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Studies on the Mechanism of the Voges-Proskauer Reaction
The Crystal Structure of Pigment A'

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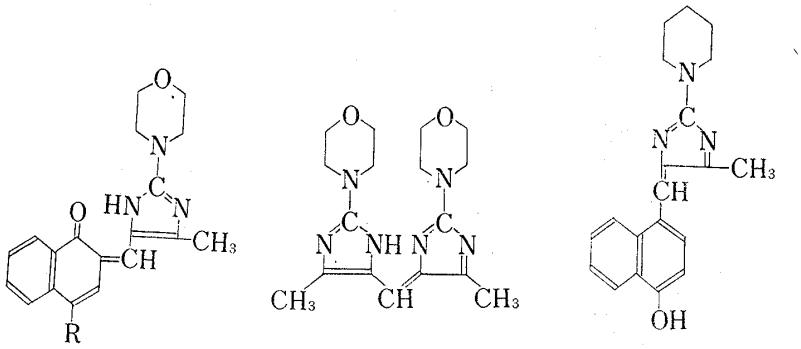
The structure of Pigment A obtained in the Voges-Proskauer reaction was determined as 2-(4-methyl-2-morpholino-1 H-5-imidazolylmethylidene)-1,2-dihydro-1-oxonaphthalene, by the X-ray analysis of Pigment A', a heavy atom derivative of Pigment A.

Pigment A' crystallizes in the triclinic system, space group $P\bar{1}$, with unit-cell dimensions $a=8.08$ Å, $b=14.63$ Å, $c=7.43$ Å, $\alpha=101.5°$, $\beta=97.2°$, $\gamma=92.1°$, $Z=2$.

The structure was solved by the heavy atom method and refined by the least-squares method to an R value of 0.065.

Previously the authors have reported on three kinds of Pigment A, B, and C prepared by the reaction of diacetyl and guanidines, in the presence of 1-naphthol (Barritt's method).

On the basis of chemical and spectroscopic data, the structures of Pigment A and C were presumed to be 2-(4-methyl-2-morpholino-1H-5-imidazolylmethylidene)-1,2-dihydro-1-oxonaphthalene[2] and 5-methyl-2-morpholino-4-(4-methyl-2-morpholino-1H-5-imidazolylmethylidene)-isoimidazol,[3] respectively, and Pigment B to be *para*-isomer[4] of Pigment A.



R=H, Pigment A
R=Br, Pigment A'

Pigment C

Pigment A

Fig. 1

In the present study, Pigment A', a bromine atom derivative of Pigment A, is prepared by the reaction of diacetyl, morpholinoamidine, and 4-bromo-1-naphthol in order to confirm the structure of Pigment A' by the X-ray diffraction method.

1) Location: *a) 1-18-1, Kamiyoga, Setagaya, Tokyo; b) 1-33, Yayoi-cho, Chiba; c) Hongo, Bunkyo-ku, Tokyo.*
2) T. Sakaguchi, K. Kijima, S. Tanabe, T. Inoue and I. Koyahara, *Yakugaku Zasshi*, **92**, 1195 (1972).
3) K. Kijima, I. Koyahara, S. Tanabe and T. Sakaguchi, *Yakugaku Zasshi*, **91**, 1150 (1971).
4) S. Tanabe, I. Koyahara, N. Takeuchi and T. Sakaguchi, *Chem. Pharm. Bull.* (Tokyo), **20**, 1026 (1972).

Experimental

Preparation of Pigment A′——To an aqueous solution (300 ml) of diacetyl (0.01 mole) and morpholinoamidine (0.01 mole), 4-bromo-1-naphthol (0.01 mole) dissolved in 100 ml 4% NaOH solution was added, and the mixture was stirred for 40 min at room temperature. The reaction mixture was neutralized with 2N HCl solution.

The crude crystals were obtained by filtration. Purification of the sample was made using alumina column chromatography (developing solvent, benzene: MeOH=19.5: 0.5) and a reddish violet fraction was separated which was further chromatographed over the silicagel column (developing solvent, benzene: AcOEt =5: 1).

Dark reddish brown flat crystals, mp 237° (decomp.) were recrystallized from an ether solution. $\lambda_{max}^{0.1NNaOH}$: 540 nm.

The molecular formula of Pigment A′ was established from the molecular ion (M^+) in high resolution mass spectrograph as $C_{19}H_{18}O_2N_3Br$. The mass spectrum indicated the peaks at *m/e* 401 (M^++2) (isotope peak), 399 (M^+), 199.5 (M^{++}).

The infrared (IR) spectrum of Pigment A′ showed the presence of a quinoid-carbonyl at 1620 cm^{-1} due to intramolecular hydrogen bonding between carbonyl oxygen and N-H, and also showed the absorption bands at 3300, 2800 (aromatic C=C and C-N streching vibration), 1105 (C-O-C vibration) and 760 (ring proton out of plane vibration) cm^{-1}.

The space group and the approximate lattice constants were determined from Weissenberg photographs. The structure factors and the accurate lattice constants were derived from the measurement using a Rigaku four circle X-ray diffractometer. The crystal data are shown in Table I.

Table I. Crystal Data

Pigment A′	Pigment A′
$C_{19}H_{18}O_2N_3Br$ mol. wt. 399	$\beta=97.2\pm0.1°$
Triclinic	$\gamma=92.1\pm0.1°$
$a=8.081\pm0.008$ Å	$U=852.5$ Å^3
$b=14.63\pm0.015$	$Z=2$
$c=7.434\pm0.007$	$Dx=1.554$ g·cm^{-3}
$\alpha=101.5\pm0.1°$	Space group P_1^-

All the intensity data for the independent reflections within the 2θ angle of 100° were collected with Ni filtered CuKα radiation by using the 2θ-ω scan method. Intensities for 1483 reflections were measured each of which has net intensity greater than three times of its standard deviation.

The number of reflections theoretically possible to observe within the same 2θ angle is 1766.

The size of the crystal specimen used for the intensity measurement was about $0.25\times0.20\times0.05$ mm and $\eta\theta$ absorption correction was applied for the intensity data. All the intensity data were then corrected for Lorentz and polarization factors and were put on an absolute scale by Wilson's method. It also gave a mean temperature factor of 4 Å^2. The statistical distribution of the intensities indicated a centrosymmetric space group.

Determination of the Structure——The structure was determined by the heavy atom method. The coordinates of the bromine atom were easily determined on a sharpened Patterson map and a Fourier synthesis phased by the bromine atom contributions revealed all the atoms on the map.

Refinement of the atomic parameters was carried out by the block-matrix least-squares method using the HBLS program.[5]

Four cycles with isotropic and further four cycles of calculations with anisotropic thermal parameters for each atom reduced the R value to 0.065. Unit weight was assigned for each reflection.

