ACTA CHEMICA SCANDINAVICA 21 (1967) 224–232

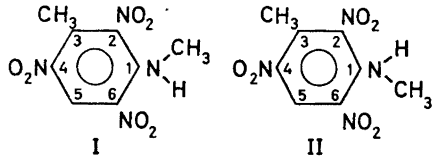
The Crystal Structure of N,3-Dimethyl-4-bromo-2,6-dinitroaniline

SIXTEN ABRAHAMSSON, MAUREEN INNES and BO LAMM

Crystallography group, University of Göteborg, Göteborg, Sweden and Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Göteborg, Sweden

The crystal structure analysis of N,3-dimethyl-4-bromo-2,6-dinitroaniline shows that the N-methyl group is in contact with the 2-nitro group thus confirming earlier NMR and IR results.

In a recent paper, Lamm and Nordfält [1] have discussed the preferred conformation of N,3-dimethyl-2,4,6-trinitroaniline. Provided that the dihedral angle between the planes defined by the methylamino group and the benzene ring is less than 90°, which is certainly a very reasonable assumption, two different conformations for the molecule are defined by the orientation of the methylamino group. In one of these (I), the N-methyl group is in van der Waals-contact with the 2-nitro group, allowing an intramolecular hydrogen bond between the amine proton and the unhindered 6-nitro group. In the other (II), the methylamino group is in the reverse position, with the N-methyl group close to the 6-nitro group. In Ref. 1, three different pieces of evidence,



two based on NMR spectroscopy and one on IR spectroscopy, all favour (I) as the preferred conformation of the molecule.

It appeared desirable to confirm this assignment by an X-ray crystallographic study of the solid compound. In order to simplify the structural analysis, the 4-nitro group was replaced by bromine in the same position. This modification can hardly influence the relative stability of (I) *vs.* (II). Therefore, if the

structural analysis showed that in N,3-dimethyl-4-bromo-2,6-dinitroaniline, the N-methyl group is in van der Waals-contact with the 2-nitro group, this would strongly confirm the assignment made in Ref. 1.

EXPERIMENTAL

3,6-Dibromo-2,4-dinitrotoluene was prepared according to Cohen and Dutt.[2] After recrystallization from ethanol, a 55 % yield was secured, m.p. 142°, (Kofler micro hot stage), lit.[2] 142–143°.

N,3-Dimethyl-4-bromo-2,6-dinitroaniline. Of the preceding compound, 12 g (0.0353 mole) was dissolved in 100 ml hot ethanol. Methylamine, 15 ml of a 33 % solution in water (approx. 0.16 mole), was added and the solution was boiled under reflux for 15 min. Orange rods separated on cooling. These were collected and recrystallized twice from ethanol-benzene (4:1) yielding 4.9 g (48 %), m.p. 137–138° (Kofler micro hot stage). The 60 MHz NMR spectrum, recorded in nitrobenzene solution containing tetramethylsilane as standard, is in agreement with the structure of the compound; singlet at $\delta = -2.14$ (3-methyl), doublet at $\delta = -2.88$, coupling constant 5.3 Hz (N-methyl). The position of the amine proton peak was located through spin decoupling [3] and has $\delta = -8.3$. The δ values (ppm) are referred to tetramethylsilane. The aromatic proton peak was swamped by the solvent absorption.

The crystals are triclinic with the following unit cell dimensions determined from precession photographs (Cu$K\alpha$-radiation).

$a = 6.14 \pm 0.02$ Å, $b = 11.22 \pm 0.04$ Å, $c = 8.28 \pm 0.02$ Å
$\alpha = 77.32° \pm 0.3°$, $\beta = 98.26° \pm 0.4°$, $\gamma = 109.66° \pm 0.3°$

The calculated density for two molecules per unit cell is 1.87 g cm^{-3} which agrees well with the value 1.83 g cm^{-3} determined by flotation of the crystals in sulphuric acid. The space group was assumed to be $P\bar{1}$ which was not contradicted during refinement.

Weissenberg photographs were taken for layers 0–3 about the a-axis and 0–3 about the b-axis. The size of the crystal used was 0.35 × 0.23 × 0.17 mm. The intensities were estimated visually and corrected for the Lorentz and polarization factors and for absorption.

STRUCTURE DETERMINATION

The bromine position was easily found from the sharpened three-dimensional Patterson series and the rest of the heavier atoms from successive electron density series. In the following block-diagonal least squares refinement [4] positional and anisotropic temperature parameters were varied. At an R-value of 11 % a difference series was calculated. Peaks showed up at the expected positions for the hydrogen atoms of the two methyl groups and the aromatic ring but it was not possible to say anything certain about the position of the amino hydrogen. The refinement was continued with the identified hydrogen atoms included in the structure factor calculation. They were given their expected coordinates and isotropic temperature factors corresponding to those of the parent atoms. No hydrogen parameters were refined. When no further improvement occurred in the refinement another difference series was calculated in order to try to locate the amine hydrogen. It seemed very likely from the calculated distances that there exists an intramolecular hydrogen bond between the amine nitrogen and one of the 6-nitro oxygens. A peak in the expected region was also present in the series and the amine proton was included in the structure factor calculation. The final R-value for the 926 observed inde-

Table 1. Fractional atomic coordinates with standard deviations $\times 10^5$ (within brackets) for the heavier atoms of the structure.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Br	0.23829	(14)	0.37062	(5)	0.17131	(8)
C(1)	0.48629	(124)	0.81115	(40)	0.11804	(66)
C(2)	0.27832	(136)	0.72766	(40)	0.19970	(61)
C(3)	0.06751	(131)	0.67151	(42)	0.12526	(73)
C(4)	0.05140	(140)	0.70221	(45)	0.95061	(67)
C(5)	0.22908	(136)	0.77928	(45)	0.86185	(65)
C(6)	0.44595	(124)	0.83315	(41)	0.94292	(58)
C(7)	0.24869	(189)	0.12938	(66)	0.63219	(78)
C(8)	0.13112	(157)	0.41827	(60)	0.77501	(89)
O(1)	0.20926	(118)	0.73272	(59)	0.46946	(66)
O(2)	0.40924	(127)	0.61237	(45)	0.43273	(56)
O(3)	0.18313	(107)	0.04417	(54)	0.10419	(54)
O(4)	0.42687	(108)	0.06255	(47)	0.31078	(45)
N(1)	0.31305	(117)	0.13595	(42)	0.80325	(56)
N(2)	0.30013	(116)	0.68784	(41)	0.38238	(56)
N(3)	0.37670	(106)	0.08629	(36)	0.16333	(57)

Table 2. Allowance was made for anisotropic vibration with

$\exp -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})$.

