Topochemical Studies. III. The Crystal and Molecular Structures of Crotonic Acid, $CH_3CH=CHCOOH$, and Crotonamide, $CH_3CH=CHCONH_2$

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Crotonic acid crystallizes in the monoclinic space group C2/c, with $a=15.30(3)$, $b=4.06(1)$, $c=16.18(2)$ Å, $\beta=107.4(1)°$ and $Z=8$; crotonamide in the monoclinic space group $P2_1/a$, with $a=9.71(2)$, $b=6.90(2)$, $c=7.75(1)$ Å, $\beta=104.0(4)°$ and $Z=4$. The structures have been solved by the Patterson method and refined by the block-diagonal least-squares method. The final R values are 0.090 for 337 observed reflections for crotonic acid, and 0.088 for 525 observed ones for crotonamide. The configuration of the molecules of crotonic acid and crotonamide is approximately planar and of *trans*-type regarding the C=C bond. Every two centrosymmetrically related molecules form a dimer through hydrogen bonds of 2.645 Å (OH···O) for crotonic acid and 2.963 Å (NH···O) for crotonamide. In the crystals of crotonamide additional NH···O hydrogen bonds (2.862 Å) link the neighboring molecules related by the a-glide plane to form a sheet parallel to (001) plane. Distances between the C=C bonds of the nearest neighbors are 3.86 Å for crotonic acid and 3.62 and 3.88 Å for crotonamide.

In the first paper of this series[1] attention has been drawn to the crystal structure of aconitic acid as an unsaturated aliphatic acid in order to test the topochemical rule[2] and to examine the relationship between the molecular geometry and the hydrogen bond system.[3] The present paper is devoted to the examination of the degree of planarity of the molecules and the packing arrangement of the simplest α,β-unsaturated acid, crotonic acid, and its amide.

Experimental

Crotonic acid crystallized from aqueous solution as soft, colorless transparent plates elongated along the b axis and became gradually sublimate. The differential thermogram showed a weak *endo*-peak at 44 °C and the melting peak at 72 °C. Crontonamide crystallized from ethanol solution as twinned plates or as prisms elongated along the a axis. Crystals of crotonic acid were sealed in glass capillaries. Single crystals of crotonamide were obtained by cutting the twinned plates with razor. Equi-inclination Weissenberg photographs were taken by using Cu$K\alpha$ radiation, $\lambda=1.5418$ Å. Crystal data are summarized in Table 1. The space group for crotonic acid was deduced from the systematic absences to be Cc or C2/c, but the latter was assumed, and confirmed by subsequent refinement. The intensities were estimated visually, and corrected for the Lorentz and polarization factors and for spot shape.

Table 1. Crystal data

	Crotonic acid	Crotonamide
Chemical formula	$CH_3CH=CHCOOH$	$CH_3CH=CHCONH_2$
Molecular weight	86.09	85.12
Melting point	72 °C	158 °C
Space group	Monoclinic, C2/c	Monoclinic, $P2_1/a$
Systematic absences	hkl for $h+k$ odd	$h0l$ for h odd
	$h0l$ for l odd	$0k0$ for k odd
Cell constants: a	15.30(3) Å	9.71(2) Å
b	4.06(1)	6.90(2)
c	16.18(2)	7.75(1)
β	107.4(1)°	104.0(4)°
Z	8	4
D_c	1.19 g/cm³	1.12 g/cm³
D_m	1.19	1.11
$F(000)$	368	184
μ for Cu$K\alpha$ ($\lambda=1.5418$ Å)	8.18 cm⁻¹	6.72 cm⁻¹
Dimension of crystals used	0.5×1.5×0.2 mm	0.3×0.1×0.1 mm
	0.7×0.5×0.2 mm	
Layers photographed	$h0l$ to $h2l$	$0kl$ to $7kl$
	$0kl$ to $7kl$	
Observed reflections	337	525

Structure Determination and Refinement

Crotonic Acid. Two-dimensional Patterson and Fourier maps projected along the b axis were used to obtain the trial structure. The y coordinates were estimated by tilting and shifting the planar molecular model against the b axis so that the calculated structure factors may suit to the observed ones. The trial structure gave an R value of 0.27. Three cycles of block-diagonal least-squares refinement of positional and isotropic thermal parameters reduced the R value to 0.15. The reflections $20\bar{4}$, $11\bar{3}$, and $11\bar{2}$, which were considered to suffer from extinction effect, were dropped off in subsequent refinements. Including the positions of hydrogen atoms obtained from a difference synthesis and the appropriate isotropic thermal parameters, further refinements were repeated with the weighting scheme:

$$w = (16.0/F_o)^2 \quad \text{for } |F_o| > 16.0$$

$$w = 1.0 \quad \text{for } 16.0 \geq |F_o| \geq 6.7$$

and

$$w = 0.5 \quad \text{for } 6.7 > |F_o| > 0.0.$$

The final R value was 0.090 for 337 observed reflections.

