The Crystal and Molecular Structures of a 3 : 2 Adduct of Acetylene and Isonitrile Derivatives

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In order to determine the structure of the 3 : 2 adduct (acetylene : isonitrile) obtained by cycloaddition reaction of dimethyl acetylenedicarboxylate with 2,6-dimethylphenylisonitrile and to elucidate the route of the reaction, a heavy atom derivative of this adduct was prepared and subjected to X-ray diffraction analysis. The crystal grown from acetone solution has the composition $C_{36}H_{34}N_2O_{12}Br_2 \cdot CH_3COCH_3$ and belongs to monoclinic system with the lattice constants: $a=34.13\pm0.04$, $b=14.66\pm0.02$, $c=8.10\pm0.01$ Å, $\beta=90.5\pm0.2°$. The space group is $P2_1/n$ containing four formula units in the cell. The structure was solved by the heavy atom method and refined by the block-matrix least-squares method for 1482 observed reflections allowing the anisotropic thermal motions for each atom. It has been shown that the chemical structure of the adduct is 1-(4-bromo-2,6-dimethylphenyl)-2-(4-bromo-2,6-dimethylphenyl)imino-1,2-dihydro-3,4,5,5,6,7-hexacarbomethoxy-5*H*-1-pyrindine.

It has been shown that isonitrile reacts as nucleophile, but substituted acetylene, especially when it has electron withdrawing groups, reacts as electrophile giving rise to cyclic products. Takizawa, Obata, Suzuki, and Yanagida[1] synthesized cyclopententriimine and biseketenimine which correspond respectively to the 1 : 3 and 1 : 2 adducts of acetylene and isonitrile and elucidated the structures of these adducts as well as the reaction mechanism. However, this cycloaddition reaction is very complicated and gives many complex compounds in addition to 1 : 3 and 1 : 2 adducts. We have chosen one of the 3 : 2 adducts obtained in the reaction of dimethyl acetylenedicarboxylate and 2,6-dimethylphenylisonitrile for structure determination. However, the structure is so complicated that it proved to be difficult to solve it merely on the basis of spectral data and chemical reactions.

It was therefore decided to carry out X-ray diffraction analysis by applying the heavy atom method. In order to introduce a heavy atom into the adduct, 4-bromo-2,6-dimethylphenylisonitrile was reacted with dimethyl acethylenedicarboxylate and the 3 : 2 adduct containing heavy atoms was prepared.

Experimental

The crystals of the 3 : 2 adduct, $C_{36}H_{34}N_2O_{12}Br_2 \cdot CH_3COCH_3$, recrystallized from acetone solution are monoclinic deep violet prisms. The amount of the solvent of crystallization was calculated from elemental analysis and NMR spectrum. The lattice constants were determined from the $0kl$ and $h0l$ precession photographs taken with Cu$K\alpha$ radiation. Intensity data were collected from the c-axis multiple-film equi-inclination Weissenberg photographs of zero to six layers and the b-axis zero layer precession photographs of various exposures. All were taken with Cu$K\alpha$ radiation. The intensities were measured with the aid of a Narumi microdensitometer. From systematic absence, the space group was found to be $P2_1/n$. The unit cell contains four molecules of the adduct together with four molecules of acetone. After Lorentz and polarization corrections were made, the structure factors of various layers of the c-axis were put on the same relative scale by use of $h0l$ structure factors obtained from the precession photographs. Since the cross-section of the crystal used for the c-axis Weissenberg photographs was about 0.08×0.10 mm and the μR value was calculated to be less than 0.2 for Cu$K\alpha$ radiation, no absorption correction was applied for the intensity data. All together 1482 independent reflections were observed out of 3085 possible reflections within the sphere of radius corresponding to $2\theta=90°$ in reciprocal space.

Crystal data

$C_{36}H_{34}N_2O_{12}Br_2 \cdot CH_3COCH_3$, MW 904.5, mp 254—255°C
Monoclinic
$a=34.13\pm0.04$, $b=14.66\pm0.02$, $c=8.10\pm0.01$ Å,
$\beta=90.5\pm0.2°$
Volume of the unit cell=4052.8 Å^3
Density (calculated)=1.483 g·cm^{-3}
Linear absorption coefficient for Cu$K\alpha$ radiation=33.2 cm^{-1}
Absent reflections: $h0l$ when $h+l$ is odd, $0k0$ when k is odd
Space group: $P2_1/n$
$Z=4$

Structure Determination

The ordinary heavy atom method was applied to phase determination. From the Harker and other vectors in the Patterson map, the positional parameters of the two independent bromine atoms were easily determined. Three-dimensional electron density map was then calculated on the basis of bromine contributions. Several cycles of Fourier and difference Fourier syntheses revealed the fifty-two atoms composing the whole molecule. Three cycles of least-squares refinement were made, in which individual isotropic temperature factors were assigned coding all atoms as carbon except for two bromine atoms. At this stage, twelve oxygen and two nitrogen atoms were distinguished by comparing their temperature factors. Using these positional parameters, difference Fourier synthesis was computed and the atomic parameters of the solvation molecule were determined. The R value at this stage was 0.17.

Refinement of the structural parameters for 1482 observed structure factors was carried out by the method of block-matrix least-squares using the program HBLS.[2] Six cycles of calculation with isotropic temperature factors and three cycles with anisotropic temperature factors for all atoms reduced the R value to

1) T. Takizawa, N. Obata, Y. Suzuki, and T. Yanagida, *Tetrahedron Lett.*, **1969**, 3407.

2) Y. Okaya and T. Ashida, *HBLSIV, The Universal Crystallographic Computing System (I)*, p. 65. Japanese Crystallographic Association (1967).

