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The Crystal and Molecular Structure of *trans-p,p'*-Dibromoazobenzene

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The crystal structure of *trans-p,p'*-dibromoazobenzene, $Br{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}Br$ has been determined by three-dimensional Fourier and full matrix least-squares methods. The crystals are monoclinic, space group $P2_1/c$, $a = 4.01$, $b = 5.88$, $c = 24.69$ Å, $\beta = 92.6°$, with two molecules in the unit cell.

The centrosymmetric molecule is planar. Observed bond distances are: N=N 1.276, C–N 1.428, C–C (average) 1.390, C–Br 1.891 Å. Some observed angles: N=N–C 112.2°, N–C–C (*cis* relative to N=N) 125.6°, N–C–C (*trans* to N=N) 114.7°. $R = 0.074$ for 780 observed reflections.

The only previously reported crystal structure determinations of aromatic azocompounds that we are aware of are those of *trans*- and *cis*-azobenzene.[1,2] It was felt that additional information on this type of structure would be of value. Preliminary investigation of *trans-p,p'*-dibromoazobenzene indicated that a determination of the crystal structure would be an uncomplicated task; we, therefore, proceeded with a structure analysis based on complete three-dimensional intensity data.

EXPERIMENTAL

Crystals of *trans-p,p'*-dibromoazobenzene suitable for X-ray analysis were obtained in the form of orange red needles from a benzene solution. The crystals were studied at room temperature by oscillation and Weissenberg techniques, using Cu$K\alpha$ radiation. Integrated equi-inclination Weissenberg photographs of all layers accessible with rotation about the *a* axis and the *b* axis, respectively, were prepared by use of the multiple film technique. The intensities were measured with a microdensitometer. The usual Lorentz and polarization corrections were applied, but no correction was made for absorption or secondary extinction.

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Scale factors used to put the different layers on a common scale were obtained by averaging the ratios between F_o's derived from intensities measured on both a-axis and b-axis photographs respectively. For all F_o's found in both sets of data the average of the two values was used in all calculations. A total of 780 unique non-zero reflections was recorded.

DETERMINATION OF THE STRUCTURE

Oscillation and Weissenberg photographs indicated the crystals to be monoclinic. The systematically absent reflections were: $0k0$ with k odd and $h0l$ with l odd; the space group therefore is $P2_1/c$. The dimensions of the unit cell were found to be, $a = 4.01$, $b = 5.88$, $c = 24.69$ Å, $\beta = 92.6°$, with two molecules in the unit cell.

Initial x,z parameters for Br were derived from a $P(v,w)$ Patterson map. A subsequent Fourier synthesis calculated with the phases determined by the Br atom revealed the positions of all other atoms (not counting hydrogens, which at no stage were included in the calculations). The y parameters were determined in a similar way. The positional parameters together with individual isotropic temperature parameters (initially set at $B = 4$ Å^2) were then adjusted through a few cycles of full matrix least-squares refinement. The process seemed to converge with the R index at about 0.1. At this stage anisotropic temperature factors were introduced for all atoms, and the least-squares refinement was continued until the largest shift in any parameter was less than 1/25 of the corresponding estimated standard deviation. The value of the R index, calculated for all observed reflections was then 0.074. As a further check of the structure a difference Fourier synthesis was calculated with all atoms subtracted. The resulting electron density map showed no disturbing features. Regions with an electron density of about 0.5 e Å^{-3} could be found around the expected hydrogen positions, but the peaks were not well defined and it was not attempted to make use of them.

The final positional parameters and thermal parameters arrived at are listed in Tables 1 and 2, respectively. (For identification of the atoms see Fig. 1(*a*).)

Table 1. Final positional parameters and their e.s.d. (in parentheses). The e.s.d. apply to the least significant digits.

Atom	x	y	z
Br	0.9172(4)	0.5945(3)	0.7977(5)
N	0.4704(31)	−0.0338(18)	0.9757(4)
C_1	0.7825(30)	0.4019(23)	0.8540(5)
C_2	0.6258(34)	0.1957(24)	0.8408(5)
C_3	0.5227(33)	0.0611(22)	0.8831(5)
C_4	0.5874(33)	0.1236(21)	0.9368(5)
C_5	0.7450(34)	0.3353(22)	0.9489(5)
C_6	0.8424(34)	0.4681(22)	0.9074(5)

Table 2. Final anisotropic temperature parameters and their e.s.d. (in parentheses). The e.s.d. apply to the least significant digits.