At the end of the refinement, a difference Fourier map was calculated which revealed all hydrogen atoms except for those belonging to the morpholine group, but no attempt has been made to refine the atomic parameters for hydrogen atoms.

The final atomic parameters and their estimated standard deviations are given in Table II, and the observed and calculated structure factors are listed in Table III.

5) Y. Okaya, & T. Ashida, HBLS IV, "The Universal Crystallographic Computing System (I)," Japanese Crystallographic Association, 1967, p. 65.

TABLE II. Final Atomic Parameters with Estimated Standard Deviations

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.7260(2)	0.8121(1)	0.7599(2)	0.0211(3)	0.0040(1)	0.0204(3)	0.0005(1)	0.0046(2)	−0.0006(1)
C(1)	0.7849(13)	0.5104(7)	0.4110(14)	0.0136(21)	0.0041(6)	0.0124(23)	0.0006(9)	0.0003(18)	−0.0002(10)
C(2)	0.7188(13)	0.5228(7)	0.5822(13)	0.0132(21)	0.0038(6)	0.0114(22)	0.0006(9)	0.0012(17)	0.0002(9)
C(3)	0.7028(13)	0.6166(7)	0.6790(13)	0.0157(22)	0.0029(5)	0.0135(23)	0.0004(9)	0.0016(18)	−0.0000(9)
C(4)	0.7515(13)	0.6919(7)	0.6173(15)	0 0141(22)	0.0039(6)	0.0172(26)	0.0004(9)	0.0002(19)	0.0006(10)
C(5)	0.8242(13)	0.6840(7)	0.4451(14)	0.0112(20)	0.0043(6)	0.0160(25)	−0.0004(9)	−0.0002(18)	0.0013(10)
C(6)	0.8747(14)	0.7612(8)	0.3748(15)	0.0171(24)	0.0046(7)	0.0190(28)	−0.0009(10)	0.0001(21)	0.0017(11)
C(7)	0.9407(14)	0.7470(8)	0.2072(16)	0.0152(23)	0.0055(7)	0.0213(29)	−0.0010(10)	−0.0014(21)	0.0031(12)
C(8)	0.9539(14)	0.6555(8)	0.1081(15)	0.0133(22)	0.0062(7)	0.0192(28)	0.0005(10)	0.0016(20)	0.0038(12)
C(9)	0.9021(13)	0.5785(7)	0.1722(14)	0.0140(21)	0.0050(6)	0.0144(24)	0.0000(9)	0.0028(18)	0.0019(10)
C(10)	0.8367(13)	0.5916(7)	0.3460(14)	0.0130(21)	0.0043(6)	0.0132(23)	0.0006(9)	0.0026(18)	0.0010(10)
C(11)	0.6610(12)	0.4506(6)	0.6703(14)	0.0117(20)	0.0031(6)	0.0150(24)	−0.0008(8)	−0.0015(17)	−0.0002(9)
C(12)	0.6613(13)	0.3575(7)	0.6240(14)	0.0133(21)	0.0041(6)	0.0142(24)	−0.0006(9)	0.0008(18)	0.0015(10)
C(13)	0.6064(13)	0.2909(7)	0.7291(14)	0.0126(21)	0.0039(6)	0.0182(26)	−0.0017(9)	0.0015(19)	0.0016(10)
C(14)	0.6919(13)	0.2147(7)	0.4855(15)	0.0148(22)	0.0034(6)	0.0199(27)	0.0004(9)	0.0031(20)	0.0016(10)
C(15)	0.5367(14)	0.3153(8)	0.9131(15)	0.0185(25)	0.0069(8)	0.0146(26)	−0.0004(11)	0.0074(21)	0.0031(12)
C(16)	0.7847(20)	0.1519(8)	0.1919(19)	0.0439(42)	0.0037(7)	0.0294(37)	−0.0006(13)	0.0197(33)	−0.0023(13)
C(17)	0.7668(30)	0.0768(10)	0.0516(24)	0.1067(80)	0.0038(9)	0.0433(53)	−0.0098(21)	0.0277(53)	−0.0012(17)
C(18)	0.6814(26)	−0.0240(9)	0.2452(23)	0.0742(62)	0.0041(8)	0.0426(50)	−0.0069(18)	0.0160(45)	0.0004(16)
C(19)	0.6829(24)	0.464 (8)	0.3899(21)	0.0668(54)	0.0022(7)	0.0403(44)	−0.0016(15)	0.0228(40)	0.0009(14)
N(1)	0.7141(10)	0.3201(5)	0.4668(12)	0.0145(18)	0.0035(5)	0.0195(22)	0.0005(7)	0.0047(16)	0.0007(8)
N(2)	0.6244(11)	0.2048(6)	0.6478(12)	0.0165(19)	0.0048(5)	0.0184(22)	0.0004(8)	0.0013(16)	0.0025(9)
N(3)	0.7282(12)	0.1396(6)	0.3678(12)	0.0221(21)	0.0030(5)	0.0228(23)	0.0009(8)	0.0083(18)	0.0009(8)
O(1)	0.8063(10)	0.4281(5)	0.3082(9)	0.0234(17)	0.0044(4)	0.0138(16)	0.0009(7)	0.0080(13)	−0.0003(7)
O(2)	0.7344(13)	−0.0135(6)	0.0800(12)	0.0402(26)	0.0060(6)	0.0295(24)	0.0007(10)	0.0141(20)	−0.0000(9)

