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THE CRYSTAL STRUCTURE OF THE POLYMERIZATION CATALYST OF ACETALDEHYDE AND ITS DERIVATIVES

I. THE CRYSTAL STRUCTURE OF DIMETHYLALUMINUM *N*-PHENYLBENZIMIDATE DIMER, $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$

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SUMMARY

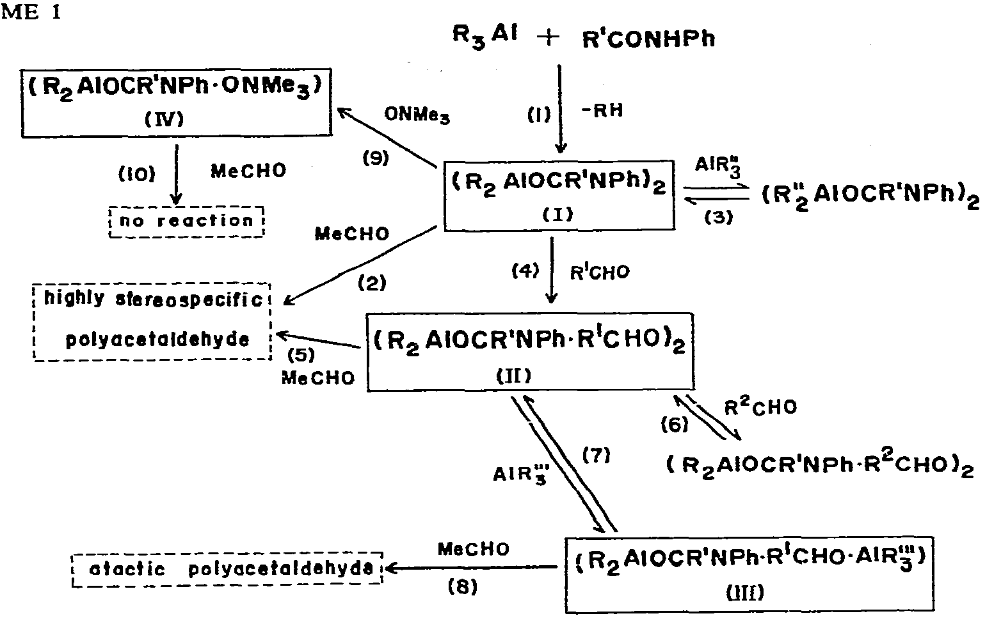
The crystal structure and molecular configuration of the highly stereospecific polymerization catalyst of acetaldehyde, dimethylaluminum *N*-phenylbenzimidate dimer, $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$ have been determined from three-dimensional X-ray data collected photographically. The crystal belongs to the monoclinic system, space group $P2_1/c$, with two dimer formula units in a cell of dimensions: $a = 6.64 \pm 0.03$, $b = 12.05 \pm 0.01$, $c = 18.28 \pm 0.01$ Å, and $\beta = 94.9 \pm 0.2°$. The structure has been refined by block-diagonal least-squares using anisotropic temperature factors for the nonhydrogen atoms. Hydrogen atoms with isotropic temperature factors were also included in the refinement. The final R index is 0.107 for 1096 non-zero reflections.

The dimeric molecule is composed of a centro-symmetrical eight-membered ring: the aluminum atoms are bridged by OCN groups. The environment of the aluminum atom is a distorted tetrahedron: Al–O = 1.805(6), Al–N = 1.947(7), Al–C = 1.940(11) and 1.940(11) Å. The environments of the N and C atoms (of the eight-membered ring) are trigonal. The configuration of the two adjacent benzene rings about the N–C bond is *cis*.

INTRODUCTION

In recent years, Tani and co-workers have reported a series of investigations of the stereospecific polymerization reaction of acetaldehyde. Among them, the catalytic system of trialkylaluminum–acid amide has posed many interesting problems[1–4]. They are summarized in Scheme 1. Reaction of equimolar amounts of trialkylaluminum and acid amide proceeds very smoothly (1). The reaction product (I) is an excellent catalyst for the stereospecific polymerization of acetaldehyde (2) and methyl methacrylate. It was also observed that the alkyl groups attached to the aluminum atom in (I) can be easily replaced reversibly by those of trialkylaluminum in solution (3).

SCHEME 1



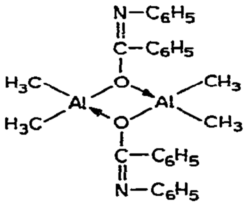
The catalyst gives a crystalline 1/1 complex with an aldehyde (II), by adding a large amount of n-hexane to a benzene solution of an equimolar mixture of (I) and aldehyde at 0° (4), a temperature above the polymerization ceiling. This complex also acts as a stereospecific catalyst under suitable polymerization conditions (5). The aldehyde moiety of (II) cannot be liberated by a strong electron donor such as pyridine or tetrahydrofuran, but it is easily replaced by free aldehyde present in the solution (6).

The catalyst-aldehyde complex again gives a crystalline 1/1 complex with a typical Lewis acid, trialkylaluminum (III) by mixing equimolar amounts of these two compounds together in n-hexane at 0° (7). Polymerization of acetaldehyde with this complex gives atactic polymer (8).

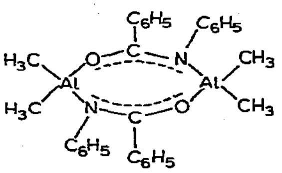
Recent investigation[4] showed the stereospecific polymerization catalyst (I) also gives the 1/1 complex with a strong electron donor, trimethylamine oxide. The reaction product (IV) which is obtained from the equimolar mixture of (I) and $ON(CH_3)_3$ in benzene at room temperature (9), does not show any catalytic activities for the polymerization of aldehyde (10).

From the chemical evidences these four characteristic complexes [(I), (II), (III) and (IV)] are assumed as the key substances to elucidate the reaction mechanism of the stereospecific polymerization of aldehyde. We have, therefore, been engaged in a series of structural studies of these complexes to obtain information about the stereospecific behavior at the initiation of isotactic polymerization[5-7].

Dimethylaluminum *N*-phenylbenzimidate $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$ which is prepared from trimethylaluminum and benzanilide (1), is one of the most effective catalysts. From the studies of NMR and IR spectra, the catalyst was found to have the imino ether type structure, $(CH_3)_2Al{-}O{-}C(C_6H_5){=}N(C_6H_5)$[1]. Cryoscopic measurement of its molecular weight in benzene showed the catalyst to be dimeric Two plausible models were proposed for the structure of the catalyst.



(A)



(B)

To determine the exact structure, an X-ray structure analysis was undertaken. The preliminary result was communicated earlier[5].

EXPERIMENTAL

The crystals which always grow in a long prismatic shape having the *a* axis as the needle axis, were prepared and supplied by Tani and Yasuda of this university. As the crystals are very unstable in the air, they were sealed in thin-walled glass capillary tubes in argon. The X-ray experiment was undertaken with nickel-filtered Cu-*K*α radiation ($\lambda = 1.5418$ Å).

The unit cell dimensions were determined from oscillation and Weissenberg photographs around the *a* axis. Debye powder lines of tungsten were superposed on the Weissenberg photographs for calibration, from which dimensions of the axial lengths, *b* and $c \cdot \sin \beta$ were determined by the least-squares procedure. Efforts were made to align the other crystal axes along the glass capillary tube wall in the inert atmosphere, but were unsuccessful because the crystals always grow along the *a* axis. Trials were repeated to take a precession photograph but, because of the twinning which will be described later, it was also unsuccessful. The dimension of the axial length, *a*, therefore, could be determined only from the oscillation photographs. The axial angle, β was determined from the zero layer and first layer Weissenberg photographs by the angular lag method. The deviations of these value were estimated from their reproducibilities, respectively. The space group was uniquely determined as $P2_1/c$ from the systematic absences of reflections ($h0l$: $l \neq 2n$; and $0k0$: $k \neq 2n$).

The crystal data are listed in Table 1. The density of the crystal was measured by the flotation method in a mixture of carbon tetrachloride and n-hexane. These data impose C_i-$\bar{1}$ point symmetry on the dimeric molecules.

