Table 7. *Anisotropic thermal vibration parameters*

The B_{ij} are coefficients in the temperature factor expression:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right]$$

$$U_{11}=B_{11}/2\pi^2a^{*2};\; U_{12}=B_{12}/4\pi^2a^*b^*;\; etc.$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	0·0399	0·0489	0·0496	0·000	−0·0015	−0·006
Pd(2)	0·0451	0·0486	0·0503	0·0000	−0·0047	0·0019
Pd(3)	0·0402	0·0489	0·0481	0·0003	−0·0026	−0·0009
S(1)	0·0494	0·0474	0·0520	0·0064	−0·0062	−0·0031
S(2)	0·0348	0·0516	0·0523	0·0005	0·0010	0·0001
S(3)	0·0457	0·0506	0·0563	0·0047	0·0109	0·0026
S(4)	0·0466	0·0551	0·0494	0·0029	−0·0078	−0·0035
S(5)	0·0444	0·0560	0·0473	−0·0020	−0·0003	0·0079
S(6)	0·0459	0·0599	0·0503	−0·0019	0·0000	0·0046
C(1)	0·0502	0·0841	0·0785	0·0046	0·0174	0·0017
C(2)	0·0683	0·0857	0·0651	0·0120	0·0176	−0·0072
C(3)	0·1049	0·1377	0·1272	0·0057	0·0290	0·0041
C(4)	0·0467	0·0890	0·0536	0·0019	−0·0019	−0·0130
C(5)	0·0879	0·1300	0·0895	−0·0247	0·0091	−0·0163
C(6)	0·0638	0·1927	0·1152	0·0340	−0·0090	0·0099
C(7)	0·0776	0·0691	0·0627	−0·0059	0·0150	−0·0005
C(8)	0·2111	0·0819	0·1163	0·0313	−0·0545	−0·0428
C(9)	0·2451	0·1225	0·0999	0·0203	−0·0841	−0·0454
C(10)	0·0747	0·0621	0·0629	−0·0063	−0·0234	0·0154
C(11)	0·0787	0·0839	0·0648	0·0032	−0·0334	−0·0021
C(12)	0·00469	0·1519	0·1819	0·0334	−0·0334	−0·0142
C(13)	0·0516	0·0604	0·0842	0·0172	0·0172	0·0082
C(14)	0·0388	0·0991	0·0570	−0·0072	−0·0015	0·0136
C(15)	0·0777	0·1553	0·1021	0·0184	−0·0138	0·0190
C(16)	0·0709	0·0874	0·0998	−0·0600	−0·0099	0·0113
C(17)	0·0840	0·0939	0·2147	−0·0096	0·0059	0·0131
C(18)	0·1264	0·1119	0·2526	−0·0426	−0·0343	−0·0337

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The Crystal and Molecular Structure of 4,4′-Diamino-3,3′-dichlorobiphenyl

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4,4′-Diamino-3,3′-dichlorobiphenyl, $C_{12}H_{10}N_2Cl_2$, crystallizes with cell dimensions $a=12·5$, $b=3·85$, $c=23·7$ Å, $\beta=108°$, space group $P2_1/c$ and $Z=4$. The structure has been determined from three-dimensional X-ray data and refined by the minimum residual method, with isotropic temperature factors for individual atoms, to give a final R index of 14%. The two phenyl rings are not coplanar, but are twisted around the linkage between them, C(1)–C(1′), so as to be mutually inclined at an angle of 21°; in addition, each phenyl ring is bent through a small angle (approximately 2·2° and 3·4° respectively) away from the line C(1)–C(1′). The length of the bond C(1)–C(1′) is 1·515 ± 0·024 Å.

Introduction and experimental

A preliminary examination of one projection of the structure of 4,4′-diamino-3,3′-dichlorobiphenyl by Toussaint (1948) gave an electron density map with spurious symmetry in addition to the true symmetry of the actual structure. The map suggested that the molecules are probably planar, or very nearly so, with chlorine atoms in the *trans* positions. We have now completed the analysis of the structure, using three-dimensional X-ray data kindly supplied by Dr Toussaint, and find that the phenyl rings are mutually inclined at an angle of 21°.

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There is a misprint in Dr Toussaint's paper. With a unit cell $a=12{\cdot}5$, $b=3{\cdot}85$, $c=23{\cdot}7$ Å and $\beta=108°$, the space group is $P2_1/c$, not $P2_1/a$ as reported; the unit cell contains four molecules.

Dr Toussaint's three-dimensional X-ray data were obtained from Weissenberg photographs with intensities estimated visually. A small crystal was used to obtain $0kl$, $1kl$ ... $5kl$ reflexions and a larger one for $h0l$ and $h1l$ reflexions. No corrections were made for absorption. The dimensions of the smaller specimen are not recorded but the larger specimen had an irregular cross-section in which linear dimensions through the centre varied from 0·3 to 0·5 mm. With a linear absorption coefficient $\mu=51$ cm^{-1} differential absorption in the larger specimen would be substantial, and since data collected from this crystal were used to scale the intensities of the other reflexions it follows that absorption errors will have been introduced into all the data.