Atom	$10^4 \times \beta_{11}$	$10^4 \times \beta_{22}$	$10^5 \times \beta_{33}$	$10^4 \times \beta_{12}$	$10^4 \times \beta_{13}$	$10^4 \times \beta_{23}$
Br	723(12)	329(5)	123(2)	− 51(14)	34(2)	32(2)
N	740(84)	191(31)	136(16)	− 85(84)	32(19)	7(11)
C_1	454(72)	283(38)	120(18)	115(107)	−13(18)	16(15)
C_2	645(89)	273(40)	118(19)	− 90(113)	− 6(20)	−20(14)
C_3	621(90)	264(43)	126(18)	−202(106)	− 3(20)	1(14)
C_4	603(85)	220(39)	125(19)	77(97)	− 9(20)	0(14)
C_5	612(89)	211(36)	121(19)	− 20(94)	9(20)	9(12)
C_6	581(89)	232(40)	149(21)	− 56(100)	−15(22)	12(14)

Table 3 is a listing of observed and calculated structure factors. The F_c's were calculated from the parameters given in Tables 1 and 2. Unobserved reflections, indicated by U, are included in the table with F_o corresponding to the minimum observable intensity.

The Fourier program used was one written by P. K. Gantzel and H. Hope and the least-squares program was ACA computer program No. 317 (UCLALS-1) written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood; both programs were adopted for use on the UNIVAC 1107 computer. The least-squares program minimizes the weighted sum of the squares of the quantity $(KF_o - GF_c)$ by a full matrix routine. Of the scale factors K and G, the latter is one of the adjustable parameters. Unobserved reflections were not used.

The weighting scheme of Hughes [3] was used with $4F_o(\text{min}) = 17$. The atomic form factors were those given by Hanson *et al.*[4] The isotropic tempera-

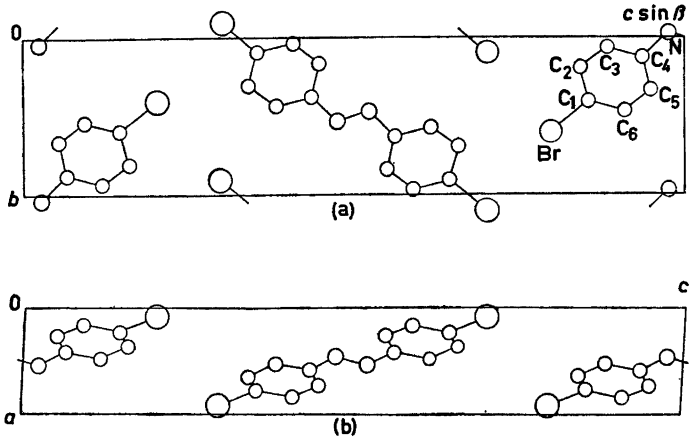

Fig. 1. (a) Projection of the structure along the *a* axis. The lettered atoms correspond to the parameters given in Table 1. (b) Projection of the structure along the *b* axis.

Table 3. Observed and calculated structure factors. The data are separated into groups having common h and k. The three columns in each group list values of l, $10F_o$ and $10F_o$, in that order.

H = 0, K = 0		
2	556	-566
4	43	66
6	298	290
8	772	-822
10	695	692
12	758	-790
14	399	373
16	57U	-33
18	330	-315
20	523	516
22	475	-471
24	170	150
26	63U	-35
28	202	-177
30	129	145

H = 0, K = 1		
1	138	-123
2	185	183
3	877	1001
4	674	731
5	752	-783
6	558	-599
7	845	861
8	563	540
9	299	-291
10	172	-163
11	176	-136
12	477	-433
13	274	295
14	323	319
15	535	-535
16	412	-407
17	560	553
18	206	161
19	313	-297
20	66U	25
21	196	-180
22	68U	-27
23	100	68
24	166	155
25	222	-214
26	147	-136
27	198	212
28	129	120
29	136	-130

H = 0, K = 2		
0	635	653
1	709	896
2	116	-110
3	541	-574
4	117	115
5	30U	-6
6	62	-39
7	323	321
8	39U	-23
9	788	-796
10	434	457
11	584	613
12	296	-294
13	432	-446
14	102	94
15	58U	27
16	92	-80
17	219	211
18	196	-174
19	239	-214
20	74	74
21	383	389
22	151	-146
23	315	-315
24	71	64
25	62U	45
26	82	-64
27	75	72
28	49U	-1
29	171	-163

