A Refinement of the Crystal Structure of *cis*-Azobenzene

ASBJØRN MOSTAD and CHR. RØMMING

Chemistry Department, University of Oslo, Oslo 3, Norway

The crystal structure of *cis*-azobenzene has been refined by three-dimensional X-ray methods to an R value of 0.039 using 411 observed reflections collected by counter methods.

The molecule is severely distorted from planarity; the dihedral angle at the $N-N$ double bond is 8.0°, the $C-N$ bond forms an angle of 4.3° with the plane of the phenyl ring, and the phenyl ring is rotated by 53.3° about the $C-N$ bond relative to a planar $N=N$-phenyl arrangement. Distances as short as 3.032 Å are observed between non-bonded carbon atoms of the two phenyl rings.

The bond lengths do not deviate from the corresponding values in *trans*-azobenzene.

The main features of the crystal structure of *cis*-azobenzene were established on the basis of two-dimensional X-ray data by Hampson and Robertson [1,2] in 1941. The methods at that time, however, did not allow an accuracy which would now seem to be desirable for a detailed discussion of bond lengths and angles in the molecule.

The reason to undertake a re-examination of the molecular structure was mainly to examine the effect of the large distortions from planarity on the bond lengths in the bridging arrangement between the phenyl rings. If a resonance in the system is destroyed by the distortion, a shorter $N=N$ bond and a longer $C-N$ bond relative to those in *trans*-azobenzene would be expected.

EXPERIMENTAL AND STRUCTURE REFINEMENT

cis-Azobenzene was formed by irradiating a solution of *trans*-azobenzene in dry benzene with intense light for a couple of hours. The isomers were separated by column chromatography in the dark with acid Al_2O_3 as adsorbant.[3] The *cis* isomer was recrystallized from petroleum ether at a temperature of 0°C; the orange prismatic crystals were as far as possible kept dry and in darkness throughout the experimental part of the investigation.

Unit cell parameters were determined from diffractometer measurements. The crystal data for *cis*-azobenzene, $C_{12}N_2H_{10}$, mol.wt. 182.2 are: orthorhombic; $a=7.587$ Å; $b=12.742$ Å; $c=10.320$ Å; (e.s.d. 0.1 %); calculated density is 1.213 g cm^{-3}; $Z=4$; $V=997.7$ Å^3; $F(000)=384$; space group *Pbcn*.

2

Three-dimensional intensity data were recorded using an automatic Picker diffractom-
eter with graphite crystal monochromated MoKα radiation. The take-off angle was 4°.
The crystal was kept in a pyrex capillary tube (wall thickness less than 0.01 mm) during
the X-ray exposure. It had dimensions $0.3 \times 0.3 \times 0.4$ mm^3 and was mounted with the
crystallographic c direction along the diffractometer ϕ axis. The $\omega - 2\theta$ scan technique
was used, the 2θ scan speed being $1°$ min^{-1} through the scan range from $0.9°$ below $2\theta(\alpha)_1$
to $0.9°$ above $2\theta(\alpha_2)$. Background counts were taken for 50 sec at each of the scan range
limits.

The intensities of three standard reflections measured for every 50 reflections of the
data set showed a decrease during the data collection of 26 ± 2 % and the intensities were
adjusted according to this. The estimated standard deviations were taken as the
square root of the total counts with a 2 % addition for the uncertainty in rescaling.

