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The Crystal and Molecular Structure of the Monomeric *C*-Nitroso Compound *N*,*N*,*N*′,*N*′-Tetramethyl-1,5-diamino-4-nitrosobenzene

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The crystal and molecular structure of the monomeric *C*-nitroso compound *N*,*N*,*N*′,*N*′-tetramethyl-1,5-diamino-4-nitrosobenzene has been determined from X-ray diffraction data collected at −170 °C and refined by least squares methods. The space group is $P2_12_12_1$ with cell dimensions $a = 15.574(5)$ Å, $b = 9.884(2)$ Å, and $c = 6.501(1)$ Å at −170 °C. The final R factor was 4.3 % and the estimated standard deviation in bond lengths is about 0.002 Å and in angles 0.2°. The conformation about the C−NO bond is *trans* with respect to the *ortho* position carrying the dimethylamino group. Sterical interaction between the nitroso group and the *ortho* dimethylamino group causes large (0.64 Å) deviation from planarity in the molecule. The bond lengths indicate a very strong intramolecular charge transfer from the dimethylamino groups to the nitroso group. The C−NO and the N−O bond length are 1.372 and 1.276 Å, respectively.

The present structure determination of *N*,*N*,*N*′,*N*′-tetramethyl-1,5-diamino-4-nitrosobenzene (I) is part of a series of structural investigations of *C*-nitroso compounds and oximes derived from these. Previously, *N*,*N*-dimethyl-*p*-nitrosoaniline (II), its hydrochloride and the oxime tautomer of *p*-nitrosophenol and three of its salts have been investigated.[1–6]

Nitrosobenzenes are found both as monomers and as azo dioxide dimers in the solid state.[7] The monomers are considered to be characterized by a strong intramolecular charge transfer of π-type to the nitroso group. This feature is very pronounced in the *p*-nitrosophenolate ion which may be termed a nitrosonate.[6] Some of the structural results of (II) indicate only a weak charge transfer to the nitroso group, but disorder prevented an accurate structure determination in this case. The structure of three other monomers is also known, but the moderate accuracy in the structural results prevents any conclusions for these compounds.[7]

Since IR spectroscopy indicates that the title compound is monomeric in the crystal and that it possesses an intramolecular charge transfer about as strong as that of (II),[8] it was decided to carry out a structure determination of this compound.

Another initiating factor for the present investigation was the fact that (I) is closely related to the not yet isolated compound *N*,*N*-dimethyl-*o*-nitrosoaniline (III).[8] It has been shown that a benzimidazole derivative is easily obtained from (I), probably by an intramolecular elimination of water.[8] The failure to isolate (III) is thought to be caused by an even more pronounced tendency towards elimination of water for this compound than for (I).[8]

EXPERIMENTAL

The title compound has been synthesized by Knieriem.[8] Suitable crystals were obtained by sublimation. At room temperature and normal humidity they disintegrate rapidly. A freshly sublimized crystal was therefore quickly transferred from the cold finger into the low temperature gas stream at the diffractometer. The crystal was needle formed and of dimensions $0.60 \times 0.25 \times 0.15$ mm. All the data were collected and the unit cell constants determined using this crystal. The measurements were made on a Syntex $P\bar{1}$ diffractometer with monochromatized Mo$K\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). The temperature at the crystal site was −170 °C. Cell constants were determined by least squares treatment of fifteen general reflections. Intensity data were

collected using the $\omega - 2\theta$ scan technique. Prior to each scan the intensity was measured with moving crystal and stationary counter and the scan speed accordingly adjusted. The scan speed varied between 2.0 and 6.0°/min and the total time for background counts at the scan limits $2\theta(\alpha_1)$ $-1.0°$ and $2\theta(\alpha_2)$ $+1.1°$ was 0.7 of the time of integration. An octant of reciprocal space was examined. All reflections having 2θ less than 45° were measured; between 45 and 70° only reflections having integrated counts larger than a preset value during a 2s scan over the peak were measured. The intensity of three test reflections measured for every 50 reflection showed no significant change during the measurements. Out of 2542 unique reflections 1893 had intensities larger than $2.5\sigma(I)$. They were regarded as observed. $\sigma(I)$ is the estimated standard deviation of the intensity based on counting statistics adding 2 % uncertainty due to experimental fluctuations. The atomic scattering factors for the heavy atoms were those of Doyle and Turner [9] and for hydrogen those of Stewart *et al.*[10] All programs except for the ORTEP program [11] and the MULTAN [12] program applied during the structure investigation are described in Ref. 13.