TABLE 1. THE FINAL ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS

The thermal parameters are of the form

$$T = \exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}.$$

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
BR(18)	0.2795	0.6016	0.3091	0.0015	0.0048	0.0127	-0.0007	0.0015	-0.0000
	(1)	(2)	(3)	(0)	(2)	(5)	(1)	(1)	(3)
BR(28)	0.5477	0.3526	0.8813	0.0013	0.0082	0.0129	-0.0004	-0.0021	-0.0007
	(1)	(3)	(4)	(0)	(2)	(5)	(1)	(1)	(3)
O(30)	0.4678	0.0926	0.4712	0.0012	0.0060	0.0091	0.0006	-0.0006	-0.0026
	(5)	(12)	(18)	(2)	(12)	(31)	(4)	(6)	(16)
O(31)	0.4927	0.1774	0.2721	0.0008	0.0061	0.0091	-0.0003	-0.0002	-0.0022
	(5)	(12)	(17)	(2)	(13)	(29)	(4)	(6)	(15)
O(34)	0.4086	-0.0763	0.2239	0.0011	0.0032	0.0064	0.0003	0.0008	-0.0009
	(4)	(10)	(16)	(2)	(11)	(27)	(4)	(6)	(13)
O(35)	0.4639	-0.0066	0.1458	0.0008	0.0045	0.0058	-0.0001	0.0007	-0.0016
	(4)	(11)	(16)	(2)	(11)	(30)	(4)	(6)	(13)
O(38)	0.4061	-0.0101	-0.1474	0.0007	0.0081	0.0052	0.0002	0.0004	-0.0003
	(4)	(12)	(17)	(2)	(13)	(28)	(4)	(6)	(15)
O(39)	0.3512	0.0087	-0.2941	0.0010	0.0070	0.0057	0.0001	-0.0006	-0.0000
	(5)	(12)	(17)	(2)	(13)	(29)	(4)	(6)	(15)
O(42)	0.3150	-0.0417	0.2044	0.0011	0.0051	0.0076	-0.0005	0.0007	0.0005
	(5)	(11)	(17)	(2)	(12)	(29)	(4)	(6)	(15)
O(43)	0.3414	-0.1228	0.0063	0.0013	0.0028	0.0086	-0.0001	0.0004	-0.0010
	(5)	(10)	(17)	(2)	(11)	(28)	(4)	(6)	(14)
O(46)	0.2724	-0.0153	-0.1523	0.0008	0.0052	0.0088	0.0000	-0.0000	-0.0004
	(5)	(11)	(17)	(2)	(12)	(31)	(4)	(6)	(14)
O(47)	0.2620	0.1278	-0.2346	0.0013	0.0057	0.0017	-0.0001	-0.0014	-0.0002
	(5)	(11)	(16)	(2)	(13)	(25)	(4)	(6)	(14)
O(50)	0.3075	0.3212	-0.1443	0.0010	0.0054	0.0086	-0.0004	0.0003	0.0011
	(5)	(11)	(17)	(2)	(12)	(30)	(4)	(6)	(15)
O(51)	0.2622	0.2701	0.0390	0.0009	0.0040	0.0034	-0.0000	0.0007	0.0005
	(4)	(10)	(15)	(2)	(11)	(26)	(4)	(5)	(13)
N(1)	0.3705	0.2514	0.2000	0.0009	0.0021	0.0034	-0.0006	0.0004	-0.0012
	(5)	(13)	(18)	(2)	(12)	(31)	(4)	(6)	(15)
N(19)	0.4158	0.3115	0.3820	0.0006	0.0043	0.0030	-0.0003	0.0006	-0.0010
	(5)	(13)	(19)	(2)	(13)	(31)	(4)	(6)	(16)
C(2)	0.4054	0.2411	0.2984	0.0005	0.0038	0.0029	0.0002	0.0001	0.0006
	(7)	(16)	(23)	(3)	(16)	(40)	(5)	(8)	(20)
C(3)	0.4248	0.1553	0.2732	0.0004	0.0037	0.0023	-0.0002	0.0005	0.0024
	(6)	(16)	(23)	(2)	(15)	(36)	(5)	(7)	(19)
C(4)	0.4076	0.0827	0.1832	0.0008	0.0037	0.0000	-0.0005	0.0016	0.0025
	(6)	(16)	(23)	(3)	(17)	(39)	(6)	(8)	(19)
C(5)	0.3476	0.0585	-0.0093	0.0008	0.0036	0.0021	0.0001	0.0002	0.0002
	(7)	(16)	(24)	(3)	(16)	(39)	(5)	(8)	(19)
C(6)	0.3149	0.0990	-0.0591	0.0008	0.0043	0.0018	-0.0003	-0.0004	0.0018
	(7)	(17)	(23)	(3)	(16)	(39)	(6)	(8)	(21)
C(7)	0.3194	0.1858	0.0052	0.0008	0.0033	0.0027	-0.0001	0.0009	0.0003
	(7)	(16)	(23)	(3)	(16)	(40)	(5)	(8)	(19)
C(8)	0.3726	0.1012	0.1025	0.0004	0.0032	0.0000	0.0007	0.0000	-0.0025
	(6)	(15)	(20)	(2)	(14)	(33)	(5)	(6)	(17)
C(9)	0.3548	0.1810	0.1082	0.0005	0.0024	0.0000	-0.0002	0.0013	0.0004
	(6)	(14)	(22)	(2)	(15)	(35)	(5)	(7)	(17)
C(10)	0.3488	0.3374	0.2226	0.0006	0.0042	0.0010	-0.0006	-0.0009	0.0006
	(6)	(17)	(22)	(3)	(16)	(38)	(6)	(7)	(19)
C(11)	0.3594	0.4151	0.1322	0.0009	0.0023	0.0026	0.0006	0.0003	-0.0020
	(7)	(15)	(24)	(3)	(16)	(39)	(5)	(8)	(18)
C(12)	0.3386	0.4943	0.1573	0.0006	0.0065	0.0121	0.0014	-0.0003	-0.0009
	(7)	(18)	(28)	(3)	(19)	(50)	(7)	(9)	(25)
C(13)	0.3080	0.4899	0.2629	0.0008	0.0048	0.0116	0.0011	0.0007	-0.0031
	(7)	(18)	(28)	(3)	(19)	(51)	(6)	(10)	(24)
C(14)	0.2965	0.4155	0.3691	0.0009	0.0019	0.0052	-0.0002	-0.0010	-0.0014
	(7)	(15)	(24)	(3)	(15)	(41)	(5)	(8)	(19)
C(15)	0.3174	0.3332	0.3406	0.0007	0.0046	0.0000	-0.0004	0.0008	-0.0016
	(6)	(16)	(22)	(3)	(16)	(37)	(6)	(7)	(19)
C(16)	0.3077	0.2500	0.4367	0.0018	0.0043	0.0005	-0.0010	0.0024	0.0022
	(8)	(18)	(25)	(4)	(17)	(42)	(7)	(10)	(21)
C(17)	0.3913	0.4123	0.0056	0.0011	0.0052	0.0000	-0.0002	0.0013	-0.0025
	(7)	(18)	(24)	(3)	(18)	(39)	(6)	(8)	(20)
C(20)	0.4481	0.3140	0.4929	0.0013	0.0016	0.0032	-0.0002	-0.0007	-0.0022
	(7)	(15)	(23)	(3)	(15)	(41)	(6)	(9)	(19)
C(21)	0.4798	0.3625	0.4524	0.0010	0.0040	0.0068	-0.0006	-0.0001	-0.0028
	(7)	(17)	(26)	(3)	(18)	(43)	(6)	(9)	(21)
C(22)	0.5111	0.3738	0.5650	0.0006	0.0062	0.0105	0.0003	-0.0005	0.0001
	(7)	(18)	(27)	(3)	(21)	(47)	(6)	(8)	(24)
C(23)	0.5069	0.3374	0.7261	0.0009	0.0028	0.0169	0.0004	0.0002	0.0007
	(7)	(17)	(29)	(3)	(18)	(51)	(6)	(10)	(24)
C(24)	0.4740	0.2898	0.7758	0.0005	0.0091	0.0095	0.0003	0.0001	0.0002
	(7)	(20)	(28)	(3)	(22)	(48)	(6)	(9)	(25)
C(25)	0.4430	0.2793	0.6572	0.0010	0.0033	0.0041	0.0002	0.0009	0.0008
	(7)	(16)	(24)	(3)	(17)	(43)	(6)	(8)	(19)
C(26)	0.4048	0.2242	0.7054	0.0013	0.0037	0.0079	-0.0003	-0.0001	0.0030
	(8)	(17)	(27)	(4)	(18)	(48)	(6)	(10)	(22)
C(27)	0.4841	0.4039	0.2755	0.0008	0.0052	0.0053	-0.0006	-0.0001	0.0013
	(7)	(18)	(25)	(3)	(18)	(43)	(6)	(8)	(23)
C(29)	0.4641	0.1395	0.3505	0.0011	0.0029	0.0105	0.0001	-0.0001	-0.0010
	(7)	(17)	(27)	(3)	(17)	(47)	(6)	(9)	(22)
C(32)	0.5318	0.1558	0.3366	0.0006	0.0113	0.0179	0.0006	0.0008	-0.0022
	(8)	(23)	(32)	(3)	(26)	(58)	(8)	(10)	(31)
C(33)	0.4265	-0.0069	0.1860	0.0006	0.0062	0.0069	-0.0005	-0.0005	-0.0027
	(7)	(18)	(27)	(3)	(19)	(44)	(6)	(9)	(23)
C(36)	0.4833	-0.0943	0.1962	0.0013	0.0056	0.0169	0.0016	0.0017	0.0018
	(8)	(20)	(31)	(4)	(20)	(56)	(8)	(11)	(28)
C(37)	0.3730	0.0066	-0.1621	0.0003	0.0048	0.0008	-0.0001	0.0005	0.0007
	(6)	(17)	(24)	(3)	(18)	(39)	(6)	(7)	(21)
C(40)	0.3732	-0.0271	-0.4487	0.0010	0.0105	0.0000	-0.0004	0.0011	-0.0032
	(8)	(20)	(25)	(3)	(24)	(42)	(7)	(9)	(25)
C(41)	0.3339	-0.0457	0.0779	0.0010	0.0034	0.0007	-0.0004	0.0007	0.0006
	(7)	(16)	(24)	(3)	(16)	(39)	(6)	(8)	(20)
C(44)	0.3304	-0.2085	0.0845	0.0019	0.0023	0.0233	-0.0005	0.0008	0.0052
	(9)	(18)	(34)	(5)	(18)	(63)	(7)	(13)	(26)
C(45)	0.2811	0.0637	-0.1512	0.0012	0.0033	0.0041	0.0000	0.0011	0.0029
	(7)	(17)	(25)	(3)	(17)	(44)	(6)	(9)	(20)
C(48)	0.2249	0.0974	-0.3160	0.0010	0.0074	0.0147	-0.0000	-0.0019	0.0015
	(8)	(20)	(31)	(3)	(21)	(53)	(8)	(10)	(29)
C(49)	0.2946	0.2664	-0.0499	0.0010	0.0041	0.0019	-0.0003	-0.0004	-0.0029
	(7)	(17)	(24)	(3)	(17)	(41)	(6)	(8)	(20)
C(52)	0.2365	0.3484	-0.0104	0.0010	0.0057	0.0210	0.0007	-0.0004	0.0041
	(8)	(20)	(33)	(4)	(20)	(61)	(7)	(11)	(29)
O(56)	0.3808	0.6260	-0.1995	0.0038	0.0114	0.0401	0.0002	0.0022	-0.0042
	(9)	(20)	(34)	(5)	(25)	(67)	(9)	(15)	(32)
C(53)	0.3860	0.5197	-0.4167	0.0027	0.0054	0.0228	-0.0010	0.0003	-0.0014
	(11)	(22)	(39)	(6)	(24)	(71)	(9)	(16)	(32)
C(54)	0.3819	0.6102	-0.3474	0.0017	0.0127	0.0292	-0.0008	-0.0001	-0.0020
	(10)	(26)	(39)	(5)	(32)	(75)	(11)	(15)	(40)
C(55)	0.3750	0.6922	-0.4561	0.0019	0.0107	0.0632	-0.0003	-0.0002	0.0148
	(12)	(28)	(55)	(6)	(35)	(127)	(11)	(22)	(54)