The intensity data were collected by the multiple-film equi-inclination Weissenberg photographs along the *a* axis only. The crystal used had the dimensions of

TABLE 1

CRYSTAL DATA OF THE DIMETHYLALUMINUM *N*-PHENYLBENZIMIDATE DIMER, $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$

Monoclinic	$M = 506.6$ (as a dimer)
$a = 6.64 \pm 0.03$ Å	$Z = 2$ (as a dimer)
$b = 12.05 \pm 0.01$ Å	$d_m = 1.148$ g·cm^{-3}
$c = 18.28 \pm 0.01$ Å	$d_x = 1.154$ g·cm^{-3}
$\beta = 94.9 \pm 0.2°$	Space Group $P2_1/c$
$V = 1457.3$ Å^3	$\mu = 12.0$ cm^{-1} (for Cu-*K*α)

0.3 × 0.3 × 1.0 mm. The crystals examined, however, always had a twinned structure; the b^*–c^* plane was the twin plane (Fig. 1). All the reflection spots on the film were examined carefully and those from one component of the twinned crystal were identified and separated, and intensities were estimated visually. As can be seen in Fig. 1, however, in the second and fourth layers some pairs of reflection spots could not be separated. Finally, 1442 independent reflections were obtained from $0kl$ to $5kl$, however 346 of these could not be distinguished from the background. Corrections for the usual Lorentz and polarization factors and for the spot-shape were made but the absorption correction was ignored ($\mu = 12$ cm^{-1} for Cu-$K\alpha$). The inter-layer scale factors were at first made proportional to the exposure time of X-ray. They were improved during the least-squares refinement of the crystal structure using the isotropic temperature factors for the nonhydrogen atoms.

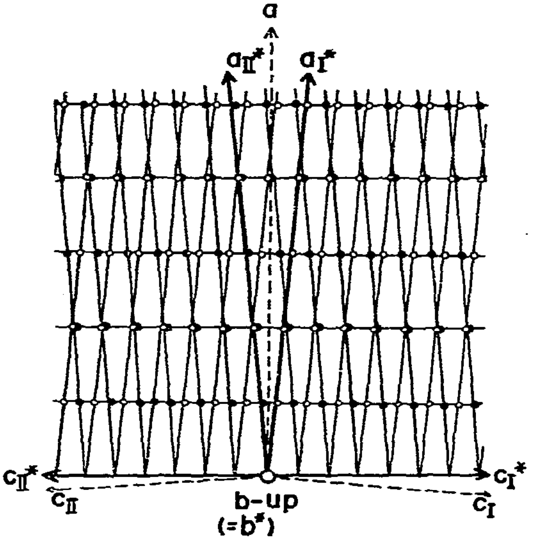


Fig. 1. Twinning in one reciprocal lattice plane of the dimethylaluminum *N*-phenylbenzimidate dimer.

STRUCTURE DETERMINATION AND REFINEMENT

The initial co-ordinates of the aluminum atom, which is the heaviest atom in the molecule, were easily determined from the three-dimensional Patterson function. Approximate co-ordinates of the oxygen atom could also be determined. The minimum function was computed by superposing four sets of Patterson maps shifted according to the four equivalent aluminum atom positions. At the same time, the Fourier synthesis was also carried out with the signs based on the aluminum atom only. Another Fourier map with the phases based on the aluminum and oxygen atoms was also computed. From these maps, the co-ordinates of the carbon and nitrogen atoms constituting the centro-symmetrical eight-membered ring and of six carbon atoms of one benzene ring were determined. Using these ten atomic locations the successive Fourier syntheses were undertaken, and all of the eighteen nonhydrogen atomic locations were found.

Then, the block-diagonal least-squares refinement proceeded using the program HBLS IV on a HITAC 5020E computer at the University of Tokyo. This program uses the block-diagonal approximation with a 9 × 9 matrix for each atom with anisotropic temperature factors and a 4 × 4 matrix for each atom with an isotropic temperature factor[8]. In this refinement the function minimized was $\sum w\cdot(\Delta F)^2$, and at the initial stage w was taken as unity for all reflections. The atomic scattering factors used were taken from those of Hanson and co-workers[9]. Using the isotropic temperature factors the refinement converged after 5 cycles to give $R=0.146$. The R index is defined as $\sum||F_0|-|F_c||/\sum|F_0|$. At this stage the interlayer scale factors were fixed. The anisotropic temperature factors for all atoms were then introduced in the refinement, and at the same time an appropriate weight was used for each reflection. After 2 cycles the R index was 0.119. At this stage the difference Fourier synthesis was carried out and the positions of the hydrogen atoms including those of the methyl groups were found. The final refinement was then carried out with all atoms including the hydrogens, and after 2 cycles the R index reduced to 0.107 for non-zero reflections ($R=0.151$ for all reflections). Through the refinement the following weighting scheme was applied;

$F_o < F_{min}$: $w = F_{wt}$;
$F_{min} \leqslant F_o \leqslant F_{max}$: $w = 1$;
$F_{max} < F_o$: $w = (F_{max}/F_o)^2$;

where, $F_{max}=14.10$, $F_{min}=4.70$ and $F_{\,t}=0.15$. The weighted R index {defined as $[\sum w\cdot(\Delta F)^2/\sum w\cdot(F_o)^2]^{\frac{1}{2}}$} is 0.157.

The final atomic co-ordinates of the heavy atoms along with their estimated standard deviations and the anisotropic temperature factors are listed in Tables 2

TABLE 2

ATOMIC CO-ORDINATES OF THE HEAVY ATOMS (IN FRACTION OF CELL EDGES) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS (in 10^{-3} Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Al	0.1413	3	0.1322	3	0.0454	2
O	0.1948	6	−0.0127	5	0.0314	5
N	0.0273	7	−0.1705	7	0.0434	6
C(1)	0.3921	11	0.2144	10	0.0442	10
C(2)	−0.0132	11	0.1506	11	0.1299	10
C(3)	0.1670	8	−0.1007	8	0.0682	8
C(4)	0.3083	9	−0.1165	9	0.1360	8
C(5)	0.2450	12	−0.1739	11	0.1975	9
C(6)	0.3813	10	−0.1823	13	0.2591	9
C(7)	0.5670	11	−0.1313	13	0.2614	10
C(8)	0.6199	10	−0.0741	12	0.2030	10
C(9)	0.4906	9	−0.0646	9	0.1401	9
C(10)	0.0154	9	−0.2822	9	0.0717	8
C(11)	−0.1484	10	−0.3119	12	0.1097	10
C(12)	−0.1598	12	−0.4217	12	0.1342	12
C(13)	−0.0153	14	−0.4957	11	0.1219	14
C(14)	0.1423	16	−0.4644	11	0.0856	14
C(15)	0.1600	11	−0.3558	9	0.0585	11

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS OF THE HEAVY ATOMS EXPRESSED IN THE FORM OF $\exp\{-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+\beta_{12}\cdot h\cdot k+\beta_{13}\cdot h\cdot l+\beta_{23}\cdot k\cdot l)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0218	0.0049	0.0023	0.0013	−0.0008	0.0002
O	0.0267	0.0046	0.0030	0.0077	−0.0002	0.0008
N	0.0247	0.0053	0.0028	−0.0021	−0.0007	0.0010
C(1)	0.0409	0.0073	0.0039	0.0039	0.0014	0.0000
C(2)	0.0370	0.0104	0.0038	0.0083	0.0028	−0.0014
C(3)	0.0137	0.0057	0.0030	0.0041	0.0000	−0.0002
C(4)	0.0242	0.0056	0.0028	0.0027	0.0006	−0.0003
C(5)	0.0456	0.0113	0.0023	−0.0148	−0.0018	0.0024
C(6)	0.0296	0.0164	0.0031	−0.0165	−0.0067	0.0022
C(7)	0.0327	0.0148	0.0042	−0.0081	−0.0089	0.0021
C(8)	0.0247	0.0129	0.0044	−0.0100	−0.0061	0.0019
C(9)	0.0271	0.0062	0.0039	−0.0035	−0.0020	0.0011
C(10)	0.0329	0.0053	0.0031	−0.0006	−0.0041	0.0026
C(11)	0.0298	0.0111	0.0046	−0.0035	−0.0011	0.0057
C(12)	0.0355	0.0112	0.0065	−0.0094	−0.0052	0.0085
C(13)	0.0568	0.0065	0.0082	−0.0145	−0.0114	0.0056
C(14)	0.0645	0.0054	0.0072	0.0093	−0.0077	0.0023
C(15)	0.0361	0.0057	0.0054	0.0052	−0.0046	0.0001

TABLE 4

ATOMIC CO-ORDINATES (IN FRACTION OF CELL EDGES) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS (in 10^{-2} Å) AND ISOTROPIC TEMPERATURE FACTORS FOR THE HYDROGEN ATOMS (in Å^2)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
H(1)	0.345	10	0.294	11	0.043	10	5.1
H(2)	0.498	10	0.204	11	0.016	10	5.6
H(3)	0.494	10	0.182	11	0.085	10	4.9
H(4)	−0.162	10	0.163	10	0.127	9	4.1
H(5)	−0.029	11	0.228	11	0.144	11	5.4
H(6)	0.031	12	0.130	11	0.175	11	6.0
H(7)	0.121	9	−0.221	10	0.200	10	4.2
H(8)	0.374	9	−0.214	10	0.302	10	4.2
H(9)	0.668	12	−0.138	12	0.310	12	6.6
H(10)	0.765	8	−0.037	9	0.205	8	2.0
H(11)	0.523	10	−0.022	11	0.094	10	4.5
H(12)	−0.277	9	−0.253	10	0.109	9	3.8
H(13)	−0.288	13	−0.433	13	0.156	13	7.7
H(14)	−0.084	14	0.583	14	0.141	14	8.8
H(15)	0.285	10	−0.514	10	0.084	9	3.6
H(16)	0.313	13	−0.335	13	0.032	13	7.7

and 3, respectively. The atomic co-ordinates and the isotropic temperature factors of the hydrogen atoms are listed in Table 4. The observed and calculated structure factors are given in Table 5.