The measurements included 603 reflections with $\sin\theta/\lambda$ less than 0.54. 411 reflections
had net intensity larger than 1.5 $\sigma(I)$. These were regarded as "observed" reflections
whereas the remaining reflections were excluded from the refinement calculations. The
ratio of the number of observations to the number of parameters refined (83) was thus
only 5. This low figure may be attributed to fairly large amplitudes of thermal vibra-
tion.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard
deviations ($\times 10^5$) for nitrogen and carbon atoms.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N1	4353	18596	30146	2762	549	1761	84	438	348
	29	13	18	75	13	41	47	79	35
C1	10583	28184	36007	1955	507	1214	217	−48	345
	34	18	28	64	18	38	58	83	48
C2	21140	35190	29514	2376	619	1018	−108	366	213
	35	21	33	68	22	40	65	93	52
C3	27955	43688	35891	2357	665	1471	−275	−341	331
	39	22	36	74	23	49	72	108	60
C4	24436	45309	48814	2385	947	1527	206	−741	−485
	46	29	42	76	31	56	84	116	66
C5	14097	38268	55245	2628	1502	1015	532	−308	−136
	47	34	33	90	40	51	98	115	78
C6	7288	29596	49196	2214	1088	1162	150	42	737
	41	30	33	76	34	46	84	99	61

Table 2. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters with
estimated standard deviations for hydrogen atoms.

Atom	x	y	z	B
H2	2374	3399	2078	4.2
	28	16	24	.6
H3	3486	4846	3153	5.7
	29	19	20	.8
H4	2964	5116	5312	6.3
	32	22	25	.8
H5	1141	3893	6351	7.4
	37	20	23	.9
H6	9	2462	5336	6.9
	35	19	24	.9

Table 3. Observed and calculated structure factors. The columns are h, k, l, $10|F_o|$, $10|F_c|$.

