May, 1984] © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57*, *1295—1298 (1984)* 1295

The Crystal Structure of *N,N,N′,N′*-Tetramethylpiperazinediium Bis(2,4-dinitrophenolate) Dihydrate

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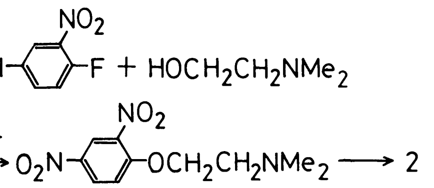
(Received September 8, 1983)

The crystal structure of *N,N,N′,N′*-tetramethylpiperazinediium bis(2,4-dinitrophenolate) dihydrate has been determined by the X-ray method. The crystals are triclinic, space group $P\bar{1}$, a=11.504(2), b=8.239(2), c=7.119(2) Å, α=106.22(2), β=99.67(2), γ=92.31(2)°, Z=1. The final R is 0.067 for 2743 reflections. Two dinitrophenolate anions are connected by hydrogen bonds, *via* the water molecules, forming a dimeric unit related by the center of symmetry. *N,N,N′,N′*-Tetramethylpiperazinediium ion has a chair conformation.

Reaction of 2,4-dinitrofluorobenzene with 2-(dimethylamino)ethanol gave 2,4-dinitrophenyl 2-(dimethylamino)ethyl ether (**1**) as a viscous liquid. On standing long at room temperature or heating in DMF, **1** gave yellow precipitates (**2**), whose NMR spectrum showed only three broad singlets at 3.3—4.0 ppm in addition to an AMX pattern in the aromatic region. In order to elucidate the character of **2** an X-ray structure analysis was undertaken.



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Experimetal

Yellow crystals were grown from an EtOH-H_2O mixed solution. Intensity data were collected on a Rigaku automatic diffractometer AFC4 using graphite-monochromated Mo$K\alpha$ radiation. A specimen with approximate dimensions 0.4×0.4×0.2 mm was used. Reflections within the range $2\theta<60°$ were measured by the ω-2θ scan technique with a scanning speed of 4°/min in 2θ and scan widths of $\Delta\omega$=1.1°+0.5°tanθ. At both ends of the scan range 10 s background counts were taken for each reflection. 2743 reflections had $|F_o|\geq3\sigma(F_o)$ and were considered as observed. No absorption correction was applied.

Structure Determination

Crystals belong to the triclinic system, and the centrosymmetric space group $P\bar{1}$ was assumed on the basis of the intensity statistics. Unsuccessful attempts were made to solve the structure with MULTAN78.[1] E-maps obtained from the four sets of signs showed honeycomb-like arrays of peaks from which unambiguous recognition of molecules was impossible.

The space group was assumed to be $P\bar{1}$ and attempts to solve the structure with MULTAN78 gave two fragments of 2,4-dinitrophenolate anion (2,4-DNP^-). Examination of the structure showed that one fragment related to the other with the center of symmetry. Reassuming the space group to be $P\bar{1}$, the parameters were refined by a block-diagonal least-squares method to R value of 0.49. A Fourier map showed two other fragments; one was assigned to the water oxygen and the other to NC_4 of the tetramethylammonium group. All non-hydrogen atoms were refined with anisotopic temperature factors. A difference synthesis was calculated from which the positions of the hydrogen atoms in 2,4-DNP^-, H_2O, and $(CH_2)_2N(CH_3)_2$ were found. Examination of the structure revealed that the cation was not a tetramethylammonium, but an *N,N,N′,N′*-tetramethylpiperazinediium whose center of inversion was coincident with that of the crystal symmetry. All the atoms were then refined with several cycles of block-diagonal least-squares using anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the H atoms. The quantity minimized was $w(|F_o|-k^{-1}|F_c|)^2$ where w=0.8 if $|F_o|<2.0$, w=1.0 if $2.0\leq|F_o|\leq8.0$ and $w=(8.0/|F_o|)^2$ if $|F_o|>8.0$. The final R value was 0.067 for all observed reflections. Scattering factors were taken from "International Tables for X-Ray Crystallography".[2] All computations were performed on a HITAC M180 computer of the Data Processing Center of the University of Electro-Communications, using the programs UNICS III,[3] MULTAN78 and ORTEP.[4] The final atomic parameters are given in Table 1.[5]

Discussion

Crystal data: $(C_8H_{20}N_2)^{2+}\cdot2(C_6H_3N_2O_5^-\cdot H_2O)$.†† Triclinic, space group $P\bar{1}$, a=11.504 (2), b=8.239 (2), c=7.119 (2) Å, α=106.22 (2), β=99.67 (2), γ=92.31 (2)°, V=636.0 (2) Å³, D_x=1.427 g cm⁻³, Z=1.

