

Crystal Structure of *N,N*-Dimethyl-*p*-nitrosoaniline Hydrochloride Hydrate

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The crystal structure of the title compound has been determined by X-ray methods using 2058 observed reflections collected by counter methods. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 7.85_2$ Å; $b = 8.51_1$ Å; $c = 9.43_2$ Å; $\alpha = 116.4_1^\circ$; $\beta = 91.8_9^\circ$; $\gamma = 112.5_8^\circ$. The structure was solved by Patterson methods and refined to a conventional R -factor of 0.044; standard deviations in bond lengths are 0.003 Å and in angles 0.2° .

The protonation of *N,N*-dimethyl-*p*-nitrosoaniline by the reaction with the acid occurs at the nitroso oxygen atom and an oxime is formed. Disregarding the methyl hydrogen atoms the organic ion is planar and has a pronounced quinonoid character.

The electron donating properties of *p*-nitroso-*N,N*-dimethylaniline have been studied by Popp and Ragsdale by means of infrared and visible spectra and by measurements of magnetic moments and molar conductances of various complexes.¹ They conclude that coordination takes place through the nitroso oxygen atom and that the basic properties of the nitroso group appear to be enhanced by the substitution of the strongly electron-donating dimethylamino group *para* to the nitroso group. The contribution of the polar resonance form of the molecule seems thus to be pronounced. From NMR studies of a solution of *N,N*-dimethyl-*p*-nitrosoaniline in trifluoroacetic acid MacNicol, Porte, and Wallace found that the protonation predominantly occurs on the oxygen atom.²

Owing to the disorder in the crystals an X-ray study of *N,N*-dimethyl-*p*-nitrosoaniline did not yield a precise determination of bond lengths and angles.³ A quinonoid structure was indicated, however, confirming the basic nature

of the nitroso group in this molecule.

The chloride of *N,N*-dimethyl-*p*-nitrosoaniline was described by Baeyer and Caro;⁴ Kaufler and Kunz reported that this salt reacts with even a second molecule of hydrochloric acid forming a hygroscopic dichloride.⁵

An X-ray study of the monochloride was undertaken in order to confirm the formation of an oxime and to obtain data for the calculation of the charge distribution in the ion.

EXPERIMENTAL

Yellow needle-formed crystals were formed by cooling a saturated solution of *N,N*-dimethyl-*p*-nitrosoaniline in hydrochloric acid (2 N) from 30–40 °C to 5 °C over a period of one or two days. The formation of crystals sufficiently large for X-ray experiments seemed to be dependent on a high degree of purity of the sample. The crystal used in the present investigation was cut from a larger prismatic crystal to the size 0.1 × 0.3 × 0.5 mm.

Oscillation, Weissenberg, and precession photographs showed that the crystals are triclinic. Cell dimensions were determined from diffractometer measurements on 15 general reflections and their Friedel equivalents. The least-squares program used in the calculations as well as all other computer programs used during the X-ray analysis are described in Ref. 6.

The intensity data were recorded with the use of a SYNTEX PI diffractometer using graphite crystal monochromated MoK radiation ($\lambda = 0.71069$ Å). The $\theta-2\theta$ scanning mode was applied with scan speeds (2θ) of 2–8° min⁻¹ depending on the peak intensity. Three standard reflections were measured for every 50 reflections; they showed a small systematic fluctuation and the data were accordingly adjusted. The standard deviations were taken as $\sigma(I) = (C_T + (0.025 C_N)^2)^{\frac{1}{2}}$, where C_T is the

total number of counts and C_N is the scan count minus background count.

2058 reflections with $\sin \theta/\lambda < 0.7$ and intensities greater than $2.5\sigma(I)$ were regarded as observed and used in the structure determination. They were corrected with Lorentz and polarization factors but not for absorption or secondary extinction.

Atomic form factors used were those of Doyle and Turner⁷ for the chloride ion and oxygen, nitrogen, and carbon atoms, and of Stewart, Davidson and Simpson⁸ for hydrogen. The full-matrix least-squares program employed minimizes the function $\sum w(F_o - F_c)^2$, where w is the inverse of the variance of the observed structure factor.

CRYSTAL DATA

N,N-Dimethyl-*p*-nitrosoaniline hydrochloride hydrate, $C_8H_{10}N_2O \cdot HCl \cdot H_2O$, triclinic.

