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The Crystal and Molecular Structure of 4,4′-diamino-3,3′- dimethylbiphenyl (*o*-Tolidine)

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4,4′-Diamino-3,3′-dimethylbiphenyl, $C_{14}H_{16}N_2$, crystallizes with cell dimensions $a=7{\cdot}44$, $b=23{\cdot}70$, $c=6{\cdot}47$ Å, space group $P2_12_12_1$ 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 11%. 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 41°; in addition each phenyl ring is bent through an angle of about 3° away from the line C(1)–C(1′). The length of the bond C(1)–C(1′) is $1{\cdot}504 \pm 0{\cdot}013$ Å.

Introduction

X-ray analyses of crystals of biphenyl (Hargreaves & Rizvi, 1962; Robertson, 1961*a*,*b*; Trotter, 1961) have established that the biphenyl molecule is planar in the solid state, although electron diffraction studies (Brockway & Karle, 1944; Bastiansen, 1949; Almenningen & Bastiansen, 1958) suggest that the two phenyl rings are mutually inclined at an angle of about 42° in the vapour phase. Substituents introduced in the 2,2′ positions produce overcrowding which must result in a nonplanar molecule (see *e.g.* Smare, 1948; Fowweather & Hargreaves, 1950; Fowweather, 1952). It is not clear, however, what will be the effect of introducing substituents in the 3,3′ and 4,4′ positions. A number of these derivatives are in course of examination by X-ray methods and we now present details of the stereochemistry of one of them, *viz.* 4,4′-diamino-3,3′-dimethylbiphenyl (*o*-tolidine).

Experimental

X-ray rotation and Weissenberg photographs about the three principal axes of the orthorhombic crystals show that the space group is $P2_12_12_1$ and that four molecules are contained in a unit cell with the following dimensions and estimated limits of error; $a=7{\cdot}44 \pm 0{\cdot}01$, $b=23{\cdot}70 \pm 0{\cdot}05$, $c=6{\cdot}47 \pm 0{\cdot}02$ Å. These results are in agreement with preliminary X-ray studies by Clark & Pickett (1931), Hargreaves (1940), Quader (1958) and Lasheen (1963).

Reflexions *hk*0, *hk*1, *hk*2, *hk*3 and *hk*4, recorded in equi-inclination Weissenberg photographs using Cu $K\alpha$ radiation, provided the data from which the atomic positions were finally determined. The intensities of the reflexions were measured by the multiple film technique and visual comparison with crystal reflected calibration spots of known relative exposures. No corrections were made for absorption, which was small in the crystal specimen used for intensity measurements ($\mu=6{\cdot}7$ cm^{-1}; dimensions of cross-section perpendicular to the axis of oscillation ~0·18 mm).

Determination and refinement of the structure

Optical transforms and Patterson maps were used to obtain the approximate orientations of the phenyl rings and the position of the centre of the molecule was determined by the molecular location technique of Bhuiya & Stanley (1964). The [001] projection agreed well with that deduced previously (Sullivan, 1960) by direct methods using Sayre's relationship.

Refinement began with an agreement index, R, of 0·44 for the *hk*0 reflexions and 0·42 for the 0*kl* reflexions. Three cycles of Fourier refinement using ϱ_o maps reduced $R(hk0)$ to 0·35. Because of overlap of the projected atoms refinement was continued by the minimum residual method of Bhuiya & Stanley (1963); six cycles of refinement reduced $R(hk0)$ to 0·12. $R(0kl)$ was similarly reduced to 0·19 by three cycles of Fourier refinement and to 0·15 by five cycles of minimum residual refinement.

At this stage $(\varrho_o-\varrho_c)$ maps indicated that the structure was basically correct and that there was no marked thermal anisotropy. Minimum residual refinement was then applied to all the 839 observed *hkl* reflexions, excepting for 6 reflexions which appeared to suffer from extinction effects. The calculated structure factors were based on the atomic scattering factors of Forsyth & Wells (1959) and isotropic temperature factors B. Four cycles of refinement reduced $R(hkl)$ from 0·17 to 0·13. Hydrogen atoms were then included in the calculations and after five more cycles of refinement, when the parameter shifts were less than one-quarter of the estimated standard deviations, a final R index of 0·11 was obtained.

The final positional and thermal parameters are given in Table 1. Estimated standard deviations of the posi-

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tional coordinates were deduced with the use of Cruickshank's (1960) formula; the z coordinates required a correction for the fact that experimental data had not been collected to the edge of the limiting sphere in this direction. The standard deviations obtained thus were

	$\sigma(x)=\sigma(y)$	$\sigma(z)$
Carbon	0·008 Å	0·017 Å
Nitrogen	0·007	0·013

The observed and calculated structure amplitudes, and the calculated phase angles α, are presented in Table 2.

Description of the structure

Fig. 1 gives the dimensions of the o-tolidine molecule deduced from the positional coordinates in Table 1. The estimated standard deviations of the bond lengths and bond angles are given within brackets; the former were calculated with the use of Ahmed & Cruickshank's (1953) formula and the latter by Darlow's (1960) formula.

The equations of the 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

Phenyl ring I

$$0·9128x+0·2403y-0·3302z-3·2001=0$$

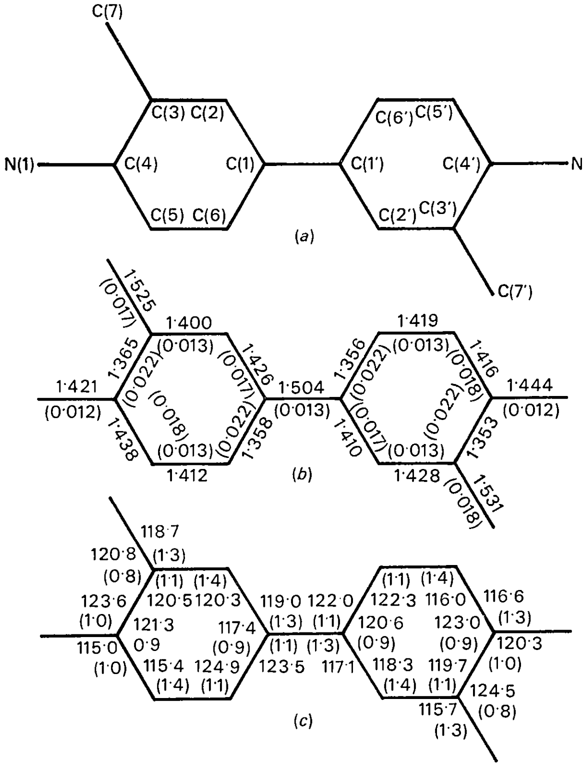

Fig. 1. Dimensions of the o-tolidine molecule. (a) Numbering of the atoms. (b) Bond lengths with standard deviations (Å). (c) Bond angles with standard deviations (°).