CRYSTAL DATA

N,N,N',N'-Tetramethyl-1,5-diamino-4-nitrosobenzene, $C_{10}H_{15}ON_3$, orthorhombic, space group $P2_12_12_1$ (No. 19). Dimensions of the unit cell at -170 °C: $a = 15.574(5)$ Å, $b = 9.884(2)$ Å, $c = 6.501(1)$ Å, $V = 1000.7$ Å^3, $M = 193.25$, $F(000) = 416$, D_{calc} $(-170$ °C$) = 1.283$ g cm^{-3}, $Z = 4$.

STRUCTURE DETERMINATION

The structure was determined by direct methods [12,13] and refined by full matrix least squares techniques. Including only heavy atoms anisotropic refinement yielded a conventional R factor of 0.08. At this stage a difference Fourier map revealing the positions of all the hydrogen atoms was calculated. The refinement including all atoms and all observed reflections converged with $R = 0.042$, a weighted R_w factor of 0.039 and a goodness of fit S of 1.77. Using 1439 reflections with $\sin\theta/\lambda$ greater than 0.45 the refinement yielded $R = 0.043$, $R_w = 0.037$ and $S = 1.23$.

The scale factor became larger (3σ), the C2 – C3, C1 – C6, and C6 – C5 bond longer (2.7σ, 2.3σ, 2.3σ, respectively) and the N – O bond shorter (2.0σ) disregarding valence electron scattering. Only the parameters obtained from the refinement with all the observed reflections will be discussed. A final difference Fourier map was calculated in the same manner as for the *p*-nitrosophenolate ions.[6] Also in the present case the highest residual peaks in the map were located in the middle of the bonds and at lone pair positions. The difference synthesis in the plane through the C – N = O group is shown in Fig. 3.

Magnitudes and directions of the principal axis of the vibrational ellipsoids are indicated in Fig. 1. The r.m.s. discrepancy between the atomic vibrational tensor component obtained in the structure determination and those calculated from a rigid body analysis was 0.0009 Å^2 in the benzene ring with the nitrogen atoms and the oxygen atom and 0.0013 Å^2 in the entire molecule. In the last case the translation r.m.s. of vibration along the principal axes are 0.13, 0.11, and 0.10 Å^2 and the r.m.s. librational amplitudes are 3.0, 2.2, and 1.6°. The largest increase in bond length was 1σ when adjusting to this libration. A list of structure amplitudes is available from the author.

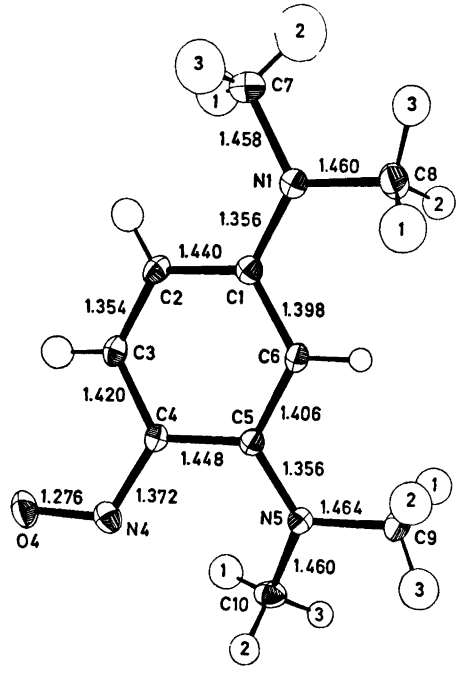

Fig. 1. 50 % probability ellipsoids, bond lengths (Å) and numbering of atoms.