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|F(OBS)|	F(CAL)
4	0	0	53.23	49.13
6	0	0	43.38	38.20
8	0	0	31.52	16.68
12	0	0	116.16	-113.61
16	0	0	104.31	-95.97
20	0	0	25.01	-11.05
22	0	0	110.19	112.99
1	1	0	45.24	-49.70
2	1	0	117.59	124.15
3	1	0	36.11	44.62
4	1	0	31.92	-34.12
5	1	0	98.85	99.31
6	1	0	33.68	-24.05
7	1	0	97.88	-87.30
8	1	0	34.76	-20.48
9	1	0	95.53	83.04
10	1	0	83.67	-79.42
11	1	0	84.56	-88.03
12	1	0	110.09	99.16
13	1	0	58.74	-58.17
15	1	0	58.88	61.15
16	1	0	113.89	115.80
17	1	0	56.53	53.11
18	1	0	49.45	47.26
19	1	0	99.61	102.06
20	1	0	73.41	-71.05
22	1	0	47.43	48.88
24	1	0	42.24	-44.73
0	2	0	53.61	60.87
1	2	0	121.19	-128.29
2	2	0	103.41	-98.74
4	2	0	83.94	-82.11
5	2	0	174.36	-193.04
7	2	0	53.99	50.48
8	2	0	60.66	52.80
9	2	0	82.19	-82.96
11	2	0	56.74	-61.47
13	2	0	148.19	154.21
14	2	0	35.22	28.30
16	2	0	93.61	-87.35
17	2	0	102.98	104.32
19	2	0	52.18	-51.55
20	2	0	49.18	-48.76
21	2	0	63.20	62.16
23	2	0	48.26	-39.08
25	2	0	43.78	-36.06
1	3	0	262.87	-253.80
2	3	0	160.70	-156.33
4	3	0	23.63	18.45
6	3	0	150.06	-130.23
7	3	0	85.13	95.76
8	3	0	130.94	134.42
10	3	0	68.60	-66.55
11	3	0	127.83	129.70
12	3	0	57.39	56.09
13	3	0	46.18	45.52
14	3	0	42.27	-41.53
16	3	0	59.28	53.69
19	3	0	46.62	-39.61
21	3	0	49.75	-42.31
23	3	0	47.78	-54.30
24	3	0	58.42	-56.70
0	4	0	173.61	-169.20
1	4	0	68.98	-70.21
2	4	0	75.06	-70.87
3	4	0	127.69	135.86
4	4	0	212.82	-205.36
5	4	0	51.96	-47.46
8	4	0	35.52	-23.99
10	4	0	28.90	32.98
12	4	0	75.84	81.52
13	4	0	42.48	33.41
15	4	0	51.34	-47.41
17	4	0	37.30	32.46
18	4	0	77.97	-73.17
1	5	0	43.05	-41.28
2	5	0	72.92	67.87
3	5	0	73.38	65.39
4	5	0	77.11	69.31
5	5	0	63.12	-52.07
6	5	0	66.12	56.64
7	5	0	32.98	29.56
9	5	0	130.69	-129.97
10	5	0	91.13	88.63
11	5	0	87.13	92.61
12	5	0	51.67	-52.41
13	5	0	78.65	-72.49
14	5	0	70.09	-65.13
16	5	0	42.02	-38.40
18	5	0	69.11	-70.72
23	5	0	40.89	-45.56
25	5	0	44.27	43.73
26	5	0	48.29	43.04
27	5	0	52.77	-49.66
0	6	0	41.81	43.43
1	6	0	147.11	152.66
2	6	0	134.88	141.14
5	6	0	158.05	153.12
6	6	0	81.94	78.69
7	6	0	55.88	44.71
8	6	0	81.70	-72.34
10	6	0	101.90	-111.10
11	6	0	33.87	31.93
12	6	0	34.08	29.06
13	6	0	53.42	-50.64
14	6	0	48.83	-37.98
15	6	0	54.45	-49.91
16	6	0	63.87	61.59
17	6	0	46.05	-37.95
20	6	0	58.01	54.44
21	6	0	48.70	-50.36
1	7	0	43.92	38.64
3	7	0	36.06	33.17
4	7	0	83.16	-73.80
6	7	0	47.10	45.95
7	7	0	29.28	28.16
9	7	0	71.81	-68.23
11	7	0	77.51	73.78
12	7	0	69.90	-66.96
13	7	0	58.31	-64.95
14	7	0	60.96	55.21
19	7	0	63.42	59.40
20	7	0	44.97	46.49
0	8	0	112.03	106.63
1	8	0	64.87	66.85
3	8	0	98.98	-111.56
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8	8	0	35.16	35.82
9	8	0	49.45	-51.05
10	8	0	34.00	-37.87
11	8	0	51.10	43.34
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16	8	0	54.21	-29.73
19	8	0	40.81	37.95
21	8	0	66.71	-69.95
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13	9	0	47.94	45.05
14	9	0	47.97	48.41
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16	10	0	44.78	-45.31
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8	11	0	51.32	47.68
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7	0	1	243.69	-212.64
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19	0	1	42.43	-40.40
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23	0	1	45.54	-47.28
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10	8	1	64.23	59.50
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13	8	1	52.10	43.36
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19	5	2	77.43	83.81
20	5	2	44.97	-51.37
23	5	2	42.02	46.43
24	5	2	39.92	-43.12
-25	6	2	31.41	-43.21
-22	6	2	48.67	52.16
-20	6	2	54.34	-55.04
-18	6	2	88.26	98.72
-17	6	2	61.55	-65.35
-14	6	2	27.01	33.45
-13	6	2	38.09	28.18
-12	6	2	32.57	32.17
-11	6	2	16.53	16.82
-10	6	2	27.04	-27.51
-9	6	2	95.82	89.97
-7	6	2	21.98	-25.36
-6	6	2	197.67	-208.86
-3	6	2	57.47	-65.77
-2	6	2	38.92	-40.93
-1	6	2	64.85	63.72
1	6	2	111.00	-102.27
6	6	2	46.99	45.84
8	6	2	57.20	54.31
9	6	2	83.27	92.29
10	6	2	53.02	51.71
11	6	2	24.04	24.66
12	6	2	82.59	-87.35
13	6	2	55.10	55.94
16	6	2	76.51	-81.05
18	6	2	30.52	-32.76
19	6	2	22.98	-32.36
26	6	2	47.45	-49.89
-17	7	2	52.37	52.83
-14	7	2	18.88	23.64
-12	7	2	52.45	-54.75
-11	7	2	41.21	-41.17
-10	7	2	76.81	75.60
-8	7	2	74.68	-74.01
-6	7	2	23.04	25.35
-4	7	2	38.32	-39.59
-1	7	2	38.62	-40.36
0	7	2	100.90	105.33
1	7	2	70.82	68.51
2	7	2	66.06	-58.82
3	7	2	87.26	83.91
4	7	2	52.37	51.92
5	7	2	82.29	88.38
6	7	2	77.41	-74.89
7	7	2	21.58	19.60
8	7	2	39.46	51.41
10	7	2	65.95	-64.57
11	7	2	47.05	-46.10
15	7	2	19.34	-25.99
17	7	2	48.51	-61.34
19	7	2	35.00	-40.51
20	7	2	40.38	-43.61
22	7	2	50.42	51.79
27	7	2	49.86	49.47
-17	8	2	29.65	-36.28
-12	8	2	36.57	39.01
-11	8	2	67.84	-67.75
-10	8	2	33.90	36.70
-9	8	2	29.63	-34.16
-8	8	2	31.38	-29.11
-7	8	2	96.36	-98.59
-5	8	2	38.35	41.04
-3	8	2	59.98	-60.73
-2	8	2	24.87	23.31
-1	8	2	115.59	121.66
0	8	2	36.68	-34.44
1	8	2	24.23	-25.26
2	8	2	29.74	27.06
3	8	2	47.59	52.38
4	8	2	60.71	62.82
5	8	2	43.29	42.75
6	8	2	48.18	53.05
7	8	2	30.52	-35.85
8	8	2	23.69	33.20
9	8	2	18.42	21.64
11	8	2	78.59	-71.98
13	8	2	42.16	37.97
14	8	2	34.06	-33.51
15	8	2	28.76	-33.88
17	8	2	82.46	82.89
21	8	2	44.75	42.90
-17	9	2	29.95	-32.58
-16	9	2	35.95	-43.04
-15	9	2	21.23	25.62
-13	9	2	33.36	-39.76
-12	9	2	79.08	-76.55
-11	9	2	43.24	41.76
-10	9	2	36.70	-35.64
-8	9	2	35.33	-34.54
-7	9	2	40.38	41.89
-2	9	2	62.04	67.35
0	9	2	52.64	54.83
1	9	2	32.19	-27.31
5	9	2	76.46	-84.75
9	9	2	19.69	-23.87
10	9	2	65.82	-70.93
13	9	2	49.91	51.52
15	9	2	32.95	-32.27
-14	10	2	42.48	-38.77
-8	10	2	42.38	-44.51
-6	10	2	72.00	73.77
-4	10	2	47.67	-49.25
-3	10	2	29.76	26.52
-2	10	2	61.98	59.79
-1	10	2	41.89	-48.35
0	10	2	30.84	-34.24
1	10	2	32.19	29.58
2	10	2	20.01	23.44
4	10	2	46.83	-45.79
6	10	2	47.37	-48.96
10	10	2	31.22	-26.01
12	10	2	39.54	40.89
16	10	2	62.63	66.68
-12	11	2	40.81	49.63
-8	11	2	48.48	51.67
-7	11	2	48.70	50.95
-5	12	2	35.03	-38.13
-1	11	2	36.68	39.59
0	12	2	36.89	-43.13
0	11	2	45.89	-47.35
1	11	2	34.14	-37.29
2	11	2	25.98	26.12
4	11	2	40.43	-43.16
5	11	2	104.58	-108.90
-21	0	3	50.72	57.88

TABLE 2 (cont.)