h	k	l	$10|F_o|$	$10|F_c|$
0	2	0	474	-476
0	4	0	30	-34
0	6	0	123	123
0	8	0	294	-297
0	12	0	100	-98
0	12	1	209	-209
0	10	1	111	112
0	8	1	24	27
0	6	1	60	58
0	4	1	220	224
0	2	1	300	301
0	0	2	242	243
0	2	2	342	340
0	4	2	259	253
0	6	2	293	-289
0	8	2	32	38
0	10	2	30	32
0	12	2	89	-87
0	10	3	41	-35
0	8	3	96	-90
0	4	3	57	-56
0	2	3	142	-139
0	0	4	304	302
0	2	4	47	-45
0	4	4	76	-74
0	6	4	217	218
0	8	5	106	108
0	6	5	22	-22
0	4	5	66	-67
0	2	5	258	-258
0	0	6	443	436
0	2	6	71	-69
0	4	6	143	149
0	6	6	35	-33
0	8	6	125	-125
0	10	7	30	34
0	8	7	33	36
0	4	7	43	43
0	2	7	43	-48
0	0	8	31	29
0	4	8	153	155
0	6	8	73	-76
0	8	8	94	-89
0	6	9	155	161
0	2	9	38	35
0	0	10	25	28
1	0	10	71	72
1	3	9	53	55
1	4	9	27	21
1	5	9	40	-48
1	6	9	43	-50
1	7	9	43	33
1	8	8	33	-44
1	7	8	84	86
1	6	8	72	-73
1	5	8	142	-145
1	4	8	105	105
1	3	8	76	79
1	0	8	24	21
1	1	7	45	-40
1	2	7	36	-33
1	3	7	70	71
1	4	7	74	-76
1	6	7	216	-218
1	7	7	36	-35
1	8	7	60	67
1	10	6	42	-46
1	9	6	36	-39
1	8	6	34	31
1	7	6	60	62
1	6	6	137	140
1	5	6	81	-87
1	4	6	23	-29
1	3	6	53	54
1	2	6	41	-46
1	0	6	46	-44
1	1	5	166	164
1	5	5	169	-167
1	3	5	53	-51
1	7	5	56	-51
1	8	5	91	-92
1	10	5	32	-24
1	11	5	46	43
1	9	4	29	33
1	8	4	39	-32
1	6	4	45	-46
1	5	4	42	37
1	4	4	217	217
1	2	4	58	59
1	1	4	49	-54
1	0	4	539	-527
1	1	3	222	219
1	2	3	50	46
1	3	3	182	176
1	5	3	167	-166
1	6	3	68	-68
1	7	3	58	56
1	8	3	22	-19
1	12	3	107	-105
1	12	2	34	-29
1	11	2	81	-81
1	10	2	66	-66
1	8	2	151	-148
1	7	2	131	127
1	6	2	44	-44
1	5	2	260	-255
1	4	2	168	166
1	3	2	436	432
1	2	2	19	-27
1	1	2	331	-321
1	0	2	670	671
1	1	1	613	-619
1	2	1	831	-848
1	3	1	401	401
1	4	1	260	-264
1	5	1	105	103
1	6	1	232	-231
1	7	1	175	-181
1	9	1	102	103
1	10	1	49	-48
1	11	1	38	-41
1	12	1	70	72
1	11	0	153	152
1	9	0	207	-213
1	7	0	81	83
1	5	0	50	56
1	3	0	267	275
1	1	0	158	-161
2	0	0	436	-437
2	2	0	889	-916
2	4	0	227	232
2	6	0	108	108
2	8	0	41	-35
2	10	0	247	250
2	11	0	90	89
2	10	1	116	112
2	9	1	47	-45
2	8	1	141	-146
2	7	1	31	-27
2	6	1	86	-85
2	5	1	62	-63
2	4	1	159	156
2	3	1	114	-115
2	2	1	608	-625
2	1	1	700	724
2	0	1	81	-80
2	1	2	220	217
2	2	2	282	-289
2	3	2	50	54
2	4	2	133	-133
2	5	2	200	-199
2	7	2	78	76
2	8	2	124	121
2	9	2	93	-98
2	10	2	37	-32
2	11	2	79	83
2	6	3	56	-58
2	5	3	53	54
2	4	3	318	-312
2	3	3	211	214
2	2	3	200	205
2	1	3	92	-90
2	1	4	82	84
2	2	4	116	-116
2	3	4	104	-107
2	5	4	152	-149
2	6	4	40	-40
2	7	4	74	75
2	8	4	80	-82
2	9	4	48	55
2	10	4	54	47
2	11	4	63	-66
2	10	5	45	-34
2	9	5	31	-25
2	8	5	51	-48
2	7	5	84	84
2	5	5	61	-61
2	4	5	90	93
2	3	5	71	-35
2	2	5	70	67
2	1	5	195	192
2	0	6	47	-45
2	1	6	52	57
2	2	6	206	-204
2	3	6	99	-98
2	5	6	42	47
2	6	6	51	48
2	7	6	44	-52
2	9	6	67	60
2	10	6	66	73
2	8	7	40	-40
2	5	7	88	92
2	3	7	158	-161
2	2	7	54	-61
2	1	7	50	40
2	1	8	44	44
2	2	8	85	-82
2	4	8	41	-40
2	5	8	74	-81
2	7	8	48	55
2	8	8	70	65