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

	x/a	y/b	z/c	B
C(1)	0·4119	0·1115	0·1097	2·60 Å^2
C(2)	0·4880	0·0705	0·2452	2·86
C(3)	0·5158	0·0151	0·1772	2·92
C(4)	0·4633	−0·0010	−0·0162	3·10
C(5)	0·3900	0·0390	−0·1605	3·40
C(6)	0·3647	0·0941	−0·0827	3·20
C(7)	0·5968	−0·0275	0·3271	3·58
N(1)	0·4847	−0·0566	−0·0944	3·98
C(1′)	0·3775	0·1701	0·1897	2·75
C(2′)	0·4060	0·2152	0·0515	2·97
C(3′)	0·3646	0·2710	0·1197	2·99
C(4′)	0·2962	0·2791	0·3111	3·16
C(5′)	0·2688	0·2346	0·4536	3·50
C(6′)	0·3095	0·1796	0·3809	3·28
C(7′)	0·3989	0·3181	−0·0374	3·52
N(1′)	0·2535	0·3353	0·3820	3·98
H(1)	0·331	0·120	−0·179	4·80
H(2)	0·360	0·023	−0·290	4·80
H(3)	0·421	−0·068	−0·232	4·80
H(4)	0·546	−0·076	0·027	4·80
H(5)	0·569	−0·031	0·464	4·80
H(6)	0·568	−0·063	0·277	4·80
H(7)	0·650	−0·014	0·465	4·80
H(8)	0·520	0·077	0·404	4·80
H(1′)	0·298	0·151	0·490	4·80
H(2′)	0·202	0·234	0·595	4·80
H(3′)	0·177	0·335	0·509	4·80
H(4′)	0·313	0·351	0·259	4·80
H(5′)	0·303	0·321	−0·121	4·80
H(6′)	0·384	0·356	−0·058	4·80
H(7′)	0·459	0·345	0·079	4·80
H(8′)	0·433	0·210	−0·108	4·80

Phenyl ring II

$$0·9300x+0·1054y+0·3522z-3·4694=0\ .$$

Deviations of atoms from these two planes are shown in Table 3 and Fig. 2.

Phenyl rings I and II are both planar within the accuracy of our measurements, but the molecule as a whole is non-planar since the two rings are mutually inclined at an angle, φ, of 41°. We may describe the relative positions of these rings by starting with a trans-planar configuration and then bringing the rings to their observed mutual positions by introducing the three 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 quite small (2·7° and 3·3° respectively) and because of this the angle between the rings, $\varphi=41°$, 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 at C(1) and C(1′); it also shows, through plots of the atomic positions determined, that these bends are real

Table 2. *Observed and calculated structure amplitudes and calculated phase angles* (°)