RESULTS AND DISCUSSION

The molecular structure is shown in Fig. 2 with the numbering of atoms. The interatomic bond distances and angles calculated using the DAPH[10] program are listed in Tables 6 and 7, respectively. Standard deviations were estimated by taking the maximum value of the standard deviations for co-ordinates of each atom, $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$.

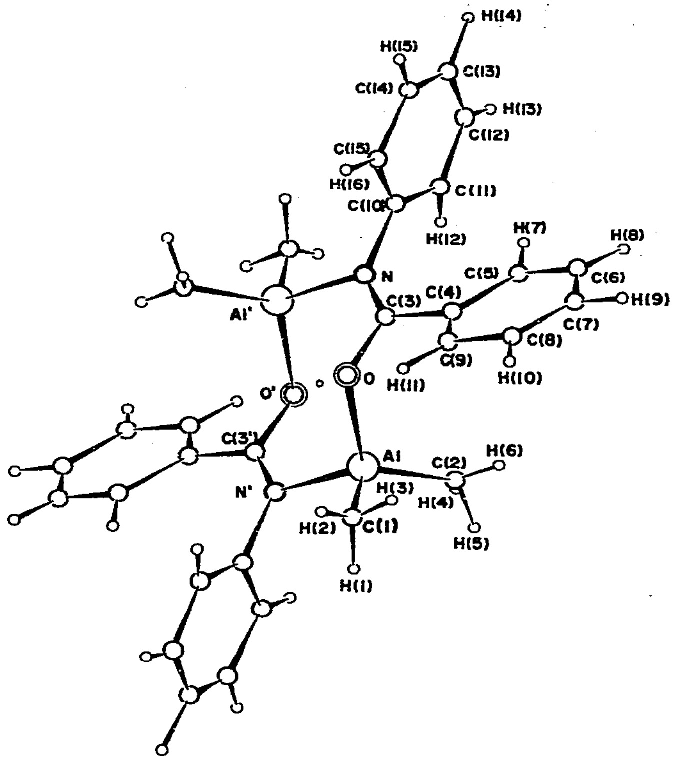


Fig. 2. Molecular structure.

The molecule is composed of a centro-symmetrical eight-membered ring, which corresponds to the proposed model (B). The NCO groups are bridging two aluminum atoms both by the oxygen and nitrogen atoms. Horder and co-workers showed the similar type of OCN bridging between two aluminum atoms and the formation of an eight-membered ring in the spectroscopic studies of the similar compounds such as $[C_2H_5ClAlNC_6H_5COC_2H_5]_2$ and $[ClAl(NC_6H_5COC_2H_5)_2]_2$[11].

The aluminum atom has a distorted tetrahedral co-ordination consisting of two methyl carbons and nitrogen and oxygen atoms. The bond lengths between the aluminum atom and two methyl carbons are both 1.940(11) Å, which are a little shorter than those obtained in the earlier stage of the refinement (1.97, 2.01 Å)[5]. This may be due to the consideration of the hydrogen atoms in the least-squares refinement. The Al–O distance of 1.805(6) Å is equal to those distances (between the aluminum and oxygen atoms in the 2-methyl-8-quinolinolato groups) of 1.804(5), 1.817(5),

(*Continued on p.* 174)

TABLE 5

OBSERVED AND CALCULATED STRUCTURE FACTORS

The values of F_o and F_c are all multiplied by the factor of 8.0. The asterisks stand for the F_o's less than F_{min} (=4.70) used in the weighting scheme in the least-squares refinement.

