3)–C(2)	122.0(4)	120.1(2)	120.1(3)	120.4(3)	120.3(3)
N(1)–C(3)–C(2)	114.5(3)	116.8(2)	116.9(3)	116.7(3)	117.4(3)
N(1)–C(5)–C(6)	108.6(4)	110.5(2)	121.5(2)	122.1(2)	121.4(3)
N(1)–C(5)–C(7)	110.0(4)	109.9(2)			
N(1)–C(5)–C(8)	106.9(4)	106.4(2)			
N(1)–C(5)–C(10)			118.1(2)	118.0(2)	120.2(3)
C(6)–C(5)–C(7)	111.4(4)	110.4(2)			
C(6)–C(5)–C(8)	111.9(4)	108.8(2)			
C(6)–C(5)–C(10)			120.3(2)	119.9(2)	118.4(3)
C(7)–C(5)–C(8)	107.8(4)	110.7(2)			
Cl(1)–C(6)–C(5)					120.4(3)
Cl(1)–C(6)–C(7)					118.7(3)
C(5)–C(6)–C(7)			118.3(3)	119.6(3)	121.0(4)
C(6)–C(7)–C(8)			121.9(4)	120.4(3)	119.3(4)
C(7)–C(8)–C(9)			119.5(4)	119.8(3)	120.4(5)
C(8)–C(9)–C(10)			120.3(3)	120.5(3)	120.1(5)
C(5)–C(10)–C(9)			119.7(3)	119.9(3)	120.7(4)

Table 4. Selected Torsion Angles (τ/°) with esd's in Parentheses

	1	**2**	**3**	**4**	**5**
	τ/°	τ/°	τ/°	τ/°	τ/°
τ_1: O(1)–C(3)–N(1)–C(5)	−2.8(6)	1.0(3)	0.8(4)	−1.3(4)	5.4(5)
τ_2: C(1)–C(2)–C(3)–O(1)	4.1(6)	153.7(2)	159.4(3)	138.5(3)	153.3(4)
τ_3: C(3)–N(1)–C(5)–C(6)	−65.3(5)	−56.1(3)	35.8(4)	−35.3(4)	−65.4(4)
τ_4: C(3)–N(1)–C(5)–C(7)	56.9(5)	66.0(3)			
τ_5: C(3)–N(1)–C(5)–C(8)	173.7(4)	−174.1(2)			
τ_6: N(1)–C(5)–C(6)–Cl(1)					−5.3(5)

solid-state to form a main product with the head-to-tail structure.[3,4] The C=C double bonds of the nearest neighboring molecules [(i) and (ii)] are related by a c glide plane with a C···C distance of 4.786(6) Å as seen from Fig. 2(a) and Fig. 2(b). The polymerization may occur between the hydrogen-bonded molecules related by the c glide plane to form a polymer of the head-to-tail structure, if a molecule rotate by about 90° with respect to the other neighboring molecule around the hydrogen bond. This rotation of the molecule may occur through the space formed by the elimination of the methyl radicals or the lattice defects caused by γ-ray irradiation.

In the crystals of **2**, **3**, and **4** neither solid-state polymerization nor dimerization has been reported. In **2** the C···C distance of 5.642(4) Å between the C=C dou-