The U_{ij}'s (Å^2) are given together with standard deviations ($\times 10^4$) within brackets.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	0.1278 (11)	0.0670 (4)	0.0710 (5)	−0.0224 (3)	−0.0097 (5)	0.0042 (4)
C(1)	0.1059 (62)	0.0363 (20)	0.0426 (29)	−0.0050 (18)	−0.0029 (30)	0.0062 (23)
C(2)	0.1566 (76)	0.0357 (20)	0.0235 (23)	−0.0023 (16)	0.0258 (32)	0.0112 (26)
C(3)	0.1253 (66)	0.0335 (20)	0.0554 (34)	−0.0049 (19)	0.0049 (33)	0.0069 (25)
C(4)	0.1338 (68)	0.0407 (21)	0.0371 (26)	−0.0104 (18)	0.0008 (31)	0.0102 (27)
C(5)	0.1267 (71)	0.0440 (22)	0.0404 (30)	−0.0066 (20)	−0.0083 (34)	0.0074 (27)
C(6)	0.1181 (62)	0.0404 (21)	0.0278 (25)	−0.0061 (17)	0.0116 (28)	0.0126 (24)
C(7)	0.1711 (89)	0.0704 (36)	0.0389 (34)	−0.0052 (26)	−0.0169 (42)	−0.0026 (40)
C(8)	0.1126 (77)	0.0620 (33)	0.0676 (42)	−0.0057 (28)	0.0192 (39)	0.0013 (34)
O(1)	0.1523 (59)	0.1348 (49)	0.0492 (32)	−0.0431 (31)	0.0391 (32)	0.0246 (36)
O(2)	0.2087 (67)	0.0623 (24)	0.0418 (24)	0.0183 (19)	0.0107 (32)	0.0206 (30)
O(3)	0.1466 (58)	0.1012 (35)	0.0334 (22)	−0.0023 (21)	0.0151 (25)	−0.0288 (31)
O(4)	0.1634 (58)	0.0873 (30)	0.0238 (21)	−0.0002 (18)	0.0060 (26)	0.0117 (30)
N(1)	0.1259 (56)	0.0565 (25)	0.0337 (26)	−0.0134 (19)	0.0046 (27)	0.0064 (26)
N(2)	0.1286 (56)	0.0488 (22)	0.0404 (26)	0.0104 (19)	0.0089 (27)	−0.0033 (24)
N(3)	0.1314 (59)	0.0377 (19)	0.0419 (24)	−0.0025 (16)	−0.0018 (28)	−0.0039 (23)

Table 3. Fractional coordinates and isotropic temperature factors for the hydrogen atoms. The first appended number refers to the parent atom.

	x	y	z	B (Å^2)
H(11)	0.8107	0.9139	0.1164	2.4
H(51)	0.2091	0.7996	−0.2715	1.7
H(71)	0.7531	0.7759	0.4396	2.9
H(72)	0.6375	0.9193	0.4175	2.9
H(73)	0.9288	0.9270	0.3730	2.9
H(81)	−0.1993	0.6393	0.3027	2.5
H(82)	−0.0761	0.5012	0.3038	2.5
H(83)	−0.2803	0.5506	0.1392	2.5

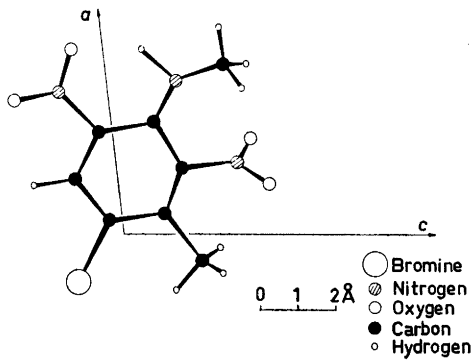


Fig. 1. Stereochemistry of N,3-dimethyl-4-bromo-2,6-dinitroaniline.

pendent reflections is 0.089. Six very strong reflections showed poor agreement and were not included in the final refinement. The R-value is then 0.082.

The calculations were performed on a Datasaab D21 computer with the integrated programme system written by Abrahamsson *et al.*[5] The form factor values given in the *International Tables for X-ray Crystallography*, Vol. III, p. 202, were used. The least-squares programme minimizes $\sum w|F_o - F_c|^2$ where the weights are [6]

$$w = \frac{1}{1 + \left[\frac{|F_o| - 2|F_{min}|}{0.8|F_{min}|}\right]^2}$$

RESULTS AND DISCUSSION

The final molecular parameters are given in Tables 1—3, observed and calculated structure factors in Table 4. A spacial drawing of the molecule is shown in Fig. 1, distances and angles in Fig. 2 and in Table 5 with standard deviations. The atomic numbering is also indicated in Fig. 2.

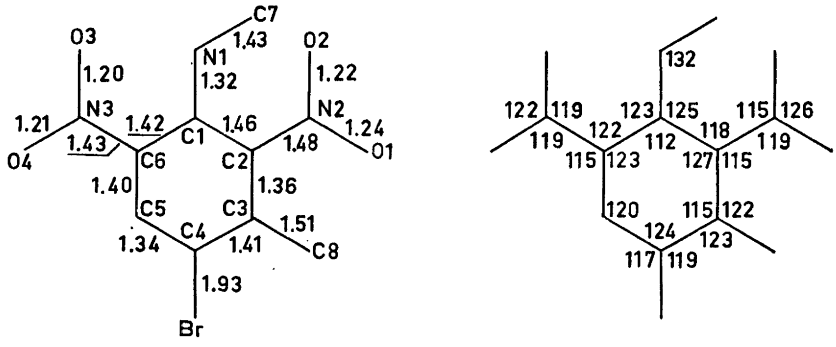


Fig. 2. Bond distances and angles. The atomic numbering used is indicated.

Relatively few substituted analines have been investigated by single crystal X-ray methods. Data exist for *p*-nitroaniline,[7] N,N-dimethyl-*p*-nitroaniline,[8] *p*-chloroaniline,[9] the *p*-iodoaniline-*s*-trinitrobenzene complex,[10] 1,3,5-triamino-2,4,6-trinitrobenzene,[14] and N-(*p*-iodophenyl)-picramide.[11] The latter of these compounds does not, however, provide any good basis for comparison since it has two substituted phenyl groups attached to the amine nitrogen.