Crotonamide. The trial structure was obtained from the Patterson maps projected along the b and a axes, and corrected by the Fourier synthesis projected along the b axis. A three-dimensional Fourier map

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gave the structure of the R value of 0.33. A diagonal least-squares refinement with isotropic thermal parameters reduced the R value to 0.178. A difference synthesis at this stage revealed all the seven hydrogen atoms. Excluding the reflections 012, 201, and 20$\bar{1}$, block-diagonal least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and with isotropic ones for the hydrogen atoms was carried out by using the weighting scheme:

$$w = (4.0/F_o)^2 \quad \text{for } |F_o| > 4.0$$

$$w = 1.0 \quad \text{for } 4.0 \geq |F_o| \geq 2.2$$

and

$$w = 0.5 \quad \text{for } 2{\cdot}2 > |F_o| > 0.0.$$

The final R value was 0.088 for 525 observed reflections.

The computations were carried out on a HITAC 8800/8700 computer at the Computer Center of the University of Tokyo and on a NEAC 2200—500 computer at the Okayama University Computer Center. The main programs used were RSSFR-5, HBLS-4, RSDLS-3, RSDA-4, and RSBP-3 of the UNICS Program System.[4] The atomic scattering factors were taken from International Tables for X-ray Crystallography.[5]

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$) FOR CROTONIC ACID

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H,K= 0	0	10	68	-48	-3	881	1208	-6	245	-209	H,K= 11		1	1	151	131	-6	92	102
2	562	617	H,K= 8		0	-2	951	1369	-5	146	140	-16	50	50	2	54	61	-5	116	123
4	592	-722	-14	48	54	-1	311	-348	-4	172	-162	-9	93	97	3	110	102	-4	96	95
6	100	84	-12	212	197	0	393	425	-3	33	-20	-8	58	61	4	154	145	-3	86	86
8	298	291	-8	311	-310	1	487	-608	-2	394	-439	-7	90	84	5	206	198	-2	125	-124
10	284	306	-6	212	195	2	170	-184	-1	84	-74	-6	57	44	7	142	124	-1	69	-66
12	105	104	-4	417	418	3	85	74	0	391	-394	-2	179	157	9	116	132	2	72	75
14	61	66	-2	290	267	4	81	89	1	422	-445	-1	83	-82	11	58	75	3	104	110
16	81	87	0	202	195	5	169	170	2	451	-439	2	150	-154	13	92	-76	4	41	49
H,K= 2	0	4	264	268	6	118	117	3	139	114	3	207	202	H,K= 4		2	5	59	59
-12	185	186	6	192	185	7	288	297	4	101	-91	H,K= 13		1	-14	111	-108	H,K= 3		3
-10	255	242	14	48	45	8	154	139	5	311	309	-10	59	-77	-12	100	-120	-12	74	-83
-8	398	-352	H,K= 10		0	9	135	130	6	164	153	-9	73	92	-11	99	101	-9	152	169
-6	355	-369	-16	192	169	12	59	60	7	174	-172	-7	85	91	-9	162	165	-8	69	75
-4	1101	1348	-14	150	133	13	42	17	8	112	-112	-6	73	87	-8	70	70	-7	97	111
-2	574	598	-12	96	-101	14	99	95	9	188	-182	-5	101	-121	-6	103	-101	-6	55	-42
0	162	-133	-8	174	170	15	40	-48	10	149	-154	-4	66	-66	-5	76	81	-5	67	-61
2	45	-21	-6	305	321	H,K= 3		1	12	42	-50	-3	124	-129	-4	190	-187	-4	66	-63
4	491	-491	-4	257	253	-13	79	94	H,K= 7		1	-2	196	-215	-3	94	85	-1	92	92
6	142	-125	0	197	190	-11	117	-93	-11	83	-87	-1	147	129	-2	163	-165	1	65	64
8	42	-48	4	46	-72	-10	174	-147	-10	97	92	0	73	-83	-1	60	-58	2	54	45
10	137	135	6	107	121	-9	69	-24	-9	192	-161	1	85	103	0	181	-168	3	67	65
12	141	148	H,K= 12		0	-8	60	-64	-8	247	-237	H,K= 15		1	1	52	43	5	68	67
14	130	-126	-6	65	60	-7	407	386	-5	195	203	-11	53	73	2	159	-158	6	40	14
16	107	-120	-4	220	189	-6	247	267	-4	55	-41	-7	91	-107	5	165	154	7	57	61
H,K= 4	0	-2	174	-162	-5	304	306	-3	227	-254	-6	91	-91	7	107	106	H,K= 5		3	
-16	47	-72	0	389	-369	-4	218	-218	-1	283	-324	H,K= 17		1	8	86	-100	-5	80	-49
-12	117	-93	4	76	78	-3	214	226	0	137	142	2	55	47	9	170	-192	-3	112	-99
-10	193	-190	H,K= 14		0	-2	258	-245	1	59	50	H,K= 0		2	10	88	-74	0	103	-101
-8	146	-142	-12	102	-111	0	67	-59	2	198	211	1	393	-428	11	87	-92	1	92	85
-6	529	-540	-8	145	136	1	229	-260	3	51	-35	2	164	160	13	49	38	2	47	35
-4	201	-199	-4	269	-282	2	360	-352	6	51	53	3	321	-338	H,K= 6		2	3	66	52
-2	87	72	-2	175	-158	3	114	99	7	88	-90	4	210	214	-8	58	54	4	67	57
0	609	-631	H,K= 16		0	4	275	-260	9	82	-90	5	216	208	-7	141	-137	5	66	-54
2	572	-612	-10	42	32	5	175	172	H,K=	9	1	6	134	134	-6	54	44	6	92	-88
4	906	-930	4	82	55	6	263	-250	-14	146	148	7	158	141	-5	123	-121	7	110	-114
6	117	-107	H,K= 18		0	7	292	295	-13	128	-132	8	79	63	-4	174	-183	H,K=	11	
8	347	358	-10	32	43	9	107	96	-12	112	-122	9	82	61	-2	104	-130	-9	46	-62
10	138	-142	-2	35	38	10	110	102	-11	176	-176	13	50	53	-1	141	-144	-8	80	70
12	237	-256	0	88	86	11	189	-189	-10	81	-60	14	34	38	2	233	219	-7	135	-158
14	57	-74	H,K=	1	1	12	117	-111	-9	92	95	15	32	46	3	68	58	-6	65	59
H,K= 6	0	-18	46	59	13	69	-62	-7	153	139	16	49	49	5	164	-176	-5	65	89
-18	57	-59	-16	43	46	14	121	-121	-6	177	157	H,K=	2	2	6	134	-116	-4	79	-93
-16	66	-66	-14	47	44	15	49	63	-5	35	-36	-10	100	-101	7	123	-141	-1	65	70
-10	225	-227	-13	38	38	H,K=	5	1	-4	244	267	-9	85	-85	H,K=	8	2	0	80	92
-8	238	-211	-12	107	105	-18	47	-44	-3	126	-113	-8	51	41	-11	116	-152	1	46	-42
-6	256	-221	-10	185	175	-16	75	-70	-2	220	214	-7	216	216	-10	115	123	3	114	-127
-4	571	-575	-9	171	-154	-14	115	-109	-1	127	-112	-6	263	280	-9	178	-193			
-2	126	127	-8	168	172	-12	60	-66	0	84	-71	-5	468	480	-8	105	-102			
0	516	-548	-7	333	-357	-10	51	-29	1	107	94	-4	116	109	-7	174	172			
2	357	-359	-6	187	-187	-9	71	-65	2	203	207	-3	197	-182	-6	154	149			
4	519	517	-5	389	412	-8	271	-269	4	120	113	-2	46	-44	H,K=	1	3			
6	55	41	-4	292	285	-7	116	102	7	73	55	0	142	-151	-8	52	-56			