h	k	l	$10\lvert F_o\rvert$	$10\lvert F_c\rvert$	α
0	2	0	47	22	180.0
0	12	0	259	248	0.0
0	20	0	187	198	180.0
*1	1	0	198	216	90.0
1	5	0	278	295	-90.0
1	9	0	110	109	90.0
1	14	0	125	108	-90.0
1	20	0	110	103	-90.0
1	29	0	68	59	90.0
*2	2	0	880	1144	0.0
2	7	0	220	228	0.0
2	11	0	220	202	0.0
2	16	0	199	185	0.0
2	21	0	154	162	180.0
2	28	0	48	43	0.0
3	4	0	45	40	90.0
3	10	0	225	211	-90.0
0	18	0	119	107	-90.0
3	23	0	110	104	90.0
3	28	0	45	48	-90.0
4	3	0	122	135	0.0
4	11	0	119	96	0.0
4	18	0	42	44	0.0
4	23	0	107	92	180.0
5	2	0	80	60	90.0
5	7	0	102	100	-90.0
5	11	0	134	132	-90.0
5	15	0	94	95	90.0
5	20	0	110	88	90.0
5	24	0	42	35	90.0
6	2	0	130	125	0.0
6	7	0	77	75	180.0
6	12	0	77	71	0.0
6	17	0	32	41	0.0
7	7	0	45	46	90.0
7	11	0	94	88	90.0
7	16	0	86	74	-90.0
8	1	0	88	105	180.0
8	10	0	53	51	180.0
9	2	0	29	26	-90.0
0	5	1	27	26	90.0
0	9	1	38	37	-90.0
0	13	1	134	117	90.0
0	17	1	51	45	-90.0
0	23	1	51	7	-90.0
1	3	1	427	465	137.6
1	7	1	205	158	-59.9
1	11	1	115	97	91.4
1	15	1	123	102	-155.4
1	19	1	269	277	-140.2
1	23	1	39	46	174.2
2	2	1	365	366	-175.3
2	6	1	180	149	174.1
2	10	1	183	147	-82.9
2	14	1	99	95	136.0
2	18	1	92	93	-126.2
3	0	1	69	96	90.0
3	4	1	114	97	139.4
3	8	1	251	280	-8.9
3	13	1	73	67	165.8
3	17	1	153	161	-171.2
3	22	1	49	68	84.7
4	2	1	57	54	123.5
4	6	1	238	230	-157.4
4	11	1	66	62	143.8
4	18	1	92	97	-121.0
4	22	1	65	69	-153.9
5	3	1	169	172	-140.0
5	8	1	61	52	104.8
5	19	1	43	41	49.0
6	2	1	132	148	-111.1
6	6	1	91	108	-158.2
6	11	1	69	77	-106.3
6	16	1	79	94	-121.0
6	20	1	61	71	-101.5
7	3	1	40	36	-142.7
7	13	1	45	61	84.6
0	1	2	183	241	-90.0
0	5	2	106	93	90.0
0	10	2	191	165	0.0
0	15	2	27	38	90.0
0	20	2	117	125	0.0
1	0	2	320	387	0.0
1	4	2	163	161	129.4
1	8	2	327	304	132.2
1	12	2	137	132	6.5
1	17	2	41	24	-110.2
1	22	2	78	78	17.3
2	2	2	13	37	167.1
2	6	2	241	228	-55.5
2	10	2	173	164	-44.9
2	14	2	130	125	-68.3
2	20	2	159	172	66.8
2	24	2	44	45	4.4
3	1	2	133	144	14.3
3	5	2	108	99	-19.6
3	9	2	154	151	100.9
3	10	2	32	34	-12.2
3	17	2	75	81	-74.0
3	21	2	24	27	-45.5
4	0	2	43	21	180.0
4	4	2	88	96	-43.0
4	8	2	126	114	-54.3
4	12	2	48	31	60.7
4	16	2	90	86	-87.8
4	20	2	24	34	7.2
4	25	2	13	16	28.9
*0	4	0	535	640	0.0
0	14	0	107	95	180.0
0	22	0	74	78	0.0
*1	2	0	297	368	-90.0
1	6	0	195	189	90.0
1	11	0	102	106	90.0
1	16	0	71	47	-90.0
1	21	0	94	82	90.0
1	30	0	86	80	-90.0
2	4	0	190	197	0.0
2	8	0	94	65	180.0
2	12	0	66	80	180.0
2	17	0	199	192	180.0
2	22	0	71	79	180.0
3	1	0	301	294	90.0
3	5	0	119	112	-90.0
3	12	0	88	87	90.0
3	19	0	273	271	90.0
3	24	0	53	48	90.0
3	29	0	39	33	90.0
4	4	0	110	102	0.0
4	12	0	145	147	0.0
4	19	0	42	39	180.0
4	25	0	45	33	180.0
5	3	0	113	110	90.0
5	8	0	116	121	-90.0
5	12	0	98	86	-90.0
5	16	0	98	100	-90.0
5	21	0	60	53	90.0
5	26	0	29	21	90.0
6	3	0	102	102	180.0
6	8	0	53	43	180.0
6	13	0	94	81	180.0
7	2	0	32	33	-90.0
7	8	0	53	52	-90.0
7	12	0	56	56	-90.0
7	17	0	60	48	90.0
8	5	0	29	41	180.0
8	11	0	98	79	180.0
9	3	0	36	47	90.0
0	6	1	114	115	0.0
0	10	1	553	439	0.0
0	14	1	165	150	0.0
0	18	1	225	224	180.0
1	0	1	504	633	-90.0
1	4	1	211	208	-140.8
1	8	1	174	107	-65.9
1	12	1	172	132	-107.8
1	16	1	45	42	137.5
1	20	1	199	211	128.6
1	24	1	49	53	107.5
2	3	1	572	575	-145.0
2	7	1	146	136	30.0
2	11	1	255	245	10.4
2	15	1	81	78	33.6
2	19	1	79	81	61.9
3	1	1	206	216	171.0
3	5	1	272	277	-170.7
3	10	1	165	154	-152.5
3	14	1	59	46	-76.1
3	18	1	121	133	64.2
3	23	1	37	41	60.5
4	3	1	139	140	-173.3
4	7	1	121	97	-154.1
4	13	1	72	76	-41.1
4	19	1	72	72	-41.1
5	0	1	94	90	-90.0
5	4	1	135	131	-30.4
5	13	1	33	43	149.3
5	20	1	29	43	143.1
6	3	1	55	73	-41.8
6	7	1	72	76	-123.1
6	13	1	32	56	123.5
6	17	1	29	32	150.8
6	21	1	38	44	5.3
7	9	1	77	84	35.3
7	19	1	49	47	54.9
0	2	2	296	308	180.0
0	7	2	335	318	90.0
0	11	2	220	188	90.0
0	16	2	97	77	0.0
0	21	2	184	195	-90.0
1	1	2	143	165	11.4
1	5	2	199	211	14.9
1	9	2	377	355	61.8
1	13	2	124	123	106.3
1	18	2	156	140	87.1
1	24	2	23	24	-2.8
2	3	2	120	86	-173.9
2	7	2	150	143	158.2
2	11	2	140	127	65.5
2	16	2	24	8	-76.5
2	21	2	25	27	67.4
2	25	2	29	21	-78.6
3	2	2	330	332	23.4
3	6	2	146	129	120.6
3	10	2	46	36	80.2
3	14	2	62	64	04.5
3	18	2	130	132	162.4
3	22	2	74	68	25.2
4	1	2	130	128	50.3
4	5	2	72	87	120.9
4	9	2	74	72	125.0
4	13	2	64	60	123.2
4	17	2	97	114	-106.9