$a = 7.852(0.001)$ Å; $b = 8.517(0.001)$ Å; $c = 9.432(0.001)$ Å; $\alpha = 116.41(0.01)^\circ$; $\beta = 91.89(0.01)^\circ$;

$\gamma = 112.55(0.01)^\circ$. $V = 505.64$ Å³, $M = 204.66$; $F(000) = 216$, $Z = 2$. $D_{\text{obs}} = 1.3$ g cm⁻³ (floatation), $D_{\text{calc}} = 1.344$ g cm⁻³. Space group $P\bar{1}$.

STRUCTURE DETERMINATION

Wilson's statistical methods showed the crystals to possess a centre of symmetry, the space group was thus proved to be $P\bar{1}$. The structure was solved by Patterson methods and refined by least-squares calculations to an R -factor of 0.07 neglecting hydrogen atoms. A difference Fourier map failed to give any indication of the positions of the hydrogen atoms and coordinates of the hydrogen atoms bonded to the ring atoms and of those presumably taking part in hydrogen bonds were calculated. Least-squares refinement of positional and isotropic thermal parameters yielded acceptable values with the exception of a fairly high B -value for one of the water hydrogen atoms. Several sets

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^4$ for chlorine, oxygen, nitrogen, and carbon and $\times 10^3$ for positional hydrogen coordinates). The anisotropic temperature factor is $\exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

Atom	x	y	z	$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	2332(2)	4865(2)	353(2)	146(4)	160(4)	115(3)	127(6)	58(5)	128(5)
C2	3220(3)	5812(3)	-542(2)	167(3)	190(4)	92(2)	150(7)	27(5)	125(6)
C3	4843(3)	7483(3)	182(2)	175(4)	198(4)	101(3)	134(7)	61(3)	171(5)
C4	5744(2)	8396(2)	1903(2)	136(4)	164(4)	101(2)	142(6)	55(5)	123(6)
C5	4839(3)	7448(3)	2798(2)	174(4)	201(4)	92(3)	131(7)	47(5)	136(6)
C6	3217(3)	5776(3)	2057(2)	193(4)	201(4)	115(3)	129(7)	88(6)	184(5)
C7	8297(3)	11025(3)	4340(2)	202(5)	253(5)	106(3)	54(8)	-3(6)	123(7)
C8	8347(3)	11036(3)	1743(2)	183(4)	242(5)	162(3)	79(8)	61(6)	249(7)
N1	776(2)	3212(2)	-228(2)	179(4)	186(4)	122(2)	128(6)	40(5)	136(5)
N2	7344(2)	10019(2)	2599(2)	135(3)	180(3)	113(2)	114(5)	50(4)	143(5)
O1	43(2)	2426(2)	-1856(2)	195(3)	203(3)	125(2)	69(5)	-4(4)	127(4)
O2	2567(2)	4906(2)	-4574(2)	206(4)	297(5)	233(3)	104(7)	80(6)	194(6)
Cl	6603(1)	8686(1)	-2940(1)	313(1)	181(1)	120(1)	41(2)	18(1)	127(1)
H2	263(2)	520(2)	165(2)	3.6(4)					
H3	540(2)	805(2)	42(2)	3.1(4)					
H5	539(2)	799(2)	393(2)	3.6(4)					
H6	267(3)	516(3)	258(2)	4.0(4)					
HO1	-119(4)	117(4)	213(3)	8.8(7)					
HW1	369(3)	601(3)	410(3)	7.8(6)					
HW2	281(5)	376(5)	527(4)	16.2(13)					
H71	948(4)	1214(5)	459(4)	13.5(11)					
H72	749(3)	1104(4)	495(3)	9.1(7)					
H73	846(4)	1012(4)	450(3)	10.2(8)					
H81	789(4)	1032(4)	62(3)	9.7(8)					
H82	831(4)	1228(4)	211(4)	12.7(10)					
H83	973(4)	1142(4)	195(4)	11.3(9)					

Table 2. Bond lengths (Å) and interbond angles (°).