TABLE III. Observed and

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
K,L=-14 0	4 42 -21	1 190 190	0 703-733	-3 452 467	1 371-339	-5 174 170	-2 161 117
1 108-120	5 306-314	2 123-124	2 430 400	-2 211 198	3 85 70	-4 54 5	-1 421-376
2 86 63	7 112 121	3 97 91	3 132-108	-1 540-527	4 117-109	-3 381-385	0 45 -57
K,L=-13 0	K,L= 2 0	4 104 88	4 162-150	0 132 144	K,L= 12 1	-1 495 482	1 587 578
1 291 271	0 438-516	K,L=-11 1	5 118 119	1 396 411	-4 110-100	0 128 83	2 185 215
2 60 13	1 87 87	-4 184 205	6 108 82	2 348-341	-3 38 68	1 288-289	3 372-398
3 139-134	2 357 366	-3 113 -90	7 115 -90	3 213-217	-2 108 85	2 288 300	4 128 115
K,L=-12 0	4 188-182	-2 191-194	K,L= -3 1	4 393 397	0 61 6	3 95 69	5 145 166
1 348 325	5 34 59	-1 400 405	-7 40 -12	6 159-148	1 59 -35	4 198-197	6 128-145
2 45 -34	6 190 204	0 211 217	-6 97 101	K,L= 4 1	2 62 44	6 110 97	K,L= 2 2
3 293-303	K,L= 3 0	1 256-243	-4 230-257	-7 94 108	3 153 161	K,L= -5 2	-7 80 101
4 131 133	0 172-212	2 151-154	-3 149 130	-6 83 -85	K,L= 13 1	-7 63 -63	-6 164 129
K,L=-11 0	1 249 282	3 239 227	-2 342 289	-5 102-101	-3 42 59	-6 118 111	-5 150-169
1 140 133	2 659 632	5 183-183	-1 416-417	-4 366 375	-2 146 122	-5 101 112	-4 82 -73
2 138-137	3 293-309	K,L=-10 1	0 255 248	-3 77 94	-1 197-186	-4 277-280	-3 511 503
3 68 -72	4 173-186	-5 182 189	1 379 350	-2 507-460	1 260 254	-3 44 10	-2 188-176
4 95 84	5 201 188	-4 91 -85	2 172 129	-1 249-252	K,L=-14 2	-2 834 817	-1 550-584
5 45 -26	6 106 120	-3 108 -99	3 224-212	0 438 464	-1 77 -89	-1 124-138	0 82 127
K,L=-10 0	7 73 -77	-2 161 143	4 160 181	2 445-437	0 82 96	0 659-667	1 378 352
1 313-302	K,L= 4 0	-1 153 131	5 213 214	3 122 122	1 130 105	1 176 185	2 355-331
2 135-128	0 181 197	0 284-286	6 105-109	4 325 320	2 83 -71	2 283 296	3 114-135
3 245 257	1 332 337	1 183-177	7 90 -96	5 88-106	K,L=-13 2	3 150-144	4 228 220
4 25 42	2 194-206	2 201 203	K,L= -2 1	6 98 -90	-3 108 90	4 206-194	5 51 49
5 153-169	3 169-160	4 129-131	-7 190 193	7 128 132	-2 213-208	5 146 143	6 205-212
6 35 17	4 192 181	K,L= -9 1	-5 338-328	K,L= 5 1	0 219 217	6 54 28	K,L= 3 2
K,L= -9 0	5 173 185	-5 43 37	-4 158 161	-6 267-265	2 202-197	7 71 -91	-7 170 174
1 184-168	6 292-289	-4 122-144	-3 594 610	-4 418 398	3 128-124	K,L= -4 2	-6 223-212
2 146 153	7 103-100	-3 43 -45	-2 96-119	-3 199-214	K,L=-12 2	-7 119 129	-5 165-181
3 207 204	K,L= 5 0	-2 264 267	-1 743-804	-2 718-691	-4 38 41	-6 182 157	-4 296 276
4 185-184	0 498 500	-1 165-148	0 857 954	-1 363 389	-2 93-102	-5 221-197	-3 50 48
6 149 158	1 101 81	0 283-284	1 809 784	0 496 498	-1 42 46	-4 115-117	-2 600-592
K,L= -8 0	2 494-518	1 118 122	2 706-782	1 227-221	1 368-346	-3 165 131	-1 70 68
1 132 130	3 92 87	2 273 293	3 254-222	2 178-171	2 57 -11	-2 75 -41	0 725 723
2 253 245	4 99 91	3 182-184	6 151-164	3 404 383	3 238 238	-1 150-194	2 395-363
4 104-102	5 174-177	4 105-116	K,L= -1 1	5 196-217	4 73 20	0 172-170	3 136 109
K,L= -7 0	7 98 106	5 176 161	-7 149 142	K,L= 6 1	K,L=-11 2	1 459 448	4 174 161
1 353 373	K,L= 6 0	K,L= -8 1	-6 102-110	-7 95 -89	-5 189 198	2 308-303	5 157-147
3 609-591	0 470 436	-6 138 154	-5 154-138	-5 203 206	-4 84 -88	3 349-376	K,L= 4 2
4 56 49	1 617-630	-5 164-170	-4 240 235	-3 266-273	-3 221-239	4 131 142	-6 148-130
5 275 264	2 291-302	-4 109-105	-3 102 123	-2 216 221	-2 254 245	5 67 111	-5 71 51
6 99 -76	3 420 425	-3 344 341	-2 647-627	-1 581 562	-1 99 87	6 71 -90	-4 324 323
7 88 -85	4 198 197	-2 32 1	-1 356-335	0 234-213	0 274-258	K,L= -3 2	-3 91 -72
K,L= -6 0	5 209-217	-1 488-454	0 714 749	1 356-347	1 88 109	-5 321-323	-2 280-249
1 192 181	K,L= 7 0	0 151 120	1 123 78	2 266 240	2 266 278	-4 105 108	-1 132 174
2 509-499	0 36 -1	1 402 439	219051883	4 192-194	4 193-192	-3 456 423	0 337 331
3 35 -38	1 246-239	2 212-224	3 74 66	6 131 130	5 98 69	-2 409-415	1 384-396
4 462 465	3 214 223	3 197-220	4 900 890	K,L= 7 1	K,L=-10 2	-1 427-474	2 201-182
5 84 64	4 96-113	4 121 136	5 218-203	-7 129-113	-4 128-123	0 418 385	3 183 191
6 230-235	5 116-100	5 253 256	6 87 -96	-6 159 174	-3 134 119	1 361 374	5 132-127