Bond distances. It has recently been shown by microwave spectroscopy [12] that the nitrogen atom in aniline is pyramidal, as has been predicted by Coulson.[13] The C—N bond distance in aniline is calculated to be 1.431 Å. In *p*-nitroaniline, where the conjugation between the lone electron pair on the nitrogen and the aromatic π electron system is far stronger than in aniline, the C—N bond distance is 1.37 Å. A similar distance, 1.36 Å, is found in N,N-dimethyl-*p*-nitroaniline. The present structure analysis gives a C—N-distance of 1.32 Å, which indicates a still higher bond order. It is of course expected that an *o*-dinitroaniline should be more conjugated than, *e.g.*, *p*-nitroaniline. Triaminotrinitrobenzene [14] has a similar C—N distance (1.31 Å).

Table 5. Bond distances and angles with standard deviations.

Bond	Length	σ	Angle	σ	δ
Br—C(4)	1.929 Å	0.007 Å	C(2)—C(1)—C(6)	112.0°	0.5°
C(1)—C(2)	1.460	0.009	—N(1)	124.5	0.5
—C(6)	1.417	0.007	C(6)—C(1)—N(1)	123.4	0.5
—N(1)	1.320	0.008	C(1)—C(2)—C(3)	127.0	0.5
C(2)—C(3)	1.359	0.009	—N(2)	117.8	0.5
—N(2)	1.481	0.007	C(3)—C(2)—N(2)	114.9	0.5
C(3)—C(4)	1.408	0.008	C(2)—C(3)—C(4)	115.0	0.6
—C(8)	1.511	0.010	—C(8)	121.6	0.5
C(4)—C(5)	1.340	0.009	C(4)—C(3)—C(8)	123.4	0.6
C(5)—C(6)	1.404	0.009	Br—C(4)—C(3)	119.4	0.5
C(6)—N(3)	1.429	0.008	—C(5)	117.1	0.4
C(7)—N(1)	1.426	0.008	C(3)—C(4)—C(5)	123.5	0.6
O(1)—N(2)	1.245	0.010	C(4)—C(5)—C(6)	120.0	0.5
O(2)—N(2)	1.219	0.010	C(1)—C(6)—C(5)	122.5	0.5
O(3)—N(3)	1.197	0.008	—N(3)	122.1	0.5
O(4)—N(3)	1.209	0.006	C(5)—C(6)—N(3)	115.4	0.4
			C(1)—N(1)—C(7)	131.7	0.7
			C(2)—N(2)—O(1)	118.8	0.6
			—O(2)	115.0	0.6
			O(1)—N(2)—O(2)	126.2	0.5
			C(6)—N(3)—O(3)	119.3	0.5
			—O(4)	118.9	0.5
			O(3)—N(3)—O(4)	121.9	0.5

The aromatic ring shows normal bond distances except between C4 and C5 and between C1 and C2. The short C4—C5 distance indicates that the orthoquinoid limiting structure must make a significant contribution to the electronic structure. In this structure C4—C5, C2—C3, C1—N1, and C6—N3 are double bonds. The distances of all these bonds agree well with such a picture.

Table 4. Observed and calculated structure factors (× 100).