Bond	Corrected	Angle	
C1—C2	1.436	C1—C6—C5	121.6
C2—C3	1.342	C1—C2—C3	121.1
C3—C4	1.456	C6—C1—C2	118.1
C4—C5	1.441	C6—C5—C4	120.6
C5—C6	1.343	C2—C3—C4	120.7
C1—C6	1.439	C3—C4—C5	117.6
N1—C1	1.314	C1—N1—O1	111.7
N2—C4	1.314	C2—C1—N1	126.6
N1—O1	1.368	C6—C1—N1	115.3
N2—C7	1.472	N2—C4—C3	120.6
N2—C8	1.471	N2—C4—C5	121.6
C—H (mean)	0.93	C4—N2—C7	122.8
O—H (mean)	0.94	C4—N2—C8	124.0
		C7—N2—C8	113.1

of positions for the methyl hydrogen atoms were tried. The best set was that given in the parameter table, but even this has high values for the thermal parameters and we cannot exclude the possibility of a disorder resulting from a rotation about the N—C(methyl) bonds. Leaving out the two largest structure factors

Table 3. Deviations (Å) from the least-squares plane through the six-membered ring.

C1	-0.005	N1	-0.030	HO1	-0.04
C2	0.004	O1	-0.060	H2	-0.01
C3	0.000	N2	-0.020	H3	-0.01
C4	-0.002	C7	0.002	H5	-0.02
C5	0.000	C8	-0.040	H6	-0.02
C6	0.003				

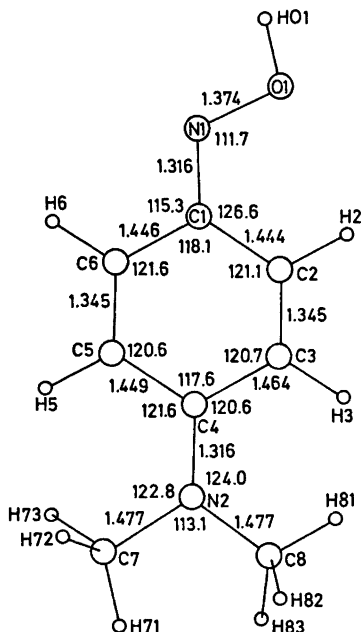


Fig. 1. Bond lengths (corrected) (Å) and angles (°).

the final refinements yielded a conventional R -factor of 0.040, $R_w = 0.045$.

The observed and calculated structure factor data are available from the authors upon request. The final parameters with their estimated standard deviations are given in Table 1.

An analysis of the thermal parameters in terms of rigid-body motion of the organic part showed this approximation to be reasonable. The translational part is nearly isotropic with r.m.s. amplitudes of 0.20, 0.17, and 0.17 Å; the main librational axes coincide closely with the main axes of the moment of inertia and the r.m.s. oscillation amplitudes are 7, 3, and 2°. The interatomic distances were corrected according to these values.

DISCUSSION

The bond distances and valency angles are listed in Table 2. The estimated standard deviations were calculated from the correlation

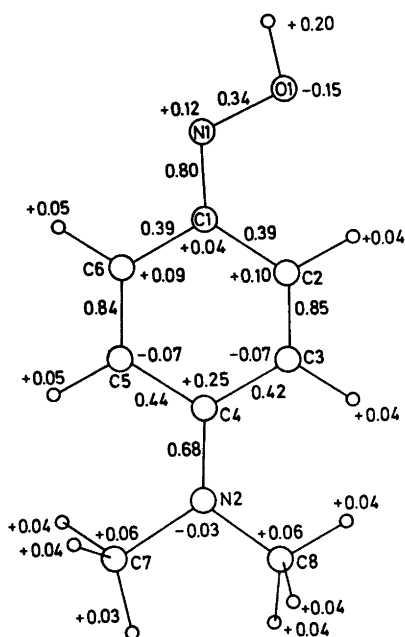


Fig. 2. CNDO/2 results for the isolated ion. π -Bond orders and atomic charges are indicated.

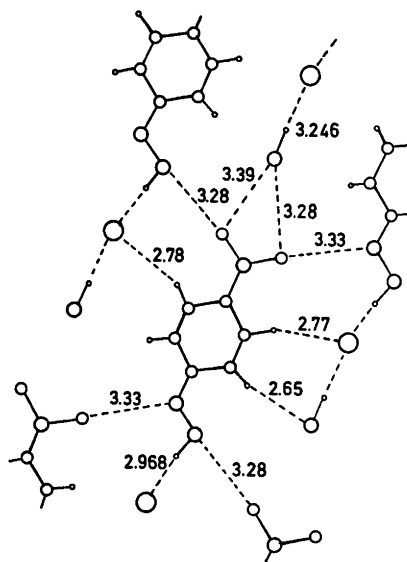


Fig. 3. Packing within one layer. Van der Waals contacts and hydrogen bonds are indicated.

matrix to be 0.003 Å for bond lengths and 0.2° for bond angles if only non-hydrogen atoms are involved. If one hydrogen atom is involved the standard deviations are 0.02–0.03 Å and 1°, respectively.