Determination and refinement of the structure

The heavy chlorine atoms enabled the structure to be determined in its a- and b-axial projections (Hasan, 1962). It is similar to that proposed by Toussaint (1948) but the two phenyl rings are not coplanar and the z coordinates differ from Toussaint's by one quarter of a lattice translation.

The structure was refined, using 851 independent hkl reflexions, by the minimum residual method of Bhuiya & Stanley (1963), with calculated structure factors based on the atomic scattering factors of Forsyth & Wells (1959) and isotropic temperature factors B. In five cycles the agreement index $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ fell from 0·23 to 0·14. A final R value of 0·14 with isotropic temperature factors appears to be quite reasonable in view of the errors due to absorption in the experimental data and the omission of the contributions of the hydrogen atoms from the calculated structure factors.

The final positional and thermal parameters are given in Table 1. Standard deviations of the positional coordinates were estimated using the formula of Cruickshank (1960) and are as follows:

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Carbon	0·016 Å	0·019 Å	0·013 Å
Nitrogen	0·013	0·015	0·011
Chlorine	0·004	0·006	0·003

The observed and calculated structure factors are given in Table 2.

Table 1. *Final positional coordinates and isotropic temperature factors*

	x/a	y/b	z/c	B
C(1)	0·2111	0·2806	0·4681	1·94 Å
C(2)	0·2517	0·3338	0·4203	2·34
C(3)	0·1780	0·4572	0·3680	2·39
C(4)	0·0686	0·5238	0·3595	2·36
C(5)	0·0256	0·4623	0·4073	2·86
C(6)	0·1015	0·3398	0·4616	2·31
N(1)	−0·0069	0·6479	0·3052	2·87
Cl(1)	0·2306	0·5245	0·3078	2·63
C(1′)	0·2919	0·1684	0·5272	1·81
C(2′)	0·2461	0·0142	0·5697	2·19
C(3′)	0·3223	−0·0657	0·6250	2.23
C(4′)	0·4351	−0·0271	0·6400	2·49
C(5′)	0·4789	0·1232	0·5975	2·56
C(6′)	0·4057	0·2197	0·5414	2·42
N(1′)	0·5105	−0·1033	0·6973	2·97
Cl(1′)	0·2673	−0·2404	0·6783	2·40

Description of the structure

Fig. 1 gives the dimensions of the molecule deduced from the atomic coordinates in Table 1. The estimated standard deviations in Fig. 1(b) and (c) were calculated using, respectively, the formulae of Ahmed & Cruickshank (1953) and of Darlow (1960). The dimensions and estimated standard deviations must be viewed with caution because there are three possible sources of systematic errors for which no corrections have been made and for which no quantitative assessments are available. These arise from the absorption errors to which reference has already been made, from uncertainties in the precision of the unit-cell dimensions and from the errors caused by libration effects. It is considered, nevertheless, that these systematic errors are

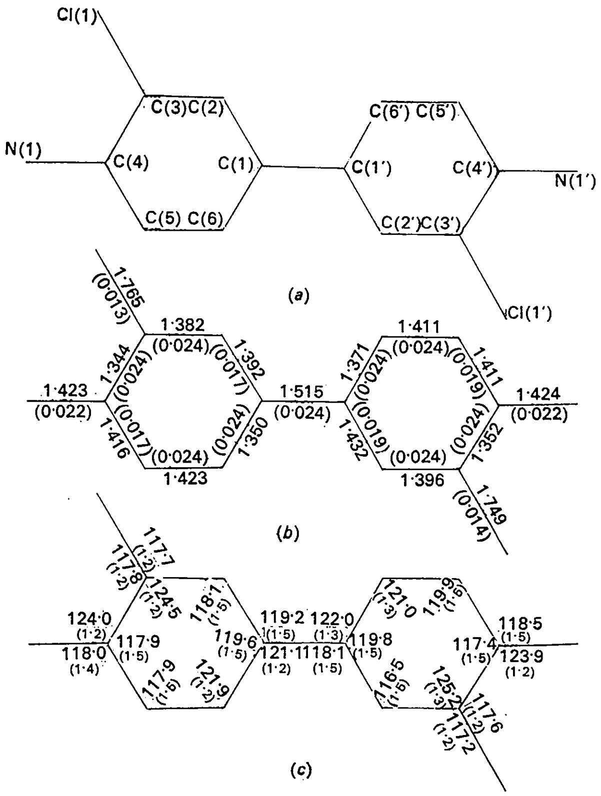

Fig. 1. Dimensions of the molecule. (a) Numbering of the atoms (b) Bond lengths with standard deviations (Å) (c) Bond angles with standard deviations.