K,L= -5 0	K,L= 8 0	6 94 -74	7 151 171	-4 214-217	-2 158 160	2 315-316	6 72 95
1 106-108	0 476-471	K,L= -7 1	K,L= 0 1	-3 192 180	-1 121-120	3 240-276	K,L= 5 2
2 265-263	1 97 111	-5 155-159	-8 82 89	-2 220 235	0 204-204	4 442 457	-7 150-158
3 311 336	2 378 384	-3 270 290	-7 120-140	-1 432-421	1 235 231	5 90 94	-5 217 210
4 68 48	3 85 -99	-2 204-218	-6 238-253	0 312-287	2 118 97	6 52 -54	-4 250-257
5 197-194	4 191-194	-1 444-420	-5 133 151	1 120 125	3 210-216	K,L= -2 2	-3 247-260
7 58 67	5 138 142	0 352 391	-4 320 327	2 287 315	4 79 -71	-6 118-128	-2 389 378
K,L= -4 0	K,L= 9 0	1 414 447	-3 443-429	3 155-166	5 83 97	-4 255 279	-1 98 94
1 493-488	0 81 -55	2 374-362	-2 250-257	4 211-224	K,L= -9 2	-3 120 -98	0 621-589
2 104 118	1 220 218	3 86 -79	-1 297 355	5 141 158	-6 94 89	-2 305-267	1 106 -86
3 267 329	2 103 112	4 296 286	0 624-661	6 57 74	-5 169-180	-1 445 393	2 383 386
4 229-226	3 243-243	5 156-157	1 54 -66	K,L= 8 1	-4 150-157	0 532 507	3 131 114
5 199-217	5 46 66	6 175-183	2 4241315	-5 109-110	-3 270 246	1 256-248	4 214-214
6 197 213	K,L= 10 0	7 54 54	3 223 182	-4 179-197	-2 121 94	2 42 -64	5 83 89
7 77 91	0 268 249	K,L= -6 1	4 197-173	-3 138 143	-1 397-386	3 281 272	6 103 112
K,L= -3 0	1 91 85	-6 171-155	5 90 -92	-2 143 175	0 84 90	4 278 272	K,L= 6 2
1 318-263	2 349-339	-5 42 -46	6 73 79	-1 285-290	1 342 331	5 169-149	-7 98 -93
2 355 366	3 149-171	-4 170 174	7 38 55	0 40 -43	2 171-167	6 294-308	-6 166 166
3 90 118	4 215 206	-3 52 25	K,L= 1 1	1 513 294	3 235-253	7 79 68	-5 76 96
4 227-230	5 58 73	-2 127 104	-7 151-169	2 158-158	4 193 200	K,L= -1 2	-4 252-256
5 73 50	K,L= 11 0	-1 78 104	-6 165 170	3 330-118	5 60 66	-7 99-114	-3 121 123
6 97 112	0 83 78	0 178 185	-5 306 301	4 113 110	6 108-105	-6 155-186	-2 338 348
7 84 -81	1 292-274	1 319-317	-4 271-271	5 126 124	K,L= -8 2	-5 382 395	-1 360-364
K,L= -2 0	2 102 -86	2 173-184	-3 206-178	K,L= 9 1	-6 90 -71	-4 260 290	0 205-210
1 63 70	3 410 398	3 178 181	-2 531 489	-5 168-174	-4 196 192	-3 448-458	1 633 598
2 354-329	4 89 80	5 153-181	-1 145 205	-4 159 158	-3 94 92	-2 389-326	2 130 153
3 363-344	K,L= 12 0	6 96 90	0 127 177	-3 201 213	-2 80-100	-1 623 594	3 290-304
4 50 -38	1 61 -50	7 133 131	1 58 14	-2 253-256	-1 42 -54	0 162-122	5 112 106
5 198 204	2 141 135	K,L= -5 1	2 285 267	-1 98-104	0 104 97	1 562-531	6 46 36
7 129-133	K,L= 13 0	-7 75 -70	3 118-137	0 328 312	1 69 67	2 391 400	K,L= 7 2
K,L= -1 0	0 147-121	-6 97 -99	4 507-506	1 114 104	2 219-209	3 198 180	-6 84 89
1 92 84	1 311-285	-5 252 259	5 118 135	2 281-252	3 53 -35	4 888-864	-5 280-283
2 333 306	2 138 132	-4 335 307	6 134 124	3 50 51	4 150 139	5 112 -98	-3 306 288
3 75 -51	K,L= 14 0	-3 431-434	7 113-112	4 277 272	6 97 -94	6 358 362	-2 40 42
4 352 364	0 66 -45	-2 136-145	K,L= 2 1	K,L= 10 1	K,L= -7 2	K,L= 0 2	-1 203-222
5 138 138	K,L=-14 1	-1 300 343	-6 95 75	-4 204 221	-6 153-151	-7 37 -22	0 39 -3
6 225-233	-1 62 -37	0 314-302	-4 270-264	-3 99-101	-5 74 41	-6 76 46	1 124 145
7 39 14	0 139-114	1 213-220	-3 146 146	-2 242-235	-4 200 206	-5 63 61	2 140-119
K,L= 0 0	1 245 220	2 152 143	-2 274 318	-1 316 297	-3 123-120	-4 388-363	3 204-203
1 155-147	2 99 87	3 226 225	-1 555-542	0 213 200	-2 250-273	-3 307-280	4 191 189
214331479	K,L=-13 1	4 188-181	0 510-536	1 417-388	-1 202 233	-2 602 571	5 60 46
3 411 413	-3 155 134	6 136 112	1 570 522	2 58 -50	0 150-135	-1 59 -51	K,L= 8 2
4 335 361	-1 127 -96	7 83 26	2 86 -72	3 266 254	1 305-321	0 651-612	-5 123-120
5 258-270	0 57 -19	K,L= -4 1	3 233-274	4 82 -66	2 124 127	1 102 91	-4 78 71
6 100-110	1 75 -85	-7 121-130	4 109-107	K,L= 11 1	3 325 329	4 166 133	-3 166 187
7 112 122	3 65 -54	-6 152 156	5 159 177	-5 149 148	4 59 -46	5 93 104	-2 344-340
K,L= 1 0	K,L=-12 1	-5 79 91	7 98-103	-4 87 86	5 146-144	6 153 170	-1 157-154
0 105-152	-4 124 132	-4 510-522	K,L= 3 1	-3 264-275	6 97 76	K,L= 1 2	0 427 408
1 499-512	-2 215-217	-3 81 -81	-6 100 95	-2 144-177	K,L= -6 2	-6 158 162	1 64 -49
2 731-726	-1 281-268	-2 485 477	-5 258-279	-1 468 344	-7 78 -81	-5 224-243	2 337-338
3 426 456	0 229 235	-1 142 151	-4 158-162	0 53 68	-6 62 -67	-3 417 412	3 86 92