h	k	l	F_{obs}	F_{calc}
0	2	0	3855	-3554
0	3	0	5057	5278
0	4	0	6226	-5795
0	5	0	1271	1127
0	7	0	1803	-1843
0	8	0	1049	1101
0	9	0	1262	-1180
0	11	0	504	557
0	12	0	522	-464
0	0	1	4069	4904
0	1	1	882	-644
0	2	1	1743	1783
0	3	1	3195	-3104
0	4	1	3639	-3620
0	5	1	2088	2139
0	6	1	3189	-3316
0	8	1	1211	1203
0	9	1	1432	-1353
0	10	1	1263	1209
0	13	1	428	439
0	-1	1	1260	1179
0	-2	1	2436	-2446
0	-3	1	3627	3990
0	-4	1	400	203
0	-5	1	733	465
0	-6	1	4735	4804
0	-7	1	2042	-1847
0	-8	1	1077	-921
0	-9	1	682	567
0	-10	1	1199	-1187
0	-11	1	647	658
0	0	2	3347	-3500
0	1	2	4722	-5054
0	2	2	2415	2331
0	3	2	3804	-4405
0	4	2	1849	1690
0	5	2	1241	1223
0	6	2	2029	-2399
0	7	2	2759	3023
0	8	2	1047	-855
0	9	2	887	-871
0	10	2	1136	1336
0	11	2	956	-1004
0	12	2	541	415
0	13	2	466	490
0	-1	2	5113	6480
0	-2	2	4432	-5450
0	-3	2	1950	2040
0	-4	2	3414	3621
0	-5	2	2213	-2176
0	-6	2	2639	2600
0	-7	2	380	-310
0	-8	2	1069	-1029
0	-9	2	671	712
0	0	3	6388	-7247
0	1	3	4164	4387
0	3	3	2878	-2762
0	4	3	4121	4031
0	5	3	3571	-3283
0	6	3	974	991
0	7	3	2045	1960
0	8	3	2630	-2957
0	9	3	621	528
0	11	3	805	-[illegible]57
0	12	3	612	519
0	-1	3	2374	2111
0	-2	3	3081	2875
0	-3	3	2269	-2602
0	-4	3	2231	2268
0	-5	3	1032	-936
0	-7	3	1492	1562
0	-8	3	956	-866
0	-9	3	388	407
0	-11	3	688	-705
0	0	4	3876	-3753
0	1	4	1740	-1039
0	2	4	3054	-3344
0	3	4	503	496
0	4	4	1747	1598
0	5	4	2872	-3138
0	6	4	2118	2001
0	7	4	509	330
0	8	4	1659	-1775
0	9	4	898	793
0	10	4	965	-843
0	11	4	427	232
0	12	4	502	488
0	13	4	396	-413
0	-1	4	497	237
0	-2	4	2766	2578
0	-3	4	2201	-2108
0	-4	4	1395	1405
0	-5	4	1385	1292
0	-6	4	2120	-1930
0	-7	4	1555	1543
0	-8	4	1310	1204
0	-9	4	521	-615
0	0	5	1923	1507
0	1	5	791	-722
0	2	5	3250	-3245
0	3	5	3235	2939
0	4	5	2243	-2412
0	6	5	2499	2508
0	7	5	1782	-1925
0	8	5	957	951
0	9	5	554	555
0	10	5	1042	-921
0	11	5	798	654
0	12	5	261	-272
0	-1	5	3232	-3597
0	-2	5	1579	1341
0	-3	5	956	-947
0	-4	5	1927	-1791
0	-6	5	1483	-1710
0	-7	5	1362	1527
0	-8	5	985	1161
0	-9	5	522	-518
0	0	6	2080	2011
0	1	6	893	-904
0	2	6	1419	1111
0	3	6	2217	2055
0	4	6	1659	-1478
0	5	6	1214	1169
0	6	6	811	-597
0	7	6	1775	-1707
0	8	6	1487	1485
0	11	6	815	596
0	12	6	612	-619
0	-1	6	524	-539
0	-2	6	1401	-1225
0	-3	6	385	374
0	-4	6	1453	-1480
0	-5	6	885	-779
0	-7	6	434	-468
0	-8	6	3[illegible]7	383
0	1	7	1683	-1773
0	2	7	1509	1673
0	3	7	890	-778
0	4	7	738	-737
0	5	7	2089	2230
0	6	7	1500	-1428
0	7	7	1171	-1192
0	8	7	753	601
0	10	7	845	772
0	-1	7	934	871
0	-2	7	618	-581
0	-3	7	1257	1282
0	0	8	1006	-1018
0	1	8	933	-958
0	2	8	473	472
0	3	8	876	-731
0	4	8	917	871
0	5	8	891	798
0	6	8	630	-626
0	9	8	468	404
0	10	8	588	694
0	-1	8	1169	1314
0	-2	8	448	-434
0	-4	8	557	466
0	0	9	460	-474
0	1	9	529	464
0	4	9	1099	1131
0	7	9	468	479
1	-3	0	9553	11672
1	0	-1	4536	6928
1	-3	-1	8891	14105
1	-3	-4	1169	-3823
1	1	0	4323	-4786
1	2	0	847	682
1	3	0	5801	-5984
1	4	0	931	606
1	5	0	2165	2065
1	6	0	2703	-2569
1	7	0	1895	1725
1	8	0	593	522
1	9	0	851	-878
1	10	0	761	728
1	11	0	608	-501
1	0	1	3772	-4137
1	1	1	1928	-1513
1	2	1	4893	4636
1	3	1	4087	-3996
1	4	1	1942	1885
1	5	1	281	201
1	6	1	2026	-1832
1	7	1	2463	2645
1	8	1	1497	-1342
1	9	1	374	331
1	10	1	1010	908
1	11	1	1717	-1736
1	-1	1	4800	4366
1	-2	1	3602	-3676
1	-3	1	2260	-2198
1	-4	1	2415	2277
1	-5	1	2631	-2635
1	-6	1	1175	1028
1	-7	1	1054	1046
1	-8	1	601	-566
1	-9	1	1645	1712
1	-10	1	364	-350
1	-11	1	679	-617
1	0	2	3910	-3435
1	1	2	5664	6510
1	2	2	4796	-5349
1	3	2	1082	709
1	4	2	4608	4423
1	5	2	5323	-4950
1	7	2	753	654
1	8	2	1958	-2068
1	9	2	1255	1277
1	11	2	974	-982
1	-1	2	684	-790
1	-2	2	2275	2347
1	-3	2	4164	-5120
1	-4	2	3193	3520
1	-5	2	1177	-1136
1	-7	2	2284	2314
1	-8	2	1355	-1339
1	-9	2	366	327
1	-10	2	617	552
1	-11	2	642	-642
1	0	3	2120	-1577
1	1	3	2315	1842
1	2	3	3895	-3779
1	3	3	1698	1543
1	4	3	396	300
1	5	3	3698	-3790
1	6	3	1889	1706
1	7	3	1019	-951
1	9	3	1222	1250
1	10	3	669	-716
1	11	3	525	469
1	-1	3	1024	-1059
1	-2	3	1626	1712
1	-3	3	4165	-4172
1	-4	3	290	-194
1	-5	3	2675	2555
1	-6	3	1307	-1321
1	-7	3	367	334
1	-8	3	838	818
1	-9	3	985	-860
1	-10	3	676	631
1	-11	3	702	565
1	0	4	3847	3923
1	1	4	1767	-1621
1	2	4	1932	-1569
1	3	4	4373	4543
1	4	4	2124	-2025
1	6	4	1226	1167
1	7	4	2008	-1996
1	8	4	1696	1565
1	10	4	545	-639
1	11	4	1224	1150
1	-1	4	4458	-4412
1	-2	4	1844	-1474
1	-3	4	435	-283
1	-4	4	2008	-1963
1	-5	4	1537	1496
1	-6	4	1225	-1140
1	-9	4	1508	-1432
1	-10	4	971	955
1	-11	4	716	694
1	0	5	1912	1804
1	1	5	2666	-2481
1	2	5	2122	1950
1	3	5	407	213
1	4	5	2475	-2414
1	5	5	2806	2681
1	8	5	986	976
1	9	5	1197	-1244
1	11	5	480	495
1	-1	5	500	370
1	-2	5	779	-745
1	-3	5	2615	2327
1	-4	5	1165	-1017
1	-5	5	454	-409
1	-6	5	658	596
1	-7	5	1369	-1337
1	-8	5	693	-620
1	0	6	492	370
1	1	6	1612	-1486
1	2	6	2280	2039
1	3	6	2306	-2213
1	4	6	2041	-1775
1	5	6	2091	1844
1	6	6	547	-503
1	7	6	1403	1374
1	8	6	568	518
1	9	6	994	-867
1	10	6	480	508
1	11	6	459	-464
1	-1	6	1869	1704
1	-2	6	1376	-1390
1	-3	6	621	707
1	-4	6	687	498
1	-5	6	521	-459
1	-6	6	510	479
1	0	7	1598	-1548
1	1	7	1056	649
1	2	7	1372	1384
1	3	7	883	-953
1	4	7	634	595
1	6	7	740	721
1	7	7	1536	1247
1	8	7	1076	-963
1	-1	7	732	812
1	-2	7	1187	-1313
1	-3	7	1024	-998
1	-4	7	1173	1207
1	-5	7	672	-607
1	-6	7	379	393
1	-7	7	489	430
1	-8	7	273	-324
1	1	8	1332	1323
1	4	8	1110	1146
1	5	8	991	-927
1	6	8	556	507
1	8	8	870	-893
1	9	8	333	356
1	-3	8	508	-471
1	-6	8	434	-447
1	0	9	544	404
1	1	9	630	551
1	2	9	631	-652
1	3	9	550	456
1	5	9	603	-510
1	7	9	884	-834
1	-2	9	556	630
1	-2	0	1465	-1559
1	-4	0	1975	1868
1	-5	0	3951	-3685
1	-6	0	3059	3300
1	-7	0	1327	-1119
1	-8	0	474	-390
1	-9	0	2093	2045
1	-10	0	873	-933
1	1	-1	5563	-6907
1	2	-1	3244	3007
1	3	-1	4547	4804
1	4	-1	4438	-4470
1	6	-1	1376	-1141
1	7	-1	1339	-1275
1	8	-1	1055	1036
1	9	-1	968	-915
1	11	-1	659	577
1	-1	-1	2431	-2183
1	-2	-1	2698	-2772
1	-4	-1	488	-333
1	-5	-1	333	401
1	-6	-1	1214	1097
1	-7	-1	2972	-3033
1	-8	-1	1243	1073
1	-9	-1	848	-763
1	-10	-1	576	-551
1	-11	-1	[illegible]	508
1	-12	-1	632	-579
1	-13	-1	313	295
1	0	-2	3941	3873
1	1	-2	4700	4482
1	2	-2	568	235
1	3	-2	4954	4849
1	4	-2	2004	-1723
1	5	-2	1373	-1066
1	6	-2	1257	1073
1	7	-2	1732	-1666
1	8	-2	1181	1065
1	10	-2	651	-673
1	11	-2	950	873
1	-1	-2	3515	-3348
1	-2	-2	2849	2595
1	-3	-2	1503	1724
1	-4	-2	2941	-2823
1	-5	-2	430	514
1	-6	-2	1963	-1781
1	-7	-2	1132	-1078
1	-8	-2	1263	1252
1	-9	-2	1497	-1462
1	-10	-2	517	399
1	-11	-2	560	475
1	-12	-2	637	-633
1	-13	-2	578	503
1	0	-3	1172	875
1	1	-3	2584	2458
1	2	-3	3450	-3502
1	3	-3	3964	3983
1	4	-3	434	411
1	5	-3	1830	-1613
1	6	-3	1784	1768
1	-1	-3	3449	-3139
1	-2	-3	4835	4754
1	-3	-3	5279	-5734
1	-4	-3	809	-645
1	-5	-3	2649	2434
1	-6	-3	3185	-3161
1	-7	-3	1772	1557
1	-9	-3	506	-522
1	-10	-3	1617	1542
1	-11	-3	923	-853
1	0	-4	3109	-3146
1	1	-4	2772	2853
1	2	-4	1109	880
1	3	-4	2260	-2147
1	4	-4	2388	2333
1	8	-4	1121	-985
1	9	-4	584	556
1	-1	-4	2944	2522
1	-4	-4	999	1049
1	-5	-4	1350	-1286
1	-6	-4	318	-272
1	-7	-4	2443	2293
1	-8	-4	1876	-1874
1	-9	-4	630	599
1	-10	-4	987	1024
1	-11	-4	1188	-1225
1	0	-5	1981	-1909
1	3	-5	2294	-2038
1	4	-5	2969	2349
1	5	-5	1539	1402
1	6	-5	880	-725
1	7	-5	575	534
1	-5	-5	2172	-2301
1	-6	-5	489	337
1	-8	-5	888	-958
1	-9	-5	1309	1336
1	1	-6	2697	-2503
1	3	-6	1207	-1057
1	4	-6	1050	984
1	5	-6	1467	1493
2	0	0	4108	-5912
2	1	0	2242	2131
2	2	0	3152	2987
2	3	0	2925	-3164
2	4	0	3160	3114
2	5	0	846	-627
2	6	0	647	-570
2	7	0	957	969
2	8	0	2149	-2195
2	10	0	466	444
2	11	0	307	-301
2	0	1	606	410
2	1	1	3034	3024
2	2	1	4673	-5592
2	3	1	354	238
2	4	1	1605	1510
2	5	1	3339	-3415
2	6	1	1951	1913
2	7	1	422	325
2	8	1	2118	-2165
2	9	1	580	576
2	11	1	247	202
2	-1	1	1279	-1072
2	-2	1	3535	3407
2	-3	1	3401	-2872
2	-4	1	2191	1936
2	-5	1	542	582
2	-6	1	2917	-3002
2	-7	1	1914	1797
2	-8	1	632	-596
2	-10	1	789	887
2	-11	1	553	-568
2	-12	1	413	394
2	0	2	1299	978
2	1	2	2120	2185
2	2	2	4553	-4788
2	3	2	805	864
2	4	2	814	-855
2	5	2	879	-807
2	6	2	1769	1850
2	7	2	845	-848
2	11	2	833	857
2	-1	2	4817	-4781
2	-2	2	2973	2769
2	-3	2	783	-680
2	-4	2	1574	-1665
2	-5	2	1521	1638
2	-6	2	1928	-1938
2	-8	2	1097	1191
2	-9	2	591	-615
2	-12	2	302	-291
2	0	3	3849	3891
2	1	3	2546	-2585
2	2	3	1648	-1280
2	3	3	2851	2780
2	4	3	2403	-2450
2	5	3	1935	1742
2	6	3	1142	1030
2	7	3	1313	-1219
2	8	3	1696	1752
2	9	3	485	-528
2	10	3	244	-225
2	11	3	562	621
2	-1	3	2266	-1726
2	-2	3	478	-451
2	-3	3	1201	1296
2	-4	3	1654	-1648
2	-5	3	405	316
2	-6	3	1225	-1330
2	-7	3	670	-730
2	-8	3	1126	1058
2	-9	3	840	-708