Results and Discussion

Observed and calculated structure factors for crotonic acid are given in Table 2, and those for crotonamide in

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$) FOR CROTONAMIDE

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H,K= 0	0	1	37	-33	H,K= 2		3	5	23	23	H,K= 4		3	1	73	-76	4	30	31
1	263	362	2	75	74	-8	19	-31	7	17	-16	-7	37	44	2	31	27	5	8	12
2	234	-242	3	46	50	-7	42	45	8	11	-7	-5	54	-52	3	35	35	H,K=	6	5
3	96	-92	4	72	70	-6	111	107	H,K=	3	4	-3	24	23	4	11	16	-4	22	26
4	169	-164	5	72	74	-5	27	-23	-7	32	-32	-2	29	-29	H,K=	5	5	-2	83	-93
5	99	-93	6	25	29	-4	29	-24	-5	80	90	-1	79	-85	-6	7	8	-1	34	-38
6	44	-43	H,K=	1	4	-2	122	-118	-4	82	87	0	28	39	-5	15	12	0	17	15
7	19	21	-8	21	21	-1	156	-160	-3	23	-30	1	118	117	-4	18	19	1	9	11
8	33	34	-6	45	-40	0	165	-163	-2	15	-15	2	45	-48	-3	16	-16	2	19	19
H,K=	0	1	-4	70	68	1	177	182	-1	27	31	3	22	-20	-2	55	-56	3	27	25
1	233	-278	-3	74	83	2	104	98	0	79	84	4	16	19	-1	36	-34	4	27	28
2	492	-739	-2	162	-150	4	24	27	1	95	91	6	15	18	1	18	19	H,K=	6	6
3	172	-176	-1	16	-18	5	52	-53	2	9	18	H,K=	4	4	2	40	40	-6	16	17
5	36	34	0	45	45	7	36	34	3	39	39	-5	31	-35	3	17	17	-4	34	-34
6	68	70	1	64	71	H,K=	2	4	4	18	18	-3	31	31	H,K=	6	5	-3	16	-15
H,K=	0	2	2	119	115	-5	53	-52	6	10	10	-2	42	42	-6	6	18	0	30	36
0	275	-338	3	54	52	-4	111	-104	7	17	-17	-1	90	90	-4	31	-35	1	29	26
1	136	-135	7	39	-38	-3	47	-47	H,K=	3	5	2	11	-11	-3	37	-41	2	17	15
2	200	-205	H,K=	1	5	-2	57	-58	-6	20	17	3	40	-40	-1	20	21	4	9	9
3	140	149	-4	14	-20	-1	91	94	-5	41	-41	H,K=	4	5	2	15	12	H,K=	6	7
4	262	287	-3	36	-50	0	121	120	-2	58	-63	-4	38	41	4	16	-15	-1	11	11
6	29	-29	-2	38	-40	1	26	27	-1	14	-11	-3	102	108	H,K=	5	7	0	28	25
7	13	-19	-1	33	32	2	67	65	0	26	30	-2	23	-25	5	25	-25	2	20	-21
8	28	-23	0	96	93	3	29	-30	1	26	29	-1	88	-87	-2	8	8	H,K=	7	1
H,K=	0	3	1	37	36	5	22	20	2	45	47	0	23	-20	-1	11	12	-6	29	29
1	64	68	4	29	-25	H,K=	2	5	3	20	26	1	33	-38	3	9	8	-4	18	-16
2	161	169	5	31	-30	-5	33	-34	4	22	-25	2	17	-17	H,K=	6	8	-3	30	26
3	10	12	H,K=	1	6	-4	52	-48	5	27	-28	5	17	13	-2	8	9	-2	47	50
4	42	39	-6	37	-34	-3	104	110	H,K=	3	6	H,K=	4	6	H,K=	6	0	-1	11	17
5	67	-67	-1	46	45	-2	133	135	-5	29	-28	-5	36	37	-6	65	-60	3	13	12
6	99	-106	0	46	51	-1	26	-24	-2	18	21	-3	50	-57	-5	52	-47	5	22	-18
7	25	23	2	25	-20	0	29	33	-1	65	72	-2	31	-34	-4	95	89	6	7	-10
8	34	30	3	29	-25	2	21	-22	0	43	44	-1	60	-67	-3	26	25	H,K=	7	2
H,K=	0	4	4	14	-16	H,K=	2	6	1	10	-14	1	32	37	-2	42	-40	-7	18	17
0	125	157	H,K=	1	7	-5	41	35	2	27	-29	H,K=	4	7	0	92	-80	-6	24	29
1	58	-37	-4	38	31	-4	34	37	3	29	-27	-5	20	-20	1	66	62	-5	22	22
2	38	-35	-1	31	28	-2	25	29	4	26	-24	-1	18	14	2	113	107	-2	25	14
3	44	-39	0	24	23	-1	58	-63	H,K=	3	7	0	25	24	3	60	57	-1	30	-29
4	65	-66	1	34	-37	0	57	-59	0	28	-26	1	58	56	4	15	20	0	41	-42
5	23	24	2	51	-49	1	45	44	1	56	-59	3	21	-18	7	25	-26	1	8	8
6	18	18	4	19	17	H,K=	2	7	2	28	-27	H,K=	4	8	H,K=	6	1	2	12	12