H = 0, K = 3		
1	103	119
2	199	-205
3	69	30
4	661	720
5	255	255
6	741	-789
7	52U	-33
8	339	330
9	61	40
10	111	-107
11	58	-40
12	293	-295
13	258	-251
14	338	323
15	118	110
16	419	-422
17	75	-39
18	319	296
19	68U	-39
20	106	-103
21	74	58
22	65U	-30
23	86	-81
24	197	192
25	70	48
26	228	-224
27	45U	-21
28	164	169

H = 0, K = 4		
0	414	-401
1	230	290
2	267	304
3	211	-230
4	83	-79
5	126	106
6	86	-76
7	86	76
8	338	333
9	305	-300
10	205	-185
11	330	318
12	271	273
13	311	-320
14	191	-166
15	75	-58
16	150	-140
17	67U	34
18	135	116
19	89	-74
20	227	-231
21	171	162
22	146	134
23	152	-137
24	48U	-23
25	107	98
26	49	-37

H = 0, K = 5		
1	83	91
2	56U	-17
3	269	-317
4	67U	-14
5	356	390
6	192	-195
7	140	-140
8	75	-44
9	120	103
10	75	-53
11	68U	33
12	74	70
13	138	-137
14	65U	22
15	213	189
16	75	-53
17	257	-250
18	57U	53
19	103	89
20	68	-78
21	46U	2
22	41U	19
23	118	-111

H = 0, K = 6		
0	182	-166
1	79	-70
2	209	197
3	65U	-3
4	64U	-36
5	110	-86
6	63U	-42
7	76	-76
8	75	75
9	115	105
10	197	-177
11	83	-84
12	168	150
13	54U	2
14	115	-96
15	48U	5
16	45U	-7
17	41U	-87
18	81	71
19	62	62

H = 0, K = 7		
1	48U	4
2	73	75
3	47U	-31
4	89	-96
5	70	68
6	68	72
7	58	-68
8	86	-91
9	38U	38

H = 1, K = 0		
-30	172	189
-28	166	-176
-26	140	136
-24	115	111
-22	94U	-49
-20	542	560
-18	641	-669
-16	303	298
-14	73U	52
-12	507	-554
-10	773	803
-8	782	-854
-6	535	555
-4	34U	-31
-2	100	-155
0	406	467
2	1986	-1944
4	644	662
6	423	-374
8	425	-422
10	847	841
12	419	-457
14	555	574
16	275	-250
18	89U	-37
20	348	344
22	269	-279
24	275	267
26	175	-164
28	70U	6
30	100	119

H = 1, K = 1		
-30	72	-57
-29	85U	-38
-28	72U	-69
-27	190	180
-26	142	140
-25	249	-256
-24	251	-232
-23	253	269
-22	188	177
-21	140	-79
-20	123	57
-19	113	74
-18	88U	-17
-17	354	339
-16	224	196
-15	537	-524
-14	366	-361
-13	575	586
-12	280	286
-11	418	-391
-10	506	-465
-9	101	-65
-8	178	-162
-7	365	357
-6	444	404
-5	624	-675
-4	634	-681
-3	591	643
-2	740	809
-1	1058	-1264
0	174	127
1	186	-159
2	144	-124
3	472	440
4	240	236
5	531	-566
6	430	-430
7	642	672
8	341	321
9	567	-570
10	360	-376
11	252	246
12	96	87
13	205	174
14	275	257
15	242	-236

16	268	-258
17	411	387
18	301	283
19	388	-399
20	140	-144
21	211	206
22	94U	10
23	139	128
24	90U	87
25	86U	-91
26	136	-130
27	164	175
28	68U	82
29	100	-110

H = 1, K = 2

-30	90	95
-29	174	190
-28	63	-61
-27	167	-152
-26	57U	-10
-25	72	64
-24	114	104
-23	89	76
-22	73	-68
-21	323	-327
-20	200	183
-19	410	417
-18	151	-126
-17	340	-346
-16	116	72
-15	141	132
-14	158	139
-13	90	93
-12	53U	-21
-11	484	-488
-10	227	226
-9	628	660
-8	539	-508
-7	691	-734
-6	40U	29
-5	313	329
-4	112	-107
-3	257	294
-2	276	-268
-1	471	-490
0	210	201
1	486	537
2	475	-495
3	782	-863
4	122	108
5	458	497
6	45	-30
7	43	53
8	45	-16
9	305	-313
10	138	134
11	653	696
12	158	-145
13	418	-422
14	224	220
15	330	327
16	196	-186
17	65U	22
18	66U	43
19	244	-229
20	204	182
21	135	124
22	90	-57
23	271	-265
24	123	101
25	206	192
26	68	-54
27	68U	-52