K	FO	FC
H,L= 0 0		
2*	21	-35
4	385	-420
6	363	351
8	143	158
10*	22	10
12	44	-54
14	59	65
H,L= 0 1		
1	439	504
2	296	327
3	378	-416
4	86	96
5	166	-169
6*	22	-19
7	228	219
8*	27	-33
9	87	77
10	83	-83
11*	0	-18
12*	22	39
13*	0	-12
14*	0	0
H,L= 0 2		
0	519	630
1	477	497
2*	0	-4
3	384	422
4	74	83
5	300	324
6	224	215
7	124	119
8	220	217
9	112	-106
10*	0	7
11*	0	14
12	58	-59
13	57	64
14*	34	43
H,L= 0 3		
1	216	221
2	729	-818
3	148	113
4	436	414
5	213	211
6	46	-38
7	169	152
8	76	-78
9	117	128
10	119	-130
11*	0	18
12	103	110
13*	0	8
14	58	49
H,L= 0 4		
0	220	-216
1	46	42
2	292	-276
3	191	-97
4	44	-50
5	58	37
6	208	180
7	145	143
8	80	75
9*	0	-19
10*	0	-18
11*	0	5
12*	0	-16
13	123	131
14*	16	9
H,L= 0 5		
1	441	436
2	41	-46
3	113	123
4*	14	-7
5	347	317
6	142	143
7*	0	-11
8	54	54
9*	0	0
10	185	-180
11*	0	4
12	114	130
13*	0	18
14	113	102
H,L= 0 6		
0	547	-586
14	80	75
H,L= 0 8		
0	176	-153
1	159	-175
2	168	155
3	50	47
4	98	90
5	40	37
6*	0	-21
7	71	78
8	69	-63
9*	31	-52
10*	0	25
11*	0	-17
12	44	48
13	107	84
14*	0	-12
H,L= 0 9		
1	271	-283
2	69	-69
3	237	167
4*	0	15
5*	0	-13
6	139	131
7	134	-96
8	49	47
9	45	-47
10*	0	9
11*	0	5
12*	19	28
13*	0	15
14*	0	15
H,L= 0 10		
0	508	-469
1	179	-163
2	60	71
3*	36	42
4	300	277
5	130	121
6	63	-56
7	73	64
8	157	-151
9	39	-36
10*	0	19
11*	0	-9
12	63	56
13*	29	39
H,L= 0 11		
1	253	-256
2*	18	-10
3	163	152
4*	0	14
5*	0	14
6	68	64
7	114	-122
8*	32	33
9*	22	-37
10*	21	40
11	93	84
12*	0	-5
13*	0	10
H,L= 0 12		
0	455	-439
1*	27	42
2*	19	-10
3	60	-58
4	152	154
5	74	-63
6	99	-111
7	91	84
8	73	-74
9*	22	37
10*	0	17
11*	0	0
12*	0	4
13*	0	8
H,L= 0 13		
1	220	-211
2	66	52
3	198	190
4	89	-93
5	74	-84
6*	22	-32
7	97	-104
8	44	41
9*	0	-27
10	77	71
H,L= 0 16		
0	64	59
1	169	169
2	60	-65
3	135	123
4	64	-65
5*	31	-28
6*	31	-25
7	66	-70
8*	0	-21
9	46	45
10*	0	9
11*	36	35
H,L= 0 17		
1	85	-84
2	141	140
3*	0	11
4*	0	-2
5	43	-54
6	86	-87
7*	0	-9
8*	0	-9
9*	0	3
10	42	39
H,L= 0 18		
0	63	-68
1*	22	37
2*	21	-37
3*	0	23
4*	21	-31
5*	0	-1
6*	0	6
7	98	-78
8*	0	10
9*	25	23
H,L= 0 19		
1*	0	14
2*	0	-2
3	50	-52
4*	19	36
5*	0	-8
6	80	-73
7*	0	2
8*	0	-12
H,L= 0 20		
0	56	68
1	48	47
2*	19	-34
3*	0	3
4	62	-70
5	41	-40
6*	21	31
7*	0	-18
H,L= 0 21		
1*	0	35
2*	0	23
3	69	-64
4*	0	-4
5*	0	1
6*	0	-7
H,L= 0 22		
0	47	46
1*	0	2
2*	0	-3
3*	0	4
4	58	-58
5*	0	-14
H,L= 1-16		
1	79	82
2*	0	-22
3*	0	6
4	39	49
5*	0	-40
6*	0	-5
7*	0	25
8*	0	-49
9*	30	-57
10*	0	26
H,L= 1-15		
1	145	-150
2	38	45
3	111	105
4*	0	-1
5*	0	-15
6*	0	18
7*	0	-13
8*	0	-51
2	59	63
3*	35	25
4	256	260
5*	0	-11
6	102	-111
7	55	-63
8	79	-93
9*	0	-2
10	62	38
H,L= 1-11		
1*	31	-47
2	65	74
3	215	193
4	60	-74
5	109	119
6	107	-115
7	87	-85
8*	0	24
9*	0	8
10*	0	-11
H,L= 1-10		
0	140	-122
1	170	143
2	43	55
3	55	60
4	177	175
5	70	-86
6*	0	4
7	101	-89
8	39	23
9	79	82
10	38	34
H,L= 1 -9		
1	170	153
2	373	356
3	95	89
4	63	-72
5*	33	44
6	225	-242
7*	0	-24
8	158	65
9	68	80
10	67	71
H,L= 1 -8		
0	146	107
1	108	94
2	143	97
3	169	147
4	164	153
5	111	-117
6	108	113
7	136	-142
8	54	64
9	112	127
10*	0	40
H,L= 1 -7		
1	116	92
2	75	65
3*	26	10
4	254	224
5	203	191
6	197	-203
7	112	125
8*	0	6
9	67	84
10	125	140
H,L= 1 -6		
0	578	591
1	362	-333
2	126	-117
3*	0	2
4	141	-128
5*	0	-26
6	268	256
7	68	-76
8	116	120
9	67	69
10*	0	4
H,L= 1 -5		
1	375	356
2	234	-200
3	46	-42
4	150	-132
5	268	255
6	92	-104
7	163	160
8	125	114
2	88	82
3	571	553
4	448	-470
5	125	117
6	273	263
7	63	-64
8	272	245
9*	37	41
10	39	-45
H,L= 1 -1		
1	135	130
2	528	642
3	602	-616
4	181	155
5	133	-130
6	130	135
7	298	281
8	48	-50
9*	0	0
10	55	-66
H,L= 1 0		
1	44	44
2*	28	5
3*	36	27
4	102	-79
5*	22	-27
6	353	327
7	152	131
8	191	182
9*	0	13
10*	0	-18
H,L= 1 1		
1	309	-325
2	611	-676
3*	16	10
4	92	70
5	249	-225
6	129	120
7	284	267
8	123	-100
9	87	-92
10	119	-119
H,L= 1 2		
0	379	415
1	47	-42
2*	0	-24
3	39	-23
4	108	-102
5	268	290
6*	0	25
7	140	137
8	114	-110
9	50	-56
10*	0	-24
H,L= 1 3		
1	93	98
2	471	-517
3	235	228
4	141	130
5	119	102
6	189	188
7*	0	-3
8*	0	-30
9	162	-150
10	154	-147
H,L= 1 4		
0	901	1174
1	385	390
2	130	-123
3	218	-202
4	39	35
5	257	241
6	89	-98
7	280	275
8	163	-163
9	168	-159
10*	0	-30
H,L= 1 5		
1	134	165
2	95	-89
3	48	54
4*	24	26
5	92	78
6	230	230
7	71	-87
8	98	91
9*	37	-44
3	71	-76
4	215	215
5*	0	16
6	114	-110
7*	0	6
8	150	-150
9*	0	0
10*	0	17
H,L= 1 9		
1	466	-439
2*	0	7
3	82	-86
4	191	-167
5*	32	38
6	48	66
7	145	-150
8	37	38
9	54	-60
10	53	65
H,L= 1 10		
0	120	-103
1*	0	-4
2	72	-53
3	43	-44
4	131	135
5	67	-67
6	94	-111
7*	0	26
8	155	-167
9*	0	33
10*	0	12
H,L= 1 11		
1	155	-167
2	129	122
3	196	194
4	216	-209
5	155	-150
6*	36	-38
7	205	-213
8	38	44
9*	0	21
10	62	71
H,L= 1 12		
0	114	-119
1	66	60
2*	0	-14
3	84	91
4*	35	12
5*	0	9
6	195	-205
7*	0	-16
8*	0	-19
9*	0	38
10*	34	19
H,L= 1 13		
1*	0	0
2	183	163
3*	0	-10
4	117	101
5	119	-102
6	156	-159
7	38	-43
8*	0	-37
9*	35	41
10	73	75
H,L= 1 14		
0	73	74
1	189	171
2	162	-164
3	130	134
4	76	-79
5	133	-133
6*	0	10
7	76	-94
8*	36	42
9	48	77
10*	0	12
H,L= 1 15		
1	37	-35
2	152	155
3	38	-40
4	101	-45
5*	0	13
6	120	-136
7*	0	19
8*	0	-6
9*	0	-5
H,L= 2-11		
2	170	183
3	87	91
H,L= 2-10		
0	216	-189
1	146	126
2	108	122
H,L= 2 -9		
1	93	73
2	75	68
H,L= 2 -8		
0	291	220
1	246	-237
2	128	115
3	74	-61
H,L= 2 -7		
1	332	323
2*	0	-19
H,L= 2 -6		
0	629	603
1	181	-169
2	211	191
H,L= 2 -5		
1	101	117
2	211	-185
H,L= 2 -4		
0	298	261
1	139	-145
H,L= 2 -3		
1*	0	17
2	239	-224
3	340	-319
H,L= 2 -2		
0	57	69
1	303	255
2	173	-160
3	98	-91
H,L= 2 -1		
1	163	153
2	76	-66
3	273	-251
4	201	-155
H,L= 2 0		
1*	10	11
2	196	-185
3*	0	10
4	105	99
5	260	236
H,L= 2 1		
1	236	-278
2	141	-133
3	242	-229
4	138	139
5	110	97
7	66	-87
H,L= 2 2		
0	168	-186
1	89	-97
2	435	-420
3	310	-307
4	117	104
5	285	292
7	164	183
H,L= 2 3		
1	201	-221
3*	20	-17
4*	0	0
5	38	60
H,L= 2 4		
0	439	-548
1	299	314
2	371	-359
3	45	-28
4	103	111
5	40	-50
6	199	-210
H,L= 2 5		
1	314	-326
2	168	180
3	123	125
4	109	-107
5	174	183
6	124	-105
7	275	-266
8	162	139
H,L= 2 6		
0	699	-795
5	51	-45
6	54	-51
7	163	-153
H,L= 2 10		
0*	0	-6
2	96	81
3	203	204
4	51	-43
5	54	-58
6	113	-106
7	41	-48
8	94	85
H,L= 2 11		
1	86	-81
2	125	107
3	64	80
4*	0	-17
9	115	108
H,L= 2 12		
0	106	93
2	93	-88
3	174	172
4	69	-59
5	58	-136
6*	0	29
7	145	-151
H,L= 2 13		
1	96	92
2	98	87
3	70	65
4*	0	-49
5*	0	-39
H,L= 2 14		
0	116	99
2*	0	13
5*	0	-73
H,L= 2 15		
1	93	86
2*	0	0
4	93	102
5	58	-63
7	38	99
H,L= 2 16		
0	102	92
1	42	-25
4	58	-62
H,L= 3-18		
0	69	-66
1	48	58
2	58	56
3	47	58
4	64	71
5	60	-64
6*	0	-6
H,L= 3-17		
1*	36	-33
2	107	112
3	86	94
4*	34	-29
5*	0	35
6	44	-43
7*	0	-10
8*	34	32
H,L= 3-16		
0	64	-52
1*	36	46
2*	36	30
3	63	72
4	80	75
5*	34	-51
6*	0	24
7*	0	-18
8*	0	0
9	41	45
H,L= 3-15		
1*	0	6
2	91	83
3*	36	45
4*	0	-19
5*	0	-23
6*	0	-32
7	47	55
8*	0	28
9*	0	2
10*	31	44
H,L= 3-14		
0	63	46
6*	0	-23
7*	0	16
8	50	51
9*	33	57
10*	30	-26
H,L= 3-11		
1*	32	25
2*	0	-6
3*	34	32
4*	0	-20
5	50	-41
6	63	-65
7	52	47
8	63	64
9*	0	23
10	55	62
11	48	-51
H,L= 3-10		
0	75	61
1*	0	8
2	78	68
3	65	-58
4	158	-139
5	70	72
6	63	-68
7*	0	0
8	97	84
9*	35	36
10*	0	-35
12*	24	-25
H,L= 3 -9		
1	155	153
2*	29	-41
3	165	-169
4	65	63
5	59	-54
6	87	82
7*	0	-40
8	52	51
9*	0	12
10*	0	32
H,L= 3 -8		
0	204	218
1	39	-43
2	40	-51
3	59	-51
4	261	-265
5	152	158
6	98	83
7*	0	10
8	117	125
9*	36	-55
10*	0	-40
12	39	-35
H,L= 3 -7		
1	68	74
2	85	-65
3	298	-300
4	42	44
5	176	-169
6	234	233
7	50	47
8*	36	-31
9	117	112
10*	0	-18
11	74	-79
H,L= 3 -6		
0	208	207
1	258	-242
2	101	-87
3	85	-82
4	270	-274
5	97	85
6*	0	1
7	60	-47
8	96	101
9*	0	7
10*	0	-23
12	74	-75
H,L= 3 -5		
1	44	-44
2	272	-282
3	176	-156
4	152	157
5	73	-59
6	111	99
7	77	-64