7	20	21	H,K=	1	8	-6	19	20	3	19	16	2	14	-20	-6	31	31	3	31	-31
8	26	24	-1	15	-16	-5	18	-13	H,K=	3	8	H,K=	5	1	-5	20	20	4	21	-24
H,K=	0	5	0	19	-16	-3	23	-18	-2	14	-14	-9	18	17	-4	41	36	H,K=	7	3
2	69	-75	H,K=	2	0	-2	12	-13	-1	17	-16	-7	25	-25	-2	99	-101	-5	18	-17
3	54	53	-7	33	32	-1	12	13	0	12	-12	-6	21	17	-1	22	23	-4	40	-42
4	66	67	-6	82	87	1	20	25	H,K=	4	0	-5	27	24	0	104	90	-3	23	-27
H,K=	0	6	-4	69	-64	3	28	-21	-7	56	64	-4	56	-45	1	74	63	-1	15	-14
0	64	-71	-3	40	-37	H,K=	2	8	-6	40	39	-3	88	-83	2	46	42	2	13	-13
1	40	40	-2	240	-235	-4	10	-11	-5	82	-84	-2	85	-84	3	17	-15	H,K=	7	4
2	48	55	-1	329	474	-3	31	24	-4	51	-45	-1	67	-47	4	23	-26	-7	8	-11
3	10	-11	1	292	-291	-2	28	31	-3	135	-132	0	51	46	5	14	-16	-6	14	13
H,K=	0	7	2	130	-120	3	37	-35	-2	261	-257	1	74	68	6	31	-32	-5	9	-15
1	13	-14	3	60	-66	H,K=	3	1	0	183	-174	2	11	9	H,K=	6	2	-3	28	30
2	12	18	4	114	-109	-5	49	49	1	71	-72	3	22	22	-8	28	25	-2	53	56
H,K=	0	8	5	81	-84	0	20	33	2	167	151	4	59	56	-7	20	20	-1	13	-12
2	30	26	7	47	59	-3	36	-31	3	105	99	6	29	-32	-5	17	-20	0	46	-44
4	26	-26	H,K=	2	1	-2	112	-115	4	11	12	H,K=	5	2	-4	37	-56	1	9	9
H,K=	1	1	-6	34	-35	-1	220	-215	6	28	29	-7	8	-11	-2	9	8	2	20	20
-4	83	-67	-5	66	-59	0	73	-75	8	23	-24	-6	78	-74	-1	39	34	5	12	12
-3	115	110	-4	172	-154	1	117	98	H,K=	4	1	-5	63	-58	0	75	79	H,K=	7	5
-2	297	334	-3	148	143	2	25	-23	-7	22	-25	-2	110	96	3	52	-50	-5	23	21
-1	17	17	-2	261	261	3	97	-104	-6	30	-31	-1	154	156	4	59	-65	-4	29	28
0	137	-147	-1	216	-204	4	14	11	-5	95	-97	0	80	82	6	21	22	-2	31	-27
1	233	261	0	27	43	5	47	50	-4	105	-96	1	53	56	H,K=	6	4	-1	18	-17
2	196	194	1	263	-282	H,K=	3	2	-3	67	64	2	53	54	-6	35	-37	0	9	-14
3	184	-192	2	221	-206	-6	24	-23	-2	34	-34	3	20	-16	-5	15	-18	2	14	11
4	146	-154	3	9	-2	-5	83	87	-1	29	27	4	52	-53	-4	37	36	H,K=	7	6
H,K=	1	2	4	15	11	-3	233	-215	0	215	223	5	22	-25	-3	66	64	-4	29	-29
-8	35	26	5	74	71	-2	91	-79	1	100	82	H,K=	5	3	-2	32	32	-3	16	-16
-6	45	-39	6	43	45	-1	137	138	2	86	80	-7	11	-15	-1	24	21	1	27	26
-5	37	-35	9	9	-15	0	101	97	4	15	-15	-4	26	23	0	57	60	2	28	27
-4	134	123	H,K=	2		1	102	94	6	25	-24	-3	69	67	1	58	58	H,K=	7	7
-3	60	49	-8	36	-41	3	30	28	H,K=	4	2	-2	94	94	2	106	-112	-1	22	22
-2	9	-18	-6	44	-37	5	17	19	-9	25	-28	-1	59	59	3	12	-12	0	19	19
-1	27	35	-4	54	52	H,K=	3	3	-8	26	-24	0	68	67	4	21	21			
0	56	-55	-4	150	136	-6	46	-53	0	17	21	-7	15	-16	-4	37	39			
1	210	-225	-3	9	-8	-5	45	-42	-3	50	48	3	53	-56	6	10	13			
2	211	-208	-2	62	55	-3	67	74	-2	102	100	H,K=	5	4	H,K=	6	4			
3	123	-127	-1	69	83	-2	131	128	0	17	21	-7	15	-16	-4	37	39			
4	48	-41	0	155	-160	-1	87	78	1	64	-74	-6	8	47	-3	21	25			
5	51	52	1	123	-130	0	36	36	2	22	-18	-5	44	47	-1	36	-37			
6	53	54	2	102	-99	1	23	17	3	35	36	-4	16	12	0	84	-92			
H,K=	1	3	3	234	219	2	44	-43	4	73	-67	-2	57	40	1	36	-34			
-1	173	-180	4	96	-92	3	40	-39	5	35	-37	-1	19	-22	2	12	-14			
0	263	-260	5	56	-52	4	14	19	6	19	21	0	128	-137	3	8	9			