Calculated Structure Factors

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
4 134 139	4 96 -95	1 328 352	-2 200 206	-7 43 -47	-5 233-239	-4 77 32	-4 81 81
K,L= 9 2	5 39 45	2 244-241	-1 146-132	-6 63 -79	-4 271 261	-3 154-135	-3 144-168
-6 228-219	6 58 79	3 73 -74	0 160-142	-5 239 227	-3 371 381	-2 232 238	-2 106 -96
-5 65 72	K,L= -6 3	4 229 231	1 230 235	-4 167-171	-2 262-284	-1 198 208	0 102 -94
-4 213 208	-6 106 98	6 70 -78	2 146 160	-3 207-214	-1 388-405	0 310-306	K,L= 7 5
-3 136-133	-4 258-264	K,L= 2 3	K,L= 11 3	-2 134 129	0 195 170	1 53 44	-4 168-167
-2 180-182	-3 65 81	-7 91 99	-3 150 136	-1 66 93	1 164 157	2 199 196	-3 152-136
-1 214 208	-2 289 329	-6 136-135	-1 115 -98	0 132-141	2 237-226	4 45 -80	-2 172 175
0 200 185	-1 226-231	-5 152-148	0 39 12	1 145-149	4 117 109	K,L= -3 5	-1 164 155
1 295-267	0 509-511	-4 370 351	1 62 45	2 108 88	K,L= 6 4	-6 200 195	0 212-208
2 86 -96	1 343 296	-3 125 133	K,L=-13 4	3 47 -6	-3 184-174	-4 263-279	2 213 221
3 312 303	2 454 440	-2 451-398	-2 154 124	4 141-152	-2 213-218	-3 212 200	K,L= 8 5
K,L= 10 2	3 266-262	-1 217 158	-1 81 73	6 71 73	-1 291 286	-2 187 181	-2 78 64
-5 104 116	4 40 -57	0 311 322	0 84 -75	K,L= -2 4	0 133 131	-1 179-192	-1 209-225
-3 227-215	5 106 139	1 238-230	K,L=-12 4	-6 159 150	1 170-170	0 262-260	0 81 83
-2 47 75	K,L= -5 3	2 372-366	-3 149 152	-5 39 -61	2 93 -75	1 260 257	K,L=-10 6
-1 230 213	-7 49 67	3 167 172	-2 150 143	-4 266-257	3 95 81	2 165 171	-2 83 98
1 155-129	-6 287 307	4 109 109	-1 258-283	-3 123 110	4 75 93	3 261-270	-1 56 56
3 74 79	-5 197-208	5 86 -99	0 49 -39	-2 490 463	K,L= 7 4	4 90-107	0 112-112
4 90 -34	-4 201-196	K,L= 3 3	1 210 223	-1 572-493	-4 115 102	5 79 104	K,L= -9 6
K,L= 11 2	-3 398 406	-7 118-101	2 76 -76	0 411-409	-2 55 -56	K,L= -2 5	-3 97 131
-4 153-138	-1 235-248	-6 97 -95	3 120-131	1 416 412	-1 181 172	-5 108-112	K,L= -8 6
-3 42 55	0 366 365	-5 237 227	K,L=-11 4	2 341 332	0 108 119	-4 86 -81	-3 96 109
-2 219 182	1 183 169	-4 46 42	-4 93 84	3 228-227	1 261-263	-3 172 172	-2 123-108
-1 185-215	2 165-156	-3 237-243	-3 61 38	4 56 -85	2 101 97	-2 42 47	-1 285-280
0 220-209	3 188-178	-2 86-101	-2 126-139	5 164 192	3 161 167	-1 240-220	0 85 108
1 250 252	4 158 153	-1 184 172	-1 92-101	K,L= -1 4	K,L= 8 4	0 81 88	1 110 108
2 65 48	5 125 143	0 76 -97	0 88 94	-6 149 158	-4 102-107	2 165-157	K,L= -7 6
3 167-169	6 129-126	1 104-127	1 49 72	-5 169-177	-3 226-239	4 179 185	-4 117 112
K,L= 12 2	K,L= -4 3	2 155 167	2 66 -68	-4 201-199	-2 282 282	K,L= -1 5	-3 193-199
-3 79 66	-7 121 132	3 207 191	K,L=-10 4	-3 214 199	-1 64 76	-5 143-136	-2 92 -87
-2 78 72	-6 145-147	4 39 -55	-5 82 -60	-2 218 187	0 269-258	-4 184 153	-1 261 279
-1 126-103	-5 52 -43	5 96 -93	-4 82 78	-1 164-169	2 135 141	-3 71 61	0 208 209
1 203 179	-4 132 147	6 60 57	-3 68 66	0 132 108	K,L= 9 4	-2 300-300	1 67 -82
K,L=-14 3	-3 174 192	K,L= 4 3	-2 177-165	1 437 435	-4 89 -77	-1 106-108	2 122-118
0 132 121	-2 330-305	-7 183-169	-1 109 87	2 266-253	-3 74 62	0 318 320	3 96 109
K,L=-13 3	-1 265-266	-6 64 71	0 223 216	3 203-206	-1 85 -75	2 102-104	K,L= -6 6
-3 92 -69	0 357 370	-5 243 238	1 107 -99	4 147 149	0 82 -99	3 163 178	-4 95 63
-1 113 97	1 171 149	-4 134-138	2 141-147	5 48 53	1 177 154	5 76 -71	-2 80 87
0 74 -62	2 377-389	-3 250-245	3 117 128	K,L= 0 4	K,L= 10 4	K,L= 0 5	-1 155 167
1 53 -41	4 97 85	-2 518 503	K,L= -9 4	-7 145 138	-2 115-101	-6 194-192	0 255-280
2 79 75	6 112-130	-1 161 156	-4 46 29	-6 51 -72	-1 214-202	-5 97 92	1 110-113
3 156 147	K,L= -3 3	0 558-533	-3 41 -21	-5 157-162	0 131 125	-4 99 84	2 119 141
K,L=-12 3	-6 220-220	1 34 22	0 63 -76	-4 211 214	K,L=-12 5	-3 98 -96	3 40 -13
-4 57 -49	-4 277 273	2 500 506	1 118-110	-3 318 308	-2 121 -97	-2 60 -63	K,L= -5 6
-3 198-191	-3 256-259	3 132-145	K,L= -8 4	-2 261-294	0 153 159	-1 213 214	-5 47 59
-2 129 119	-2 346-338	4 276-296	-4 204-223	-1 82 -68	K,L=-11 5	0 89 77	-4 134-170
-1 190 172	-1 373 349	6 99 99	-3 73 -60	0 53 60	0 44 23	1 84 -96	0 97 -93
0 248-252	0 178 145	K,L= 5 3	-2 315 341	1 77 -78	2 61 -59	2 152-135	1 66 -80
1 74 -71	1 478-482	-6 235 234	-1 46 41	2 165-132	K,L=-10 5	3 94 92	2 184 181
2 204 213	2 96-116	-5 52 -57	0 217-240	4 128 123	-4 77 -31	K,L= 1 5	K,L= -4 6
3 147-160	3 303 314	-4 274-288	2 264 253	5 46 -34	-3 111-112	-5 225 240	-4 168-166
4 139-150	5 214-215	-3 114 89	K,L= -7 4	6 94 -90	-2 95 79	-4 73 -4	-2 255 251