4	22	2	21	32	46.4
4	26	2	22	26	-36.6
0	6	0	261	278	0.0
0	16	0	110	103	180.0
0	24	0	50	46	180.0
1	3	0	31	50	90.0
1	7	0	137	144	-90.0
1	12	0	214	204	-90.0
1	17	0	63	60	90.0
1	22	0	66	64	90.0
*2	0	0	294	320	0.0
2	5	0	179	101	0.0
2	9	0	29	21	180.0
2	13	0	232	203	0.0
2	19	0	107	87	0.0
2	25	0	36	34	180.0
3	2	0	204	195	90.0
3	6	0	94	85	-90.0
3	14	0	127	109	-90.0
3	20	0	56	52	-90.0
3	25	0	50	41	90.0
4	1	0	63	65	180.0
4	9	0	29	12	0.0
4	14	0	228	227	0.0
4	20	0	45	40	0.0
4	27	0	39	26	180.0
5	5	0	42	33	90.0
5	9	0	182	173	90.0
5	13	0	98	78	90.0
5	17	0	98	102	90.0
5	22	0	66	54	-90.0
6	0	0	80	69	180.0
6	5	0	53	45	180.0
6	9	0	53	38	180.0
6	14	0	107	108	0.0
7	4	0	56	49	-90.0
7	9	0	83	102	-90.0
7	14	0	56	55	-90.0
7	19	0	48	31	-90.0
8	7	0	53	58	180.0
8	12	0	53	51	0.0
0	2	1	342	217	180.0
0	7	1	89	66	-90.0
0	11	1	566	477	90.0
0	15	1	105	86	90.0
0	20	1	118	136	180.0
1	1	1	787	870	-129.2
1	5	1	141	126	43.0
1	9	1	296	231	-177.5
1	13	1	95	77	-132.2
1	17	1	120	107	108.2
1	21	1	52	49	85.5
2	0	1	741	909	-90.0
2	4	1	177	170	-156.5
2	8	1	46	54	-12.5
2	12	1	143	133	16.5
2	16	1	94	96	118.6
2	20	1	134	152	177.2
3	2	1	396	400	-97.5
3	6	1	91	73	56.1
3	11	1	37	42	-106.3
3	15	1	71	73	166.7
3	19	1	46	60	-60.4
4	0	1	388	380	-90.0
4	4	1	377	397	-166.6
4	9	1	130	131	8.2
4	16	1	97	96	-157.4
4	20	1	50	63	17.9
5	1	1	40	40	-135.3
5	5	1	74	77	-158.7
5	14	1	73	61	-79.1
6	0	1	167	183	90.0
6	4	1	71	87	178.5
6	8	1	122	143	-165.0
6	14	1	59	85	-103.8
6	18	1	28	37	-173.4
7	1	1	46	55	154.4
7	11	1	48	58	152.7
8	0	1	41	8	90.0
0	3	2	421	498	-90.0
0	8	2	138	137	0.0
0	12	2	122	69	0.0
0	18	2	87	69	0.0
0	22	2	122	118	0.0
1	2	2	211	237	124.3
1	6	2	178	201	37.7
1	10	2	266	216	-100.0
1	14	2	74	74	-164.1
1	19	2	168	163	6.5
2	0	2	40	36	180.0
2	4	2	220	217	-83.1
2	8	2	84	72	-64.3
2	12	2	107	79	-159.0
2	18	2	93	93	6.2
2	22	2	73	76	-18.2
2	28	2	24	31	22.9
3	3	2	265	264	47.1
3	7	2	151	155	30.9
3	11	2	48	04	68.1
3	15	2	87	80	112.5
3	19	2	90	93	91.8
3	23	2	63	63	3.9
4	2	2	137	134	75.6
4	6	2	119	100	-28.4
4	10	2	138	139	-144.6
4	14	2	89	86	-149.4
4	18	2	43	55	55.7
4	23	2	20	15	20.4
5	0	2	117	111	0.0
0	8	0	281	269	180.0
0	18	0	317	304	0.0
0	28	0	56	52	0.0
1	4	0	91	74	-90.0
1	8	0	169	187	90.0
1	13	0	134	128	-90.0
1	18	0	50	30	90.0
1	27	0	42	11	-90.0
*2	1	0	900	1231	0.0
2	6	0	80	83	180.0
2	10	0	193	139	0.0
2	14	0	187	172	0.0
2	20	0	83	68	0.0
2	27	0	74	54	180.0
3	3	0	160	170	-90.0
3	8	0	143	126	90.0
3	16	0	163	162	-90.0
3	21	0	102	95	-90.0
3	26	0	53	43	90.0
4	2	0	148	145	0.0
4	10	0	125	117	180.0
4	16	0	166	167	0.0
4	22	0	80	68	180.0
5	1	0	39	33	-90.0
5	6	0	32	32	-90.0
5	10	0	91	93	90.0
5	14	0	66	68	-90.0
5	18	0	193	193	-90.0
5	23	0	42	39	-90.0
6	1	0	68	61	180.0
6	6	0	42	53	180.0
6	11	0	39	52	180.0
6	16	0	91	83	0.0
7	5	0	39	44	90.0
7	10	0	66	62	90.0
7	15	0	63	59	90.0
8	0	0	119	144	0.0
8	9	0	48	45	180.0
8	15	0	36	9	0.0
0	3	1	203	192	90.0
0	8	1	22	3	180.0
0	12	1	83	77	180.0
0	16	1	35	34	180.0
0	22	1	65	64	180.0
1	2	1	184	182	160.1
1	6	1	255	244	-23.1
1	10	1	130	118	-60.7
1	14	1	56	53	-94.0
1	18	1	216	202	-11.1
1	22	1	119	125	50.7
2	1	1	528	576	118.2
2	5	1	165	169	-114.2
2	9	1	201	179	147.4
2	13	1	192	172	99.4
2	17	1	136	142	-18.5
2	21	1	57	70	-137.9
3	3	1	153	150	-135.6
3	7	1	101	84	126.1
3	12	1	51	40	-67.9
3	16	1	31	53	-32.5
3	21	1	32	55	-143.7
4	1	1	410	468	-98.2
4	5	1	156	150	-124.3
4	10	1	154	144	-154.8
4	17	1	113	130	85.6
4	21	1	57	63	120.9
5	2	1	28	10	-86.4
5	7	1	47	48	157.4
5	15	1	57	69	173.4
6	1	1	45	57	-73.3
6	5	1	56	55	-166.1
6	10	1	52	54	3.3
6	15	1	38	64	109.3
6	19	1	55	56	-165.1
7	2	1	65	75	-16.9
7	12	1	59	62	-72.4
9	0	1	47	54	-90.0
0	4	2	42	55	0.0
0	9	2	95	88	90.0
0	13	2	59	51	90.0
0	19	2	142	130	90.0
0	26	2	20	16	0.0
1	3	2	108	109	16.2
1	7	2	194	180	-76.6
1	11	2	173	164	864.2
1	15	2	22	48	-35.3
1	21	2	95	99	10.4
2	1	2	152	150	-44.2
2	5	2	68	45	179.7
2	9	2	294	275	121.1
2	13	2	67	53	-96.2
2	19	2	94	97	-100.1
2	23	2	78	64	-30.3
3	0	2	358	358	180.0
3	4	2	173	157	85.2
3	8	2	138	126	-122.1
3	12	2	79	89	-111.9
3	16	2	125	110	41.5
3	20	2	121	120	23.1
3	25	2	42	38	-1.6
4	3	2	134	127	135.6
4	7	2	42	48	92.6
4	11	2	77	63	-14.9
4	15	2	114	118	-75.5
4	19	2	60	57	-52.3
4	24	2	44	44	15.3
5	1	2	207	182	158.3