Table 2. *Observed and calculated structure factors*

h	k	l	$10\|F_o\|$	$10F_c$
-12	0	4	457	-640
-11	0	12	195	200
-10	0	8	185	156
-9	0	12	265	-287
-8	0	10	261	373
-7	0	8	148	-130
-6	0	2	687	-687
-6	0	16	257	-178
-5	0	14	335	267
-4	0	2	459	-460
-4	0	16	373	329
-3	0	14	352	-317
-3	0	28	134	124
-2	0	12	310	-261
-1	0	8	289	253
-1	0	24	228	200
0	0	10	548	402
0	0	24	143	-92
1	0	14	184	-153
1	0	28	67	72
2	0	14	208	145
3	0	2	126	94
3	0	16	250	-218
4	0	4	387	304
5	0	4	46	65
6	0	4	297	-297
7	0	8	131	120
8	0	10	365	379
12	0	2	166	-239
-8	1	9	114	-126
-7	1	2	102	-207
-7	1	11	55	90
-7	1	20	131	-38
-6	1	4	102	97
-6	1	13	249	291
-6	1	23	182	17
-5	1	7	393	-386
-5	1	14	441	465
-5	1	21	100	80
-4	1	2	292	302
-4	1	10	300	-308
-4	1	18	154	140
-3	1	3	291	-297
-3	1	10	186	-163
-3	1	18	231	219
-3	1	27	102	103
-2	1	6	78	-9
-2	1	13	329	320
-2	1	22	165	170
-1	1	5	85	79
-1	1	14	362	308
-1	1	22	212	-236
0	1	4	305	-287
0	1	11	242	211
0	1	18	245	232
0	1	25	48	52
1	1	4	353	308
1	1	11	186	170
1	1	19	249	-215
2	1	1	184	140
2	1	9	70	-91
2	1	17	128	106
3	1	0	413	-444
3	1	8	231	213
3	1	19	102	84
4	1	4	256	-273
4	1	12	67	78
4	1	21	78	106
5	1	8	166	-180
5	1	17	110	112
6	1	4	196	195
6	1	12	182	-191
7	1	5	309	-291
-5	2	5	156	-150
-5	2	18	165	-170
-4	2	4	103	80
-4	2	12	170	-146
-4	2	21	49	17
-3	2	2	387	447
-3	2	14	165	-142
-3	2	25	82	-37
-2	2	8	154	182
-2	2	16	372	-407
-1	2	2	269	-304
-1	2	9	142	87
-1	2	18	169	-169
-1	2	26	40	26
0	2	6	198	-165
0	2	13	154	176
0	2	21	92	-112
1	2	1	128	-86
1	2	9	104	77
1	2	16	134	-121
2	2	1	220	-236
2	2	12	113	125
3	2	1	128	-84
3	2	12	271	-331
4	2	2	152	125
4	2	9	58	66
4	2	18	95	-99
5	2	4	501	-526
5	2	12	386	416
-4	3	1	73	130
-4	3	9	100	16
-4	3	16	62	80
-3	3	1	68	85
-3	3	15	312	-330
-2	3	3	186	216
-2	3	13	262	256
-2	3	21	137	-102
-1	3	12	224	230
-1	3	21	80	-72
0	3	8	77	-63
0	3	16	117	102
1	3	1	163	147
1	3	10	98	-78
1	3	20	104	130
2	3	10	168	-154
4	3	2	235	-221
4	3	16	122	123
5	3	6	61	-107
5	3	14	140	176
-12	0	6	137	204
-11	0	16	138	56
-10	0	10	289	322
-9	0	14	137	115
-8	0	12	602	665
-7	0	12	306	303
-6	0	4	191	174
-6	0	20	367	402
-5	0	16	243	-209
-4	0	4	620	-671
-4	0	20	145	-81
-3	0	16	328	284
-3	0	30	188	-207
-2	0	14	528	476
-1	0	10	215	-190
-1	0	26	110	-82
0	0	12	382	-349
0	0	26	83	68
1	0	16	379	332
2	0	0	634	-898
2	0	16	379	-342
3	0	4	75	-48
3	0	18	260	262
4	0	8	829	-892
5	0	8	321	-315
6	0	6	179	-192
7	0	10	233	-229
8	0	12	99	-91
12	0	4	263	299
-8	1	10	200	-231
-7	1	3	176	-38
-7	1	12	189	143
-7	1	22	130	85
-6	1	5	153	-180
-6	1	14	227	-251
-5	1	1	154	-154
-5	1	8	172	148
-5	1	15	144	93
-5	1	22	164	-150
-4	1	3	395	-443
-4	1	11	258	277
-4	1	19	181	-179
-3	1	4	49	-39
-3	1	11	421	400
-3	1	19	157	180
-3	1	28	89	95
-2	1	7	89	21
-2	1	14	85	-85
-2	1	23	69	61
-1	1	6	473	-441
-1	1	15	301	250
-1	1	24	122	97
0	1	5	351	372
0	1	12	96	101
0	1	19	128	-123
0	1	26	40	-60
1	1	5	153	-155
1	1	12	233	229
1	1	20	111	-109
2	1	2	516	-518
2	1	10	315	318
2	1	18	182	-154
3	1	1	274	-297
3	1	9	479	504
3	1	22	188	-174
4	1	5	272	299
4	1	13	112	-120
4	1	23	79	-93
5	1	9	120	-129
5	1	19	208	-219
6	1	5	241	-249
6	1	13	157	161
7	1	6	357	-359
-5	2	6	121	-82
-5	2	19	68	68
-4	2	5	135	69
-4	2	13	104	16
-4	2	23	124	4
-3	2	4	581	-741
-3	2	16	266	-266
-3	2	26	89	-70
-2	2	9	121	-62
-2	2	17	194	-221
-1	2	3	102	-38
-1	2	10	250	285
-1	2	20	218	215
0	2	0	202	173
0	2	7	160	-135
0	2	14	368	427
0	2	22	40	-44
1	2	2	388	414
1	2	10	240	-267
1	2	18	130	134
2	2	2	242	240
2	2	13	182	164
3	2	3	184	-154
3	2	14	152	170
4	2	3	353	348
4	2	10	58	64
4	2	19	44	34
5	2	5	80	-53
5	2	13	145	-171
-4	3	2	233	-250
-4	3	10	172	157
-4	3	17	58	80
-3	3	2	68	60
-3	3	16	98	-91
-2	3	4	265	-317
-2	3	15	132	-91
-2	3	23	76	42