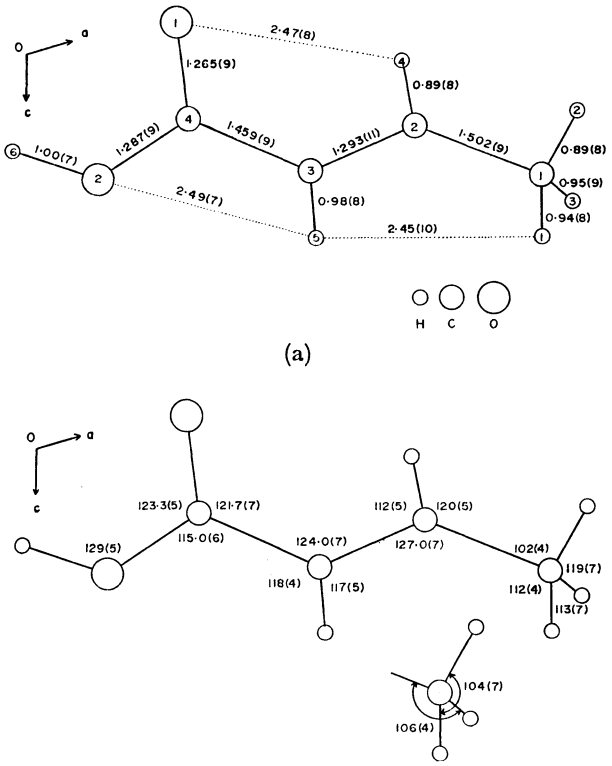
TABLE 4. FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS ($\times 10^4$) FOR NON-HYDROGEN ATOMS