H = 1, K = 3

-28	58	-62
-27	59U	27
-26	161	180
-25	74U	64
-24	270	-282
-23	85U	-54
-22	205	212
-21	96	100
-20	93U	9
-19	94U	-12
-18	138	-124
-17	94U	35
-16	309	287
-15	91U	36
-14	509	-528
-13	135	-130
-12	370	358
-11	100	104
-10	234	-222
-9	131	-129
-8	208	-209
-7	75U	-12
-6	391	379
-5	150	141
-4	612	-655
-3	229	-236
-2	598	640
-1	69U	6
0	167	-184
1	69U	-66
2	70U	-31
3	132	-119
4	233	273
5	73U	68
6	482	-532
7	200	-192
8	570	620
9	111	-93
10	295	-332
11	84U	-34
12	86U	67
13	89U	90
14	328	349
15	214	214
16	274	-288
17	94U	-30
18	217	225
19	94U	91
20	214	-217
21	90U	19
22	93	76
23	128	-83
24	77U	43
25	71U	56
26	126	-142

H = 1, K = 4

-26	65	-71
-25	56U	-17
-24	64U	20
-23	112	121
-22	76U	53
-21	174	-171
-20	157	-154
-19	190	184
-18	222	232
-17	93U	-73
-16	142	-131
-15	94U	-16
-14	127	122
-13	94U	9
-12	209	199
-11	258	-253
-10	293	-270
-9	262	225
-8	177	168
-7	428	-420
-6	374	-370
-5	120	105
-4	85U	7
-3	210	207
-2	100	95
-1	223	-218
0	283	-281
1	292	288
2	350	373
3	232	-235
4	255	-257
5	214	229
6	87U	24
7	89U	41
8	119	127
9	98	-90
10	228	-220
11	166	152
12	191	183
13	256	-257
14	184	-180
15	236	242
16	122	103
17	92U	-2
18	99	88
19	87U	-43
20	93	-96
21	98	101
22	182	180
23	113	-118
24	89	-99
25	92	87
26	33U	1

H = 1, K = 5

-23	123	-147
-22	52U	-30
-21	101	105
-20	66U	38
-19	72U	-7
-18	96	-94
-17	80U	-86
-16	83U	-4
-15	275	287
-14	89U	-99
-13	237	-244
-12	92U	29
-11	125	124
-10	100	101
-9	94U	16
-8	94U	-40
-7	169	-162
-6	94U	-10
-5	151	134
-4	148	-135
-3	356	-330
-2	94U	1
-1	258	241
0	94U	-34
1	120	-101
2	94U	-4
3	94U	-78
4	94U	47
5	290	297
6	94U	23
7	317	-311
8	134	133
9	153	155
10	93U	4
11	92U	-77
12	91U	67
13	89U	-67
14	87U	11
15	172	159
16	82U	-7
17	129	-128
18	74U	-5
19	148	154
20	63U	-75
21	56U	-66
22	46U	63

H = 1, K = 6

-18	87	102
-17	52U	29
-16	80	-70
-15	79	-80
-14	67U	-42
-13	71U	28
-12	85	81
-11	77U	4
-10	141	-150
-9	87	-102
-8	143	159
-7	84U	75
-6	101	-101
-5	86U	-84
-4	87U	35
-3	88U	-27
-2	141	94
-1	88U	59
0	103	-152
1	88U	-98
2	143	156
3	87U	52
4	160	-186
5	86U	59
6	85U	-5
7	84U	82
8	82U	46
9	80U	62
10	78U	-71
11	87	-87
12	105	127
13	69U	42
14	101	-108
15	60U	-12
16	96	104
17	47U	0

H = 1, K = ?