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factors are expressed as: $\exp -2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$. Estimated standard deviations in parentheses.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O4	,66262(7)	,33394(14)	,42882(20)	,0154(5)	,0365(7)	,0264(6)	-,0047(5)	,0016(5)	-,0020(7)
N1	,29988(8)	,34485(14)	,05558(22)	,0172(6)	,0213(6)	,0179(6)	-,0024(5)	-,0008(5)	,0032(6)
N4	,59648(9)	,27284(15)	,49787(22)	,0172(6)	,0229(7)	,0185(6)	,0006(5)	,0006(6)	-,0041(6)
N5	,43892(9)	,15937(15)	,64887(22)	,0161(6)	,0201(6)	,0283(7)	,0005(5)	,0014(5)	,0065(7)
C1	,36805(10)	,34197(17)	,18489(24)	,0158(6)	,0153(7)	,0154(7)	,0015(6)	,0021(6)	-,0012(7)
C2	,43979(11)	,43128(16)	,15118(26)	,0225(7)	,0151(7)	,0159(7)	-,0033(6)	,0014(7)	,0030(7)
C3	,51185(11)	,41396(17)	,26464(28)	,0188(8)	,0159(7)	,0190(7)	-,0039(6)	,0026(7)	,0006(6)
C4	,51881(9)	,31347(15)	,41979(25)	,0157(6)	,0149(7)	,0147(6)	-,0011(5)	,0017(6)	-,0004(6)
C5	,44224(9)	,24028(15)	,47983(24)	,0154(6)	,0122(6)	,0162(7)	,0019(6)	,0034(6)	-,0002(6)
C6	,36958(10)	,25395(16)	,35310(26)	,0153(6)	,0139(7)	,0174(7)	-,0012(6)	,0031(6)	,0007(7)
C7	,29353(13)	,44105(22)	-,11371(31)	,0253(9)	,0323(10)	,0221(9)	-,0001(8)	-,0048(8)	,0073(9)
C8	,23214(11)	,24336(20)	,07508(31)	,0181(7)	,0314(9)	,0206(8)	-,0064(7)	-,0009(7)	,0003(8)
C9	,36451(12)	,07117(21)	,67889(34)	,0211(8)	,0246(9)	,0328(10)	-,0027(8)	,0048(8)	,0109(9)
C10	,49896(12)	,16542(21)	,82031(27)	,0250(8)	,0280(9)	,0161(7)	,0064(8)	,0001(7)	,0020(8)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H2	,4380(11)	,4958(19)	,0497(31)	1,8(4)	H3	,5616(12)	,4705(19)	,2438(31)	1,9(4)
H6	,3214(19)	,2048(16)	,3876(27)	,9(3)	H71	,3279(15)	,4172(25)	-,2196(39)	3,7(5)
H72	,2324(16)	,4373(23)	-,1596(40)	4,3(5)	H73	,3099(13)	,5322(24)	-,0765(38)	3,4(5)
H81	,1949(12)	,2624(20)	,1983(30)	1,7(4)	H82	,2567(13)	,1518(21)	,0861(37)	3,0(4)
H83	,1987(12)	,2449(20)	-,0537(31)	2,0(4)	H91	,3524(13)	,0199(22)	,5517(37)	2,7(4)
H92	,3116(13)	,1202(20)	,7134(32)	2,4(4)	H93	,3765(13)	,0877(23)	,7861(35)	2,8(4)
H101	,5276(12)	,2575(22)	,8246(33)	2,5(4)	H102	,5464(12)	,0949(19)	,8151(31)	1,8(4)
H103	,4650(11)	,1494(18)	,9495(28)	1,5(3)					

Final parameters from the refinement with all the observed reflections are given in Table 1. Bond lengths and angles with their estimated standard deviations are given in Table 2. Fig. 1 shows numbering of atoms and bond lengths. The estimated standard deviations were calculated from the correlation matrix. Deviations from least squares planes are given in Table 3.