15

-17	0	3	34.98	-38.93
-15	0	3	44.40	-43.24
-13	0	3	80.30	-78.62
-11	0	3	119.62	-113.05
-9	0	3	83.40	83.37
-7	0	3	148.90	139.41
-5	0	3	7.62	-12.48
-3	0	3	125.18	136.08
-1	0	3	90.15	94.79
1	0	3	89.64	105.58
3	0	3	10.83	18.27
5	0	3	122.83	-137.22
7	0	3	77.73	-79.09
9	0	3	191.97	-196.51
11	0	3	13.04	-11.55
13	0	3	64.63	-69.95
15	0	3	59.58	68.98
17	0	3	72.71	73.16
21	0	3	54.66	48.56
-20	1	3	45.59	51.35
-19	1	3	75.27	-73.97
-16	1	3	41.11	42.53
-15	1	3	101.87	-101.66
-14	1	3	38.84	-42.38
-13	1	3	86.70	82.95
-12	1	3	66.52	70.15
-11	1	3	46.48	-45.11
-10	1	3	201.99	-175.56
-9	1	3	48.72	43.24
-8	1	3	57.37	-57.24
-7	1	3	18.80	-17.50
-6	1	3	167.10	150.93
-5	1	3	67.49	55.67
-4	1	3	21.53	19.50
-3	1	3	22.36	26.41
-2	1	3	90.96	95.49
-1	1	3	34.06	-38.28
0	1	3	110.09	-129.42
1	1	3	48.18	-47.09
2	1	3	33.33	47.90
3	1	3	100.44	-115.50
4	1	3	150.11	-161.43
5	1	3	80.48	-78.66
6	1	3	104.25	103.79
7	1	3	21.34	-18.38
8	1	3	28.47	-30.91
9	1	3	138.85	130.03
10	1	3	78.11	-79.87
11	1	3	27.49	30.54
15	1	3	32.95	38.42
16	1	3	31.57	32.51
19	1	3	40.43	-42.71
20	1	3	96.61	93.78
21	1	3	40.03	-33.14
22	1	3	32.95	-30.27
23	1	3	54.80	-53.70
-20	2	3	65.31	-66.67
-16	2	3	54.85	-56.92
-12	2	3	73.81	72.25
-11	2	3	41.35	41.17
-10	2	3	50.02	49.02
-9	2	3	74.14	68.07
-8	2	3	83.97	84.52
-7	2	3	45.21	-47.56
-6	2	3	29.92	-21.41
-5	2	3	82.89	-77.72
-4	2	3	137.07	115.21
-2	2	3	52.48	-53.91
-1	2	3	12.99	17.56
0	2	3	50.99	-48.77
1	2	3	132.96	140.95
2	2	3	76.65	-78.54
3	2	3	24.82	22.09
4	2	3	105.36	-94.27
5	2	3	20.45	23.50
6	2	3	37.49	43.60
7	2	3	69.38	-66.51
8	2	3	56.26	-58.26
10	2	3	127.34	125.92
11	2	3	60.39	59.11
12	2	3	58.66	52.70
13	2	3	39.49	41.70
14	2	3	111.76	110.58
15	2	3	81.70	-73.25
16	2	3	27.44	31.50
18	2	3	42.32	38.70
19	2	3	49.94	-43.95
20	2	3	46.51	-46.63
21	2	3	25.60	-21.86
22	2	3	42.40	-40.99
23	2	3	49.72	49.07
26	2	3	43.21	-44.35
-19	3	3	35.43	-32.97
-18	3	3	23.71	27.71
-17	3	3	51.32	53.96
-15	3	3	60.20	-68.17
-14	3	3	77.30	83.23
-13	3	3	47.94	42.35
-12	3	3	41.08	40.86
-11	3	3	34.46	-27.98
-9	3	3	75.87	74.58
-7	3	3	31.73	32.28
-6	3	3	54.50	-59.75
-5	3	3	67.66	-61.36
-4	3	3	120.27	-116.52
-2	3	3	137.12	-132.03
-1	3	3	69.11	-63.75
0	3	3	163.91	-149.79
1	3	3	59.58	69.10
2	3	3	89.50	-88.97
3	3	3	120.67	-123.17
4	3	3	92.75	99.04
5	3	3	27.33	29.00
6	3	3	91.91	84.43
7	3	3	75.35	-73.01
8	3	3	123.59	119.48
9	3	3	62.09	58.41
11	3	3	33.76	-36.66
12	3	3	86.64	78.58
15	3	3	72.25	72.90
16	3	3	46.89	-46.64
17	3	3	57.55	-56.76
21	3	3	40.35	-38.96
-24	4	3	40.76	-35.79
-23	4	3	42.83	38.02
-21	4	3	60.98	-67.35
-18	4	3	24.47	32.26
-15	4	3	47.94	56.20
-13	4	3	42.43	45.01
-11	4	3	31.03	-38.18
-10	4	3	76.87	-75.97
-8	4	3	33.27	-33.07
-7	4	3	40.46	-37.57
-3	4	3	163.64	-151.33
-2	4	3	96.61	-88.83
1	4	3	26.61	23.74
2	4	3	30.49	-32.64
5	4	3	84.89	85.62
8	4	3	49.07	-44.08
9	4	3	116.13	110.45
10	4	3	58.93	-53.37
11	4	3	38.54	36.70
12	4	3	129.53	-121.99
15	4	3	75.33	-73.29
16	4	3	44.67	-40.63
19	4	3	45.99	-47.35
21	4	3	67.39	-71.18
27	4	3	55.77	50.56
-21	5	3	69.28	72.43
[illegible]	5	3	76.59	74.76
-16	5	3	64.68	-61.99
-15	5	3	41.30	51.35
-14	5	3	65.33	66.13
-12	5	3	60.66	-62.85
-10	5	3	115.92	111.02
-9	5	3	54.48	-53.85
-8	5	3	31.87	-35.36
-7	5	3	49.37	-49.79
-6	5	3	39.70	40.41
-5	5	3	44.83	-43.47
-4	5	3	76.76	71.59
-2	5	3	82.32	-78.12
-1	5	3	96.47	98.96
0	5	3	58.72	66.13
1	5	3	41.40	45.36
3	5	3	53.26	56.55
5	5	3	28.82	29.36
8	5	3	44.46	44.59
13	5	3	71.30	-66.14
15	5	3	51.72	-50.35
-11	6	3	84.70	-85.34
-9	6	3	37.87	45.00
-8	6	3	46.18	-47.34
-7	6	3	84.51	-79.25
-5	6	3	70.49	70.67
-1	6	3	56.37	57.49
0	6	3	43.51	46.26
1	6	3	19.34	26.22
2	6	3	98.39	98.53
3	6	3	54.75	-59.70
4	6	3	42.97	49.35
5	6	3	20.09	-25.07
7	6	3	14.11	-116.75
8	6	3	95.15	90.02
10	6	3	92.39	-94.32
11	6	3	65.09	-62.04
13	6	3	23.66	25.47
14	6	3	51.40	-49.66
17	6	3	80.78	79.46
19	6	3	50.56	55.73
-20	7	3	37.78	39.14
-18	7	3	29.95	31.25
-17	7	3	38.97	-35.40
-16	7	3	46.51	-52.47
-15	7	3	47.10	50.08
-13	7	3	37.84	-40.61
-12	7	3	41.70	-31.20
-11	7	3	29.41	34.82
-7	7	3	30.14	33.40
-6	7	3	35.03	40.58
-5	7	3	41.54	-43.44
-4	7	3	70.25	69.09
-2	7	3	33.81	37.60
-1	7	3	71.95	81.42
0	7	3	74.97	76.90
1	7	3	88.18	-85.25
5	7	3	26.87	-32.42
6	7	3	39.13	-30.76
7	7	3	29.38	36.15
8	7	3	49.07	-58.56
10	7	3	38.92	-38.70
11	7	3	41.08	37.09
14	7	3	31.30	31.08
18	7	3	38.81	35.65
19	7	3	38.41	-39.74
21	7	3	40.38	41.65
-24	8	3	42.89	54.62
-22	8	3	35.52	-43.19
-10	8	3	59.61	62.22
-7	8	3	33.41	34.73
-6	8	3	35.54	40.99
-4	8	3	23.55	-28.56
-3	8	3	43.81	38.08
0	8	3	66.12	-65.32
2	8	3	41.08	45.41
3	8	3	23.44	29.73
5	8	3	56.31	-54.69
8	8	3	53.88	50.04
9	8	3	36.11	-44.44
12	8	3	64.28	61.44
-13	9	3	33.79	-36.12
-12	9	3	57.88	61.62
-5	9	3	81.48	82.08
-4	9	3	55.56	-61.14
0	9	3	72.71	-70.69
1	9	3	80.19	-84.05
2	9	3	30.82	30.47
4	9	3	31.09	-37.11
5	9	3	39.59	-36.66
6	9	3	75.95	74.51
10	9	3	41.46	24.27
-5	10	3	71.68	-76.80
-3	10	3	45.78	46.60