The anisotropic thermal parameters are defined as: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Crotonic acid									
O(1)	1113(3)	−719(14)	72(3)	61(3)	1246(46)	52(2)	2(21)	34(4)	−154(19)
O(2)	533(3)	2121(15)	978(3)	55(3)	1437(54)	66(3)	−3(24)	37(5)	−165(21)
C(1)	3824(5)	1335(21)	1821(5)	58(4)	1151(80)	64(4)	−49(35)	17(7)	69(32)
C(2)	2874(5)	698(18)	1236(4)	63(4)	779(55)	58(3)	−5(31)	37(6)	30(26)
C(3)	2114(5)	1698(18)	1345(4)	68(4)	838(60)	51(3)	54(31)	40(6)	25(24)
C(4)	1211(4)	952(18)	753(4)	42(4)	820(56)	58(3)	−20(28)	4(6)	86(26)
Crotonamide									
O	−561(3)	2038(4)	1263(4)	120(5)	254(6)	302(7)	−11(7)	106(8)	−31(11)
N	1613(4)	1505(5)	797(5)	138(6)	252(7)	315(9)	5(9)	118(10)	−12(13)
C(1)	898(6)	7542(6)	3790(8)	281(10)	252(10)	284(11)	−68(14)	109(16)	−59(18)
C(2)	415(5)	5650(5)	2921(6)	210(8)	214(8)	226(8)	−28(12)	82(11)	31(14)
C(3)	1232(5)	4415(5)	2313(6)	172(7)	236(8)	197(8)	−53(11)	80(10)	28(13)
C(4)	668(4)	2547(5)	1419(5)	115(6)	219(8)	204(7)	8(9)	74(9)	54(12)

TABLE 5. FINAL FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS (Å^2) FOR HYDROGEN ATOMS
Their estimated standard deviations are in parentheses.

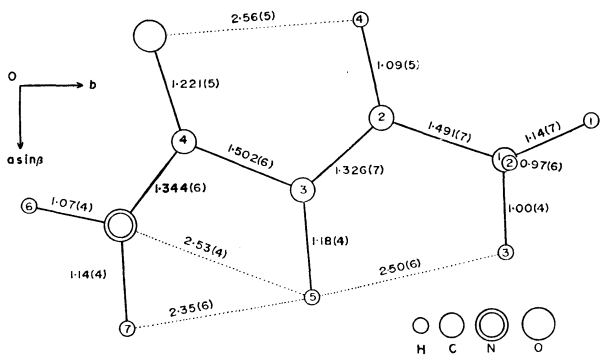
	x/a	y/b	z/c	B
Crotonic acid				
H(1)	383(5)	294(22)	224(4)	6.3(2.0)
H(2)	409(4)	231(19)	147(4)	5.2(1.8)
H(3)	405(5)	−73(24)	206(5)	8.2(2.5)
H(4)	278(6)	−63(21)	78(5)	7.2(2.1)
H(5)	216(5)	329(19)	181(5)	6.0(1.9)
H(6)	−10(5)	162(20)	62(5)	6.7(2.1)
Crotonamide				
H(1)	46(6)	895(10)	308(8)	8.1(1.6)
H(2)	95(6)	764(8)	506(8)	6.1(1.3)
H(3)	196(4)	758(5)	401(6)	3.7(1.0)
H(4)	−72(5)	535(7)	268(7)	5.0(1.2)
H(5)	247(4)	456(5)	252(5)	2.7(0.8)
H(6)	138(5)	12(6)	20(6)	4.4(1.1)
H(7)	282(4)	164(7)	111(6)	4.5(1.1)



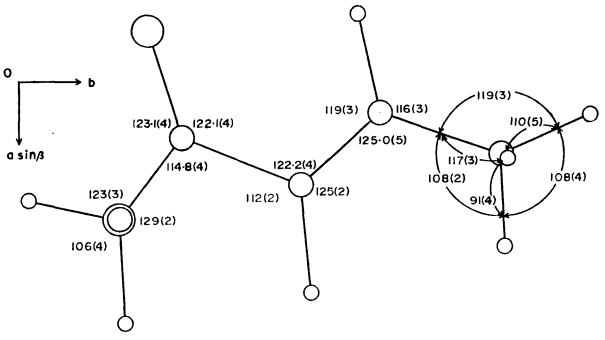
(a)

(b)

Fig. 1. The molecular structure of crotonic acid.
(a) Bond lengths (Å) and numbering of atoms.
(b) Bond angles (°). The estimated standard deviations are given in parentheses.



(a)



(b)

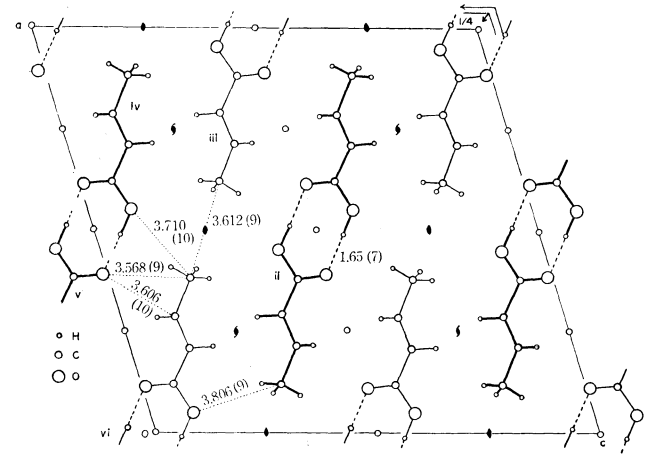
Fig. 2. The molecular structure of crotonamide.
(a) Bond lengths (Å) and numbering of atoms.
(b) Bond angles (°). The estimated standard deviations are given in parentheses.