-1	3	13	311	209
0	3	1	64	54
0	3	9	107	52
0	3	17	31	-22
1	3	2	95	74
1	3	11	96	-82
1	3	21	104	102
2	3	12	261	243
4	3	5	183	185
4	3	17	110	-92
5	3	8	124	135
5	3	16	103	-106
-12	0	12	196	196
-11	0	18	192	86
-10	0	14	236	-280
-9	0	16	136	-76
-8	0	14	458	-487
-7	0	14	212	-210
-6	0	6	395	-303
-6	0	22	220	-191
-5	0	20	307	287
-4	0	6	603	653
-4	0	24	325	-321
-3	0	18	130	-113
-2	0	2	781	-1135
-2	0	16	483	-420
-1	0	14	291	246
-1	0	28	110	-103
0	0	14	433	-407
0	0	28	76	69
1	0	18	331	-314
2	0	2	775	1137
2	0	20	169	165
3	0	6	120	-72
3	0	22	180	-152
4	0	10	696	651
5	0	10	169	145
6	0	8	468	521
8	0	0	284	354
8	0	16	141	158
12	0	6	123	-157
-8	1	11	165	213
-7	1	7	256	230
-7	1	13	130	95
-7	1	24	148	82
-6	1	8	153	-150
-6	1	16	212	203
-5	1	2	128	107
-5	1	9	446	499
-5	1	16	66	-74
-5	1	23	222	-219
-4	1	4	95	-50
-4	1	12	132	87
-4	1	21	200	207
-3	1	5	126	148
-3	1	13	222	184
-3	1	21	131	154
-2	1	1	134	-145
-2	1	8	53	-73
-2	1	15	168	-172
-2	1	24	130	-124
-1	1	7	321	-275
-1	1	16	461	-492
-1	1	25	115	90
0	1	6	102	59
0	1	13	229	-227
0	1	20	100	-93
0	1	27	36	31
1	1	6	380	424
1	1	13	296	-267
1	1	21	95	88
2	1	3	451	450
2	1	11	158	-157
2	1	20	166	172
3	1	2	291	313
3	1	10	254	-250
3	1	24	111	107
4	1	6	208	205
4	1	15	128	143
5	1	1	608	644
5	1	10	165	184
5	1	21	66	63
6	1	6	249	-235
7	1	0	227	-145
7	1	8	280	53
-5	2	7	231	-141
-5	2	20	145	117
-4	2	6	174	-160
-4	2	14	230	-88
-4	2	24	113	-128
-3	2	5	238	250
-3	2	18	267	276
-2	2	1	64	57
-2	2	10	176	-191
-2	2	20	154	-156
-1	2	4	652	676
-1	2	11	103	-64
-1	2	21	70	-84
0	2	1	265	-228
0	2	8	223	204
0	2	15	177	167
0	2	23	91	-67
1	2	3	131	30
1	2	11	108	64
1	2	19	74	47
2	2	3	146	-115
2	2	14	230	-250
3	2	4	560	660
3	2	15	86	45
4	2	4	80	94
4	2	11	190	-210
4	2	20	137	165
5	2	6	283	323
5	2	14	123	-170
-4	3	3	146	-182
-4	3	11	182	174
-4	3	18	130	-143
-3	3	3	137	112
-3	3	17	95	-21
-2	3	5	349	-352
-2	3	16	42	-66
-1	3	1	210	-220
-1	3	14	42	45
0	3	2	133	-128
0	3	10	282	285
0	3	18	121	-116
1	3	3	242	-220
1	3	12	180	-170
2	3	1	132	102
2	3	13	247	253
4	3	6	146	-227
4	3	18	77	-75
5	3	10	124	-131
5	3	17	103	127
-12	0	16	253	283
-11	0	20	161	-200
-10	0	20	236	224
-9	0	18	139	-92
-8	0	16	95	124
-7	0	16	130	129
-6	0	8	430	417
-5	0	6	147	-147
-5	0	22	196	-144
-4	0	8	919	-1035
-3	0	6	147	147
-3	0	20	325	-290
-2	0	4	283	-357
-2	0	18	136	123
-1	0	16	408	-353
0	0	2	141	-149
0	0	16	304	287
1	0	6	187	175
1	0	20	196	-177
2	0	6	449	-423
2	0	22	67	-80
3	0	8	255	255
3	0	24	205	180
4	0	12	173	-101
5	0	16	240	251
6	0	10	63	92
8	0	2	449	-490
10	0	2	272	284
12	0	8	139	-146
-8	1	13	184	-200
-7	1	5	323	35
-7	1	14	158	-120
-7	1	25	184	-142
-6	1	9	197	210
-6	1	17	110	-100
-5	1	3	516	-577
-5	1	10	277	269
-5	1	17	266	-243
-5	1	25	185	185
-4	1	5	164	151
-4	1	13	280	-272
-4	1	22	235	-255
-3	1	6	73	-22
-3	1	14	319	-283
-3	1	22	242	225
-2	1	2	780	-687
-2	1	9	74	24
-2	1	16	233	245
-1	1	1	178	-190
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-1	1	26	104	103
0	1	7	127	-150
0	1	14	37	33
0	1	21	250	247
1	1	0	111	-85
1	1	7	308	300
1	1	14	67	8
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2	1	4	276	290
2	1	12	192	-188
2	1	21	200	-199
3	1	3	123	141
3	1	14	398	390
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4	1	7	181	-201
4	1	16	55	-69
5	1	2	520	-517
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7	1	1	271	-218
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-5	2	24	146	-169
-4	2	7	500	-489
-4	2	17	148	-31
-4	2	25	284	106
-3	2	7	174	123
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-2	2	2	125	-94
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-1	2	22	66	-42
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0	2	9	244	232