-9	46U	26
-8	50U	-6

-7	96	-33
-6	55U	-109
-5	57U	47
-4	59U	55
-3	60	-86
-2	77	-79
-1	61U	39
0	61U	77
1	61U	-3
2	60U	37
3	59U	-37
4	58U	-21
5	56U	42
6	96	103
7	51U	-22
8	79	-84

H = 2, K = 0

-28	192	-215
-26	189	202
-24	86U	-71
-22	181	-176
-20	93U	55
-18	440	-466
-16	510	523
-14	277	-287
-12	72U	29
-10	588	598
-8	642	-637
-6	602	672
-4	326	-348
-2	81	87
0	391	398
2	555	-549
4	687	725
6	428	-439
8	293	285
10	257	253
12	530	-550
14	298	304
16	325	-324
18	148	167
20	92U	51
22	261	-276
24	137	152
26	123	-130
28	62	67

H = 2, K = 1

-28	58U	41
-27	67U	57
-26	74U	59
-25	179	-198
-24	130	-108
-23	179	189
-22	231	259
-21	251	-280
-20	184	-179
-19	127	133
-18	92U	-38
-17	123	72
-16	136	92
-15	310	-318
-14	257	-252
-13	416	414
-12	258	245
-11	442	-447
-10	217	-196
-9	375	357
-8	291	275
-7	157	142
-6	128	121
-5	344	-351
-4	243	-251
-3	414	430
-2	429	439
-1	397	-408
0	458	-463
1	822	802
2	114	101
3	79	69
4	69	56
5	313	-310
6	333	-328
7	443	424
8	308	287
9	517	-503
10	223	-207
11	206	191
12	161	147
13	172	-151
14	85U	-6
15	87U	-80
16	146	-135
17	177	179
18	181	169
19	252	-256
20	139	-116
21	172	201
22	118	96
23	108	-99
24	79U	-31
25	73U	-36
26	66U	-60
27	69	82
28	44U	79

H = 2, K = 2

-28	104	-97
-27	176	-189
-26	79	53
-25	147	153
-24	57U	-4
-23	60U	-32
-22	126	-101
-21	197	-152
-20	90	76
-19	257	259
-18	169	-170
-17	337	-327
-16	165	151
-15	322	350
-14	65U	-9
-13	86	-70
-12	130	-118
-11	98	-88
-10	121	119
-9	438	447
-8	158	-153
-7	533	-521
-6	230	227
-5	510	519
-4	56	-48
-3	311	-301
-2	229	205
-1	401	-372
0	282	235
1	393	389
2	246	-212
3	333	-353
4	276	256
5	487	485
6	137	-127
7	242	-239
8	63	43
9	59U	47
10	82	71
11	225	219
12	196	-189
13	463	-494
14	66U	-3
15	267	251
16	120	-105
17	187	-180
18	129	130
19	66U	-32
20	65U	-29
21	166	160
22	118	-89
23	123	-94
24	52U	53
25	147	150
26	81	-67
27	64	-68

H = 2, K = 3

-26	99	90
-25	61U	-22
-24	158	-165
-23	74U	-76
-22	242	260
-21	83U	60
-20	168	-182
-19	89U	-101
-18	91U	-23
-17	92U	7
-16	157	152
-15	92U	-19
-14	247	-245
-13	91U	-99
-12	409	415
-11	88U	104
-10	307	-297
-9	85U	52
-8	223	219
-7	185	186
-6	202	202
-5	79U	32
-4	428	-443
-3	77U	-80
-2	427	433
-1	156	130
0	370	-379
1	100	-94
2	133	138
3	78U	23
4	79U	38
5	80U	62
6	235	-267
7	131	-122
8	286	320
9	135	120
10	337	-339
11	90U	78
12	222	237
13	92U	-1
14	92U	-68
15	93U	-9
16	240	-255
17	104	-96
18	205	234
19	86U	-36
20	98	-115
21	89	-95
22	84	112
23	67U	-1
24	60U	-26
25	50U	59
26	29U	-27

H = 2, K = 4

-24	45U	73
-23	55U	36
-22	63U	-1
-21	113	-119
-20	74U	-66
-19	164	170
-18	143	149
-17	145	-148
-16	188	-194
15	90U	102
-14	131	131
-13	92U	33
-12	92U	-48
-11	130	-123
-10	185	-175
-9	181	174
-8	233	214
-7	142	-117
-6	143	-140
-5	320	313
-4	265	260
-3	123	-100
-2	89U	19
-1	136	-134
0	89U	-63
1	173	180
2	196	202
3	211	-242
4	258	-292
5	139	145
6	164	171
7	163	-176
8	92U	16
9	92U	-63
10	93U	-105
11	92U	92
12	129	134
13	120	-128
14	146	-157
15	124	139
16	85U	66
17	82U	-77
18	78U	-49
19	74U	53
20	69U	-37
21	62U	12
22	54U	72
23	70	-84