2	6	9	28	-27
2	4	9	113	-114
2	3	9	32	-39
2	2	9	37	41
2	3	10	47	37
2	1	9	53	-64
3	4	9	45	43
3	5	8	34	22
3	3	8	66	64
3	2	8	97	-94
3	1	8	57	-59
3	1	7	38	-52
3	2	7	38	-42
3	3	7	29	-23
3	4	7	234	238
3	6	7	29	-35
3	7	7	54	46
3	8	6	85	-78
3	6	6	26	-23
3	5	6	30	36
3	4	6	31	35
3	3	6	26	32
3	1	6	32	-38
3	0	6	61	-51
3	1	5	74	-76
3	2	5	136	141
3	4	5	27	-3
3	5	5	44	38
3	7	5	50	47
3	8	5	72	75
3	10	5	44	-58
3	9	5	81	-78
3	8	4	42	40
3	7	4	28	31
3	5	4	72	-74
3	4	4	47	-50
3	3	4	29	-15
3	2	4	71	72
3	1	4	112	114
3	0	4	44	-116
3	1	3	54	-55
3	2	3	221	-229
3	3	3	205	-205
3	4	3	188	191
3	5	3	53	52
3	6	3	36	26
3	7	3	65	64
3	8	3	36	-23
3	9	3	60	-62
3	10	3	91	96
3	10	2	112	115
3	9	2	46	45
3	6	2	57	44
3	5	2	187	-194
3	4	2	215	218
3	3	2	193	197
3	2	2	368	-380
3	1	1	52	-57
3	3	1	86	-92
3	4	1	371	384
3	5	1	60	-65
3	7	1	65	-71
3	8	1	174	181
3	9	1	96	100
3	10	1	85	-87
3	9	0	30	26
3	7	0	68	68
3	5	0	48	51
3	3	0	470	-490
3	1	0	196	199
4	0	0	138	136
4	6	0	64	66
4	8	0	138	-146
4	10	0	124	-127
4	11	1	29	24
4	10	1	31	-29
4	9	1	78	-82
4	8	1	97	92
4	7	1	66	67
4	6	1	121	-119
4	5	1	75	77
4	4	1	164	164
4	3	1	154	-154
4	2	1	105	107
4	1	1	199	202
4	0	2	106	-109
4	1	2	58	-56
4	2	2	157	163
4	3	2	104	-108
4	4	2	188	194
4	5	2	56	51
4	6	2	83	-85
4	7	2	106	109
4	8	2	29	-14
4	9	2	34	-35
4	10	2	29	-31
4	11	2	36	42
4	9	3	53	55
4	5	3	101	-101
4	4	3	101	101
4	3	3	71	-71
4	2	3	94	93
4	1	3	35	-36
4	0	4	135	140
4	1	4	83	-81
4	2	4	62	-63
4	3	4	184	184
4	4	4	69	70
4	5	4	51	-49
4	6	4	29	22
4	7	4	35	-37
4	9	5	79	-89
4	8	5	36	-36
4	7	5	42	50
4	4	5	61	-65
4	3	5	113	-111
4	2	5	77	74
4	1	5	73	75
4	0	6	62	70
4	1	6	65	67
4	2	6	98	100
4	3	6	87	-86
4	4	6	49	-45
4	5	6	54	52
4	2	7	57	61
4	1	7	108	106
4	1	8	59	-62
4	2	8	91	94
4	3	8	47	57
4	4	8	28	-21
4	6	8	40	-38
5	2	8	42	28
5	0	8	45	35
5	2	7	79	-83
5	7	6	51	-57
5	6	6	44	33
5	5	6	48	42
5	2	6	54	-50
5	0	6	126	122
5	1	5	95	-95
5	2	5	27	-27
5	4	5	36	-33
5	8	4	54	61
5	7	4	44	47
5	6	4	50	-56
5	2	4	67	62
5	1	4	72	-77
5	1	3	111	115
5	2	3	50	-53
5	4	3	97	98
5	6	3	149	-149
5	7	3	41	32
5	8	2	39	-42
5	7	2	68	60
5	4	2	53	-50
5	3	2	106	-107
5	1	2	45	44
5	0	2	191	191
5	3	1	51	-47
5	4	1	67	-71
5	5	1	178	175
5	6	1	135	-135
5	8	1	34	-32
5	9	1	59	-53
5	9	0	57	64
5	7	0	185	-188
5	5	0	110	109
5	3	0	29	-36
5	1	0	92	88
6	0	0	195	-195
6	2	0	45	42
6	4	0	94	-91
6	8	0	67	71
6	7	1	37	38
6	6	1	41	-35
6	3	1	41	-44
6	2	1	44	-48
6	0	2	27	-72
6	1	2	41	33
6	4	2	56	55
6	5	2	64	67
6	6	2	30	-10
6	7	2	112	-111
6	8	2	42	45
6	8	3	47	20
6	6	3	32	-29
6	5	3	130	125
6	2	3	39	-43
6	1	4	43	-36
6	3	4	37	31
6	5	4	31	-24
6	7	4	57	59
6	5	2	29	-32
6	1	5	120	113
6	0	6	101	-103
6	1	6	54	-58
6	3	6	44	33
6	4	6	37	-20
6	1	1	53	-52
7	1	5	39	36
7	4	5	57	50
7	6	6	60	66
7	5	2	62	52
7	4	2	42	-44
7	1	1	59	49
7	2	1	55	55
7	5	1	71	-64
7	6	1	71	65
7	5	0	72	59
7	3	0	53	-50