TABLE 6. LEAST-SQUARES PLANES
Each plane is represented by $lX+mY+nZ=p$, where X, Y and Z (in Å) are referred to the crystallographic axes.

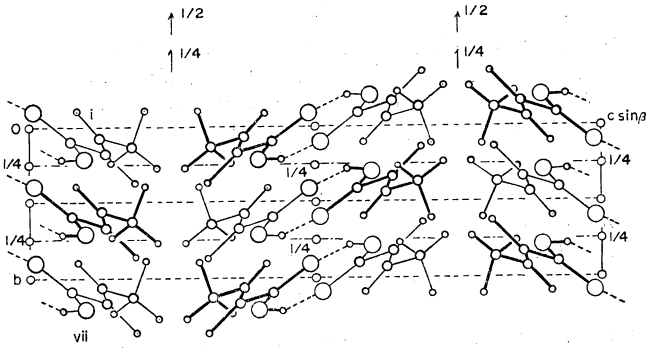
	Crotonic acid		Crotonamide	
	(1) Best plane through the ethylenic group	(2) Best plane through the carboxyl group	(1) Best plane through the ethylenic group	(2) Best plane through the amide group
l	0.2068	0.1931	0.0153	0.0597
m	0.8316	0.8390	−0.4587	−0.4781
n	−0.5536	−0.5431	0.8584	0.8358
p	0.0336	0.0208	0.1541	0.1146
Deviation (Å)				
C (1)	−0.004	O (1) 0.0002	C (1) −0.006	O −0.001
C (2)	0.004	O (2) 0.0002	C (2) 0.007	N −0.001
C (3)	0.003	C (3) 0.0002	C (3) 0.006	C (3) −0.001
C (4)	−0.004	C (4) −0.0006	C (4) −0.006	C (4) 0.003

Table 3; the final atomic parameters in Tables 4 and 5. Bond lengths and angles along with the numbering scheme for atoms are shown in Fig. 1 for crotonic acid, and in Fig. 2 for crotonamide.

Molecular Shape. The equations of best planes and the deviations of the atoms from each plane are listed in Table 6. Dihedral angle between the ethylenic and carboxylic planes of crotonic acid is only 1.0°, and that between the ethylenic and amide planes of crotonamide is 2.9°, which are rather smaller than the corresponding value (3.6°) found in *trans*-β-2-furylacrylamide.[6] Thus the configurations of both crotonic acid and crotonamide are nearly planar. The bond length C(2)=C(3) of crotonic acid is rather shorter. The difference between the bond lengths C(4)=O(1) and C(4)–O(2) in crotonic acid is very small as observed in β-methyl-*cis*-cinnamic acid and β-chloro-*cis*-cinnamic acid.[7] On the other hand, the C(4)=O and C(4)–N distances in crotonamide are very close to the values (1.225 and 1.349 Å, respectively) predicted from hybridization effect.[8] The C=O bonds of both carboxyl and amide groups adopt the *cis*-configuration with respect to the ethylenic C=C bonds. Some intramolecular contacts are shown in Figs. 1 and 2.

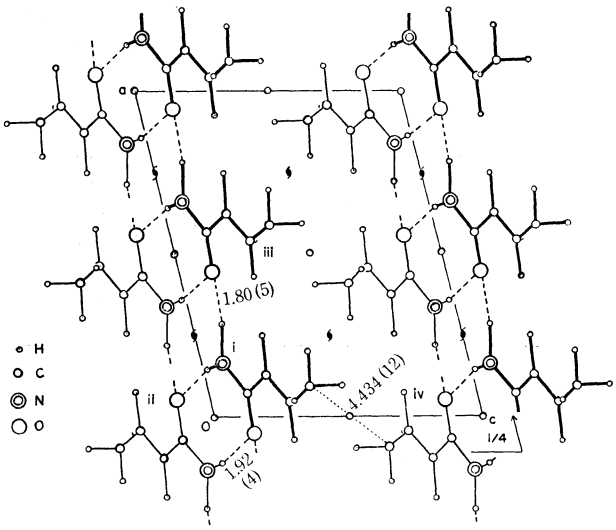


(a)

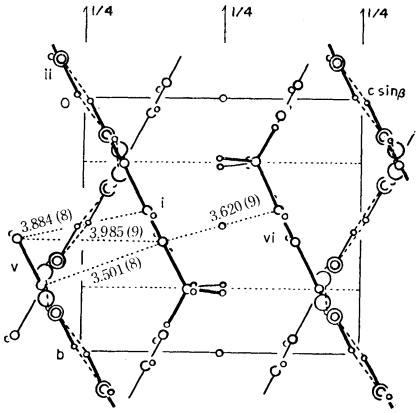


(b)

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



(a)



(b)

Fig. 4. Projections of the crystal structure of crotonamide.
(a) Viewed along the b axis.
(b) Viewed along the a axis.
Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.
Symmetry code: i $x/a, y/b, z/c$; ii $-x/a, -y/b, -z/c$; iii $1/2+x/a, 1/2-y/b, z/c$; iv $-x/a, 2-y/b, 1-z/c$; v $-x/a, 1-y/b, -z/c$; vi $-x/a, 1-y/b, 1-z/c$.