H = 2, K = 5

-14	79U	19
-13	226	-233
-12	84U	79
-11	214	216
-10	87U	-3

-9	138	-112
-8	90U	-43
-7	90U	-7
-6	91U	32
-5	204	179
-4	92U	-67
-3	191	-160
-2	92U	33
-1	251	210
0	92U	5
1	204	-139
2	92U	45
3	92U	70
4	91U	-20
5	91U	78
6	90U	-72
7	178	-208
8	88U	-4
9	174	178
10	86U	-42
11	113	-117
12	81U	34
13	79U	54
14	75U	-54
15	72U	37
16	67U	-38
17	138	-131
18	56U	3
19	104	96

H = 2, K = 6

-10	66U	-83
-9	69U	-21
-8	115	131
-7	71U	80
-6	74U	-85
-5	75U	-33
-4	76U	97
-3	77U	64
-2	77U	-32
-1	77U	-13
0	77U	-95
1	77U	-61
2	78	106
3	76U	72
4	92	-137
5	74U	-64
6	81	109
7	70U	-47
8	68U	8
9	66U	-29
10	63U	-33

H = 3, K = 0

-26	149	186
-24	158	-164
-22	147	50
-20	134	141
-18	139	-149
-16	296	322
-14	270	-267
-12	161	189
-10	70U	-56
-8	405	-425
-6	391	419
-4	330	-371
-2	147	188
0	141	-122
2	268	-315
4	409	423
6	301	-303
8	226	229
10	76U	-40
12	113	-108
14	227	240
16	180	-181
18	146	153
20	100	-91
22	67U	-33
24	119	142

H = 3, K = 1

-25	72	-74
-24	62U	-49
-23	164	184
-22	99	77
-21	118	-103
-20	160	-181
-19	192	205
-18	119	124
-17	123	-127
-16	84U	-27
-15	123	-98
-14	125	-98
-13	199	217
-12	227	222
-11	327	-338
-10	177	-174
-9	260	261
-8	129	127
-7	169	-181
-6	107	-94
-5	108	-95
-4	109	-78
-3	230	224
-2	214	188
-1	313	-283
0	223	-223
1	257	251
2	176	171
3	312	-314
4	110	-99
5	62U	-2
6	66U	-18
7	127	113
8	163	165
9	260	-287
10	164	-172
11	298	325
12	156	163
13	84U	-18
14	85U	-38
15	85U	55
16	85U	-23
17	83U	20
18	81U	82
19	132	-103
20	103	-99
21	127	145
22	64U	25
23	64	-84
24	47U	-41

H = 3, K = 2

-25	98	136
-24	38U	-10
-23	123	-144
-22	49U	16
-21	53U	16
-20	70	61
-19	159	174
-18	73	-75
-17	194	-199
-16	121	115
-15	221	227
-14	114	-106
-13	196	-201
-12	68U	9
-11	68U	22
-10	68U	29
-9	67U	28
-8	187	-185
-7	336	-322
-6	132	129
-5	340	334
-4	66U	-42
-3	288	-290
-2	65U	18
-1	208	186
0	113	-121
1	245	239
2	97	-115
3	244	-247
4	146	127
5	265	269
6	122	-116
7	208	-207
8	82	96
9	74	44
10	68U	-33
11	68U	-60
12	67U	-48
13	112	-107
14	124	126
15	241	269
16	62U	-6
17	120	-143
18	57U	56
19	54U	76
20	62	-27
21	71	26
22	40U	7
23	69	-79

H = 3, K = 3

-22	128	148
-21	60U	45
-20	167	-185
-19	71U	-54
-18	116	114
-17	78U	70
-16	80U	10
-15	82U	-28
-14	135	-146
-13	84U	13
-12	182	204
-11	97	117
-10	222	-237
-9	84U	-75
-8	151	155
-7	83U	-56
-6	165	-170
-5	82U	-107
-4	101	-98
-3	81U	-79
-2	317	351
-1	80U	-9
0	242	-274
1	81U	-38
2	179	194
3	82U	101
4	82U	-55
5	83U	1
6	84U	-45
7	84U	-13
8	155	162
9	85U	85
10	171	-179
11	85U	-59
12	153	168
13	83U	-4
14	86	-102
15	79U	15
16	76U	31
17	72U	-49
18	87	114
19	62U	26
20	116	-135
21	46U	37