-16	11	3	40.92	55.10
0	11	3	60.28	-61.43
-6	12	3	76.70	-75.65
-4	12	3	44.83	36.37
-24	0	4	75.03	-73.22
-20	0	4	36.84	-40.07
-16	0	4	69.82	70.90
-12	0	4	202.64	199.90
-10	0	4	74.11	-71.34
-8	0	4	209.02	204.68
-6	0	4	13.37	-19.60
-4	0	4	92.48	92.11
-2	0	4	75.46	-77.87
2	0	4	42.86	-43.88
4	0	4	53.21	-60.28
6	0	4	85.48	82.48
8	0	4	15.75	-14.72
10	0	4	164.72	167.89
12	0	4	64.68	57.87
14	0	4	54.58	55.14
16	0	4	66.74	-63.30
22	0	4	100.01	-90.50
-18	1	4	56.61	42.57
-15	1	4	51.72	-45.03
-14	1	4	44.91	47.95
-12	1	4	69.33	-63.69
-11	1	4	43.29	-40.34
-10	1	4	32.30	-31.56
-9	1	4	155.97	119.98
-8	1	4	73.49	-71.72
-7	1	4	31.98	-15.95
-6	1	4	80.69	-79.70
-5	1	4	66.57	-63.45
-4	1	4	109.98	-97.34
-3	1	4	69.19	55.34
-2	1	4	70.63	-78.07
-1	1	4	97.18	-110.04
0	1	4	56.88	72.86
1	1	4	35.19	40.12
2	1	4	14.75	-22.51
4	1	4	73.08	79.85
5	1	4	52.80	54.84
6	1	4	79.05	72.63
7	1	4	47.32	43.51
8	1	4	47.91	39.45
9	1	4	51.13	42.96
10	1	4	34.71	32.90
11	1	4	56.50	54.52
12	1	4	72.98	-66.61
15	1	4	27.33	19.09
16	1	4	98.14	-96.37
17	1	4	33.45	-31.09
19	1	4	42.66	-38.22
21	1	4	62.31	-63.65
-25	2	4	46.97	-42.12
-24	2	4	45.48	-40.55
7	7	4	43.67	47.61
8	7	4	70.92	69.13
10	7	4	47.10	-46.25
11	7	4	43.46	39.38
13	7	4	32.87	-30.14
14	7	4	34.49	-33.97
17	7	4	44.10	-45.85
19	7	4	40.08	-41.21
20	7	4	47.24	45.85
-12	8	4	39.00	37.70
-11	8	4	60.93	58.13
-9	8	4	75.27	-67.18
-8	8	4	62.28	61.00
-5	8	4	59.44	-59.36
-4	8	4	32.14	-27.28
-3	8	4	37.46	31.29
-2	8	4	68.92	-66.26
2	8	4	80.46	-72.63
3	8	4	73.76	69.27
7	8	4	85.02	86.63
8	8	4	40.03	-39.86
13	8	4	74.65	-76.43
14	8	4	42.97	38.04
15	8	4	45.27	-37.74
18	8	4	41.46	-38.16
-20	9	4	44.46	40.28
-19	9	4	48.37	-49.79
-17	9	4	43.67	41.43
-15	9	4	41.35	-44.07
-8	9	4	27.76	30.17
-4	9	4	48.45	-41.75
-3	9	4	47.51	43.66
1	9	4	69.01	61.75
2	9	4	64.82	63.01
5	9	4	45.62	41.38
6	9	4	48.29	49.02
7	9	4	42.78	-43.23
12	9	4	46.32	-39.57
13	9	4	36.60	-35.76
15	9	4	38.16	38.98
-10	10	4	71.92	-62.24
-7	10	4	52.23	-50.83
-4	10	4	86.72	76.55
2	10	4	41.05	39.64
8	10	4	77.03	-71.22
-23	0	5	65.22	62.83
-19	0	5	78.67	68.32
-17	0	5	42.48	34.87
-13	0	5	69.17	67.34
-11	0	5	117.76	-99.27
-7	0	5	73.44	-82.10
-5	0	5	70.68	64.40
-3	0	5	44.54	38.93
-1	0	5	63.71	61.06
1	0	5	54.42	66.11
3	0	5	68.36	68.16
5	0	5	86.56	81.47
11	0	5	129.77	-119.48
13	0	5	82.70	-72.94
15	0	5	60.34	-53.03
17	0	5	33.98	-25.10
23	0	5	48.64	38.96
-22	1	5	69.82	70.51
-18	1	5	67.74	57.42
-6	1	5	51.50	-43.54
-5	1	5	80.19	80.01
-4	1	5	81.35	60.90
-2	1	5	58.96	-62.42
-1	1	5	74.25	86.40
0	1	5	67.14	75.37
1	1	5	15.99	-21.94
3	1	5	57.66	60.95
4	1	5	53.29	56.56
5	1	5	59.39	-44.69
7	1	5	53.80	-46.48
8	1	5	95.10	-82.50
9	1	5	44.64	-44.82
11	1	5	52.31	-41.90
12	1	5	64.87	-56.13
15	1	5	45.27	38.12
17	1	5	77.08	68.91
-12	2	5	82.05	-69.01
-8	2	5	66.71	-58.58
-6	2	5	52.96	42.46
-5	2	5	62.36	40.69
-4	2	5	36.70	29.33
-3	2	5	37.65	-19.82
-2	2	5	74.79	70.33
-1	2	5	41.13	-39.13
0	2	5	58.99	61.53
1	2	5	30.33	-31.82
2	2	5	93.37	-90.98
3	2	5	27.74	-27.32
5	2	5	32.36	22.71
6	2	5	107.20	-98.29
7	2	5	55.07	51.01
8	2	5	42.43	-33.50
9	2	5	43.78	40.15
10	2	5	108.28	-94.13
11	2	5	51.80	-46.74
18	2	5	76.16	67.91
22	2	5	49.86	37.70
28	2	5	58.47	-52.13
-22	3	5	46.97	-43.55
-21	3	5	46.40	-42.94
-18	3	5	80.13	-65.40
-17	3	5	114.97	-109.94
-15	3	5	52.37	38.31
-12	3	5	64.52	51.90
-8	3	5	75.65	70.86
-7	3	5	30.57	-31.90
-5	3	5	101.50	82.02
-1	3	5	34.46	34.76
0	3	5	39.35	-33.69
3	3	5	78.59	74.16
4	3	5	93.96	-86.38
5	3	5	50.88	-48.77
6	3	5	42.89	-36.64
10	3	5	84.18	74.66
12	3	5	70.14	62.18
14	3	5	88.99	81.67
17	3	5	48.67	49.68
-15	4	5	64.14	-60.81
-12	4	5	84.89	69.45
-11	4	5	74.03	64.02
-10	4	5	80.08	69.07
-9	4	5	57.23	-48.18
-8	4	5	41.73	-44.85
-7	4	5	46.56	40.45
-4	4	5	78.24	-63.14
-3	4	5	56.28	-52.75
1	4	5	115.43	-105.45
4	4	5	52.42	47.73
5	4	5	95.12	-91.29
6	4	5	35.03	-29.75
7	4	5	63.60	61.34
8	4	5	58.28	51.82
10	4	5	41.59	39.74
11	4	5	110.27	102.06
12	4	5	31.98	38.32
13	4	5	48.75	53.90
23	4	5	62.40	-78.64
-18	5	5	58.04	-48.79
-16	5	5	107.55	91.54
-14	5	5	86.75	-82.67
-12	5	5	63.25	-55.27
-9	5	5	38.11	35.20
-6	5	5	66.60	51.44
-5	5	5	60.88	-46.85
-4	5	5	28.25	-26.15
-23	2	4	31.01	30.76
-21	2	4	48.53	-50.34
-19	2	4	40.67	37.54
-17	2	4	59.69	55.41
-15	2	4	38.35	31.62
-14	2	4	39.97	37.34
-13	2	4	99.50	90.41
-11	2	4	103.36	-91.51
-10	2	4	90.96	-79.52
-7	2	4	104.20	-95.52
-6	2	4	31.49	25.15
-3	2	4	121.86	-100.35
-1	2	4	43.10	41.95
0	2	4	40.16	-35.50
1	2	4	45.10	51.26
3	2	4	71.81	78.52
4	2	4	49.37	-52.78
5	2	4	93.04	89.80
8	2	4	113.68	-118.31
9	2	4	144.44	127.98
10	2	4	37.51	38.69
11	2	4	113.68	-104.18
12	2	4	33.87	-27.87
14	2	4	46.53	-37.05
15	2	4	73.44	-68.67
17	2	4	96.36	-85.21
20	2	4	54.64	48.02
23	2	4	55.45	50.35
27	2	4	54.34	49.98
-20	3	4	44.21	-47.49
-18	3	4	51.69	51.04
-16	3	4	67.55	-63.87
-15	3	4	33.71	-26.50
-14	3	4	30.98	32.88
-13	3	4	52.69	-43.41
-12	3	4	30.30	-22.31
-11	3	4	34.89	45.36
-9	3	4	37.24	-30.53