DISCUSSION

The crystal structure is characterized by an efficient close packing of the molecules. The packing coefficient (0.82) is somewhat higher than that of (II) (0.76).[14] If one considers the molecule a strong dipole with the negative pole in the vicinity of the nitroso group and the positive pole midway between the dimethyl-

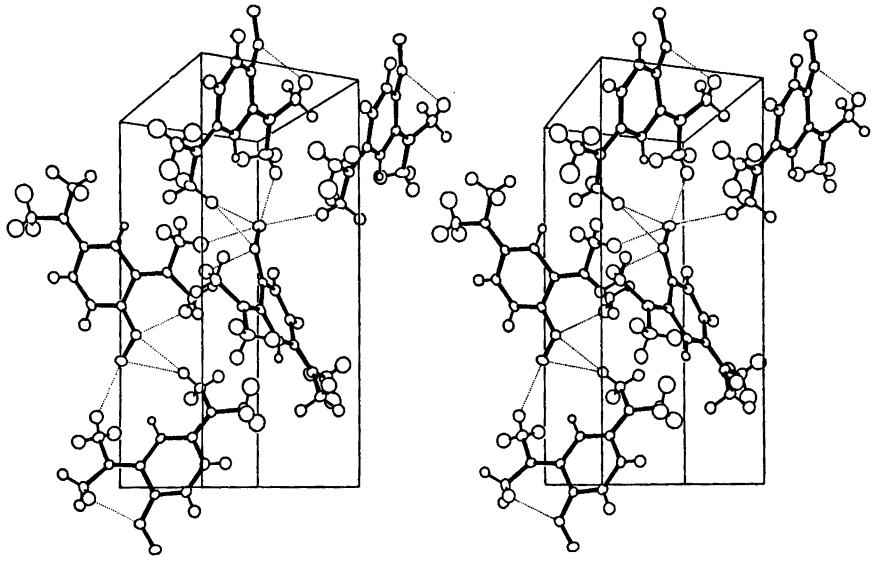

Fig. 2. A stereoscopic illustration of the structure. The unit cell axis y is nearly normal to the paper-plane. The contacts to the nitroso group atoms are indicated by dotted lines.

Table 2. Bond lengths (Å) and angles (°). Estimated deviations in parentheses.

Bond lengths. (Libration corrected bond lengths are given in the second row).

O4–N4	1.276(2)	1.277	N4–C4	1.372(2)	1.373
C1–C2	1.440(2)	1.443	N1–C1	1.356(2)	1.357
C2–C3	1.354(2)	1.355	N1–C7	1.458(2)	1.459
C3–C4	1.420(2)	1.422	N1–C8	1.460(2)	1.463
C4–C5	1.448(2)	1.451	N5–C5	1.356(2)	1.358
C5–C6	1.406(2)	1.408	N5–C9	1.464(2)	1.466
C6–C1	1.398(2)	1.400	N5–C10	1.460(2)	1.461

Bond angles

C1–C2–C3	118.9(2)	N1–C1–C2	120.1(1)	C1–N1–C7	122.3(1)
C2–C3–C4	122.6(2)	N1–C1–C6	120.8(1)	C1–N1–C8	119.8(1)
C3–C4–C5	118.6(1)	N4–C4–C3	122.3(1)	C7–N1–C8	117.7(1)
C4–C5–C6	117.2(1)	N4–C4–C5	118.7(1)	C5–N5–C9	119.5(1)
C5–C6–C1	122.1(1)	N5–C5–C4	122.9(1)	C5–N5–C10	124.8(1)
C6–C1–C2	119.2(1)	N5–C5–C6	119.9(1)	C9–N5–C10	115.2(2)
				C4–N4–O4	116.3(1)