h	k	l	F_{obs}	F_{calc}
2	-12	3	541	-514
2	0	4	1542	1477
2	1	4	1776	-1835
2	2	4	2465	2462
2	3	4	878	-801
2	4	4	1007	-936
2	5	4	1816	1753
2	6	4	1483	-1420
2	8	4	1294	1292
2	9	4	457	-535
2	10	4	458	436
2	11	4	206	-204
2	-1	4	1282	1181
2	-2	4	1964	-2081
2	-3	4	2559	2520
2	-4	4	646	-632
2	-5	4	1379	-1350
2	-6	4	1595	1469
2	-7	4	697	-704
2	-9	4	391	319
2	-10	4	532	-470
2	0	5	1976	-1889
2	1	5	2256	-2247
2	2	5	2833	2954
2	3	5	452	-478
2	4	5	1174	1065
2	5	5	1028	864
2	6	5	1802	-1728
2	7	5	942	948
2	10	5	738	573
2	-1	5	1755	1766
2	-2	5	1529	-1665
2	-4	5	770	834
2	-6	5	604	665
2	0	6	1627	-1731
2	1	6	289	304
2	2	6	416	284
2	3	6	471	356
2	4	6	2099	2117
2	5	6	743	-639
2	7	6	682	501
2	8	6	1272	-1258
2	[illegible]	6	480	[illegible]
2	-1	6	[illegible]	[illegible]
2	-2	6	[illegible]	[illegible]
2	-3	6	846	-912
2	-4	6	1014	1063
2	-5	6	1126	-1221
2	-6	6	483	-449
2	-7	6	735	757
2	-8	6	499	-453
2	-9	6	212	285
2	1	7	993	1074
2	2	7	773	-760
2	3	7	798	839
2	4	7	500	466
2	5	7	1386	-1458
2	6	7	599	622
2	7	7	239	-240
2	8	7	644	-709
2	9	7	477	479
2	-1	7	287	325
2	-2	7	1179	1226
2	-3	7	343	-394
2	-6	7	465	-430
2	0	8	459	376
2	1	8	323	273
2	2	8	983	-909
2	3	8	526	532
2	4	8	769	-702
2	5	8	412	-443
2	6	8	649	599
2	7	8	835	-859
2	8	8	189	165
2	-1	8	690	-629
2	-2	8	608	650
2	0	9	501	448
2	1	9	206	-303
2	4	9	847	-857
2	5	9	298	314
2	-1	9	340	-363
2	-2	9	315	-261
2	-3	9	366	387
2	-2	0	1412	-1147
2	-3	0	2171	-2166
2	-4	0	752	933
2	-5	0	1481	-1598
2	-6	0	1570	1405
2	-7	0	945	915
2	-8	0	1452	-1583
2	-9	0	441	448
2	-12	0	720	727
2	0	-1	2005	-1590
2	1	-1	349	-396
2	2	-1	358	256
2	3	-1	2525	-2632
2	4	-1	1700	1473
2	6	-1	1350	-1505
2	7	-1	1193	1245
2	9	-1	560	-490
2	10	-1	535	494
2	11	-1	307	-311
2	-1	-1	2459	2265
2	-2	-1	4087	-5590
2	-3	-1	249	-13
2	-4	-1	217	273
2	-5	-1	2539	-2645