-8	3	4	27.71	-17.07
-7	3	4	152.81	-131.42
-6	3	4	81.13	-72.00
-5	3	4	42.11	34.43
-2	3	4	65.36	-58.64
-1	3	4	118.70	110.95
0	3	4	53.07	56.70
1	3	4	54.53	53.63
2	3	4	84.13	-82.84
3	3	4	64.52	64.34
4	3	4	116.67	113.53
7	3	4	86.80	-87.82
8	3	4	60.07	53.14
9	3	4	22.31	-25.66
11	3	4	61.44	-54.90
13	3	4	25.95	-29.86
16	3	4	110.09	-97.20
17	3	4	91.88	78.89
18	3	4	31.52	28.68
21	3	4	94.77	89.37
22	3	4	34.60	37.42
23	3	4	37.43	40.14
-20	4	4	54.29	51.48
-19	4	4	45.81	-44.08
-18	4	4	40.67	-39.55
-16	4	4	36.08	37.66
-13	4	4	37.43	-36.65
-12	4	4	139.17	-135.05
-11	4	4	49.75	-49.02
-9	4	4	147.19	138.35
-8	4	4	89.86	-85.57
-6	4	4	99.23	87.47
-5	4	4	83.13	73.21
-4	4	4	62.77	-59.35
-3	4	4	45.37	-40.05
-2	4	4	77.49	72.56
-1	4	4	42.08	-38.43
1	4	4	30.98	-27.54
3	4	4	51.99	-47.88
4	4	4	49.75	51.86
6	4	4	48.99	-46.64
7	4	4	118.86	-103.72
8	4	4	27.79	-22.20
9	4	4	50.07	-41.48
10	4	4	62.44	-57.56
13	4	4	77.65	69.73
17	4	4	69.19	71.01
22	4	4	64.06	52.71
-19	5	4	40.05	41.06
-17	5	4	89.50	-88.09
-15	5	4	40.78	34.65
-14	5	4	47.45	-39.53
-13	5	4	36.46	-36.05
-9	5	4	41.16	-38.83
-8	5	4	25.93	22.25
-7	5	4	45.81	-32.87
-6	5	4	87.80	82.58
-5	5	4	41.67	43.04
-4	5	4	46.26	41.43
-3	5	4	45.64	-46.59
-1	5	4	100.69	99.87
0	5	4	14.69	26.21
1	5	4	67.52	-65.10
2	5	4	28.41	-23.41
3	5	4	46.21	45.01
4	5	4	104.06	-101.07
5	5	4	29.63	-31.91
6	5	4	56.18	-50.90
8	5	4	21.31	-24.89
11	5	4	81.65	-76.39
12	5	4	34.22	30.97
14	5	4	61.36	61.69
15	5	4	78.92	-74.31
16	5	4	62.28	53.29
17	5	4	33.76	25.84
19	5	4	35.16	-34.12
21	5	4	49.69	45.56
-14	6	4	118.75	112.02
-13	6	4	31.09	-26.32
-12	6	4	56.12	-52.75
-11	6	4	45.51	32.95
-10	6	4	66.98	60.93
-9	6	4	23.36	-30.21
-7	6	4	79.59	70.21
-6	6	4	87.48	81.87
-5	6	4	30.87	-30.76
-4	6	4	37.35	-30.41
-3	6	4	89.88	81.33
-2	6	4	68.41	-67.96
0	6	4	65.17	-63.39
1	6	4	38.41	-36.17
3	6	4	30.28	-28.93
5	6	4	34.65	-25.93
8	6	4	60.53	56.18
9	6	4	45.81	-45.77
11	6	4	72.62	62.19
12	6	4	99.07	97.36
15	6	4	59.47	53.58
16	6	4	47.75	42.14
17	6	4	45.37	46.36
20	6	4	53.99	-43.95
-12	7	4	90.61	85.48
-11	7	4	55.42	51.22
-10	7	4	25.41	-29.22
-9	7	4	51.91	39.92
-4	7	4	51.02	-43.62
-2	7	4	51.96	51.83
0	7	4	74.38	-72.01
1	7	4	47.53	-42.97
2	7	4	84.56	-78.72
4	7	4	41.54	-42.45
5	7	4	29.20	-32.83
-3	5	5	27.90	-26.82
-2	5	5	46.26	34.95
-1	5	5	55.72	-38.60
0	5	5	84.35	-72.46
1	5	5	27.55	-17.58
2	5	5	42.05	36.42
3	5	5	28.03	27.28
5	5	5	78.03	73.37
7	5	5	52.02	44.51
9	5	5	31.38	32.01
15	5	5	39.24	-42.31
16	5	5	74.81	65.06
19	5	5	79.05	-69.48
-15	6	5	59.39	50.81
-12	6	5	78.40	68.09
-9	6	5	74.38	-65.54
-6	6	5	66.57	-44.65
-5	6	5	52.42	-46.59
-2	6	5	51.96	-42.38
-1	6	5	52.67	49.57
3	6	5	63.12	58.61
4	6	5	43.97	-43.95
5	6	5	33.00	17.36
6	6	5	42.81	41.40
-5	7	5	58.47	-45.59
-3	7	5	45.89	39.01
0	7	5	16.50	24.76
1	7	5	33.08	40.20
2	7	5	33.19	33.05
3	7	5	69.17	-58.92
10	7	5	35.89	-44.72
12	7	5	43.56	-48.46
13	7	5	70.68	-51.19
14	7	5	53.29	-48.64
15	7	5	38.05	34.87
-10	8	5	72.76	-64.85
-8	8	5	63.58	53.45
-7	8	5	70.03	-64.20
-4	8	5	60.82	48.04
8	8	5	77.22	-68.58
17	8	5	57.64	-46.38
9	9	5	74.70	-67.81
14	9	5	38.86	40.37
15	9	5	38.81	40.10
-16	0	6	74.49	-60.86
-12	0	6	81.73	-64.86
-10	0	6	94.37	74.57
-6	0	6	103.55	80.94
-4	0	6	38.95	39.80
2	0	6	47.83	-52.76
4	0	6	41.78	-46.70
6	0	6	161.67	-150.50
8	0	6	85.24	-70.23
10	0	6	90.45	-73.28
14	0	6	41.75	35.78
18	0	6	46.26	40.50
24	0	6	77.49	-55.51
-10	1	6	71.25	61.26
-5	1	6	41.05	36.81
-4	1	6	51.96	-50.98
-3	1	6	33.19	-26.63
-1	1	6	34.95	37.84
0	1	6	39.65	-50.70
1	1	6	88.56	-97.64
3	1	6	56.91	-56.76
5	1	6	26.41	-27.80
6	1	6	45.05	38.33
8	1	6	60.61	45.94
12	1	6	73.22	64.19
17	1	6	92.12	67.46
18	1	6	62.25	-51.75
-17	2	6	67.52	-58.93
-16	2	6	66.03	-58.64
-15	2	6	64.39	55.26
-14	2	6	48.10	39.61
-13	2	6	40.86	-29.78
-12	2	6	57.23	-19.11
-11	2	6	74.14	63.15
-7	2	6	44.91	45.52
-5	2	6	32.57	-33.61
-1	2	6	96.47	-78.47
0	2	6	60.98	49.55
1	2	6	88.29	-87.08
3	2	6	44.75	49.81
4	2	6	27.71	25.05
5	2	6	41.38	-36.25
7	2	6	90.13	84.18
11	2	6	58.66	41.49
-9	3	6	82.29	-61.32
-6	3	6	73.89	53.62
-5	3	6	97.77	-67.65
-4	3	6	96.18	-75.07
1	3	6	55.88	-49.47
3	3	6	56.61	48.63
5	3	6	110.49	83.28
7	3	6	118.73	87.42
8	3	6	46.10	49.24
12	3	6	87.13	74.54
13	3	6	42.73	-41.73
14	3	6	43.83	-28.46
15	3	6	69.46	-66.09
16	3	6	61.42	47.83
17	3	6	98.80	-72.48
18	3	6	87.13	-69.18
-12	4	6	96.66	68.16
-10	4	6	111.54	-94.01
-6	4	6	65.74	-51.31
-1	4	6	71.11	57.75
2	4	6	124.67	101.60
5	4	6	56.18	-44.21
-14	5	6	71.44	-50.59
-9	5	6	83.37	-64.73
-8	5	6	72.95	-49.79
-7	5	6	71.63	61.10
-6	5	6	56.55	46.45
-3	5	6	88.40	62.92
-1	5	6	49.42	-39.81
0	5	6	66.14	61.55
2	5	6	68.36	59.06
8	5	6	74.73	-66.10
9	5	6	60.23	-44.77
12	5	6	77.92	-67.19
-14	6	6	47.32	-51.75
-11	6	6	69.38	-61.66
-1	6	6	50.72	35.88
4	6	6	80.13	-72.55
5	6	6	52.26	45.58
-6	7	6	79.94	-59.10
-4	7	6	85.05	68.14
-2	7	6	75.70	-66.35
0	7	6	54.31	25.64
-9	8	6	67.66	55.24
-6	8	6	68.47	52.55
-1	8	6	73.71	-55.70