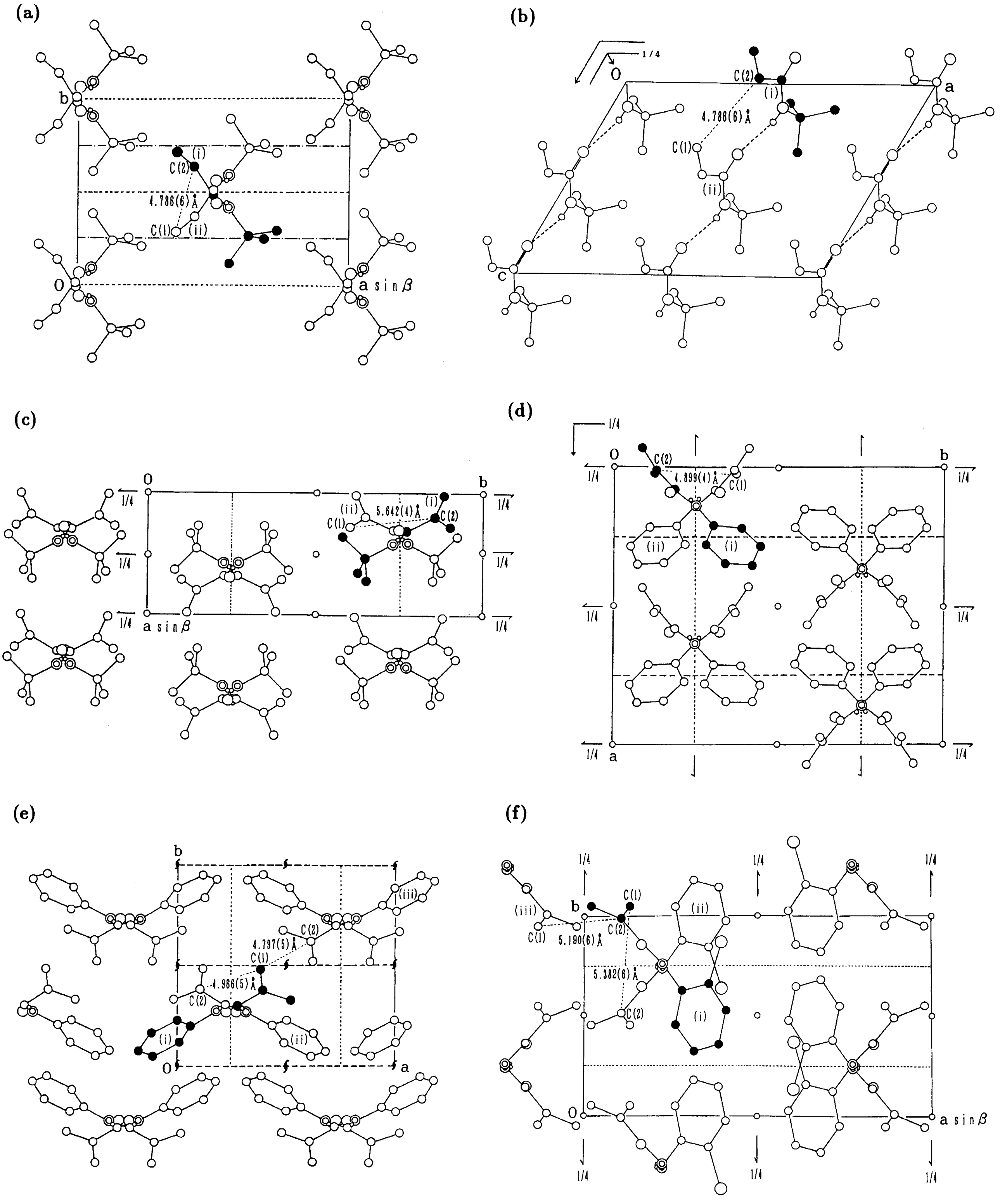

Fig. 2. Projections of the crystal structures. (a) viewed along c for (**1**), (b) viewed along a for (**1**), (c) viewed along a for (**2**), (d) viewed along c for (**3**), (e) viewed along a for (**4**), and (f) viewed along c for (**5**). Symmetry codes: (i) x, y, z for **1**—**5**, (ii) x, $1-y$, $1/2+z$ for (**1**), x, $1/2-y$, $-1/2+z$ for (**2**), x, $1/2-y$, $-1/2+z$ for (**3**), $1/2-x$, y, $1/2+z$ for (**4**) and x, $3/2-y$, $-1/2+z$ for (**5**), (iii) $1-x$, $1-y$, $1/2+z$ for (**4**) and $-x$, $1/2+y$, $1/2-z$ for (**5**).

Table 5. The Geometry of N(1$^{\rm i}$)–H(1$^{\rm i}$)···O(1$^{\rm ii}$) Hydrogen Bonds with esd's in Parentheses

	N···O l/Å	H···O l/Å	∠N–H···O ϕ/°	∠C=O···N ϕ/°
1	2.887(4)	2.04(3)	178(3)	135.9(3)
2	3.013(3)	2.12(2)	169(2)	148.6(2)
3	2.978(3)	2.06(2)	164(2)	147.9(2)
4	2.861(3)	2.01(3)	163(3)	162.3(2)
5	2.888(4)	2.08(3)	166(3)	156.2(3)

Symmetry codes: (i) x, y, z for **1**—**5**, (ii) x, $1-y$, $1/2+z$ for (**1**), x, $1/2-y$, $-1/2+z$ for (**2**), x, $1/2-y$, $-1/2+z$ for (**3**), $1/2-x$, y, $1/2+z$ for (**4**) and x, $3/2-y$, $-1/2+z$ for (**5**).

ble bonds of the molecules [(i) and (ii)] related by a c glide plane seems to be too long for the polymerization [Fig. 2(c)]. In **3** and **4** the corresponding distances are 4.899(4) and 4.966(5) Å, respectively [Fig. 2(d) and (e)]. The nearest C=C double bonds in **4** are found between the molecules [(i) and (iii)] related by a 2_1 axis with a C···C distance of 4.797(5) Å. However, the solid-state polymerization between these molecules would be unfavorable, because the hydrogen bonds should be broken to approach the molecules together.

The C···C distance between the C=C double bonds of the molecules [(i) and (ii)] related by the c glide plane is 5.382(6) Å for **5** [Fig. 2(f)], which is rather longer than the corresponding distances in **3** and **4**. The hydrogen-bond type in the crystals of **5** is the same as that found in **3** and **4**. These facts indicate that the higher reactivity of the *o*-substituted compounds is ascribed neither to the difference in the hydrogen-bond type nor to the difference in the distances between C=C bonds. The dihedral angle between the amide and phenyl groups in **5** is much larger than in **3** and **4**. The larger dihedral angle may cause smaller intermolecular steric hindrance between the phenyl groups in the hydrogen-bonded chain for the rotation of the reactant molecules around the hydrogen bond. It is considered that this is a reason why the reactivity of **5** and the other *o*-substituted *N*-phenylmethacrylamides is higher than the unsubstituted or *m*- and *p*-substituted analogs. In **5** the other short C···C distance is 5.190(6) Å between the molecules [(i) and (iii)] related by a 2_1 axis. However, the polymerization between the molecules may be unfavorable because these belong to the different chains of hydrogen-bonding.

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