H = 3, K = 4

-19	69	85
-18	69U	51
-17	128	-141
-16	108	-118
-15	114	86
-14	138	141
-13	77U	-93
-12	79U	-100
-11	81U	-16
-10	82U	-7
-9	107	121
-8	84U	105
-7	111	-129
-6	146	-161
-5	99	111
-4	85U	108
-3	122	-122
-2	99	-110
-1	85U	31
0	85U	-17
1	85U	36
2	85U	35
3	88	-107
4	86	-112
5	133	160
6	153	184
7	127U	-75
8	82U	-92
9	81U	90
10	79U	-26
11	78U	17
12	75U	55
13	72U	-50
14	69U	-80
15	86	124
16	84	102

H = 3, K = 5

-14	117	-76
-13	111	-82
-12	60U	11
-11	168	151
-10	66U	-33
-9	142	-135

-8	70U	-25	-16	92U	-54	-13	175	-161	-8	138	124
-7	72U	65	-15	97U	55	-12	85	48	-7	123U	46
-6	73U	-12	-14	101U	32	-11	70	66	-6	125U	-61
-5	74U	-17	-13	105U	52	-10	58U	-9	-5	127U	-6
-4	75U	-21	-12	108U	59	-9	59U	16	-4	128U	69
-3	134	-119	-11	117	-95	-8	60U	16	-3	129U	28
-2	76U	83	-10	133	-114	-7	61U	-2	-2	129U	32
-1	152	140	-9	247	247	-6	149	131	-1	130U	82
0	76U	4	-8	137	120	-5	186	172	0	174	-179
1	176	-122	-7	161	-140	-4	63U	-84	1	129U	29
2	75U	-5	-6	119	-83	-3	202	-181	2	178	150
3	74U	83	-5	120U	44	-2	63U	21	3	127U	4
4	74U	-13	-4	121U	21	-1	170	141	4	156	-110
5	72U	-20	-3	121U	53	0	63U	-5	5	123U	-54
6	71U	35	-2	121U	39	1	112	-75	6	120U	5
7	69U	-73	-1	121U	-100	2	63U	13	7	117U	-12
8	67U	48	0	156	-134	3	128	-112	8	113U	48
9	175	115	1	179	162	4	62U	39			
10	62U	-10	2	155	106	5	135	119	H =	4, K =	4
11	113	-89	3	140	-145	6	60U	-47	-12	54U	-90
			4	119U	-53	7	183	-164	-11	66U	46
H =	4, K =	0	5	118U	83	8	72	52	-10	74U	54
-18	80U	-59	6	117U	30	9	87	85	-9	79U	13
-16	142	161	7	115U	-4	10	54U	-53	-8	84U	22
-14	188	-195	8	113U	30	11	52U	7	-7	87U	-47
-12	122	136	9	111U	-34	12	50U	1	-6	90U	-43
-10	112U	-75	10	108U	-31	13	47U	15	-5	92U	76
-8	115U	1	11	129	143	14	44U	15	-4	110	108
-6	245	217	12	100U	70	15	40U	47	-3	95U	-117
-4	247	-226	13	142	-160	16	35U	-37	-2	95U	-66
-2	135	164	14	116	-103	17	26U	-106	-1	96U	28
0	134	-78	15	85U	-2				0	95U	28
2	118U	69	16	77U	15	H =	4, K =	3	1	95U	14
4	161	151	17	68U	-11	-17	47U	39	2	93U	5
6	195	-199	18	56U	11	-16	71U	-55	3	92U	-15
8	153	179				-15	83U	-31	4	89U	-30
10	147	-132	H =	4, K =	2	-14	92U	-8	5	87U	49
12	100	-81	-18	36U	-30	-13	99U	30	6	83U	48
			-17	115	-114	-12	105U	100	7	78U	-72
H =	4, K =	1	-16	45U	57	-11	110U	-8	8	72U	-89
-18	101	91	-15	145	142	-10	114U	-136	9	64U	35
-17	86U	-108	-14	84	-58	-9	118U	-66	10	50U	42

ture factors are of the form $\exp(-B \sin^2 \theta/\lambda^2)$, and the anisotropic ones of the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}))$. The R index is defined by $R = \sum||F_o|-|F_c||/\sum|F_o|$, including observed reflections only. The standard deviations were estimated from the inverse matrix of the normal equations, using a program which is part of the least-squares package.

DESCRIPTION OF THE STRUCTURE

Projections of the structure along the a axis and b axis are shown in Figs. 1(a) and 1(b), respectively. Bond distances and angles calculated from the final positional parameters are listed in Table 4.