Distances and angles involving hydrogen atoms

C–H		(N)C–C–H		(H)C–C–H	
C2–H	0.92(2)	C1–C2–H	120.8(1.2)	C3–C2–H	120.3(1.2)
C3–H	0.97(2)	C2–C3–H	121.1(1.2)	C4–C3–H	116.3(1.2)
C6–H	0.92(2)	C5–C6–H	117.5(1.1)	C1–C6–H	120.3(1.1)
C7–H1	0.90(3)	N1–C7–H1	111.4(1.6)	H1–C7–H2	109.0(2.1)
C7–H2	1.00(3)	N1–C7–H2	105.4(1.5)	H1–C7–H3	108.4(2.2)
C7–H3	0.97(2)	N1–C7–H3	111.7(1.5)	H2–C7–H3	110.9(1.9)
C8–H1	1.01(2)	N1–C8–H1	110.9(1.2)	H1–C8–H2	109.7(1.8)
C8–H2	0.99(2)	N1–C8–H2	111.1(1.2)	H1–C8–H3	111.7(1.5)
C8–H3	0.99(2)	N1–C8–H3	107.3(1.2)	H2–C8–H3	106.2(1.8)
C9–H1	0.99(2)	N5–C9–H1	110.0(1.3)		
C9–H2	0.98(2)	N5–C9–H2	113.7(1.2)		
C9–H3	0.96(2)	N5–C9–H3	109.6(1.3)		
C10–H1	1.01(2)	N5–C10–H1	109.9(1.2)		
C10–H2	1.02(2)	N5–C10–H2	114.3(1.2)		
C10–H3	1.01(2)	N5–C10–H3	107.3(1.0)		

Intermolecular contact

N1..C7(a) 3.349

Dihedral angles

C1–C6–C5–N5	176.2(2)
C1–C6–C5–C4	4.8(2)
N1–C1–C6–C5	−174.5(2)
C2–C1–C6–C5	6.1(2)
C3–C2–C1–N1	−171.1(2)
C3–C2–C1–C6	−9.5(2)
C4–C3–C2–C1	1.7(3)
N4–C4–C3–C2	−163.1(2)
C5–C4–C3–C2	9.4(3)

Dihedral angles

C4–C5–N5–C10	19.3(2)
C4–C5–N5–C9	−169.6(2)
C6–C5–N5–C10	−161.8(2)
C6–C5–N5–C9	9.3(2)
N4–C4–C5–N5	18.5(2)
N4–C4–C5–C6	−160.4(1)
C3–C4–C5–N5	−168.7(2)
C3–C4–C5–C6	12.4(2)
C3–C4–N4–O4	−2.5(2)
C5–C4–N4–O4	−175.0(1)
C6–C1–N1–C7	176.1(2)
C6–C1–N1–C8	−8.1(2)
C2–C1–N1–C7	−3.3(2)
C2–C1–N1–C8	172.5(2)

Symmetry Code

(a): $\frac{1}{2}-x,\ 1-y,\ -\frac{1}{2}+z$.

Table 3. Deviation (Å) of atoms from least squares planes defined by the benzene ring atoms (A), by the atoms in the fragments C6C1(N1)C2 (B), C3C4(N4)C5 (C), and C4C5(N5)C6 (D) and by the atoms of the dimethyl amino groups (E and F). Asterisks denote atoms defining the planes.

Atom/Plane	A	B	C	D	E	F
C1	−0.063 *	−0.003 *			−0.009 *	
C2	0.048 *	0.001 *				
C3	0.023 *		−0.013 *			
C4	−0.075 *		0.040 *	−0.002 *		
C5	0.059 *		−0.013 *	0.006 *		−0.019 *
C6	0.009 *	0.001 *		−0.002 *		
N1	−0.221	0.001 *			0.021 *	
N4	−0.437		−0.012 *			
N5	0.205			−0.002 *		0.044 *
O4	−0.638		−0.062			
C7	−0.216	0.081			−0.008 *	
C8	−0.496	−0.168			−0.008 *	
C9	0.104			−0.224		−0.016 *
C10	0.644			0.379		−0.017 *

Atom/Plane	A
H2	0.09
H3	0.07
H6	0.06

Atom/Plane	A	E
H71	−0.99	−0.84
H72	−0.12	0.26
H73	0.51	0.61
H81	0.33	0.88
H82	−1.22	−0.72
H83	−0.84	−0.25

Atom/Plane	A	F
H91	−0.71	0.63
H92	0.86	−0.90
H93	0.04	0.22
H101	1.15	−0.46
H102	−0.11	0.89
H103	1.24	−0.55

amino groups the dipole-dipole interactions should stabilize the crystal structure considerably.[14] Fig. 2 shows the content of the unit cell and the coordination about the nitroso group atoms.