K,L=-11 3	K,L= -2 3	-2 155 169	-6 165 168	K,L= 1 4	-1 84 102	-3 297-266	-1 173-176
-4 191-199	-7 148-149	-1 268-288	-5 199 193	-6 87 -77	0 98-137	-2 121 114	1 195 209
-3 186 198	-5 174 168	0 201-207	-4 201-225	-4 149 162	2 104 127	-1 220 215	3 79 -83
-2 116 105	-4 157 167	1 309 341	-2 237 279	-3 84 -71	K,L= -9 5	0 200-194	K,L= -3 6
-1 226-231	-3 393-387	3 346-351	-1 180-197	-2 325-307	-4 151-170	1 196-182	-5 143-123
1 166 170	-2 165-143	5 200 219	0 201-251	-1 36 22	-3 129-120	2 232 231	-4 45 32
3 95 -98	-1 437 449	K,L= 6 3	1 257 267	0 339 347	-2 197 251	4 117-111	-3 149 120
K,L=-10 3	0 125 118	-6 134-147	2 151 130	1 259-243	-1 45 47	K,L= 2 5	-2 84 -83
-5 44 -51	1 259-249	-5 335-352	3 247-232	2 90 -74	0 254-281	-6 93 110	-1 62 -44
-3 196 212	2 246 248	-3 461 479	4 171-160	3 252 252	2 134 153	-5 67 -80	0 69 60
-1 186-192	3 205 203	-2 118-102	5 136 133	5 121-122	K,L= -8 5	-4 125-106	1 109 91
1 204 188	4 166-171	-1 337-312	K,L= -6 4	K,L= 2 4	-4 76-104	-3 121 119	2 124-133
2 138-139	6 293 301	0 195 176	-6 47 56	-7 191-191	-3 122-122	-2 238 228	K,L= -2 6
3 115 -98	K,L= -1 3	1 151 137	-5 228-232	-5 275 259	-2 132 136	-1 181-182	-5 67 -36
4 125 123	-7 61 -54	2 138-130	-4 236-255	-4 44 25	1 139 133	0 173-185	-4 82 87
5 48 39	-6 153 152	4 147 140	-3 166 165	-3 390-362	2 64 65	1 131 148	-3 40 30
K,L= -9 3	-4 286-273	5 39 23	-2 88 101	-2 112 100	3 123-125	2 134 131	-2 159-145
-4 171 192	-3 418 390	K,L= 7 3	-1 296-311	-1 321 324	K,L= -7 5	3 100 -97	-1 57 41
-2 318-321	-2 459 474	-6 39 -34	0 90 83	0 154-163	-5 223-220	4 90 -95	0 206 200
-1 70 31	-1 200-178	-5 48 70	1 181 164	1 145-134	-4 93 70	K,L= 3 5	1 43 -70
0 233 233	0 637-678	-4 205 209	2 291-289	2 171 173	-3 336 355	-6 193 210	2 142-131
1 151-148	1 246 265	-3 41 -24	3 68 -49	3 55 52	-1 109-113	-5 203-196	K,L= -1 6
2 41 -62	2 323 312	-2 139-117	4 191 210	4 175-202	0 41 56	-4 237-248	-5 149 147
3 115 131	3 269-274	0 305 269	K,L= -5 4	K,L= 3 4	1 98 88	-3 371 375	-4 207 197
4 66 59	5 129 131	1 50 -2	-6 220-209	-5 124 117	2 129-138	-2 91 82	-3 210-201
5 68 -94	6 210-213	2 289-284	-5 114-114	-4 197-188	4 138 133	-1 395-418	-2 52 -37
K,L= -8 3	K,L= 0 3	3 86 83	-4 410 413	-3 74 -77	K,L= -6 5	0 84 -99	-1 138 136
-6 125-126	-7 74 54	4 160 165	-3 48 -29	-2 222 203	-5 164 151	1 295 299	0 38 -75
-4 152 177	-6 216 216	K,L= 8 3	-2 300-294	-1 80 50	-4 199 186	2 94 -84	1 175-166
-3 68 -56	-5 48 -67	-5 61 -57	-1 106 109	0 380-382	-3 91 -90	3 155-160	2 63 72
-2 92-109	-4 290-306	-4 207 227	0 260 290	2 306 310	-2 416-441	4 79 118	K,L= 0 6
-1 194 187	-3 376 384	-3 179-190	2 110-121	3 73 -78	-1 60 58	K,L= 4 5	-5 80 87
0 165 158	-2 110 -88	-2 216-221	3 50 41	4 174-180	0 253 271	-3 124 151	-4 163-169
1 176-206	-1 828-748	-1 306 296	4 127 147	5 119 131	1 190-199	-2 202-202	-3 135-145
3 174 202	0 177 185	1 257-245	K,L= -4 4	K,L= 4 4	2 131-140	-1 166-165	-2 91 107
4 111-130	1 416 406	3 140 128	-6 58 47	-6 117 127	3 103 98	0 356 354	-1 133 139
5 138-144	2 154-150	K,L= 9 3	-5 112 124	-5 223-227	K,L= -5 5	1 128 142	0 151-160
6 59 71	3 275-303	-5 145 165	-4 127 116	-4 191-176	-6 126-126	2 130-142	1 48 -40
K,L= -7 3	5 165 177	-4 174-182	-2 253-221	-3 336 334	-5 47 57	K,L= 5 5	2 156 154
-5 97 84	K,L= 1 3	-3 149-144	-1 244 277	-2 256 257	-4 69 -75	-4 83 87	K,L= 1 6
-4 108-106	-7 128 144	-2 166 147	0 108 118	-1 317-310	-3 254-256	-3 86-103	-4 195-183
-3 146-135	-6 49 -54	-1 196 179	1 355-328	1 275 289	-2 141 167	-2 137 137	-3 180 175
-2 154 141	-5 271-285	0 181-198	2 67 18	2 63 -57	-1 51 87	-1 259 255	-2 214 197
-1 243 238	-3 165 177	1 103 -94	3 257 261	3 196-203	1 99 -99	0 47 -1	-1 225-236
0 249-268	-2 78 64	2 157 168	4 100 -98	4 119 124	3 152 153	1 307-316	0 135-137
1 216-202	-1 363-342	K,L= 10 3	5 164-141	5 104 108	5 90 -79	3 145 161	1 218 209
2 42 33	0 290 286	-4 138-139	K,L= -3 4	K,L= 5 4	K,L= -4 5	K,L= 6 5	2 66 74
3 138-143	K,L= 3 6	K,L= 4 6	K,L= 5 6	K,L= -5 7	-1 94 -73	-1 172 179	-1 135-139
K,L= 2 6	-4 179 174	-4 62 76	-3 166-164	-1 45 -40	0 163 157	1 94 -97	0 120-116
-4 134-138	-2 153-156	-3 117-120	-1 120 127	0 133-104	K,L= -3 7	K,L= -1 7	K,L= 1 7
-3 163 141	-1 68 68	-2 89 -91	0 83 66	1 62 63	-2 105-107	-2 254 246	-1 52 -39
-2 203 198	0 120 108	-1 161 170	K,L= -6 7	K,L= -4 7	K,L= -2 7	0 126-137	
-1 226-231	1 72 -77	0 117-105	-2 144 163	-3 136 122	-3 164-167	K,L= 0 7	
1 205 219	2 213-220	1 184-201	-1 51 44	-2 104-110	-2 93 -73	-2 88 68	