Of main interest in this study was the geometry of the azo group and adjacent parts of the molecule. The asymmetric half of the molecule is very nearly planar, as indicated by the individual deviations from the least-squares plane. The plane defined by the positional parameters has the equation $(0.22147\mathbf{a} - 0.07836\mathbf{b} + 0.000634\mathbf{c}) \cdot \mathbf{r} - 1.1174 = 0$. The corresponding deviations are: Br −0.006, N −0.001, C_1 0.003, C_2 0.012, C_3 −0.016, C_4 0.012, C_5 −0.008 and C_6 0.004 Å, with a distance from the center at $\frac{1}{2}$,0,1 of 0.003 Å,

Table 4. Observed distances and angles in *trans-p,p'*-dibromoazobenzene. (Standard deviations in parentheses.)

Distances (in Å)			Angles (in degrees)		
N—N'	1.276	(0.014)	N—N'—C_4	112.2	(1.2)
N—C_4	1.428	(0.016)	N—C_4—C_3	114.7	(1.6)
C_1—Br	1.891	(0.013)	N—C_4—C_5	125.6	(2.1)
C_1—C_2	1.397	(0.019)	Br—C_1—C_2	119.3	(1.6)
C_1—C_6	1.385	(0.018)	Br—C_1—C_6	119.2	(1.5)
C_2—C_3	1.388	(0.018)	C_2—C_1—C_6	121.5	(2.0)
C_3—C_4	1.389	(0.017)	C_1—C_2—C_3	117.7	(1.9)
C_4—C_5	1.422	(0.018)	C_2—C_3—C_4	121.2	(1.9)
C_5—C_6	1.360	(0.018)	C_3—C_4—C_5	119.6	(1.9)
			C_4—C_5—C_6	119.0	(1.9)
			C_1—C_6—C_5	120.8	(1.9)

indicating that the molecule as a whole does not deviate significantly from planarity.

The observed N—N double bond distance of 1.276 Å and the C—N distance of 1.428 Å are reasonably close to the corresponding distances found in *trans*-azobenzene [2] (1.23 (assumed) and 1.41 Å, respectively). It is also interesting to compare these distances with those found in *p*-nitrophenyl azide [5] where in the grouping >C—N=N≡N, N=N and C—N were found to be 1.270 and 1.417 Å, respectively. As one would expect, the N—N distance in *trans-p,p'*-dibromoazobenzene is somewhat longer than the N—N double bond distance in compounds where the bond is not part of a larger conjugated system. Kuczkowski *et al.*[6] reported N=N to be 1.214 Å in *cis*-difluorodiazine (F—N=N—F) and Bohn [7] gave N=N distances of 1.209 Å for *cis* F—N=N—F and 1.224 Å for *trans* F—N=N—F.

The angle N—C_4—C_5 is found to be 125.6°, the deviation from the regular 120° angle presumably being caused by the space requirements of the N=N group and neighboring parts of the benzene ring. In this case one would expect the N=N—C angle to open up by a similar amount, and this actually seems to be the case.

For the difluorodiazines the N—N—F angle is 114.5° in the *cis* isomer [6,7] and 106.3 in the *trans* isomer,[7] indicating that for an unstrained N=N—X angle one should expect a value around 106°. The presently determined N=N—C angle is 112.2° so that both C—C—N and the N=N—C seem to deviate by about five or six degrees from the unstrained angles. Quite similar values for C—C—N and N=N—C are found in *p*-nitrophenyl azide (124.3° and 115.0°, respectively).[5] In all, there is little experimental support for the common belief that the N=N—X angle should normally be 120°. It should be mentioned, however, that in *trans*-azobenzene the corresponding angle is reported to be about 120°.

The distances within the benzene ring (average 1.39 Å) as well as the C—Br distance (1.89 Å) are normal within the experimental limits of error.

From the anisotropic temperature factors for each atom the vibrational ellipsoids were calculated. Inspection of these seemed to indicate that a

significant contribution to the anisotropy could be ascribed to an individual librational motion of each benzene ring in the plane of the molecule, but no further attempt was made to analyze the thermal motion.

It would appear to be of interest to compare the present structure with *p*-azotoluene, the structure of which is the subject of a publication by Padmanabhan *et al.*[8] Unfortunately, a closer study of that paper reveals so many errors and inconsistencies that we feel that the results reported cannot be considered trustworthy.

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