h	k	l	F_{obs}	F_{calc}
2	-6	-1	4634	5594
2	-7	-1	971	930
2	-8	-1	1350	-1310
2	-9	-1	1191	1326
2	-10	-1	847	-940
2	-12	-1	594	534
2	-13	-1	342	-285
2	0	-2	4018	4385
2	1	-2	4179	-4909
2	2	-2	329	335
2	3	-2	509	-367
2	4	-2	3004	-2971
2	5	-2	2086	2093
2	6	-2	1000	-893
2	7	-2	302	-286
2	8	-2	1056	1114
2	9	-2	789	-759
2	-1	-2	2446	1813
2	-2	-2	1156	-949
2	-3	-2	4640	4577
2	-4	-2	2615	-2656
2	-5	-2	542	-481
2	-6	-2	3539	4581
2	-7	-2	880	-812
2	-10	-2	770	-786
2	-11	-2	444	474
2	-12	-2	366	-416
2	0	-3	4480	4958
2	1	-3	905	-805
2	2	-3	1374	-1008
2	3	-3	1766	1586
2	4	-3	817	-801
2	5	-3	864	722
2	6	-3	373	-305
2	7	-3	729	-721
2	8	-3	967	908
2	9	-3	461	-381
2	10	-3	523	-485
2	-1	-3	923	-756
2	-3	-3	2002	2155
2	-4	-3	1600	-1218
2	-5	-3	1295	1717
2	-6	-3	[illegible]	[illegible]
2	-7	-3	[illegible]	-1099
2	-8	-3	778	859
2	-9	-3	1116	-1128
2	-10	-3	289	-303
2	-11	-3	529	513
2	-12	-3	363	-330
2	-13	-3	306	262
2	0	-4	1609	1133
2	1	-4	1087	1056
2	2	-4	1361	-1149
2	3	-4	1885	1818
2	4	-4	356	-250
2	5	-4	707	-661
2	6	-4	997	931
2	-1	-4	1970	-2100
2	-4	-4	1584	-1769
2	-5	-4	2330	2867
2	-6	-4	2445	-2385
2	-7	-4	266	-181
2	-8	-4	640	490
2	-9	-4	729	-804
2	-10	-4	933	1004
2	-11	-4	438	-386
2	-13	-4	617	624
2	0	-5	2054	-1843
2	1	-5	2623	2553
2	2	-5	445	345
2	3	-5	872	-736
2	4	-5	803	579
2	5	-5	743	-695
2	6	-5	363	308
2	8	-5	369	-329
2	-1	-5	345	281
2	-6	-5	1606	-1739
2	-7	-5	619	517
2	-8	-5	592	-589
2	-10	-5	686	665
2	-11	-5	421	-437
2	0	-6	1772	-1731
2	1	-6	2525	2660
2	2	-6	1616	1429
2	3	-6	720	-684
2	4	-6	577	601
2	6	-6	291	-255
3	0	0	966	-863
3	1	0	1784	1791
3	2	0	2469	-2514
3	3	0	1411	1382
3	4	0	208	-131
3	5	0	2450	-298[illegible]
3	6	0	1076	1079
3	9	0	796	825
3	10	0	256	-264
3	-1	0	1633	-1626
3	-2	0	2361	2624
3	-3	0	1698	-1768
3	-4	0	347	319
3	-5	0	1505	1420
3	-6	0	1343	-1356
3	-7	0	508	858
3	-9	0	579	[illegible]
3	-10	0	590	567
3	-11	0	438	-479
3	0	1	[illegible]	[illegible]