0	2	16	205	217
0	2	24	92	-107
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1	3	14	182	141
2	3	2	132	140
3	3	0	137	124
4	3	7	104	-120
5	3	0	151	-115
5	3	10	124	-131
5	3	18	58	-62
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-10	0	22	132	-126
-8	0	4	125	-241
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-5	0	8	215	188
-5	0	24	192	192
-4	0	10	828	905
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1	2	13	100	-123
1	2	22	163	163
2	2	5	145	-125
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3	2	7	79	87
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5	3	1	148	133
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6	0	14	139	109
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10	0	10	228	-280
12	0	12	87	-111
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-7	1	17	201	196
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-4	1	16	209	-214
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1	1	16	219	190
1	1	26	92	-117
2	1	7	221	229
2	1	15	178	-169
2	1	23	95	109
3	1	6	604	-647
3	1	16	230	-262
4	1	2	150	178
4	1	10	238	-277
4	1	18	146	172
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6	1	9	218	-239
7	1	3	124	298
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-2	2	14	70	-78
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-1	2	7	70	79
-1	2	14	170	153
-1	2	24	115	-123
0	2	4	468	-408
0	2	11	80	-82
0	2	18	216	-224
0	2	26	30	45
1	2	6	192	234
1	2	14	100	-220
1	2	23	77	-152
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2	2	22	170	197
3	2	8	80	94
3	2	22	99	-102
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4	2	23	56	-33
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0	3	13	182	-181
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1	3	6	103	-185
1	3	17	113	170
2	3	4	164	-200
4	3	0	73	-103
4	3	13	122	-164
5	3	4	71	77
5	3	12	113	-143
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-9	0	8	123	71
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-7	0	6	114	115
-7	0	24	133	-142
-6	0	14	202	130
-5	0	12	207	-254
-5	0	30	191	196
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-3	0	26	87	60
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0	0	22	304	263
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1	0	26	124	138
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3	0	14	141	125
4	0	2	692	-735
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-3	1	9	573	-571
-3	1	17	217	174
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-2	1	12	249	-220
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-1	1	21	316	283
0	1	3	377	-427
0	1	10	292	-279
0	1	17	123	-115
0	1	24	115	112
1	1	3	238	-199
1	1	10	353	353
1	1	17	192	166
2	1	0	132	-138
2	1	8	67	-78
2	1	16	100	129
2	1	24	130	-139
3	1	7	509	-539
3	1	17	349	-341
4	1	3	170	-171
4	1	11	169	176
4	1	20	85	-101
5	1	5	168	178
5	1	16	202	235
6	1	0	142	-143
6	1	10	234	260
7	1	4	241	-137
-5	2	4	388	411
-5	2	16	264	273
-4	2	3	187	106
-4	2	10	182	170
-4	2	20	50	280
-3	2	1	67	-76
-3	2	12	345	425
-3	2	24	150	151
-2	2	7	229	-225
-2	2	15	249	-230
-1	2	1	127	106
-1	2	8	170	-145
-1	2	16	108	75
-1	2	25	83	57
0	2	5	437	399
0	2	12	180	-170
0	2	20	205	224
1	2	0	162	128
1	2	8	125	70
1	2	15	79	-12
2	2	0	147	153
2	2	7	103	-95
3	2	0	200	-108
3	2	10	144	160
4	2	1	108	-212
4	2	8	58	35
4	2	17	123	-102
5	2	0	204	222
5	2	10	55	-49
-5	3	7	135	-151
-4	3	8	378	-313
-4	3	15	64	-97
-4	3	24	96	-85
-3	3	10	202	107
-2	3	2	254	203
-2	3	12	135	137
-2	3	20	106	-112
-1	3	9	104	211
-1	3	20	68	-81
0	3	6	217	-212
0	3	14	92	-40
0	3	23	31	-30
1	3	9	90	-138
1	3	18	73	-17
2	3	5	332	-413
4	3	1	73	-42
4	3	14	151	157
5	3	5	90	-71
5	3	13	107	-124