K	FO	FC
1	115	-107
2	198	173
3	126	-117
4	47	40
5•	0	-17
6	80	-71
7	198	212
8•	29	-23
9	49	-49
10•	0	11
11	59	-62
12•	29	30
13	130	125
14•	0	1
H,L= 0 7		
1•	0	-5
2	132	-121
3	42	-25
4	45	48
5	96	93
6	315	295
7•	28	16
8	90	68
9•	0	-41
10	148	-143
11	63	-72
12	80	83
13•	0	-4
0	266	-347
1	45	49
2	259	-243
3	168	180
4	175	140
5	117	102
6	97	-82
7	131	123
8	135	-129
9	90	-79
10•	0	-9
H,L= 3 -1		
1	230	-252
2	269	-274
3	146	-134
4	43	44
5	115	97
6	91	82
7	127	-112
8•	0	6
10	98	-89
H,L= 3 0		
1	74	-157
2	216	-288
3	148	-147
4	169	165
5	85	72
6	86	28
7	39	52
8•	0	-94
9•	32	-45
10	106	55
11•	0	-30
H,L= 3 1		
1•	26	-78
2•	27	19
3	167	-160
4	58	-49
5	37	-45
6•	25	-12
7	84	-58
8•	30	43
H,L= 3 2		
0	178	-309
1	58	-72
2	107	-104
3	63	-50
4	154	161
5	148	-133
6	51	-43
7	80	-67
8	174	-170
H,L= 3 3		
1	230	-206
2	167	177
3	228	234
4	93	-90
5	143	165
6	161	-138
7	132	-98
8	124	124
H,L= 3 4		
0	266	-307
1	70	81
2	82	69
3	132	-150
4	133	126

K	FO	FC
11	52	49
12•	0	-26
H,L= 0 14		
0	74	-84
1•	30	-37
2	57	47
3•	0	-3
4•	0	-10
5•	0	-11
6	155	-157
7•	31	-38
8•	31	-40
9	85	89
10•	0	4
11•	27	26
12•	0	0
H,L= 0 15		
1•	0	24
2	100	110
3	81	-70
4•	22	22
5	94	-84
6	71	-77
7•	31	-32
8•	0	13
9	47	-47
10	59	57
11•	0	24
5	145	-146
6	141	-110
7•	0	15
8	195	-219
H,L= 3 5		
1	75	-64
2	116	114
3	245	259
4	99	-99
5•	0	-29
6	170	-156
7	105	-82
8	165	173
H,L= 3 6		
0	58	-57
1	184	179
2	146	134
3	145	141
4•	24	-23
5	140	-123
6•	0	-9
7•	0	-23
8•	0	-30
H,L= 3 7		
1•	22	16
2	227	225
3	55	-55
4	83	-69
5•	0	6
6	141	-140
7•	0	-35
8•	33	40
H,L= 3 8		
0•	0	17
1	182	166
2	156	136
3	45	42
4	110	-97
5	182	-185
6	88	86
7•	0	5
8	200	209
H,L= 3 9		
1	83	66
2	189	176
3•	0	9
4	117	-114
5	130	-125
6	159	-163
7	66	54
8	88	-75
H,L= 3 10		
0	160	153
1•	0	-4
2	162	149
3	163	120
4	75	-60
5	122	-110
6•	0	-30
7	133	-143
8	105	117
H,L= 3 11		
1	129	115
2	97	81
3	62	49
4•	0	-2
5•	0	5

K	FO	FC
9	58	-15
10•	0	-22
H,L= 1 -14		
0	176	-173
1	65	50
2•	0	23
3•	0	-27
4	163	180
5•	0	-37
6	68	-89
7•	0	-32
8•	0	-45
9•	35	-18
10	64	38
H,L= 1 -13		
1	124	-124
2•	0	-13
3	150	152
4•	0	-1
5	95	93
6	79	-103
7	56	-69
8	38	-51
9•	0	-20
10•	0	21
H,L= 1 -12		
0	253	-248
1	144	128
6•	0	-17
7	47	59
8	103	-110
H,L= 3 12		
0	159	153
1	63	72
2•	0	-3
3	79	71
4•	33	-42
5•	0	16
6•	33	32
7	87	-30
8	70	66
H,L= 3 13		
1	73	57
2•	0	9
3	47	59
4•	0	-2
5•	33	-42
6	46	35
7•	0	152
8	52	-22
H,L= 3 14		
0	74	60
1•	0	-20
2•	0	-30
3•	33	-38
4•	0	-2
5•	33	33
6	64	47
7	43	-70
8•	28	85
H,L= 3 15		
1	88	89
2	141	-139
3•	33	-40
4	46	49
5•	0	-11
6	43	41
7	80	78
8•	0	-22
H,L= 3 16		
0	149	132
1•	0	-35
2•	0	4
3	96	-89
4•	31	-38
5	67	58
6	48	44
7•	0	10
8•	0	45
H,L= 3 17		
1	54	45
2	81	-75
3•	29	-42
4	41	40
5•	0	16
6•	25	31
7•	22	31
8•	0	-12
H,L= 3 18		
0•	0	-2
1	40	-53
2•	28	21
3	47	-48
4•	26	34
5	54	55

K	FO	FC
9	101	112
10	137	138
H,L= 1 -4		
0	326	321
1	454	-380
2	412	386
3	107	-108
4	178	-164
5	66	-56
6	42	-54
7•	32	28
8	195	165
9•	0	18
10•	0	-42
H,L= 1 -3		
1	792	809
2	381	-365
3	84	90
4	279	261
5	243	-269
6	153	146
7	91	79
8	49	49
9	119	120
10	39	49
H,L= 1 -2		
0	041	1365
1	411	-381
6•	0	9
H,L= 4 -19		
2	67	67
3•	28	28
H,L= 4 -18		
0•	33	-39
H,L= 4 -17		
2	62	73
H,L= 4 -16		
0	38	36
H,L= 4 -15		
2	55	68
H,L= 4 -14		
0	88	77
H,L= 4 -12		
0	67	63
1	38	-33
2	38	-35
3•	0	-30
6	55	-59
H,L= 4 -11		
1•	0	-6
2	120	-117
3	54	-59
4	111	115
5	68	-64
6•	0	33
H,L= 4 -10		
0	87	86
1	95	-85
2	81	-77
3	91	-82
4	154	-151
5	87	98
6•	0	-24
8	54	49
H,L= 4 -9		
1•	0	46
2	152	-148
3	175	-197
4•	0	17
5	68	-76
6•	0	47
H,L= 4 -8		
0	45	41
1	86	-72
2•	0	25
3•	0	1
4	176	-174
5•	0	19
6	67	-73
8	55	60
H,L= 4 -7		
1•	0	2
3	99	-80
4	152	137
5	52	-59
6	38	42
H,L= 4 -6		
0	85	-77
1	242	-225
2	60	-54
3	77	64
4•	0	11
5	184	177
6•	37	36
H,L= 4 -5		