Discussion of the Structure

Molecular Structure

The result of the present X-ray structure determination fully confirms the previously proposed chemical structure. As shown in Fig. 2, the molecule consists of a bromonaphthol group, a methylimidazole group which links to bromonaphthol through a methylidyne bridge, and a morpholine group.

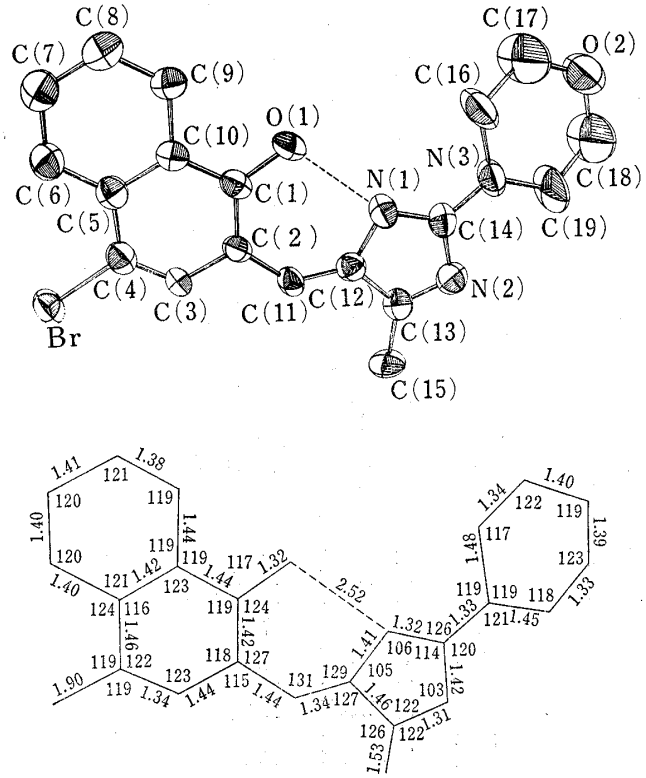


Fig. 2. Perspective drawing of the Molecular Structure viewed along the *a* Axis

The ellipsoid covers the area of finding the center of the atom with 50% probability. The Figure was drawn by ORTEP program by Johnson.[6]

The bond lengths and angles are given in Table IV. The values are in general agreement with the reported values for each component compound except for those found in the morpholine group. A strong intramolecular hydrogen bond (2.52Å) is formed between the imidazole nitrogen atom N (1) and the naphthol hydroxyl group O (1) H.

It is clearly seen that the cyclic group formed by the intramolecular hydrogen bond, O(1), C(1), C(2), C(11), C(12), N(1), is strongly strained, because O(1) and N(1) cannot be situated close enough to form a regular hexagon. Thus the bond angles, O(1)-C(1)-C(2) (124°), C(1)-C(2)-C(11) (127°), C(2)-C(11)-C(12) (131°) and C(11)-C(12)-N(1) (129°), are all significantly larger than the usual values.

The molecule is, as a whole, roughly planar. The mean plane is calculated by the leastsquares method for each part of the molecule and deviations of atoms from the plane are listed in Table V.

The interplanar angle between the A plane (naphthalene ring) and the B plane (imidazole ring) is 3.5° and that between B and C (formed by the four carbon atoms of morpholine) is 13.5°.

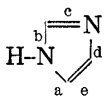
The planarity of the molecule suggests the extension of the conjugated system to the different part of the molecule.

Several canonical forms can be considered which account for the observed bond lengths.

Fig. 3 shows the two representative forms having different configuration of the hydrogen atom involved in the intramolecular hydrogen bond. To find the location of the hydrogen atom, a difference Fourier map was calculated. It showed a low and diffused single peak, about 0.3 $e\text{Å}^{-3}$ in height, lying just equi-distant from O(1) and N(1). In view of the difficulty in finding accurate positions for hydrogen atoms, especially when the hydrogen atom holds less electrons near its nucleus as commonly observed for the one involved in strong hydrogen bonds, it cannot be said, in the present case, to which atom the hydrogen atom is covalently bonded.

6) C.K. Johnson, (1965). ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Table IV. Bond Lengths and Angles

Imidazole		Present compound	Imidazol at-150°C	L-Histidine	L-Histidine HCl	DL-Histidine HCl $2H_2O$
	a	1.407 Å	1.369 Å	1.374 Å	1.386 Å	1.403 Å
	b	1.322	1.349	1.339	1.319	1.306
	c	1.416	1.326	1.327	1.314	1.331
	d	1.305	1.378	1.382	1.359	1.381
	e	1.455	1.358	1.361	1.358	1.355
	σ	±0.015	±0.005	±0.003	±0.03	±0.01
	ab	105.7°	107.2°	106.9°	108.5°	108.6°
	bc	114.4	111.3	112.2	108.7	108.3
	cd	103.5	105.4	104.9	109.6	110.5
	de	111.8	109.8	109.6	106.9	105.1
	ea	104.7	106.3	106.4	106.2	107.5
	σ	±0.8	±0.3	±0.2	±0.4	±0.6
State of protonation reference			N_1H 7)	N_1H 8)	N_1H, N_2H 9)	N_1H, N_2H 10)

Morpholine group		Present compound	Morpholinium complex
	a	1.48 Å	1.474 Å
	b	1.34	1.494
	c	1.40	1.415
	d	1.39	1.413
	e	1.33	1.500
	f	1.45	1.484
	σ	±0.02	±0.004
	ab	117.1	109.8
	bc	121.8	111.4
	cd	118.9	110.2
	de	118.2	110.9
	ef	118.2	109.5
	σ	±1	±0.2
Reference			11)

The bond lengths and angles in the morpholine groups are unusual. The two C-C bond C(16)-(17) and C(18)-C(19) are significantly shorter than those reported for the C-C single bonds.

The conformation of the ring may be described as a chair form, but as is clearly seen in Table V, N(3) is not so much deviated as O(2) from the mean plane formed by the four carbon atoms.

Furthermore, the N(3) atom takes almost completely planar configuration as is evidenced by the fact that the sum of the three valency angles subtended at N(3) amounts to 359°.