The geometry of the cation as found in the present analysis is shown in Fig. 1, in which the numbering of the atoms is also indicated.

The protonation has occurred at the oxygen atom of the nitroso group and the cation has thus the expected oxime structure.

With the exception of the methyl hydrogen atoms the ion is nearly planar. The deviations from the least-squares plane through the atoms of the six-membered ring are listed in Table 3. The amino group is thus planar and the torsion angle about the C4–N2 bond is less than 1°.

The ion has a pronounced *para*-quinonoid structure. The average C–C “single” bond in the ring is 1.450 Å and the double bonds are 1.345 Å. The corresponding mean values for a number of compounds with a pure *p*-quinonoid geometry are 1.484 and 1.336 Å, respectively,⁹ and the present ion is thus only slightly more aromatic in character. In accordance with this the two exocyclic C–N bonds are found to be 1.316 Å indicating a high degree of double bond character. The N1–O1 bond length of 1.374 Å is consistent with the corresponding bonds in aromatic oximes.^{10,11}

The considerable difference between the external angles at the C1 atom is probably to be ascribed to steric repulsion between the O1 and C2 atoms. The value found for the angle C1–N1–O1, 111.7°, agrees well with the corresponding angle in quinone-4-oxime¹¹ and is a normal valence angle for nitrogen bonded to two other atoms.

In order to obtain information of the charge distribution CNDO/2 calculations¹² were performed on the isolated ion. Fig. 2 shows the resulting π -bond orders and the net charges. The bond orders for the C–C bonds, 0.39 and 0.44, and for the C=C bond, 0.84, may be compared to the corresponding figures for *p*-benzoquinone, 0.25 and 0.94 for the two kinds of bonds, respectively. The theoretical results correspond closely to the observations from the X-ray analysis and reflect the quinonoid character of the ion.

The calculated electronic charge density shows the positive charge to be mainly dis-

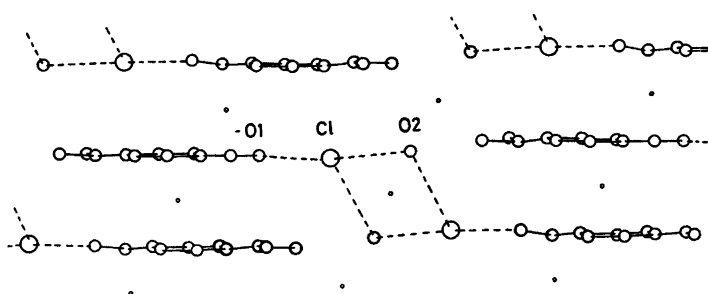


Fig. 4. The packing of the molecular layers. Hydrogen bonds are indicated by broken lines.

tributed on the C4, N1, and the hydroxy hydrogen atom with smaller contributions on the hydrogen atoms forming the surface of the ion. Since the largest negative charge is situated on the oxygen atom, it may be inferred that in the case of the formation of the dichloride⁵ a second protonation may occur on this atom. Reservations must be taken, however, for the possibility of shifts in the electronic charge distribution if a surrounding field is incorporated in the calculations to imitate the actual field in the crystal or in a solution.

The crystal is built up by layers parallel to (1-1 0). All the heavy atoms are situated close to planes nearly coinciding with every second of the crystallographic (4-4 0) planes; this is even the case for the oxygen atom of the water molecule (O2) and the chlorine ions. The spacing of the planes is 3.30 Å. The situation of the ions and the water molecule in the plane is visualized in Fig. 3 in which the distances from the atoms of the organic moiety to the neighbouring ions and molecules are indicated. Within the layer there exist hydrogen bonds between O1 atoms and chlorine ions [2.968(2) Å] and between water molecules (O2) and chlorine ions [3.246(2) Å]. The hydrogen bonds are nearly linear with O-H...Cl angles of 171(2) and 177(2)°, respectively. The other contacts within the plane are of the normal van der Waals type. Pairs of layers (Fig. 4) are connected through hydrogen bonds between water molecules of one layer and chlorine ions of the other [3.197(3) Å]. Between the same layers there are probably weak π - π charge transfer interactions between quinonoid rings related by a centre of symmetry.

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