Corrections were made for Lorentz and polarization effects but not for absorption or secondary extinction.

Calculations were performed on a CD 3300 computer with the use of a set of programs described in Ref. 4. Atomic form factors were those of Hanson et al.[5] for nitrogen and carbon and of Stewart et al.[6] for hydrogen.

Refinements of the parameters given by Hampson and Robertson were carried out by full-matrix least-squares methods to an R value of 0.12. Anisotropic thermal parameters were then introduced for nitrogen and carbon atoms, using the expression exp $-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$. Hydrogen positions were postulated and

Table 4. The root mean square amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and B-values (Å²) along the principal axes of the ellipsoids of vibration given by the components of a unit vector **e** in fractional coordinates.

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
N1	.318	8.01	.0518	.0156	.0870
	.277	6.06	−.1212	.0064	.0373
	.206	3.36	.0005	−.0766	.0208
C1	.265	5.54	.0117	.0303	.0890
	.241	4.60	.1274	.0149	−.0168
	.189	2.82	.0317	−.0708	.0345
C2	.269	5.71	.1214	.0012	.0378
	.243	4.66	−.0388	.0536	.0647
	.209	3.46	.0337	.0573	−.0614
C3	.296	6.92	−.0561	.0285	.0803
	.256	5.17	.1156	−.0047	.0462
	.223	3.91	.0293	.0730	−.0284
C4	.321	8.12	.0534	.0434	−.0706
	.262	5.43	−.0812	.0592	.0222
	.241	4.59	.0890	.0279	.0626
C5	.357	10.06	.0338	.0756	−.0079
	.273	5.87	−.1233	.0211	.0223
	.231	4.20	.0320	.0014	.0940
C6	.323	8.24	.0118	.0673	.0491
	.254	5.08	−.1309	.0032	.0104
	.219	3.79	.0094	−.0403	.0829

Table 5. Results of the rigid-body analysis for (I) the molecule and (II) one half of a molecule. The coordinate system is defined by the (orthorhombic) crystal axes. Estimated standard deviations in parentheses.

	I				II		

$$L=\begin{Bmatrix} 33.0(1.5) & 0 & 11.5(1.8) \\ & 3.9(1.2) & 0 \\ & & 15.3(2.3) \end{Bmatrix} (°)^2 \qquad L=\begin{Bmatrix} 46.2(4.2) & 15.3(4.9) & 10.9(2.8) \\ & 33.2(7.9) & 7.0(4.1) \\ & & 21.4(5.6) \end{Bmatrix} (°)^2$$

	r.m.s. amplitude	Direction cosines (× 10³)			r.m.s. amplitude	Direction cosines (× 10³)		
L	6.2°	898	0	441	7.8°	793	523	314
	3.1°	441	0	−898	4.8°	543	−839	26
	1.8°	0	1000	0	4.1°	277	150	−949
T	0.25 Å	−963	0	−268	0.25 Å	457	563	689
	0.23 Å	268	0	963	0.24 Å	853	−56	−520
	0.20 Å	0	−1000	0	0.19 Å	−254	824	−506

given individual (isotropic) thermal parameters. Additional cycles of least-squares calculations with variation of all parameters brought the conventional R-factor down to the final value of 0.039. The value of the weighted R was 0.029.

Table 6. Intra-molecular distances and bond angles.