These observations together with the fact that the lengths of the C(14)-N(3), C(16)-N(3) and C(19)-N(3) bonds are remarkably shorter than that of the normal C-N single bond, may indicate that the resonance structure is extended to the morpholine group.

However, as seen in Fig. 2, the thermal vibration of C(17) and C(18) are so large and the axes of maximum vibrations are oriented nearly perpendicular to the molecular plane that the apparent contraction of the bond lengths may take place to some extent by the anisotropy of these violent thermal motions.

7) S. Martinez-Carrera, *Acta Cryst.*, **20**, 783 (1966).
8) J.J. Madden, E.L.Mc Gandy and N.C. Seeman, *Acta Cryst.*, **B28**, 2377 (1972).
9) J. Donohue and A. Caron, *Acta Cryst.*, **17**, 1178 (1964).
10) I. Bennett, A.G.H. Davidson, M.M. Harding and I. Morelle, *Acta Cryst.*, **B26**, 1722 (1970).
11) T. Sundaresan and S.C. Wallwork, *Acta Cryst.*, **B28**, 491 (1972).

TABLE V. Deviations of Atoms from the Least-squares Planes

Plane forming atoms and distance from the plane		Distance from the plane		Coefficients			
Naphthalene ring							
C (1)	0.002 Å	Br	−0.023 Å	*A*	0.864	*L*	0.920
C (2)	0.012	O (1)	0.024	*B*	−0.142	*M*	−0.005
C (3)	−0.013	C (11)	0.016	*C*	0.391	*N*	0.391
C (4)	−0.009	C (12)	0.078	*D*	5.605	*D*	5.605
C (5)	0.014						
C (6)	0.001						
C (7)	0.004						
C (8)	−0.001						
C (9)	−0.016						
C (10)	0.006						
Imidazol ring							
C (12)	0.003	C (11)	0.017	*A*	0.868	*L*	0.923
C (13)	−0.002	C (15)	0.000	*B*	−0.085	*M*	0.052
C (14)	0.002	N (3)	0.016	*C*	0.381	*N*	0.381
N (1)	−0.003			*D*	5.957	*D*	5.957
N (2)	0.000						
Morpholine ring							
C (16)	0.024	O (2)	0.133	*A*	0.930	*L*	0.964
C (17)	−0.025	N (3)	−0.087	*B*	−0.271	*M*	−0.172
C (18)	0.025	C (14)	−0.480	*C*	0.203	*N*	0.203
C (19)	−0.024			*D*	5.563	*D*	5.563

The planes are expressed by the equation, $AX+BY+CZ=D$, where X, Y, Z and D are in Å units taken parallel to the a, b and c axes.

An alternative expression refered to the Cartesian axes are, $LX'+MY'+NZ'=D$, where X', Y' and Z' are in Å units measured parallel to the axes, $Z' \parallel c$, X' in ac plane and $Y' \perp$ to X' and Z'.

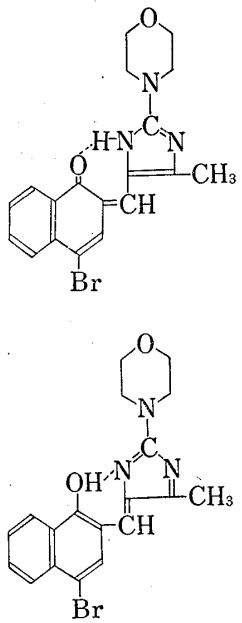


Fig. 3. Two Representative Canonical Forms

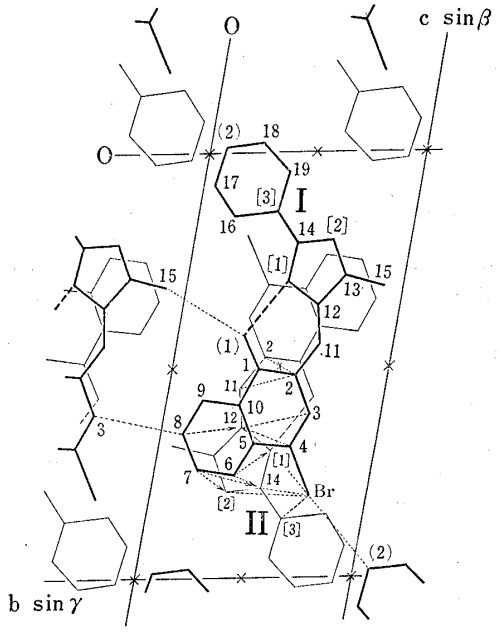


Fig. 4. Projection of Crystal Structure along the a Axis

Each × indicates a center of symmetry.

The numbers in ( ) indicate those for oxygen atoms and in [ ] indicate those for nitrogen atoms. Intramolecular hydrogen bonds are shown by broken lines and intermolecular short contacts are shown by dotted lines.

Crystal Structure

The projection of the crystal structure along the a axis is shown in Fig. 4. In this Figure, intermolecular short contacts less than 3.6 Å are shown by dotted lines.

In case of the contacts involving the bromine atom, the limit is extended to involve those less than 4 Å.

The distances are also listed in Table VI in which the molecules are designated by the Roman numerals specifying the equivalent positions, followed by the subscript in parentheses denoting the translations along *a*, *b* and *c*. The equivalent positions are: I at *x*, *y*, *z* and II at 1-*x*, 1-*y*, 1-*z*.

TABLE VI. Intermolecular Short Contacts

From atom At I (000)	To atom	At	Distance
Br	C (14)	II (000)	3.597±0.009 Å
Br	N (1)	II (000)	3.896
Br	N (2)	II (000)	3.836
Br	N (3)	II (000)	3.802
Br	O (2)	I (011)	3.114
C (2)	C (2)	II (000)	3.583±0.015 Å
C (2)	C (11)	II (000)	3.467
C (3)	C (12)	II (000)	3.553
C (4)	C (12)	II (000)	3.557
C (6)	C (14)	II (100)	3.508
C (6)	N (1)	II (100)	3.600
C (7)	C (14)	II (100)	3.462
C (7)	N (2)	II (100)	3.543
C (8)	C (12)	II (100)	3.503
C (8)	C (3)	I (00$\bar{1}$)	3.487
O (1)	C (15)	I (00$\bar{1}$)	3.502

As seen in the Figure, the molecules are stacked along the a axis with *anti*-parallel arrangement. Close approaches of the stacked units are seen mostly between the bromonaphthol and imidazolylmethylidene groups. The latera close approaches of the molecules are seen between C(15) and O(1), C(3) and C(8), and Br and O(2). The morpholine groups do not participate in the stacking of the molecules. They are held in their position mainyl through the short contacts to the bromine atoms.

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