K	FO	FC
10	101	-100
H,L= 1 6		
0	753	-827
1	294	287
2	53	56
3	192	-197
4•	25	34
5	88	-74
6	140	-138
7	105	114
8	100	-98
9•	0	-22
10•	0	7
H,L= 1 7		
1	353	-361
2	384	382
3•	0	-23
4	71	-68
5	101	97
6	151	165
7	193	-197
8•	36	62
9	65	-76
10•	0	15
H,L= 1 8		
0	616	-574
1	144	-143
2	104	99
1	160	-144
2	131	-113
3	42	-36
4	73	69
5	70	62
6	154	166
8	137	-132
H,L= 4 -4		
0	281	-327
1	157	-142
2	104	-78
3•	0	-21
4	110	106
5•	0	31
6•	0	5
8	148	-127
H,L= 4 -3		
1	243	-230
2	203	-169
3	209	157
4	61	-42
5	75	68
6•	0	9
H,L= 4 -2		
2	77	-70
3	72	-58
4	132	133
5•	0	-26
6•	35	-23
8	159	-145
H,L= 4 -1		
2	53	43
3	38	33
4	118	-108
5	66	60
6	80	-78
7•	0	7
8•	0	22
H,L= 4 0		
1	77	158
2•	11	22
3•	14	4
4	179	192
5	138	-123
6	48	50
7•	30	-52
8	81	-68
H,L= 4 1		
1•	0	-12
2	96	111
3	72	65
4	95	-76
5	110	107
6	97	-90
7	76	-70
8	105	91
9	119	-116
H,L= 4 2		
0•	20	-29
1	77	88
2	60	57
3	113	-127
4	138	134
5	76	-76
6•	0	24
7•	0	-10
8	47	-47

K	FO	FC
10	38	34
H,L= 1 16		
0	38	43
1•	0	31
2•	0	0
3•	0	14
4	38	-46
5•	37	-59
6•	36	-21
7	69	-80
8•	32	45
9•	0	34
10•	0	-19
H,L= 2 -18		
0	43	-41
H,L= 2 -16		
0	63	-52
4	125	139
H,L= 2 -14		
0•	0	-32
1	61	52
H,L= 2 -13		
3	95	112
H,L= 2 -12		
0•	0	4
1	88	88
2	80	75
3	82	81
9•	0	4
H,L= 4 3		
1•	0	23
2	236	280
3	123	132
4	80	-91
5•	26	18
6	78	-62
7•	0	0
8	67	75
9	69	56
H,L= 4 4		
0•	0	-5
1	130	127
2	92	93
3•	0	11
4•	0	4
5	83	-86
6•	0	-13
7	65	-49
8•	33	37
9	48	47
H,L= 4 5		
1•	19	19
2	135	117
3•	23	44
4	115	-103
5	71	71
6	126	-123
7	46	53
8•	0	40
9	140	142
H,L= 4 6		
0	300	326
1	215	217
2	76	63
3•	0	-1
4	136	-149
5	178	-161
6	55	60
7•	0	-6
8	84	92
9•	0	25
H,L= 4 7		
1	194	202
2	167	187
3•	0	-5
4	132	-124
5	99	-106
6	138	-149
7•	0	15
8•	0	-2
H,L= 4 8		
0	173	145
1	163	146
2	143	137
3	178	193
4•	31	-20
5	65	-72
6•	0	14
7•	34	-54
8	118	128
H,L= 4 9		
1	103	92
2•	0	17
3	44	-42
4	122	121

K	FO	FC
1	101	97
2	54	-48
3	151	-169
4	235	243
5	165	-174
6	129	-121
H,L= 2 7		
1	147	-144
2	65	66
3	75	-72
4	92	-93
5•	33	41
6	124	-116
7	236	-261
8	114	129
H,L= 2 8		
0	112	90
1	84	-83
2	117	98
3•	0	23
4•	32	43
6	83	-79
8	71	-85
H,L= 2 9		
1	115	-115
2	310	315
3•	32	-47
4	120	-119
5	47	38
6•	0	6
7•	0	16
8	95	-106
H,L= 4 10		
0	109	96
1	33	-44
2•	31	-33
3•	0	19
4•	0	-31
5•	0	28
6	91	90
7•	0	24
8	113	126
H,L= 4 11		
1	81	48
2	58	-34
3•	33	-28
4•	0	-21
5•	0	4
6	83	79
7	105	111
8•	0	-30
H,L= 4 12		
0•	33	23
1	127	-112
2•	0	5
3•	34	-34
4•	0	3
5•	0	15
6	47	-52
7•	0	-5
8	51	54
H,L= 4 13		
1	59	49
2	143	-135
3•	0	10
4	48	41
5•	0	-21
6	85	76
7	52	57
8•	0	-5
H,L= 4 14		
0	90	89
1	90	-69
2•	0	-32
3•	0	-31
4•	0	-11
5	90	83
6•	0	3
7•	0	0
8•	0	-9
H,L= 4 15		
1•	0	2
2	73	-72
3•	0	-2
4	44	39
5•	0	-24
H,L= 4 16		
0•	31	-36
1	70	-64
2•	0	-6
3	52	-50
4•	29	37
5	81	72
H,L= 4 17		
2	118	-99

K	FO	FC
1	43	63
2•	0	9
3	52	50
4•	0	-7
5•	36	-53
6•	36	29
7•	0	-15
8•	33	48
9	42	61
10•	0	-2
H,L= 3 -13		
1•	35	21
2	102	104
3•	0	22
4•	0	10
5•	37	-48
6	90	-100
7	88	92
8•	0	19
9•	0	27
10•	0	65
H,L= 3 -12		
0•	0	-11
1	103	100
2•	0	15
3•	0	-17
4•	0	-14
5•	36	-26
H,L= 5 -14		
1	40	-43
2•	0	-16
3•	0	-16
H,L= 5 -13		
1•	0	-4
2	116	-104
3•	0	-9
5	86	-82
H,L= 5 -12		
1	109	-104
2•	0	-24
3	71	-74
H,L= 5 -11		
1	40	40
2	108	-100
4•	0	35
5	81	-88
H,L= 5 -10		
2	40	46
3•	0	-15
4	58	-47
H,L= 5 -9		
1	77	-64
2	38	-37
3	56	42
4	91	97
H,L= 5 -8		
0	161	-142
1•	37	-47
4	80	71
H,L= 5 -7		
1	79	-71
2	150	-121
3•	0	-38
4•	0	-3
H,L= 5 -6		
0	158	-162
1	66	-65
2•	0	23
3	72	-56
4	133	103
5	39	25
H,L= 5 -5		
2	66	-61
H,L= 5 -4		
0	89	-79
1	88	-81
2•	0	3
3•	0	-20
H,L= 5 -3		
2	140	119
4	62	-72
H,L= 5 -2		
1	124	99
2	41	-17
3•	0	10
H,L= 5 -1		
2	42	109
3	75	99
4	58	-51
5	132	100
6	125	-100
H,L= 5 0		
1	62	128
2•	7	-21
3•	28	5

K	FO	FC
8	219	-198
9•	36	43
10•	0	32
12	76	86
H,L= 3 -4		
0	228	232
1	197	-170
2	237	-209
3•	34	15
4	75	-78
5	153	155
6	89	-84
7•	33	57
8	217	-229
9	104	-89
10•	0	-32
H,L= 3 -3		
1	129	-122
2	167	-156
3	84	-63
4	68	69
5	75	49
6	163	160
7	67	-58
8	136	-128
9	116	-126
10	104	-104
H,L= 3 -2		
4	105	72
5	125	-79
H,L= 5 1		
1•	0	76
2	73	125
3•	0	-26
4	56	-69
5	54	31
H,L= 5 2		
0	38	68
1	52	98
2•	33	55
3•	0	-3
H,L= 5 3		
1	111	140
2•	37	32
3	38	-21
H,L= 5 4		
0	278	305
1	83	67
2	75	60
3	69	33
4	150	-142
H,L= 5 5		
1	147	150
2	258	245
3•	0	-28
4•	0	-6
H,L= 5 6		
1	124	126
2	66	58
3	174	168
4	68	-60
H,L= 5 7		
1	49	-48
2	50	-43
3•	0	-8
4	64	59
H,L= 5 8		
2•	0	-33
3•	0	-10
4	88	-71
H,L= 5 9		
1	72	62
2	135	-96
3	66	-62
4•	0	-17
H,L= 5 10		
0	66	-53
1	106	-78
2•	33	41
3•	33	-23
H,L= 5 11		
1•	0	4
2	128	-111
3•	0	9
H,L= 5 12		
0	48	-40
1	108	-96
2•	0	-23