0.077. In the final calculation, the following weight system was adopted.

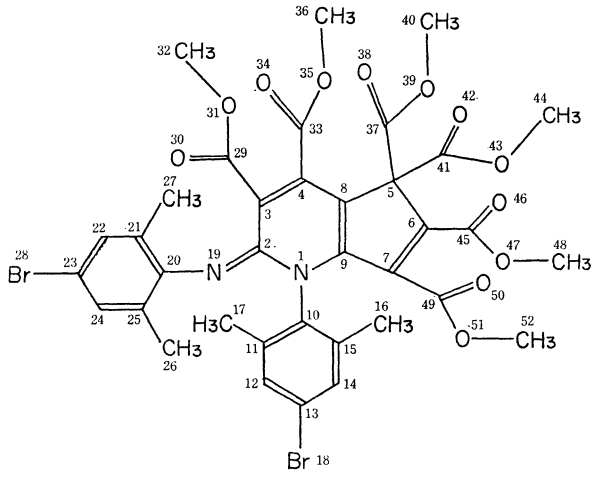
$$\sqrt{w} = 76/F_o \quad \text{when } F_o > 76,$$
$$\sqrt{w} = 1.0 \quad \text{when } 76 \geq F_o \geq 7,$$
$$\sqrt{w} = 0 \quad \text{when } 7 \geq F_o.$$

The final atomic parameters and their standard deviations are given in Table 1 and the observed and calculated structure factors in Table 2.

Discussion of the Structure

The present X-ray structure determination has shown the chemical structure of the 3 : 2 adduct to be 1-(4-bromo-2,6-dimethylphenyl)-2-(4-bromo-2,6-dimethylphenyl)imino-1,2-dihydro-3,4,5,5,6,7-hexacarbomethoxy-5*H*-1-pyrindine (I). The chemical structure and conformation of the molecule are shown in Fig. 1. From the result of X-ray analysis, the mechanism of the reaction was clarified which enabled us to suppose the chemical structures of other reaction products. Details of the study have been published in a separate paper.[3]

The bond lengths and angles are shown in Figs. 2 and 3 along with their standard deviations. The average C–C, C–C(methyl) and C–Br bond lengths found in the substituted phenyl groups are 1.41 Å, 1.54 Å and 1.91 Å, respectively, which agree well with the standard values. The average bond lengths found in the ester groups are 1.50 Å for C(ring)–C, 1.20 Å



I

Fig. 1. Chemical structure (I) and conformation of the adduct.

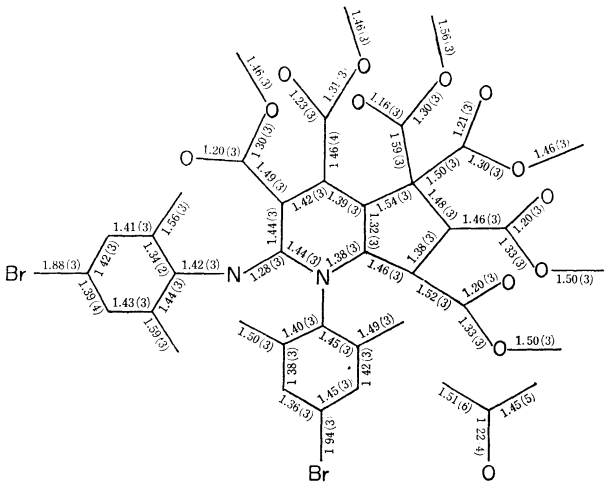


Fig. 2. Bond lengths and their estimated standard deviations. The e.s.d.'s are given in parentheses denoting the least significant digits in the bond lengths.

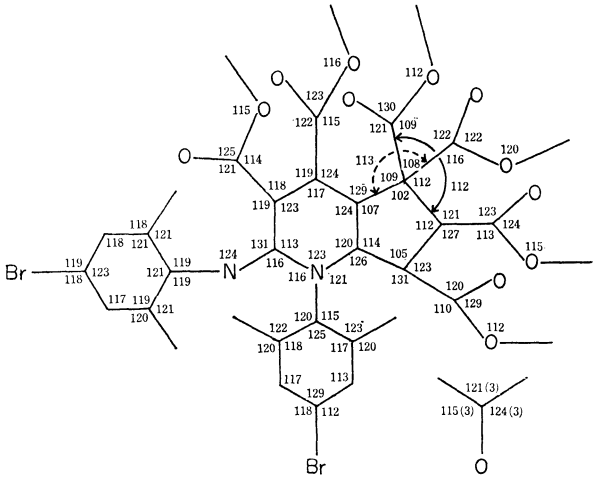
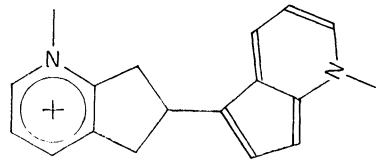


Fig. 3. Bond angles and their estimated standard deviations. The e.s.d.'s are 2° except those in acetone.

for C=O, 1.31 Å for C–O and 1.49 Å for O–C(methyl) which are also in good agreement with those of normal carbomethoxy groups. The C–C bond lengths found in the pyrindine ring vary from 1.32 Å to 1.46 Å except for C(8)–C(5) and C(6)–C(5) bonds which correspond undoubtedly to single bonds. There are few examples of X-ray analysis of a compound containing the pyrindine ring. The only one we found is 1-methyl-6-[5-(1-methyl-1*H*-1-pyrindinyl)]-1-azoniaindan iodide (II)[4] which was found to consist of 1-methyl-1*H*-1-pyrindine and 1-methyl-1-azoniaindan iodide groups. The bond lengths in the former group



II

3) Y. Suzuki, N. Obata, and T. Takizawa, *Tetrahedron Lett.*, **1970**, 2667.

4) H. L. Ammon and L. H. Jensen, *J. Amer. Chem. Soc.*, **88** 681 (1966).

TABLE 3. LEAST-SQUARES PLANES AND DEVIATIONS OF THE ATOMS

The planes are of the form $AX+BY+CZ=D$, where X, Y, Z, and D are in Å unit relative to the axes a^*, b, and c.

Best plane through pyridine ring			
$-0.517X-0.311Y+0.798Z=-6.470$			
N(1)	−0.001 Å	C(6)	0.012 Å
C(2)	0.058	C(7)	−0.047
C(3)	−0.060	C(8)	0.015
C(4)	−0.005	C(9)	0.007
C(5)	0.023		
Distances from the above plane			
C(10)	0.141 Å	C(37)	−1.273 Å
N(19)	0.093	C(41)	1.223
C(29)	−0.191	C(45)	0.180
C(33)	0.084	C(49)	−0.330
Best planes through phenyl groups			
$0.637X+0.272Y+0.722Z=10.158$		$-0.419X+0.855Y+0.306Z=-1.261$	
C(10)	−0.006 Å	C(20)	−0.029 Å
C(11)	0.003	C(21)	0.023
C(12)	0.020	C(22)	−0.007
C(13)	−0.039	C(23)	−0.003
C(14)	−0.032	C(24)	−0.002
C(15)	−0.011	C(25)	0.017
Distances from the above planes			
C(16)	0.012 Å	C(26)	−0.003 Å
C(17)	−0.062	C(27)	0.040
Br(18)	0.064	Br(28)	−0.015
C(52)	−3.745	C(32)	−3.603