probably small because of the excellent agreement between the molecular dimensions of 4,4′-diamino-3,3′-dichlorobiphenyl and those of a very similar molecule, *viz.* 4,4′-diamino-3,3′-dimethylbiphenyl (Chawdhury, Hargreaves & Sullivan, 1968); comparative details of the molecular dimensions are given in Fig. 3, which is discussed later.

The least-squares best planes passing through the atoms in phenyl ring I [C(1), C(2), ... C(6)] and phenyl ring II [C(1′), C(2′), ... C(6′)], respectively, are:

$$\text{I} \quad 0{\cdot}2247x+0{\cdot}9420y+0{\cdot}2495z=4{\cdot}1359\ \text{Å}$$

$$\text{II} \quad -0{\cdot}0993x+0{\cdot}9119y+0{\cdot}3982z=4{\cdot}7712$$

The displacements of individual atoms from the two planes are shown in Fig. 2 and Table 3.

Table 3. *Displacements from the best planes through the atoms in phenyl rings* I *and* II *respectively*

I	Displacement	II	Displacement
C(1)	0·010 Å	C(1′)	0·001 Å
C(2)	−0·010	C(2′)	−0·014
C(3)	0·002	C(3′)	0·020
C(4)	0·006	C(4′)	−0·010
C(5)	−0·007	C(5′)	−0·002
C(6)	−0·001	C(6′)	0·006
N(1)	0·017	N(1′)	0·058
Cl(1)	−0·020	Cl(1′)	0·059
C(1′)	0·090	C(1)	0·057
C(4′)	0·293	C(4)	0·274
N(1′)	0·484	N(1)	0·402

Both phenyl rings are planar within the accuracy of the atomic parameters but the molecule as a whole is non-planar since the two rings are mutually inclined at an angle (φ) of 21°. The relative positions of the rings may be described by starting with a trans-planar configuration and then bringing the rings to their observed mutual positions by the following operations: (i) rotation of one ring with respect to the other about the axis C(1)–C(1′) through an angle φ_1, (ii) rotation of ring I through an angle φ_2 about an axis which is in the plane of ring I and passes through C(1) in a direction at right angles to the line C(1)–C(1′), (iii) rotation of ring II through an angle φ_3 about an axis which is in the plane of ring II and passes through C(1′) in a direction at right angles to the line C(1)–C(1′). The angles φ_2 and φ_3 are small (approximately 3·4° and 2·2° respectively) and as a result the angle between the rings, $\varphi = 21°$, differs from φ_1 by only a few minutes. Fig. 2 shows that the angles φ_2 and φ_3 represent bends in the length of the molecule which are real and may not be attributed merely to uncertainties in the atomic parameters determined. The molecules of 4,4′-diamino-3,3′-dimethylbiphenyl show similar features in the solid state (Chawdhury, Hargreaves & Sullivan, 1968); corresponding values of φ_1, φ_2 and φ_3 are 41°, 2·7° and 3·3° respectively. It is possible that steric hindrance, resonance energy and crystal forces all play a part in determining the values of φ_1, φ_2 and φ_3 and it may well be that in the latter molecule the larger methyl group is responsible for enhanced steric effects and an increase in the value of φ_1. When crystal forces are absent (in the vapour phase) the angle φ_1 in the dichloro-molecule is reported to be 52 ± 10° (Bastiansen, 1949). Similar variations are observed in molecules of biphenyl with values $\varphi_1 = 0°$ in the solid phase (Robertson, 1961*a*,*b*) and $\varphi_2 = 42°$ in the vapour phase (Brock-

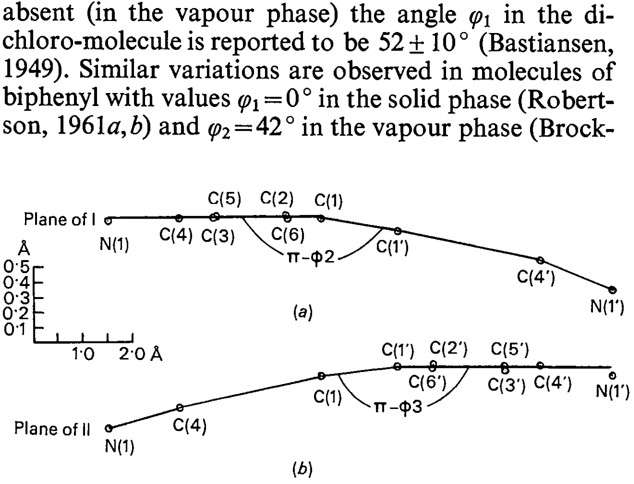


Fig. 2. (*a*) Displacements from the best plane through atoms in phenyl ring I. (*b*) Displacements from the best plane through atoms in phenyl ring II. In both (*a*) and (*b*) the best plane is viewed end-on and in a direction at right angles to the length of the molecule. The best planes are shown by horizontal lines and the displacements of individual atoms are measured by vertical displacements from this line; for clarity, vertical displacements are magnified by plotting them on a scale which is three times as large as the horizontal scale.