TABLE 6

INTERATOMIC DISTANCES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Distance (Å)	σ (Å)	Atoms	Distance (Å)	σ (Å)
Al–O	1.805	0.006	O–C(3)	1.277	0.010
Al–C(1)	1.940	0.011	C(3)–C(4)	1.501	0.012
Al–C(2)	1.940	0.011	C(3)–N	1.305	0.011
Al–N′	1.947	0.007	N–C(10)	1.447	0.012
C(4)–C(5)	1.415	0.015	C(10)–C(11)	1.387	0.015
C(5)–C(6)	1.388	0.017	C(11)–C(12)	1.401	0.017
C(6)–C(7)	1.376	0.018	C(12)–C(13)	1.343	0.019
C(7)–C(8)	1.343	0.018	C(13)–C(14)	1.340	0.021
C(8)–C(9)	1.380	0.015	C(14)–C(15)	1.407	0.019
C(9)–C(4)	1.359	0.013	C(15)–C(10)	1.344	0.015
C(1)–H(1)	1.00	0.11	C(2)–H(4)	1.00	0.10
C(1)–H(2)	0.92	0.11	C(2)–H(5)	0.98	0.11
C(1)–H(3)	1.04	0.11	C(2)–H(6)	0.89	0.12
C(5)–H(7)	1.01	0.10	C(11)–H(12)	1.12	0.10
C(6)–H(8)	0.88	0.10	C(12)–H(13)	0.98	0.13
C(7)–H(9)	1.07	0.12	C(13)–H(14)	1.21	0.14
C(8)–H(10)	1.06	0.09	C(14)–H(15)	1.12	0.10
C(9)–H(11)	1.02	0.11	C(15)–H(16)	1.19	0.13

1.820(5) and 1.809(5) Å in $[Al_2O(C_{10}H_8NO)_4]$[12], but it is shorter than the Al–O (oxygen in the dioxane) distance of 2.02(2) Å in $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$[13]. The Al–N′ distance of 1.947(7) Å is slightly longer than those of 1.916(10) Å and 1.918(10) Å in $[(C_6H_5)_2AlN{=}C(C_6H_5)C_6H_4Br]_2 \cdot 2C_6H_6$[14] but it is shorter than 2.085 (average) Å in $[Al_2O(C_{10}H_8NO)_4]$[12]. Among the bond angles around the aluminum atom, the C(1)–Al–C(2) angle of 117.6(0.6)° is larger than the N′–Al–O angle of 102.6(0.3)°; such a feature is usually observed for a tetrahedral aluminum atom which is a member of a ring[15–18].

The O–C(3) distance of 1.277(10) A is significantly longer than the C=O distances in the usual aldehydes and ketones, 1.23 Å. The O–C(3) bond seems to have a large double bond character considering that the usual $C(sp^2)$–O bond distances lie within 1.40–1.34 Å[19]. The C(3)–N distance of 1.305(11) Å is close to that found in acetanilide (1.330(6) Å)[20]. This fact suggests that the C(3)–N bond also has large double bond character. These facts may suggest that the molecule can be represented by the resonance between the two structures shown below.

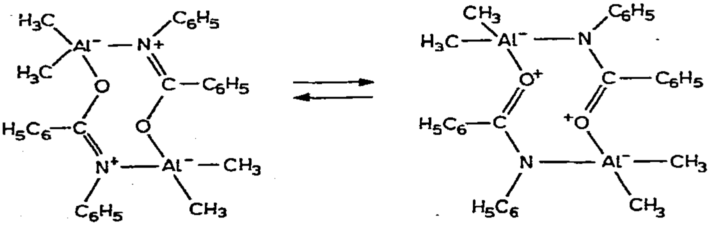


TABLE 7

INTERATOMIC ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS, (σ)

Atoms	Angle (°)	σ (°)	Atoms	Angle (°)	σ (°)
O–Al–C(1)	108.3	0.4	Al–O–C(3)	133.6	0.6
O–Al–C(2)	110.3	0.4	O–C(3)–N	118.8	0.8
O–Al–N′	102.6	0.3	O–C(3)–C(4)	115.6	0.7
C(1)–Al–C(2)	117.6	0.5	N–C(3)–C(4)	125.6	0.8
C(1)–Al–N′	107.7	0.4	C(3)–N–C(10)	122.3	0.7
C(2)–Al–N′	109.3	0.4	Al′–N–C(3)	118.6	0.6
			Al′–N–C(10)	118.2	0.6
C(3)–C(4)–C(5)	120.7	0.8	N–C(10)–C(11)	119.2	0.9
C(3)–C(4)–C(9)	118.6	0.8	N–C(10)–C(15)	119.3	0.9
C(5)–C(4)–C(9)	120.3	0.9	C(11)–C(10)–C(15)	121.5	1.0
C(4)–C(5)–C(6)	117.6	1.0	C(10)–C(11)–C(12)	118.0	1.0
C(5)–C(6)–C(7)	120.9	1.2	C(11)–C(12)–C(13)	121.0	1.2
C(6)–C(7)–C(8)	120.0	1.2	C(12)–C(13)–C(14)	119.7	1.4
C(7)–C(8)–C(9)	121.2	1.1	C(13)–C(14)–C(15)	121.9	1.4
C(4)–C(9)–C(8)	119.8	0.9	C(10)–C(15)–C(14)	117.9	1.1
H(1)–C(1)–H(2)	111	9	H(4)–C(2)–H(5)	75	9
H(1)–C(1)–H(3)	124	9	H(4)–C(2)–H(6)	111	10
H(2)–C(1)–H(3)	83	9	H(5)–C(2)–H(6)	93	10
H(1)–C(1)–Al	103	6	H(4)–C(2)–Al	124	6
H(2)–C(1)–Al	130	7	H(5)–C(2)–Al	113	7
H(3)–C(1)–Al	108	6	H(6)–C(2)–Al	123	8
H(7)–C(5)–C(4)	127	6	H(12)–C(11)–C(10)	118	5
H(7)–C(5)–C(6)	114	6	H(12)–C(11)–C(12)	123	5
H(8)–C(6)–C(5)	132	7	H(13)–C(12)–C(11)	109	8
H(8)–C(6)–C(7)	107	7	H(13)–C(12)–C(13)	129	8
H(9)–C(7)–C(6)	119	7	H(14)–C(13)–C(12)	104	7
H(9)–C(7)–C(8)	121	7	H(14)–C(13)–C(14)	136	7
H(10)–C(8)–C(7)	119	5	H(15)–C(14)–C(13)	124	5
H(10)–C(8)–C(9)	120	5	H(15)–C(14)–C(15)	113	5
H(11)–C(9)–C(4)	116	6	H(16)–C(15)–C(10)	126	6
H(11)–C(9)–C(8)	124	6	H(16)–C(15)–C(14)	116	6

The environments of the N and C(3) atoms are trigonal. The angles N–C(3)–C(4) and C(3)–N–C(10) are 125.6(0.8)° and 122.6(0.7)° respectively, and they are a little greater than 120°. The distance between the N and C(10) atoms of 1.447(12) Å is similar to that of acetanilide, 1.426(6) Å[20], The C(3)–C(4) distance is a normal value 1.501(12) Å which can be compared to that of 1.48(2) Å in benzamide[21] for example. The average C–C(benzene) and C–H bond distances are 1.374 Å and 1.03 Å respectively. The configuration of the two adjacent benzene rings about the C(3)–N bond is *cis*, however twisted by 11.4° from the exact *cis*-position. The dihedral angle between the best planes of the two benzene rings is 70.2°. These facts may result from the repulsion between the carbon atoms of the two benzene rings; several short non-bonded distances such as C(4)–C(10)=2.961(13) Å and C(5)–C(10)=2.955(15) Å are found.

Figs. 3 and 4 show the projections of the crystal structure along the *a* and *b* axes, respectively. Interatomic contacts less than 4.0 Å are indicated by broken lines.