h	k	l	F_{obs}	F_{calc}
3	1	1	310	-275
3	2	1	1335	-1723
3	3	1	1891	1965
3	5	1	606	-567
3	6	1	578	576
3	8	1	836	889
3	10	1	284	-297
3	-1	1	4073	-4338
3	-2	1	957	841
3	-3	1	1409	1269
3	-4	1	1907	-1974
3	-5	1	1526	1385
3	-6	1	480	-365
3	-7	1	410	-383
3	-8	1	719	791
3	-9	1	943	-965
3	-11	1	376	354
3	0	2	1859	1802
3	1	2	1842	-1997
3	2	2	1371	1337
3	3	2	1481	1464
3	4	2	1690	-1784
3	5	2	1733	1860
3	6	2	237	-223
3	7	2	338	-358
3	8	2	1051	1126
3	9	2	553	-564
3	-1	2	1865	-1617
3	-2	2	441	-426
3	-3	2	1780	1800
3	-4	2	1982	-1757
3	-5	2	717	638
3	-6	2	281	280
3	-7	2	636	-640
3	-8	2	426	442
3	-9	2	688	-671
3	-11	2	442	434
3	0	3	368	296
3	1	3	1368	-1221
3	2	3	1651	1626
3	3	3	773	-657
3	5	3	1430	1559
3	6	3	938	[illegible]
3	7	3	474	[illegible]
3	9	3	706	[illegible]
3	10	3	459	579
3	-1	3	1190	1128
3	-2	3	2031	-2048
3	-3	3	1528	1527
3	-4	3	664	591
3	-5	3	1315	-1186
3	-6	3	1500	1402
3	-7	3	324	-259
3	-8	3	472	-482
3	-9	3	453	303
3	-10	3	355	-316
3	0	4	1119	-1096
3	1	4	370	351
3	2	4	1234	1155
3	3	4	1750	-1974
3	4	4	915	1079
3	5	4	594	592
3	6	4	292	-300
3	7	4	791	843
3	8	4	720	-717
3	9	4	295	-281
3	10	4	243	336
3	-1	4	2060	2087
3	-2	4	1003	-1101
3	-3	4	852	-802
3	-4	4	826	826
3	-5	4	959	-837
3	-6	4	328	326
3	-8	4	279	-242
3	-9	4	390	363
3	0	5	274	216
3	1	5	1689	1820
3	2	5	334	-338
3	3	5	450	-479
3	4	5	875	876
3	5	5	1272	-1311
3	6	5	514	476
3	7	5	366	323
3	8	5	932	-907
3	9	5	468	533
3	-1	5	1204	1205
3	-2	5	454	-405
3	-3	5	1554	-1580
3	-4	5	1014	998
3	-5	5	402	-338
3	-6	5	545	-496
3	-7	5	662	630
3	-8	5	450	-487
3	-10	5	226	285
3	0	6	672	703
3	1	6	801	883
3	2	6	958	-1128
3	3	6	538	574
3	5	6	968	-1063
3	6	6	609	577
3	7	6	453	-436
3	9	6	371	-351
3	-1	6	555	-567
3	-2	6	509	531
3	-5	6	791	734
3	0	7	579	562
3	1	7	468	-497

h	k	l	F_{obs}	F_{calc}
3	2	7	875	-825
3	3	7	779	692
3	4	7	879	-852
3	6	7	519	419
3	7	7	443	-472
3	-1	7	623	-679
3	-2	7	481	432
3	-5	7	505	490
3	1	8	665	-698
3	2	8	309	301
3	3	8	270	303
3	4	8	550	-564
3	5	8	414	423
3	-2	8	244	-259
3	-3	8	426	391
3	-4	8	334	-333
3	0	-1	1836	-2008
3	1	-1	2638	2544
3	2	-1	815	-732
3	3	-1	1428	-1335
3	4	-1	1185	1233
3	5	-1	1450	-1437
3	7	-1	627	609
3	8	-1	440	-424
3	9	-1	228	286
3	-1	-1	1348	1262
3	-2	-1	1062	965
3	-3	-1	1567	-1912
3	-4	-1	1329	1281
3	-5	-1	1277	-1352
3	-6	-1	769	-871
3	-7	-1	364	374
3	-8	-1	762	-911
3	-9	-1	895	992
3	-10	-1	378	439
3	-11	-1	526	-514
3	0	-2	1953	-1950
3	1	-2	245	-173
3	2	-2	873	1001
3	3	-2	1130	-1057
3	4	-2	1062	854
3	5	-2	233	[illegible]
3	6	-2	531	-732
3	7	-2	558	472
3	8	-2	548	-528
3	-1	-2	738	804
3	-2	-2	1498	-1374
3	-3	-2	373	-379
3	-4	-2	1802	1577
3	-5	-2	2061	-1910
3	-6	-2	881	735
3	-7	-2	485	-521
3	-8	-2	1260	-1339
3	-9	-2	1759	2176
3	-11	-2	488	-466
3	-12	-2	331	333
3	-13	-2	243	-262
3	0	-3	755	685
3	1	-3	1754	-1885
3	2	-3	1483	1590
3	3	-3	1044	-1051
3	4	-3	720	-676
3	5	-3	1145	1271
3	6	-3	967	-1043
3	7	-3	273	-289
3	-1	-3	684	-621
3	-2	-3	2397	-2570
3	-3	-3	2977	3228
3	-4	-3	496	374
3	-5	-3	603	-571
3	-6	-3	1799	1707
3	-7	-3	633	-582
3	-9	-3	802	722
3	-12	-3	282	-230
3	0	-4	1298	1237
3	1	-4	677	-661
3	2	-4	380	335
3	3	-4	286	248
3	4	-4	422	-393
3	5	-4	489	471
3	6	-4	230	-306
3	7	-4	455	-430
3	8	-4	304	281
3	-2	-4	298	-335
3	-4	-4	670	-764
3	-5	-4	1122	1146
3	-6	-4	334	280
3	-7	-4	1267	-1137
3	-8	-4	1156	997
3	-9	-4	380	-347
3	-10	-4	452	-441
3	-11	-4	339	341
3	-12	-4	276	-297
3	0	-5	847	873
3	1	-5	520	453
3	2	-5	752	-724
3	3	-5	959	991
3	5	-5	406	429
3	7	-5	332	-388
3	-1	-5	1124	-1085
3	-5	-5	458	-497
3	-6	-5	604	698
3	-9	-5	1004	-936
3	0	-6	674	-634
3	1	-6	395	312

The aromatic carbon-carbon distance in triaminotrinitrobenzene [14] is 1.44 Å. The C1—C2 bond is still longer (1.46 Å). Strain in the molecule might be a contributing factor. The C7—O2 intramolecular contact is 2.94 Å with a twist of 73° of the 2-nitro group to the benzene ring. The strain is also evident from the large angle at N1 and the fact that C7 is displaced 0.24 Å and N2