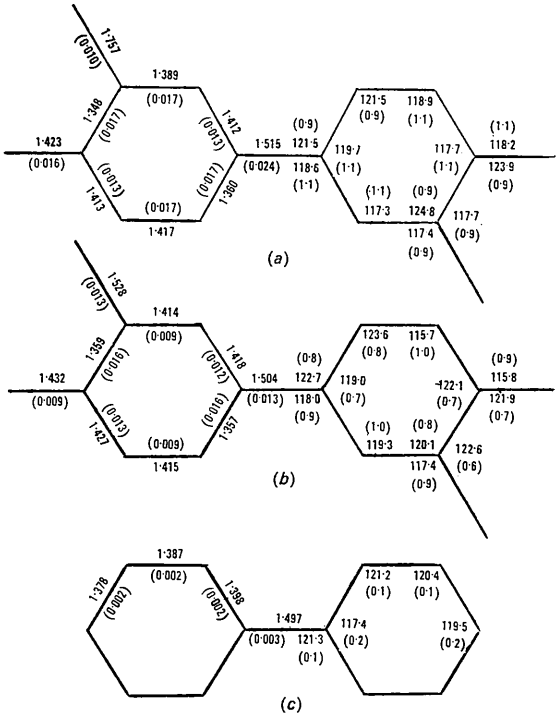
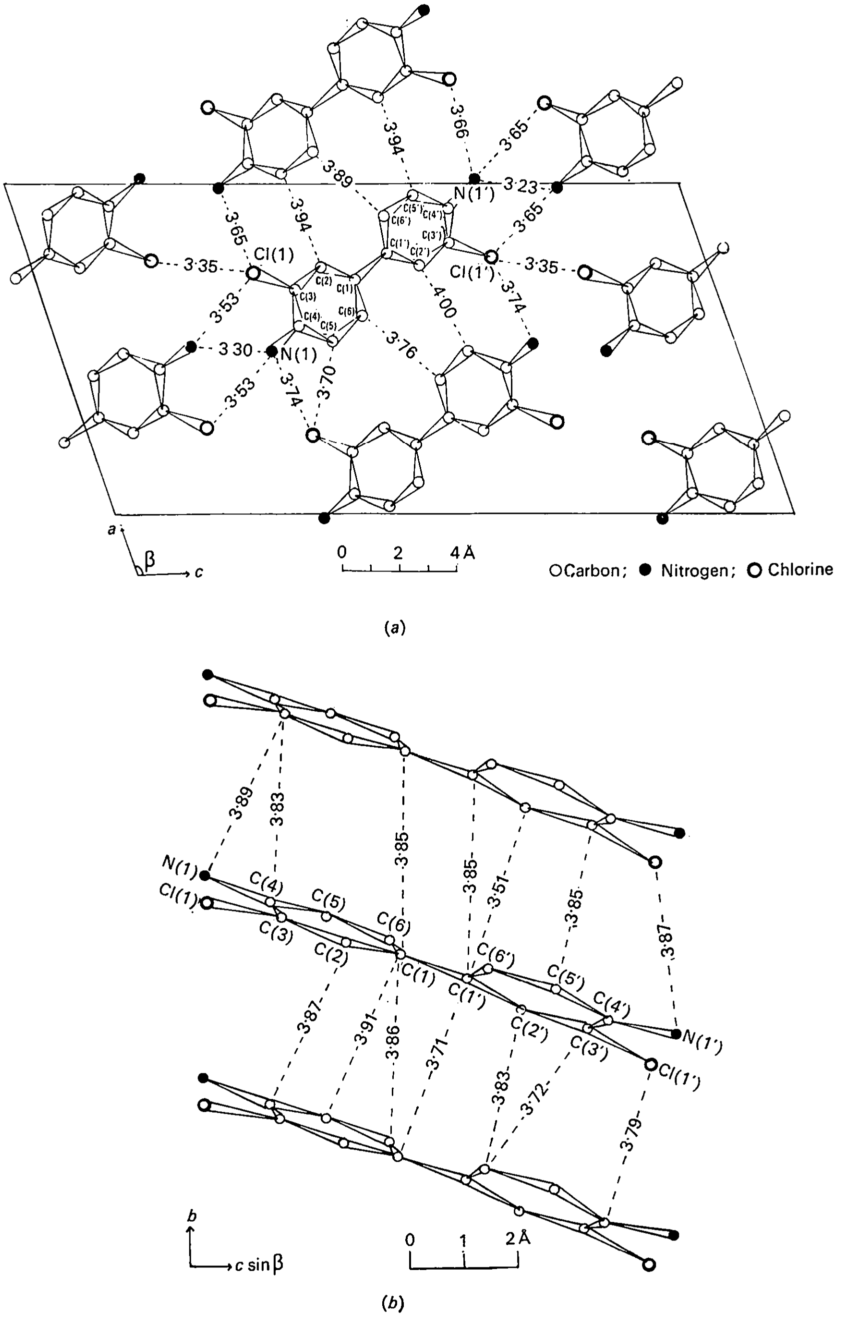