Table 2 (*cont.*)

h	k	l	$10\lvert F_o\rvert$	$10\lvert F_c\rvert$	α
5	2	2	101	88	173.2
5	6	2	72	69	11.9
5	11	2	25	47	-171.5
5	15	2	25	13	-137.2
5	19	2	89	85	169.0
6	0	2	96	98	180.0
6	4	2	100	111	101.2
6	8	2	69	65	-76.5
6	12	2	65	69	-104.5
6	18	2	69	62	-105.9
7	1	2	74	78	33.8
7	5	2	69	82	61.3
7	9	2	33	37	-49.6
7	14	2	28	29	70.4
8	1	2	26	42	-168.3
8	5	2	32	49	90.0
8	9	2	71	80	-62.7
8	14	2	12	23	-101.5
9	3	2	19	37	72.4
0	4	3	127	126	0.0
0	8	3	61	44	0.0
0	12	3	16	26	180.0
0	16	3	90	86	0.0
0	22	3	19	28	180.0
0	26	3	66	51	0.0
1	1	3	195	218	-59.4
1	5	3	44	35	171.9
1	10	3	69	75	-101.1
1	14	3	73	62	45.3
1	18	3	29	29	-120.9
1	22	3	24	31	156.1
1	28	3	18	10	-52.7
2	3	3	137	144	-153.4
2	7	3	135	135	-82.7
2	11	3	78	80	-97.8
2	15	3	94	82	-61.2
2	19	3	76	70	-88.0
2	23	3	18	12	174.3
2	27	3	56	52	2.7
3	3	0	86	65	16.9
3	7	3	142	134	95.9
3	11	3	139	148	-89.5
3	15	3	20	33	-69.3
3	19	3	72	62	-150.1
3	24	3	43	39	-82.6
4	1	3	96	82	98.5
4	5	3	75	58	-174.9
4	9	3	100	94	30.2
4	13	3	35	49	163.1
4	17	3	121	124	-106.7
4	21	3	56	54	-114.0
5	0	3	82	81	90.0
5	4	3	64	59	146.3
5	8	3	67	64	161.2
5	13	0	97	109	-31.5
5	17	3	89	80	144.8
5	23	3	37	35	178.4
6	3	3	69	71	145.5
6	7	3	29	29	-144.5
6	11	3	19	17	83.6
6	17	3	22	20	-82.4
7	0	3	100	111	90.0
7	4	3	54	58	-58.7
7	8	3	68	75	-152.6
7	12	3	48	49	149.9
7	17	3	30	32	-123.9
8	3	3	15	39	34.5
8	7	3	56	66	-26.2
0	1	4	79	97	-90.0
0	5	4	56	26	-90.0
0	9	4	74	64	-90.0
0	13	4	198	205	-90.0
0	18	4	62	57	180.0
1	0	4	85	88	0.0
1	4	4	76	91	-136.9
1	8	4	55	47	133.6
1	12	4	227	247	50.7
1	16	4	52	56	-45.6
1	24	4	28	19	116.5
2	2	4	52	33	168.7
2	6	4	137	161	42.2
2	10	4	111	114	70.1
2	14	4	93	94	-61.8
2	18	4	32	25	-22.4
2	24	4	36	45	-42.3
3	3	4	119	119	58.6
3	7	4	28	21	-40.5
3	11	4	92	91	-176.1
3	15	4	116	108	136.5
4	1	4	136	133	-67.1
4	5	4	138	133	-93.5
4	9	4	100	98	-134.7
4	15	4	32	24	-103.9
5	2	4	83	78	-92.3
5	7	4	56	75	46.3
5	11	4	88	92	119.9
5	15	4	24	25	156.5
6	1	4	98	118	-77.4
6	5	4	89	105	-30.2
6	9	4	25	35	-23.8
6	14	4	21	20	95.2
7	3	4	65	57	97.4
7	8	4	21	23	94.5
7	12	4	41	55	153.6
8	3	4	48	60	5.6
5	3	2	146	142	13.9
5	7	2	86	86	41.7
5	12	2	56	63	-7.5
5	16	2	112	106	88.2
5	20	2	90	79	121.1
6	1	2	35	54	-122.4
6	5	2	53	44	118.2
6	9	2	64	81	19.1
6	13	2	54	57	8.0
6	19	2	70	59	-94.9
7	2	2	55	55	86.1
7	6	2	84	79	80.5
7	10	2	69	59	31.2
7	17	2	55	46	79.7
8	2	2	56	63	-140.8
8	6	2	32	46	144.9
8	10	2	18	23	-75.8
9	0	2	35	38	0.0
9	4	2	19	25	148.5
0	5	3	233	229	-90.0
0	9	3	274	295	-90.0
0	13	3	141	148	-90.0
0	17	3	46	25	-90.0
0	23	3	19	29	90.0
0	27	3	48	42	-90.0
1	2	3	293	330	59.7
1	7	3	38	18	-42.6
1	11	3	49	34	65.2
1	15	3	90	72	152.3
1	19	3	96	82	-99.3
1	25	3	39	36	121.1
2	0	3	130	112	90.0
2	4	3	39	31	-146.1
2	8	3	73	82	163.1
2	12	3	61	58	-113.9
2	16	3	114	102	-55.0
2	20	3	66	66	-152.3
2	24	3	29	27	157.9
3	0	3	215	190	90.0
3	4	3	134	124	82.2
3	8	3	111	112	-38.5
3	12	3	121	120	0.4
3	16	3	125	123	121.0
3	20	3	53	52	-128.4
3	25	3	46	46	154.1
4	2	3	30	28	-23.6
4	6	3	54	57	-138.9
4	10	3	70	69	-140.6
4	14	3	86	83	-122.6
4	18	3	19	19	-23.6
4	22	3	65	53	-159.1
5	1	3	64	70	-92.3
5	5	3	65	58	32.9
5	9	3	137	138	1.0
5	14	3	111	120	77.4
5	18	3	81	70	78.1
6	0	3	160	167	-90.0
6	4	3	80	87	-76.4
6	8	3	112	119	-166.6
6	12	3	19	23	-76.5
6	18	3	54	56	-66.4
7	1	3	51	48	38.2
7	5	3	19	32	44.5
7	9	3	56	57	162.5
7	13	3	40	41	-121.1
8	0	3	42	38	-90.0
8	4	3	21	35	-117.5
8	8	3	50	58	-106.1
0	2	4	67	62	0.0
0	6	4	20	6	180.0
0	10	4	54	58	0.0
0	14	4	199	191	0.0
0	21	4	49	42	-90.0
1	1	4	51	37	-118.1
1	5	4	100	120	43.0
1	9	4	48	30	93.2
1	13	4	236	260	144.8
1	17	4	95	94	177.4
1	25	4	32	34	113.5
2	3	4	146	152	-107.9
2	7	4	126	132	-67.8
2	11	4	120	110	-126.1
2	15	4	95	96	-74.3
2	19	4	36	38	-99.7
2	25	4	38	33	-5.4
3	4	4	110	102	-119.6
3	8	4	60	75	-161.6
3	12	4	75	75	-14.6
3	18	4	25	19	-138.6
4	2	4	104	110	61.9
4	6	4	168	181	137.7
4	10	4	101	100	67.9
4	17	4	24	30	-28.5
5	4	4	124	121	-60.6
5	8	4	27	26	48.0
5	12	4	26	28	139.3
5	16	4	45	40	34.5
6	2	4	61	58	13.0
6	6	4	77	64	-93.1
6	10	4	76	74	-92.8
7	0	4	23	30	180.0