Best planes through ester groups		Distances from the planes	
$-0.107X+0.815Y+0.569Z=1.495$			
C(3)	−0.004 Å		
C(29)	0.013	C(32)	−0.115 Å
O(30)	−0.005		
O(31)	−0.004		
$0.256X+0.139Y+0.957Z=5.030$			
C(4)	0.000 Å		
C(33)	−0.001	C(36)	0.069 Å
O(34)	0.000		
O(35)	0.000		
$0.247X+0.954Y-0.168Z=3.496$			
C(5)	0.005 Å		
C(37)	−0.019	C(40)	−0.098 Å
O(38)	0.008		
O(39)	0.006		
$0.857X-0.049Y+0.514Z=10.045$			
C(5)	−0.003 Å		
C(41)	0.010	C(44)	0.064 Å
O(42)	−0.004		
O(43)	−0.003		
$-0.585X+0.153Y+0.796Z=-6.521$			
C(6)	−0.002 Å		
C(45)	0.007	C(48)	0.155 Å
O(46)	−0.003		
O(47)	−0.002		
$-0.443X+0.532Y+0.721Z=6.232$			
C(7)	0.013 Å		
C(49)	−0.049	C(52)	−0.048 Å
O(50)	0.020		
O(51)	0.016		

show a characteristic of aromatic systems, and most C–C bond lengths (average value of the seven peripheral bonds is 1.394 Å and the length of the transannular bond is 1.482 Å) are in good overall agreement with those found in azulenes. The bond lengths and angles in the latter group indicate that the five-membered ring can be best described as cyclopentenyl while the six-membered ring can be described as positively charged pyridinum, since the bond lengths involved in the six-membered ring agree with similar parameters in heterocyclic molecules having the character of sp^2 hybridization and electron delocalization. The structure of the pyrindine group in the present compound differs from that of the above two cases in that it has many substituents such as six carbomethoxy, a phenyl and a phenylimino group. Furthermore, the C(2)–N(19) bond length (1.28 Å) is significantly shorter than any other C–N lengths in the present molecule while the bond lengths of C(8)–C(5) and C(6)–C(5) (1.54 Å and 1.48 Å, respectively) are much longer than other C–C lengths involved in the ring. It is therefore reasonable to assume that the six-membered ring has an aromatic nature and the resonance structure is extended to N(19) on one side and to C(6) through C(7) on the other side of the ring. The mean C–C bond length in the six-membered ring (1.39 Å) is almost equal to that in 2-pyridone[5] (1.39 Å) and in pyridine[6] (1.395 Å) while the C–N bond lengths (1.38 Å and 1.44 Å) are longer than those in 2-pyridone (1.34 Å and 1.40 Å) and in pyridine (1.340 Å). The nitrogen atom, N(1), is undoubtedly in a state of sp^2 hybridization as evidenced by the nearly planar configuration of the substituent atoms (C(2), C(9) and C(10), see Table 3).

Least-squares planes through various groups of atoms and the deviations of atoms from each plane are shown in Table 3. Each of the pyrindine ring and the two substituted phenyl groups is almost planar within experimental error. These substituted phenyl groups are twisted with respect to the plane of the pyrindine ring at angles of 77° and 82°, respectively. Each C(ring)–COO– group is planar and the terminal methyl carbon deviates slightly from the plane. The six carbomethoxy groups are also twisted with respect to the plane of the pyrindine ring in various degrees ranging from 28° to 79°.

In the NMR spectrum of the present compound, two signals at 6.7 τ (s. 3H) and 6.9 τ (s. 3H) which are assigned to the methyl protons of C(32) and C(52), appear at a higher field than would be expected for

5) B. R. Penfold, *Acta Crystallogr.*, **6**, 591 (1953).
6) B. Bak, L. Hansen, and J. R. Rastrup-Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).

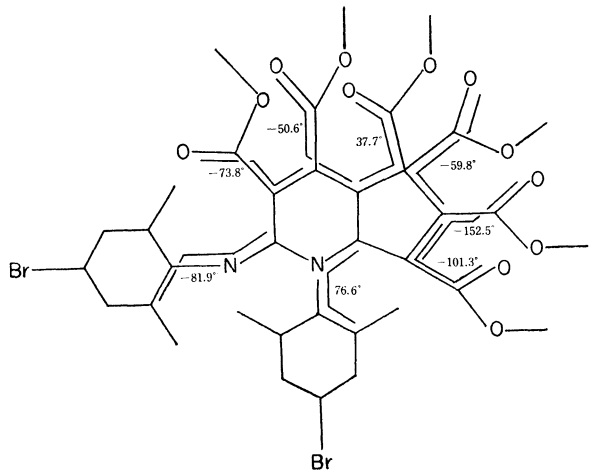


Fig. 4. Internal rotation angles about the bonds joining the pyrindine ring and the substituted groups.
Internal rotation angle A–B–C–D shown in Fig. 4 by bold line, is defined as the angle between the projections of A–B and C–D, when the projection is taken along the B–C bond. The positive angle is taken in the same sense as that of the turning direction of a right handed screw advancing along the B–C bond.

this kind of proton. The reason for this may be the effect of ring current of the proximate phenyl groups which are situated with their planes facing the methyl groups (see Fig. 1).

The crystal structure projected along the *b*-axis is shown in Fig. 5. Intermolecular short distances less than 3.6 Å are indicated in the Figure by dotted lines and are listed in Table 4. The molecules are denoted by Roman numerals and the subscript in parentheses indicates translations along the three edges of the unit cell. It is seen that the molecules lie along ($\bar{4}01$) plane and stack on top of the other mainly by the van der Waals force between the substituents of the phenyl group and carbomethoxy groups. The present molecule has so many bulky substituent groups of the pyrindine ring that there remains a wide space between the stacked molecules. The molecule of acetone is enclosed in the space as a solvent of crystallization and interacts with the surrounding adduct molecules by van der Waals force, the shortest distance being 3.55 Å found between O(56) I(000) and Br(28) III(000). Within ($\bar{4}01$) plane, the molecules are bound together through

Table 4. Intermolecular distances less than 3.6 Å

From molecule I	To atom	Of molecule	Translation	Distance
Br(18)	O(51)	II	010	3.11 Å
	C(45)	II	010	3.52
Br(28)	O(56)	III	000	3.55
O(30)	O(30)	III	0$\bar{1}$0	3.52
	C(36)	III	0$\bar{1}$0	3.44
O(35)	O(35)	III	0$\bar{1}\bar{1}$	3.46
	C(36)	III	0$\bar{1}\bar{1}$	3.40
O(38)	C(32)	III	0$\bar{1}\bar{1}$	3.39
O(42)	C(52)	II	000	3.45
O(46)	C(14)	II	000	3.45
	C(52)	II	00$\bar{1}$	3.40
O(47)	C(16)	I	00$\bar{1}$	3.58
O(50)	C(16)	I	00$\bar{1}$	3.55
C(17)	O(56)	I	000	3.56
C(22)	C(27)	III	000	3.51
C(24)	C(36)	III	0$\bar{1}$0	3.26
C(37)	C(26)	I	00$\bar{1}$	3.54
C(40)	O(34)	I	00$\bar{1}$	3.01
	O(42)	I	00$\bar{1}$	3.43
	C(4)	I	00$\bar{1}$	3.60
	C(33)	I	00$\bar{1}$	3.50

Molecule I at (x, y, z)
Molecule II at ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)
Molecule III at ($1-x$, $1-y$, $1-z$)
x, y and z are the fractional coordinates of atoms given in Table 1.

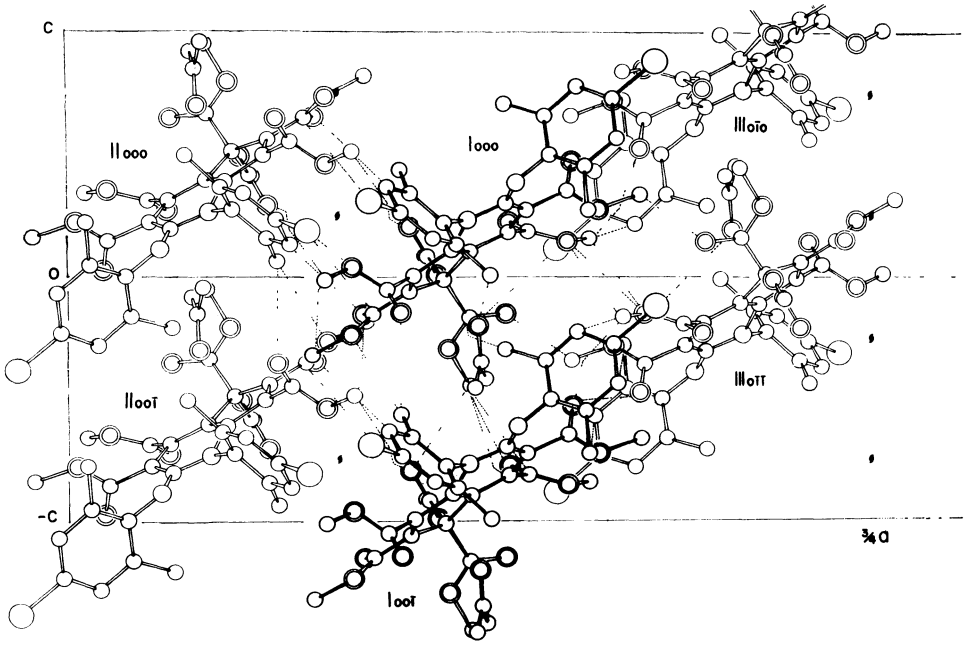


Fig. 5. Projection of the crystal structure along the *b* axis. Intermolecular short distances oi less than 3.6 Å are shown by dotted lines.

van der Waals interactions among the phenylimino groups and methyl groups. Remarkably short intermolecular distances to be noted are 3.01 Å found between C(40) I(000) and O(34) I(00$\bar{1}$) and 3.11 Å between Br(18) I(000) and O(51) II(010). Bolton[7] has already noted that very short distances are often found between a carbonyl oxygen atom and a carbon atom. In the present structure, the four atoms mentioned above belong to the ester carbon, carbonyl oxygen, *p*-substituent bromine of phenyl and ether oxygen atoms, respectively, indicating that they should be highly polarizable.

7) W. Bolton, *Nature*, **201**, 987 (1964).

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