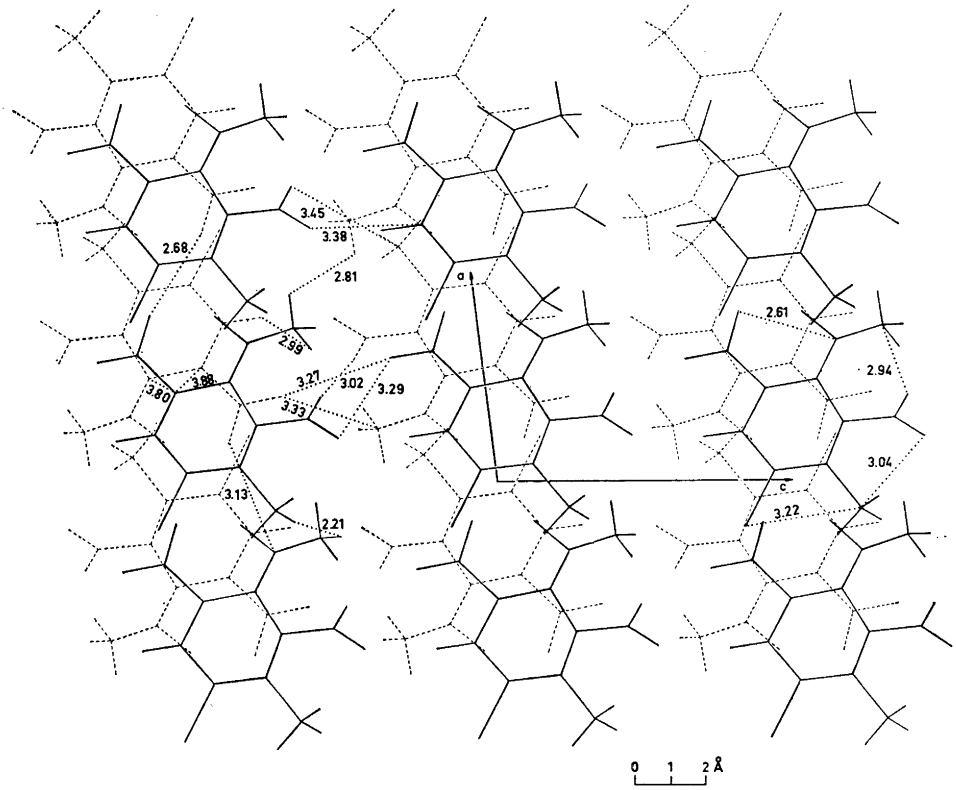


Fig. 3. Molecular packing of N,3-dimethyl-4-bromo-2,6-dinitroaniline. Dashed lines belong to symmetry related molecules. Some short intermolecular distances (to the left) and intramolecular distances (to the right) are indicated by dotted lines.

0.10 Å from the benzene plane. N1 on the other hand is close to the ring plane as are N3, Br, and C8 (Table 6).

Table 6. Least-squares plane through the benzene ring.

Equation of plane (referred to crystal axes)	Out of plane deviations (Å) for atoms defining plane.		Out of plane deviations (Å) for other atoms.	
$-0.30687X + 0.93294Y +$	C(1) −0.004,	C(2) 0.011	Br(1) −0.024,	C(7) 0.241
$0.18832Z - 0.63010 = 0$	C(3) −0.009,	C(4) −0.001	C(8) −0.055,	O(1) 0.899
	C(5) 0.007,	C(6) −0.005	O(2) −1.191,	O(3) −0.100
			O(4) 0.117,	N(1) 0.026
			N(2) −0.098,	N(3) 0.004

In accordance with the high contribution of the orthoquinoid resonance structure the 6-nitro group is almost coplanar with the benzene ring (6° twist), O3 is then close to the amino nitrogen (2.61 Å). As mentioned earlier this

represents an intramolecular hydrogen bond. O3 of a different molecule is also fairly close to N1 (3.13 Å) but the difference map and geometrical considerations seem to exclude this contact from being a hydrogen bond. Some of the shorter intra- and intermolecular contacts are given in Fig. 3 which also illustrates the molecular packing. All benzene rings pack with parallel planes. Infinite layers with rings run parallel to the *ab* plane. Interaction between these layers is provided by the ring substituents only. In the ring region there is a very short unbonded contact (2.68 Å) between O3 and its equivalent over a centre of symmetry. This cannot for chemical reasons be a hydrogen bond and as mentioned above there exists no intermolecular hydrogen bonds to link the molecules together. However, a reduction in the van der Waals radius is expected as the two oxygens approach each other in the N3—O3 bond direction.

Acknowledgements. Financial support from the *Swedish Natural Science Research Council* and the *U. S. Public Health Service* (GM-11653) is gratefully acknowledged.

REFERENCES

1. Lamm, B. and Nordfält, K. *Acta Chem. Scand.* **20** (1966) 1221.
2. Cohen, J. B. and Dutt, P. K. *J. Chem. Soc.* **105** (1914) 501.
3. Lamm, B. *Acta Chem. Scand.* **19** (1965) 2316.
4. Abrahamsson, S. *Arkiv Kemi* **25** (1966) 211.
5. Abrahamsson, S., Aleby, S., Larsson, K., Nilsson, B., Selin, K. and Westerdahl, A. *Acta Chem. Scand.* **19** (1965) 758.
6. Mills, O. S. and Rollett, J. S. *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Pergamon, London 1960, p. 107.
7. Trueblood, K. N., Goldish, E. and Donohue, J. *Acta Cryst.* **14** (1961) 1009.
8. Mak, T. C. W. and Trotter, J. *Acta Cryst.* **18** (1965) 68.
9. Trotter, J., Whitlow, S. H. and Zobel, T. *J. Chem. Soc.* **1966** 353.
10. Powell, H. M., Huse, G. and Cooke, P. W. *J. Chem. Soc.* **1943** 153.
11. Grison, E. *Acta Cryst.* **2** (1949) 410.
12. Lister, D. G. and Tyler, J. K. *Chem. Commun.* **1966** 152.
13. Coulson, C. A. *Valence*, 2nd Ed., Oxford University Press 1961, p. 263.
14. Cady, H. H. and Larson, A. C. *Acta Cryst.* **18** (1965) 485.

Received October 10, 1966.