7	5	4	22	30	-63.0
7	9	4	28	48	58.5
7	13	4	33	21	-145.2
5	4	2	191	203	60.2
5	9	2	62	65	74.5
5	13	2	53	52	125.5
5	17	2	96	92	47.2
5	21	2	52	47	19.7
6	2	2	50	74	9.0
6	6	2	59	61	60.5
6	10	2	83	87	107.3
6	14	2	41	45	156.4
6	20	2	59	50	-37.0
7	3	2	85	87	175.0
7	7	2	86	94	50.4
7	11	2	77	84	130.9
7	18	2	53	52	46.9
8	3	2	26	49	-67.8
8	7	2	68	77	81.6
8	11	2	71	85	71.9
9	1	2	14	11	53.2
0	2	3	34	42	180.0
0	6	3	136	138	180.0
0	10	3	146	142	180.0
0	14	3	190	183	0.0
0	18	3	20	33	180.0
0	24	3	37	33	180.0
0	28	3	42	39	180.0
1	3	3	187	187	123.1
1	8	3	212	219	-82.9
1	12	3	133	124	114.3
1	16	3	140	135	140.2
1	20	3	29	28	49.5
1	26	3	43	40	-58.4
2	1	3	108	79	-98.1
2	5	3	110	105	8.5
2	9	3	48	53	-54.9
2	13	3	146	139	-141.1
2	17	3	29	34	-1.3
2	21	3	68	59	-166.8
2	25	3	37	28	-141.4
3	1	3	64	65	100.5
3	5	3	78	92	-99.5
3	9	3	45	39	-87.0
3	13	3	153	146	99.8
3	17	3	54	48	120.9
3	21	3	53	47	-107.3
3	26	3	27	24	83.0
4	3	3	62	65	110.9
4	7	3	66	79	80.6
4	11	3	28	36	-86.1
4	15	3	48	45	-123.4
4	19	3	30	32	2.2
4	23	3	68	56	-102.5
5	2	3	53	67	80.3
5	6	3	114	126	-92.9
5	11	3	107	116	174.6
5	15	3	15	10	44.5
5	21	3	49	49	-149.0
6	1	3	16	10	-104.0
6	5	3	20	47	65.2
6	9	3	55	56	35.5
6	15	3	98	98	-152.7
6	19	3	52	42	-134.9
7	2	3	72	80	148.2
7	6	3	23	43	-97.6
7	10	3	57	60	14.1
7	15	3	37	41	66.1
8	1	3	76	84	-141.6
8	5	3	26	34	-98.3
8	9	3	48	47	-154.0
0	3	4	11	10	-90.0
0	7	4	39	27	90.0
0	11	4	61	57	-90.0
0	16	4	100	100	0.0
0	22	4	23	4	180.0
1	2	4	57	30	78.0
1	6	4	116	127	-59.4
1	10	4	22	33	136.3
1	14	4	117	108	-175.7
1	18	4	42	49	-138.2
2	0	4	114	124	0.0
2	4	4	74	62	109.4
2	8	4	117	110	133.9
2	12	4	150	152	19.4
2	16	4	65	51	47.3
2	20	4	39	36	177.7
3	1	4	85	68	-55.8
3	5	4	98	100	123.5
3	9	4	81	86	134.2
3	13	4	95	90	57.2
3	19	4	30	42	-137.1
4	3	4	114	109	-107.5
4	7	4	89	89	29.7
4	11	4	121	119	118.8
4	23	4	42	38	40.9
5	5	4	62	54	135.6
5	9	4	65	52	-143.3
5	13	4	25	44	55.5
5	21	4	26	31	173.0
6	3	4	41	38	-31.7
6	7	4	54	40	164.7
6	12	4	23	37	84.2
7	1	4	67	53	136.6
7	6	4	27	43	-155.6
7	10	4	19	12	88.2
8	1	4	16	27	-96.5
5	5	2	152	155	63.9
5	10	2	84	92	162.5
5	14	2	43	40	-13.1
5	18	2	68	71	-2.2
5	23	2	23	32	33.7
6	3	2	153	168	91.5
6	7	2	62	65	43.2
6	11	2	39	43	-102.9
6	17	2	76	72	-87.7
7	0	2	82	80	0.0
7	4	2	25	31	-0.6
7	8	2	24	22	-38.4
7	12	2	31	51	-108.7
8	0	2	30	23	180.0
8	4	2	29	49	86.4
8	8	2	66	70	76.4
8	12	2	16	30	-142.4
9	2	2	52	71	21.3
0	3	3	205	213	-90.0
0	7	3	17	13	-90.0
0	11	3	110	97	-90.0
0	15	3	19	18	-90.0
0	21	3	24	21	-90.0
0	25	3	40	30	90.0
1	0	3	138	190	90.0
1	4	3	112	116	-169.2
1	9	3	159	165	-149.8
1	13	3	97	93	-175.2
1	17	3	53	48	47.8
1	21	3	20	29	-175.9
1	27	3	41	30	-136.7
2	2	3	129	144	115.6
2	6	3	97	75	-57.3
2	10	3	150	153	-84.9
2	14	3	136	144	-69.0
2	18	3	95	90	-9.2
2	22	3	53	43	-101.5
2	26	3	50	39	134.0
3	2	3	57	57	51.1
3	6	3	102	110	-152.6
3	10	3	185	180	-152.7
3	14	3	131	136	150.9
3	18	3	61	54	90.3
3	23	3	62	60	174.2
4	0	3	53	39	90.0
4	4	3	76	78	-138.2
4	8	3	93	93	-44.4
4	12	3	89	87	-51.5
4	16	3	95	91	-38.4
4	20	3	92	87	-29.8
4	24	3	39	46	-162.3
5	3	3	99	100	-36.0
5	7	3	69	61	178.5
5	12	3	86	98	-120.8
5	16	3	27	07	179.6
5	22	3	56	60	-76.1
6	2	3	70	62	-40.9
6	6	3	76	84	-86.0
6	10	3	59	65	-15.0
6	16	3	16	31	71.3
6	20	3	29	30	74.0
7	3	3	61	49	-32.3
7	7	3	76	85	-53.1
7	11	3	47	50	7.8
7	16	3	55	56	14.6
8	2	3	112	118	-55.7
8	6	3	38	35	-82.2
8	10	3	21	28	-166.6
0	4	4	67	89	0.0
0	8	4	19	25	0.0
0	12	4	72	66	0.0
0	17	4	101	103	-90.0
0	24	4	25	30	0.0
1	3	4	57	43	-178.2
1	7	4	97	90	171.8
1	11	4	99	86	-89.5
1	15	4	37	43	-142.0
1	19	4	26	24	147.7
2	1	4	140	128	-144.6
2	5	4	59	50	142.1
2	9	4	108	97	113.5
2	13	4	62	58	-179.3
2	17	4	70	65	-11.7
2	21	4	23	27	-7.1
3	2	4	128	122	-68.8
3	6	4	106	93	-18.9
3	10	4	134	143	79.1
3	14	4	86	80	114.5
4	0	4	126	87	0.0
4	4	4	42	61	-22.0
4	8	4	88	96	-27.1
4	14	4	56	48	62.1
5	1	4	74	75	66.9
5	6	4	27	26	145.6
5	10	4	56	60	148.5
5	14	4	30	40	67.4
6	0	4	37	23	0.0
6	4	4	45	62	151.9
6	8	4	43	36	58.9
6	13	4	22	35	127.6
7	2	4	46	51	-61.1
7	7	4	21	22	58.3
7	11	4	31	41	141.9
8	2	4	16	27	-105.3