A characteristic feature of the molecular structure is the non planarity of the molecule (see Table 3). The only two planar arrangements are those of the atoms in the C2C1(N1)C6 and the C6C5(N5)C4 fragments (Planes B and D). The benzene ring is slightly boat formed with the C1 and the C4 atoms as prow and stern. Considering the locations of the nitrogen atoms bonded to C1 and C4, the boat form becomes even more pronounced. Each of the two dimethylamino nitrogen atoms have a slight pyramidal hybridization and the best plane through the 1-dimethylamino group makes an angle of 5.9° to Plane B while the corresponding angle for the 5-dimethylamino group is 14.2°.

Although the NO bond, as expected, is *anti* to the C4−C5 bond, repulsion between the nitroso group and the methyl group next to it (C10) apparently causes severe conformational strain in the molecule. This is revealed by deviation from trigonal hybridization of the N5 and the C4 atoms, by angular distortions at the N5, C5 and C4 atoms and by a large twist about the C4−C5 bond (ϕ(NCCN) = 18.5°). The C10···N4 distance (2.798 Å) is about 0.20 Å shorter than a normal van der Waals contact. The N5 atom deviates 0.061 Å from the plane through its three bonded atoms while the N1 atom which participates in bonds having lengths about identical to those to N5, deviates only 0.029 Å from a corresponding plane. Usually the nitrogen atom of dialkylamino groups is found to deviate insignificantly from similar planes when the $C_{ar}-N$ bond is as short as the C5−N5 and the C1−N1 bonds (1.356 Å).

The length of the C−NMe_2 bonds corresponds to a π-bond order of about 0.63 and the length of the C5−C6 and the C6−C1 bonds which differ only by 0.008 Å correspond to a π-bond order of about 0.65. As to the O−N−C−CH−CH−C fragment there is a striking similarity in bond lengths between corresponding bonds in (I) and the *p*-nitrosophenolate ions.[5,6] The C−NO bond is only 0.013 Å longer and the

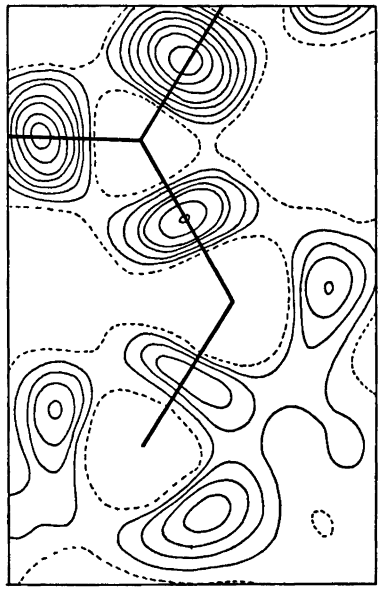

Fig. 3. The final difference Fourier synthesis in the C–N–O plane. A data set with a highest sin θ/λ value of 0.45, positional and temperature parameters from the refinement with high angle data (above 0.45 in sin θ/λ) and a scale factor from a separate refinement using the low angle data and fixing the other parameters on their high angle values were used in the calculation of the synthesis. The dotted line runs through points at 0.0 eÅ^{-3}, and the difference between the contours is 0.05 eÅ^{-3}.

N–O bond only 0.006 Å shorter than the corresponding bond in the anion of the magnesium salt.[6] Hence, the two main zwitterionic VB structures seem to contribute with approximately equal weights to the π-resonance in (I) and apparently the sum of the two weights mounts to about half the total weight.

It is noteworthy that the C–NO bond is longer (5σ) than the C–NMe$_2$ bonds. One would perhaps expect the opposite considering that the two C_{ar}–N bonds in the oxime cation have identical lengths [2] and that the two dimethylamino groups mutually counteract each other as to their electron-releasing effect.

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