Fig. 3. Comparison of the molecular dimensions of (*a*) 4,4′-diamino-3,3′-dichlorobiphenyl (*b*) 4,4′-diamino-3,3′-dimethylbiphenyl (*c*) biphenyl.

way & Karle, 1944; Bastiansen, 1949; Almenningen & Bastiansen, 1958).

There are no significant differences (Cruickshank, 1949) between the dimensions of equivalent bonds and angles in the two halves of the molecule. Assuming that the two aromatic rings have identical configurations, and taking mean values, we obtain the molecular dimensions shown in Fig. 3(*a*). For comparison the molecular dimensions of 4,4′-diamino-3,3′-dimethylbiphenyl and of biphenyl are shown in Figs. 3(*b*) and 3(*c*) respectively.

The similarity in the dimensions of the dichloro- and dimethyl-molecules is somewhat surprising in view of the unexpectedly large variations in the C–C distances within the benzenoid rings; the greatest difference between equivalent bonds in the two molecules is only 0·025 Å, yet there are variations of 0·07 Å in the C–C distances within each benzenoid ring. It is



(*a*)

(*b*)

Fig. 4. (*a*) The structure viewed along [010], showing the shorter intermolecular distances. (*b*) The structure viewed along [100], showing the shorter intermolecular distances.

difficult to account for these observed variations in terms of systematic errors in the two structure determinations since the cell dimensions, space groups and crystal structures of the two materials are completely different.

There appear to be some similarities between corresponding bond angles in the two molecules but the agreement is much less obvious than the agreement between bond lengths.

The carbon atoms linking the two aromatic rings, C(1) and C(1′), are separated by a distance (1·515 ± 0·024 Å) in the dichloro-molecule which is not significantly different from that observed in the dimethyl molecule (1·504 ± 0·013 Å) and in biphenyl itself (1·497 ± 0·003 Å) and which probably represents a C(sp^2)–C(sp^2) single bond.

The chlorine and nitrogen atoms are attached to the aromatic rings by bonds of normal lengths but all four atoms are displaced out of the planes of the rings and for ring II (Table 3) the displacements appear to be significant.

Fig. 4(*a*) and (*b*) show the structure viewed along the directions [010] and [100] respectively and indicate all distances of 4·0 Å or less between atoms in neighbouring molecules. The shortest distances are 3·23 and 3·30 Å between two pairs of nitrogen atoms, 3·35 and 3·35 Å between two pairs of chlorine atoms, and 3·51 Å between a pair of carbon atoms.

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The Structure of *cis*-Cobalt Diazidobisethylenediamine Nitrate, $Co(C_2N_2H_8)_2(N_3)_2NO_3$

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The crystal structure of *cis*-cobalt diazidobisethylenediamine nitrate has been determined from two-dimensional X-ray diffraction data. The cell has dimensions $a = 12·106$, $b = 23·620$, $c = 8·801$ Å, space group *Pnma* and $Z = 8$. The cobalt ion has a distorted octahedral coordination with four N atoms of the ethylenediamine group and two N atoms of the azide group. The ethylenediamine molecule is in *gauche* configuration. The azido groups are linear with N–N distances 1·11–1·23 Å. The valence angle Co–N–N is ~120°. The two nitrate ions are stacked one above the other to form a close packing with the complex ions.

Very few structures of compounds coordinating an azide group have been reported in the literature. The present note describes the structure of a cobalt compound coordinating ethylenediamine and azide groups.

Orthorhombic crystals of the cobalt complex were obtained from solution by the method described by Staples & Tobe (1960). Crystal data were determined from various rotation and Weissenberg films using Fe $K\alpha$ radiation, and were as follows:

$a = 12·106 \pm 0·010$, $b = 23·620 \pm 0·010$, $c = 8·801 \pm 0·01$ Å
D_o (flotation method) $= 1·60$, $Z = 8$, $D_c = 1·58$ g.cm^{-3}.

The space group is *Pnma* or $Pna2_1$. *Pnma* was confirmed by the structure analysis.

The intensities of the $hk0$, $0kl$ and $h0l$ reflexions were measured visually from Weissenberg films from crystals rotating about the three respective axes. The position of the cobalt atom was determined from Patterson projection maps, and from a series of four electron-density projections the coordinates of all the other atoms were determined. The structure was refined by least squares on the CDC 3600 computer. The final R value for 293 reflexions was 0·10. The atomic co-