Bond distances (Å)		Corrected	*Inter*-bond angles (°)		Other short *intra*-molecular distances (Å)	
N′−N	1.251	1.253	N′−N−C1	121.9	N−C2	2.482
N−C1	1.443	1.449	N−C1−C2	122.5	N−C6	2.433
C1−C2	1.374	1.385	N−C1−C6	117.3	N−C1′	2.364
C2−C3	1.369	1.377	C6−C1−C2	119.8	N−C2′	3.044
C3−C4	1.376	1.389	C1−C2−C3	120.0	C1−C1′	2.788
C4−C5	1.364	1.374	C2−C3−C4	120.8	C1−C2′	3.032
C5−C6	1.370	1.378	C3−C4−C5	119.0	C2−C2′	3.348
C1−C6	1.396	1.410	C4−C5−C6	121.7		
C̄−C̄	1.375	1.386	C5−C6−C1	118.7		
C−H distances (average) 0.93 Å						

The final positional and thermal parameters for nitrogen and carbon atoms are given in Table 1 and those of hydrogen atoms in Table 2. Observed and calculated structure factors are listed in Table 3.

Magnitudes and directions of the principal axes of the vibrational ellipsoids are given in Table 4. The molecule consists of two asymmetric units related by a twofold axis. Rigid-body motion analysis were made both by considering the complete molecule (I) and the asymmetric part (II) as the rigid unit. The r.m.s. discrepancy between the atomic vibration tensor components arrived at in the structure analysis and those calculated from the rigid-body parameters obtained are 0.0042 Å² (I) and 0.0026 Å² (II), respectively; all differences are less than twice the standard deviation from the average in both cases. Results of the rigid body analysis are given in Table 5. The sets of eigenvalues for T are almost identical. The vibrations are nearly isotropic; the directions of the principal axes are thus badly defined and the difference in direction may be ignored. The librational motion found when considering the molecule as a unit has the axis of the largest oscillation amplitude nearly parallel to the N=N bond, while the oscillation about the two-fold axis is rather small. Considering the half molecule, the primary motion is about an axis not far from the line through N−C1−C4. This oscillation could not be allowed for considering the thermal motion of the whole molecule as the vibrational unit. The corrections of the N−N bond length for librational effects would, however, probably be incorrect using the L-tensor from case II.

The bond lengths were corrected for librational effects using model I when correcting the N′=N and N−C1 bond lengths and model II when correcting dimensions in the benzene ring.

Bond lengths, valence angles and *intra*-molecular distances are given in Table 6.

Standard deviations were calculated from the correlation matrix ignoring the standard deviations in cell parameters. The estimated standard deviation in the distances between non-hydrogen atoms are 0.003−0.004 Å, in C−H bonds 0.025 Å, and in angles involving carbon or nitrogen atoms 0.3°.

DISCUSSION

Corrected bond lengths and the bond angles are shown in Fig. 1. For comparison results from some of the more accurate structure determinations of *trans*-azobenzene and analogous compounds are presented in Table 8.

The *cis*-azobenzene molecule is severely distorted from the planar arrangement usually preferred for molecules having π delocalization. The distortions are distributed on several bond angles and torsions in such a way that the molecule retains a two-fold axis of symmetry running normal to the N=N bond and between the phenyl groups.
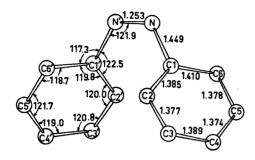
Fig. 1. Bond lengths and angles in cis-azobenzene.

Table 7. Deviations (Å) from a least-squares plane defined by the carbon atoms of the benzene ring.

C1	0.012	N	−0.108
C2	−0.004	H2	−0.03
C3	−0.004	H3	0.00
C4	0.003	H4	−0.03
C5	0.005	H5	0.11
C6	−0.013	H6	−0.01

Table 8. Structure data for various trans-azocompounds.