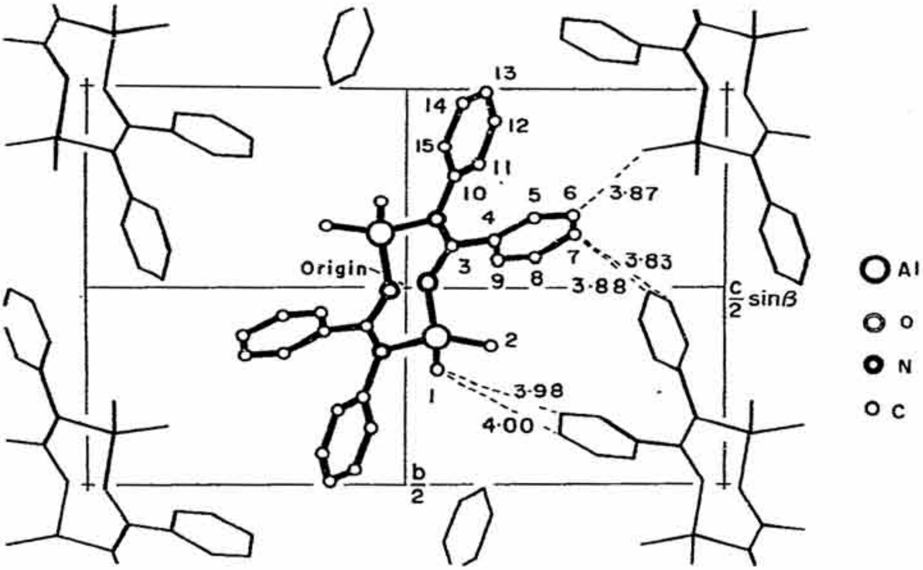


Fig. 3. Crystal structure viewed along the *a* axis.

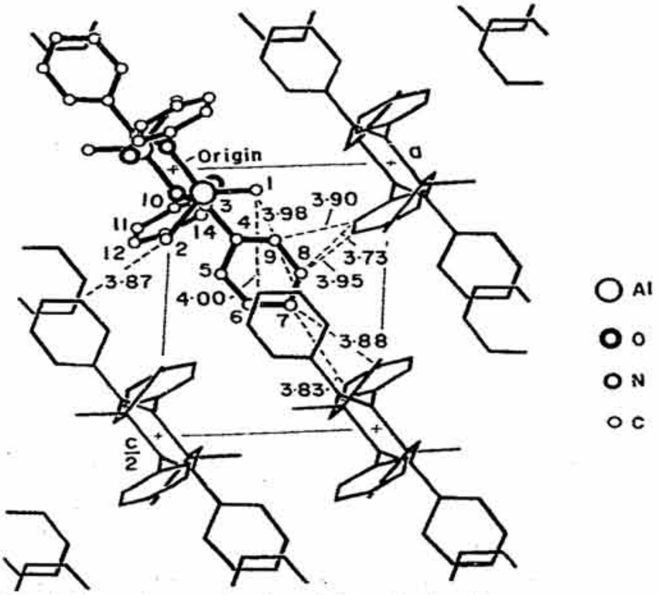


Fig. 4. Crystal structure viewed along the *b* axis.

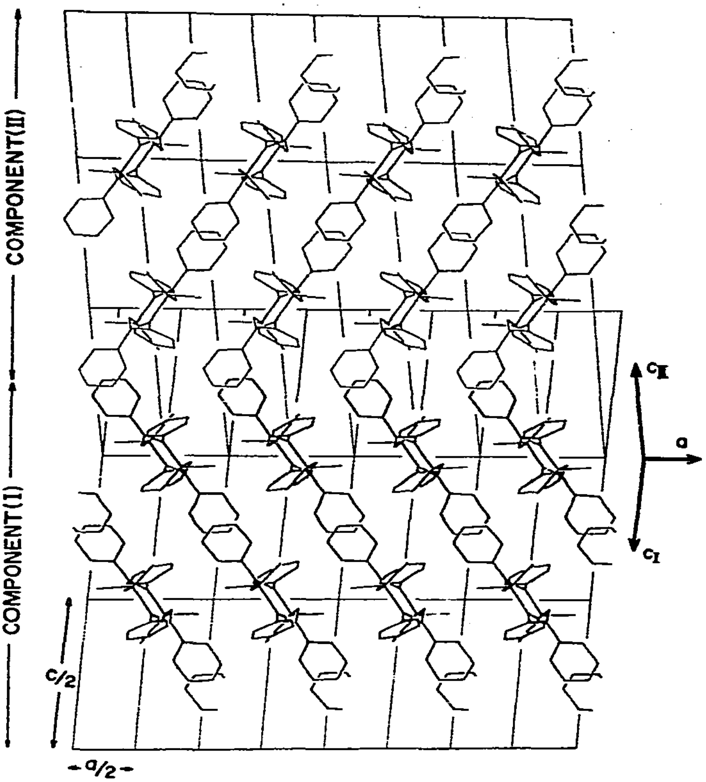


Fig. 5. A model for the boundary area of the twinning.

There are no distances shorter than the normal van der Waals' contacts.

For the interpretation of the twinned structure the molecular packing was then examined at the boundary area where each component of the twinned crystal joins. Fig. 5 shows the projection of plausible model of the twinned structure along the *b* axis (*cf.* Fig. 4). In this model the *a* axis is taken as the common axis for convenience, and the *c* axes of the two components are represented as c_I and c_{II} respectively. Fig. 6 shows the details of molecular packing and intermolecular atomic contacts at the postulated boundary area. The thick and thin lines show the molecules which belongs to the component (I) and to the component (II) respectively, and the broken lines show the postulated continuation of the molecular arrangement in the latter component. Some shorter contacts than those in the ordinary structure (Figs. 3 and 4) are found in the boundary area in this model: $C(6')_{(I)}$–$C(2)_{(II)}$ = 3.31 Å (each subscript identifies the twin component to which the molecule belongs), $C(12')_{(I)}$–$C(7)_{(II)}$ = 3.42 Å and $C(13')_{(I)}$–$C(7)_{(II)}$ = 3.50 Å. In the real crystal, however, the boundary area of the twinned crystal may have longer contacts than this model; nearly the same magnitude of the contacts as in the ordinary molecular arrangement may be taken. During the crystal growth of the component (II), when a molecule happens to take a new arrangement like one of the molecules drawn by thick lines in Fig. 6 at the growing sites, the growth of the component (I) may proceed.

Besides the structure analysis of $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$, the

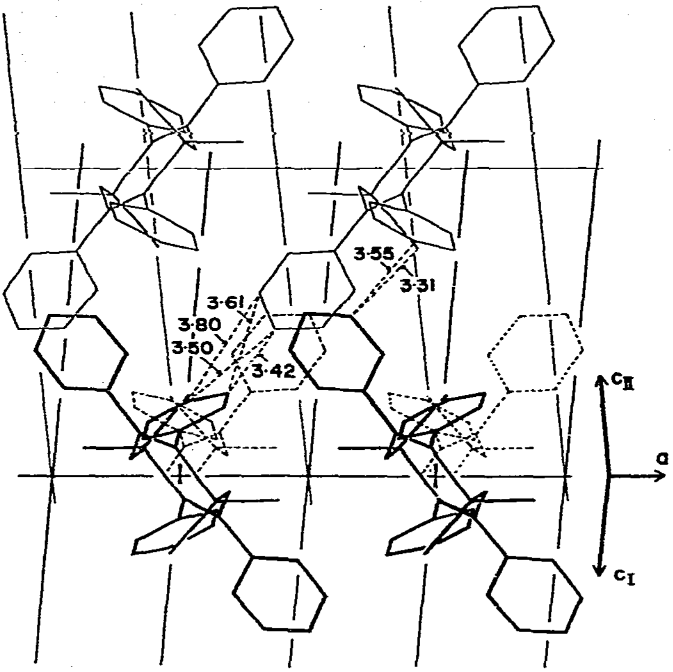


Fig. 6. Intermolecular atomic contacts at the boundary area. Thick and thin lines show molecules of components (I) and (II), respectively. Broken line shows the ordinary molecular packing of the twin component (II) without twinning.

preliminary X-ray examinations of two similar complexes have been carried out. Crystal data for these complexes are listed in Table 8.

TABLE 8

CRYSTAL DATA OF COMPLEXES SIMILAR TO $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$

$[(CH_3)_2AlOC(CH_3)N(C_6H_5)]_2$	$[(C_2H_5)ZnOC(C_6H_5)N(C_6H_5)]_2$
$M = 382.5$ (as a dimer)	$M = 581.3$ (as a dimer)
Orthorhombic	Monoclinic
$a = 8.42$ Å	$a = 25.85$ Å
$b = 21.93$ Å	$b = 15.24$ Å
$c = 18.32$ Å	$c = 17.52$ Å
	$\beta = 113.4°$
$V = 3383$ Å^3	$V = 6334$ Å^3
If $Z = 8$ (as a dimer)	If $Z = 8$ (as a dimer)
$D_x = 1.50$ g·cm^{-3}	$D_x = 1.22$ g·cm^{-3}
$P2_12_12_1$ or $P2_12_12$	$P2_1/c$

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