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

Ring I		Ring II	
C(1)	0·001 Å	C(1′)	0·003 Å
C(2)	−0·004	C(2′)	−0·002
C(3)	0·015	C(3′)	0·006
C(4)	−0·021	C(4′)	−0·011
C(5)	0·017	C(5′)	0·012
C(6)	−0·008	C(6′)	−0·009
C(7)	−0·001	C(7′)	0·006
N(1)	−0·028	N(1′)	−0·004
C(1′)	−0·070	C(1)	−0·087
C(4′)	−0·262	C(4)	−0·299
N(1′)	−0·381	N(1)	−0·468

and are not, in the main, to be attributed to uncertainties in the atomic positions.

It is interesting to compare the molecular configuration of *o*-tolidine with that of biphenyl, which is planar in the crystalline phase (see *Introduction*). Planarity requires an unusually close approach of the hydrogen atoms attached to the two pairs of atoms C(2), C(6′) and C(6), C(2′) and it would appear that, in biphenyl, crystal forces and the resonance energy of a planar structure are sufficient to overcome the effects of steric hindrance; the observed C(1)–C(1′) distance of 1·497 ± 0·003 Å indicates that the phenyl rings are linked by a C(sp^2)–C(sp^2) single bond and suggests that the planarity of the molecule may be largely determined by crystal forces.

In *o*-tolidine the C(1)–C(1′) distance is virtually the same, *viz.* 1·504 ± 0·013 Å, but it is likely that steric effects are enhanced by the amino and methyl groups in the 4,4′ and 3,3′ positions respectively and that the resulting stresses are reduced by the rotations φ_1, φ_2 and φ_3; again crystal forces may play an important part in determining the configuration adopted. The hydrogen atoms attached to C(2) and C(6′) are separated by a distance of 2·3 Å and those attached to C(6) and C(2′) by 2·4 Å. These distances suggest there is no serious strain due to steric interaction between the hydrogen atoms, but little significance can be attached to the value observed because of their very low precision – a very crude treatment gives an e.s.d. of 0·3 Å.

Non-coplanar phenyl rings have been reported in two similar biphenyl derivatives, *viz.* 4,4′-diamino-3,3′-dichlorobiphenyl [Hasan (1962) – the structure has been refined and a paper is now in preparation] and 4,4′-dinitrobiphenyl (Boonstra, 1963).

There are no significant differences (Cruickshank, 1949) between the lengths of equivalent bonds in the two halves of the molecule – although there appear to be some significant differences in bond angles – but there are marked differences between the bond lengths within each aromatic ring. Assuming that the two aromatic rings are identical, and taking mean values, we find that there are two short bond lengths [C(1)–C(6), 1·357 Å and C(3)–C(4), 1·359 Å] and four long ones [C(1)–C(2), 1·418 Å; C(2)–C(3), 1·414 Å; C(4)–C(5), 1·427 Å; and C(5)–C(6), 1·415 Å]. The differences between the long and short bond lengths appear to be significant, although some uncertainty exists because no libration corrections have been applied to the bond lengths. In biphenyl (Robertson, 1961*a*,*b*) the variations in corresponding bond lengths show much smaller variation, ranging from 1·344 to 1·385 Å when uncorrected for libration and from 1·378 to 1·398 when corrected for libration.

The carbon atoms of the methyl groups and the nitrogen atoms of the amino groups form bonds of the usual lengths with the carbon atoms to which they are attached in the aromatic rings and, within experimental error, lie in the plane of the aromatic ring.

Fig. 3 shows the structure viewed along the direction [001] and indicates all distances less than 4·1 Å between atoms in neighbouring molecules; the intermolecular distances are quite normal, the shortest being 3·44 Å.

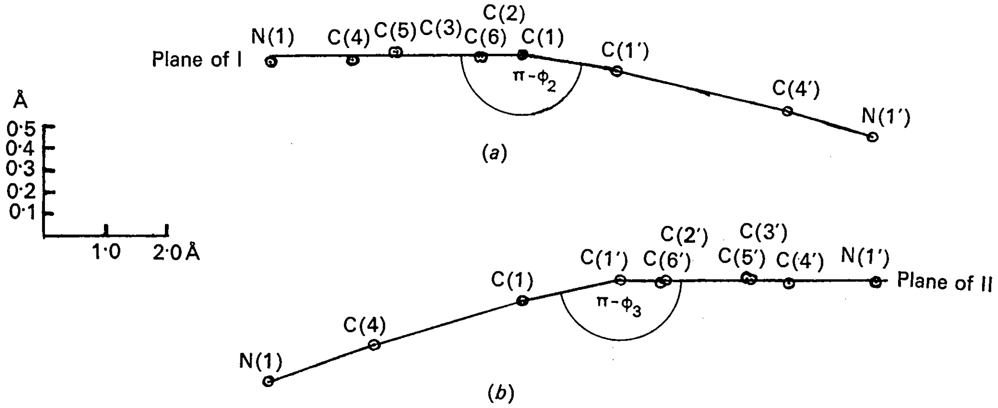

Fig. 2. Displacements from the best plane through atoms in (*a*) phenyl ring I, (*b*) phenyl ring II. In both (*a*) and (*b*) the best plane is viewed end-on and in a direction at right angles to the length of the molecule. The best planes are shown by horizontal lines and the displacements of individual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