Compound	C−N(Å)	N=N(Å)	$\overline{\text{C}-\text{C}}$(Å)	C−N=N(°)	Ref.
trans-Azobenzene	1.434	1.247	1.386	113.3	7
trans-Azotoluene	1.433	1.244	1.382	113.8	8
trans-p,p′-dichloroazobenzene	1.443	1.255	1.384	112.6	9
p-Chlorobenzene-trans-diazoimidoglyoxynitrile	1.447	1.264	1.385	112.9	10
trans-p,p′-Dibromoazobenzene	1.428	1.276	1.390	112.2	11
Mean values	1.437	1.257	1.385	113.0	

The dihedral angle C1′−N′=N−Cl is 8.0° and the N′=N−Cl angle 121.9°. The latter value is nearly 10° larger than the corresponding value in the trans-compounds in which the angle is close to 113°.

The N−Cl−C4 angle is 174.4°. The distortion from linearity is a combined effect of the in-plane opening of the angle N−Cl−C2 by 2.5° and the N−Cl direction being bent by 4.3° out of the plane of the phenyl ring, moving the C4 atom away from the two-fold axis.

Finally, the phenyl ring is rotated about the C1−C4 axis, giving an angle of 57.5° between the plane defined by the carbon atoms of the phenyl ring and the plane through the nitrogen atoms and the two-fold axis. The angle between the plane of the phenyl group and the plane through the N′, N, and Cl atoms is 53.3°.

The geometry of the molecule is a result of a compromise between the tendency to planarity and the repulsion between non-bonded carbon and nitrogen atoms of the two phenylazo groups. The critical distances between carbon atoms of the benzene rings are $C1-C1'$ (2.788 Å), $C2-C1'$ (3.032 Å), and $C2-C2'$ (3.348 Å), and between carbon and nitrogen atoms $N-C1'$ (2.364 Å) and $N-C2'$ (3.044 Å). All these distances are below the sum of the accepted van der Waals radii.

The average $C-C$ bond length in the benzene ring is 1.386 Å. This is less than in benzene itself but is in complete agreement with the mean value in the *trans*-compounds. The $N-C1$ (1.449 Å) and $N=N$ (1.253 Å) bond lengths are within the accuracy of the determinations the same as the corresponding bond lengths in the *trans*-azo compounds, the mean values found in these being 1.437 and 1.257 Å, respectively. Thus, the distortion from a planar arrangement does not seem to be accompanied by any significant changes in the bond lengths.

The planarity of the phenyl ring is demonstrated by the small deviations from a least-squares plane through the carbon atoms (Table 7). The hydrogen
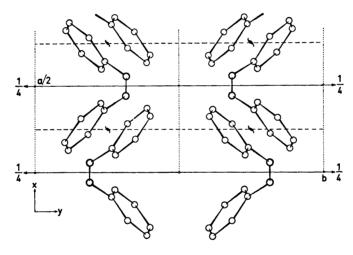

Fig. 2. The crystal structure as seen along the *c*-axis.

atoms also lie close to this plane; this is to be expected since there are no short *intra*-molecular contacts involving hydrogen atoms.

Inter-molecular distances are normal for a crystal in which molecules are bonded by van der Waals interactions.

REFERENCES

1. Robertson, J. M. *J. Chem. Soc.* **1939** 232.
2. Hampson, G. C. and Robertson, J. M. *J. Chem. Soc.* **1941** 409.
3. Zechmeister, L., Frehden, O. and Fischer Jørgensen, P. *Naturwiss.* **26** (1938) 495.
4. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.

 5. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
 6. Stewart, R. F., Davidsen, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
 7. Brown, C. J. *Acta Cryst.* **21** (1966) 146.
 8. Brown, C. J. *Acta Cryst.* **21** (1966) 153.
 9. Hope, H. and Victor, D. *Acta Cryst.* **B 24** (1969) 1849.
10. Erichson, H. H. and Rømming, Chr. *Acta Chem. Scand.* **22** (1968) 1430.
11. Amit, A. G. and Hope, H. *Acta Chem. Scand.* **20** (1966) 335.