A significant difference in the C=O bond lengths has been pointed out between the carboxyl (1.209 Å) and the amide (1.247 Å) groups in fumaramic acid,[9] but the situation has reversed in the case of crotonic acid and crotonamide.

Molecular Packing. Projections of the crystal structure of crotonic acid viewed along the b and a axes and some intermolecular contacts are shown in Fig. 3 and those of crotonamide in Fig. 4. Geometry of the hydrogen bonds is listed in Table 7. The crystal structure of crotonic acid consists of two identical stacks of centrosymmetrically hydrogen-bonded pairs of the molecules, which are held together by van der Waals interactions between the methyl groups at a distance of 3.61 Å to form infinite chains along the

Table 7. Hydrogen-bond distances (Å) and angles (°)
Symmetry code is given in Figs. 3 and 4.

Crotonic acid			
O(1)···O(2^{vi})	2.645(6)	C(4)–O(2)···O(1^{vi})	115.6(4)
O(2)–H(6)	1.00(7)	C(4)–O(2)–H(6)	129(8)
H(6)···O(1^{vi})	1.65(7)	O(2)–H(6)···O(1^{vi})	174(8)
		C(4)–O(1)···O(2^{vi})	121.1(4)
		C(4)–O(1)···H(6^{vi})	123(8)
Crotonamide			
N···O^{ii}	2.963(8)	C(4)–N···O^{ii}	117.3(3)
N–H(6)	1.07(4)	C(4)–N–H(6)	123(3)
H(6)···O^{ii}	1.92(4)	N–H(6)···O^{ii}	165(4)
		C(4)–O···N^{ii}	119.5(3)
		C(4)–O···H(6^{ii})	122(2)
N···O^{iii}	2.862(7)	C(4)–N···O^{iii}	118.9(3)
N–H(7)	1.14(4)	C(4)–N–H(7)	129(2)
H(7)···O^{iii}	1.80(5)	N–H(7)···O^{iii}	153(4)
		N···O^{iii}–C(4^{iii})	142.7(3)
		H(7)···O^{iii}–C(4^{iii})	133(2)
		O^{ii}···N···O^{iii}	123.6(2)
		H(6)–N–H(7)	106(4)

[201] direction. The corresponding contact in α-tetronic acid[10] is 3.81 Å, and that in *p*-toluic acid[11] 3.50 Å. The hydrogen-bonded carboxyl groups are not fully coplanar, being offset 0.04 Å.

Crotonamide molecules related by a center of symmetry are linked by N–H···O hydrogen bonds to form pairs at (000) and (1/2, 1/2, 0), which are held together side by side through the a-glide plane by additional N–H···O hydrogen bonds. This packing mode belongs to the glide-plane packing type.[12] The intrapair amide groups are distinctly not planar, the separation between the two corresponding parallel planes being 0.23 Å. The inclination of the amide pair to the glide plane is 61.5° and the nearest methyl-methyl distance is 4.43 Å. The interpair angles C–N···O and C=O···N are 118.9 and 142.7°, respectively, which are close to those found in furylacrylamide.[6]

The structures of crotonic acid and crotonamide show short enough distances between ethylenic groups (C(3)···C(2^{vii}) 3.86 and C(3)···C(3^{v}) 3.88 Å, respectively) to dimerize or polymerize on irradiation with ultraviolet light, and the parallel alignment of double bonds considered as a pre-requisite for cycloaddition occurs in both compounds.

References

1) K. Fukuyama, S. Kashino, and M. Haisa, *Chem. Lett.*, **1972**, 599.
2) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 1996.
3) M. A. Higgs and R. L. Saas, *Acta Crystallogr.*, **16**, 657 (1963).
4) "Universal Crystallographic Computation Program System," ed. by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1967).
5) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.
6) L. Leiserowitz and D. Rabinovich, *J. Chem. Soc., Ser. A*, **1969**, 2367.
7) S. E. Fillippakis, L. Leiserowitz, D. Rabinovich, and G. M. J. Schmidt, *J. Chem. Soc., Perkin II*, **1972**, 1750.
8) M. G. Brown, *Trans. Faraday Soc.*, **55**, 694 (1959).
9) V. Benghiat, H. W. Kaufman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc., Perkin II*, **1972**, 1758.
10) V. Benghiat and L. Leiserowitz, *ibid.*, **1972**, 1763.
11) M. G. Takwale and L. M. Pant, *Acta Crystallogr.*, **B27**, 1152 (1971).
12) L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc., Ser. A*, **1969**, 2372.