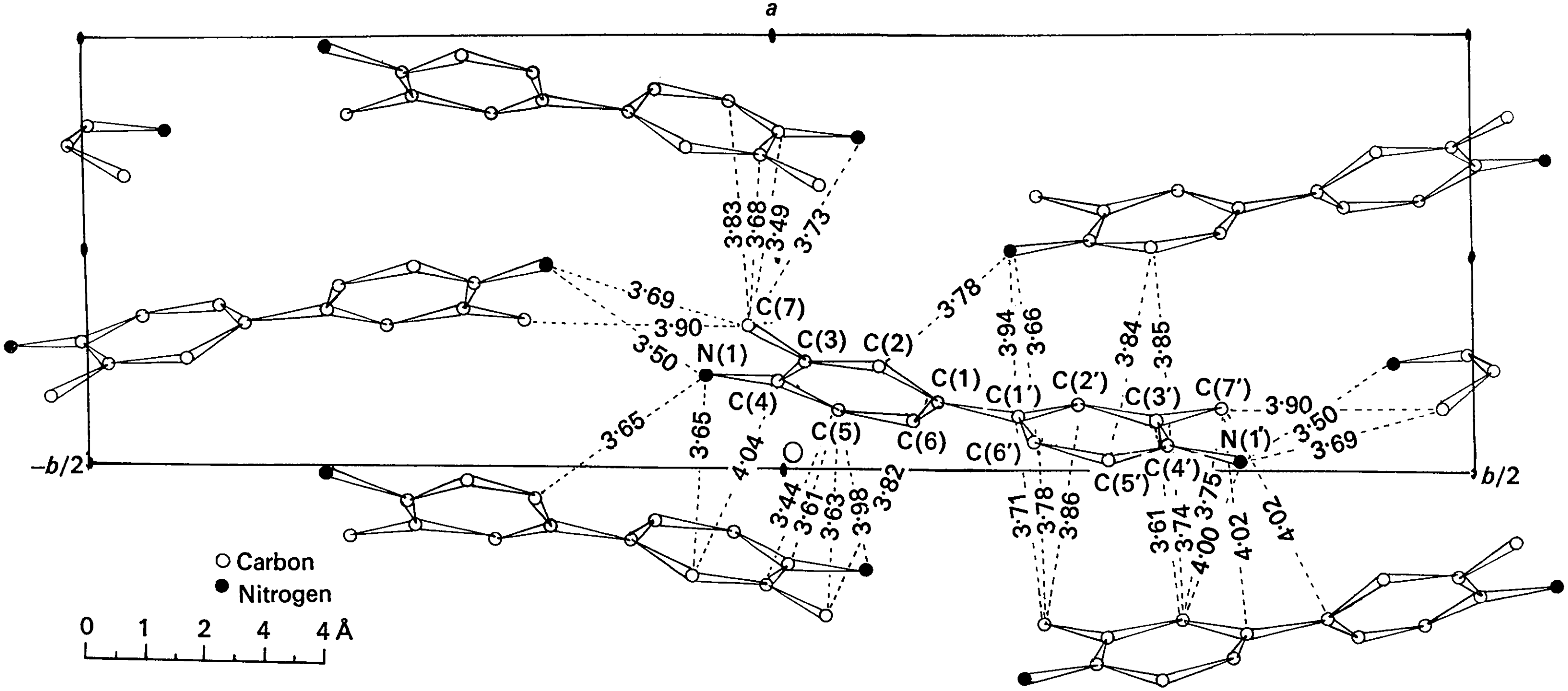

Fig. 3. The structure of *o*-tolidine viewed along [001], showing all intermolecular distances (excluding hydrogen atoms) of less than 4·1 Å.

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A New Class of Compound $M_x^+A_x^{3+}Ti_{2-x}O_4$ $(0{\cdot}60<x<0{\cdot}80)$ Typified by $Rb_xMn_xTi_{2-x}O_4$

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$Rb_xMn_xTi_{2-x}O_4$ is a non-stoichiometric compound with orthorhombic symmetry, space group *Imm*2, and at the composition $x=0{\cdot}75$ has the unit-cell dimensions $a=3{\cdot}934$, $b=15{\cdot}918$, $c=2{\cdot}933$ Å. Its structure contains (Ti, Mn)–oxygen octahedra sharing edges in puckered sheets normal to (010) similar to those in lepidocrocite, FeO(OH), except that the correspondence between sheets has been altered to give Rb^+ an irregular eightfold coordination. A number of isomorphous compounds have been prepared and the field of occurrence so far examined, while restricted to the alkali metals Rb^+ and Cs^+, includes a wide range of trivalent and divalent metals substituting for Ti^{4+} in the octahedral positions. The isomorphism of the member $Cs_xMg_{x/2}Ti_{2-x/2}O_4$ is confirmed by a least-squares refinement of powder diffractometer data.

Introduction

Oxycompounds containing alkali, trivalent and quadrivalent metals offer a useful means of studying stereochemical relations in solid state chemistry. We recently showed that a number of compounds $NaA^{3+}B^{4+}O_4$ isomorphous with calcium ferrite could be synthesized, but only when *A* and *B* were metal ions of spherical symmetry averaged over two virtually identical, but crystallographically different octahedral positions (Reid, Wadsley & Sienko, 1967). Other classes of structure with different stoichiometries were generated when the trivalent ions A^{3+} ordered into positions of special symmetry. For example $NaTi_2Al_5O_{12}$ (Mumme & Wadsley, 1967) and $Na_4Mn_4Ti_5O_{18}$ (Mumme, 1968) formed instead of '$NaAlTiO_4$' and '$NaMnTiO_4$', where Al was present in tetrahedral as well as octahedral sites in the one, and Mn^{3+} octahedral and square pyramidal in the other. One other factor limiting the formation of calcium ferrite structures was the size of the alkali metal ion, the available positions being too large for Li^+ and too small for K^+, Rb^+ or Cs^+.

When a stable compound of a new kind emerges from such experimental studies, the composition is often established more rapidly by determining its crystal structure than by isolating enough of it for chemical analysis; thereafter its confirmation by synthesis as a single phase is usually straightforward. However the possibility of a lattice compound being non-stoichiometric is a variable to be considered in a structure analysis, which provides *ab initio* an ideal composition based on point symmetry.

In the present study two classes of oxide phases of variable composition containing Rb^+ or Cs^+, Ti^{4+}, and a number of tri- or divalent metals were recognized. The composition limits of both types were determined experimentally by treating each multicomponent system as a quasi-binary. Fig. 1 shows the Rb–Ti–Mn^{3+}–O system reduced to the join $RbMnO_2$–TiO_2. One phase had the hollandite structure (Byström & Byström,