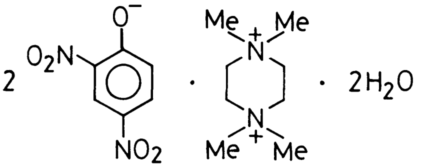

Figure 1 shows the atomic numbering of the crystal-chemical unit. Stereoscopic view of the structure and the projection along the b axis are shown in Figs. 2 and 3 respectively. The structure analysis established that the compound consists of two 2,4-dinitrophenolate

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†† From the structure analysis.

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic temperature factors

For non-H atoms $B = B_{eq} = 4/3\sum_i\sum_j\beta_{ij}a_i \cdot a_j$.

The e.s.d.'s in parentheses refer to last digits.

Atom	*x*	*y*	*z*	$B/\text{Å}^2$
C(1)	2840(2)	171(3)	1493(4)	3.9
C(2)	3611(2)	-1065(3)	1924(3)	3.2
C(3)	4823(2)	-713(2)	2472(3)	3.1
C(4)	5325(2)	866(2)	2611(3)	3.1
C(5)	4627(2)	2127(3)	2207(4)	3.7
C(6)	3440(2)	1779(3)	1669(4)	4.1
N(2)	3148(2)	-2760(2)	1777(3)	4.5
N(4)	6591(2)	1206(2)	3136(3)	3.9
O(1)	1734(1)	-67(3)	996(4)	6.4
O(21)	2098(2)	-3157(3)	1416(4)	6.3
O(22)	3828(2)	-3773(3)	2026(7)	12.1
O(41)	7189(1)	147(2)	3610(3)	5.4
O(42)	7036(2)	2571(2)	3059(3)	5.7
OW	-350(1)	-1995(2)	692(3)	4.0
NP	9193(1)	6256(2)	4550(2)	2.7
CP(1)	9088(2)	5427(2)	6154(3)	2.9
CP(2)	9748(2)	5080(2)	2988(3)	2.8
CP(3)	9903(2)	7961(2)	5394(4)	3.9
CP(4)	7982(2)	6521(3)	3592(4)	4.2
H(3)	530(2)	-155(3)	267(4)	4.7(6)
H(5)	497(2)	318(3)	236(4)	4.9(6)
H(6)	297(2)	262(3)	132(4)	5.0(6)
HW(1)	-78(2)	-139(3)	28(4)	5.1(6)
HW(2)	33(2)	-162(3)	79(4)	4.9(6)
H(11)	882(2)	621(3)	717(4)	3.8(5)
H(12)	849(2)	449(3)	558(3)	2.5(4)
H(21)	987(2)	570(3)	206(4)	3.8(5)
H(22)	916(2)	414(3)	233(3)	2.7(4)
H(31)	946(2)	863(3)	632(4)	4.8(6)
H(32)	1068(3)	784(4)	617(4)	5.5(6)
H(33)	997(3)	837(4)	433(4)	5.7(7)
H(41)	806(3)	707(4)	262(4)	5.7(7)
H(42)	762(3)	719(4)	468(4)	5.5(6)
H(43)	751(2)	541(3)	306(4)	4.8(6)

anion (2,4-DNP$^-$), one *N,N,N′,N′*-tetramethylpiperazinediium (TMP^{2+}) ion and two water molecules. Thus the substance is a salt of 2DNP$^-$ and TMP^{2+}. Many picrate compounds have been known,⁶⁾ but this is the first example of the existence of 2,4-DNP$^-$ in the crystal. Two 2,4-DNP$^-$ anions are connected by the hydrogen bonds, *via* the water molecules, forming a dimeric unit related by the center of symmetry at (0,0,0) as shown in Fig. 3.

The result of the structure analysis suggests that 2,4-dinitrophenyl(dimethylamino)ethyl ether (**1**) cleaved between -O- and -CH_2- in the course of the reaction, and two -$CH_2CH_2NMe_2$ associated to form a TMP^{2+} ring. Thus the formation of **2** is nucleophilic cleavage of either C–O bond in Ar–O–CH_2 moiety intramolecularly or intermolecularly by the dimethylamino group. Primary and secondary amines usually displace the OCH_2 group through the Meisenheimer complexes, while tertiary amines can also cleave the O–CH_2 bond.⁷⁾

Bond lengths and bond angles are listed in Table 2. The dimensions of 2,4-DNP$^-$ anion are close to those in the picrate anion. The C=O length (1.254 Å) is shorter than that of C–O (1,343 Å) in 2,4-dinitrophenol⁸⁾ and only slightly longer than the corresponding ones in the picrates. The angle at C(1) is typically low at 114.3° and the C–C bonds show characteristic variations in length. The C(1)–C(2) and C(1)–C(6) distances show some single-bonded character and the C(5)–C(6) length is shorter than the normal C–C aromatic length. The

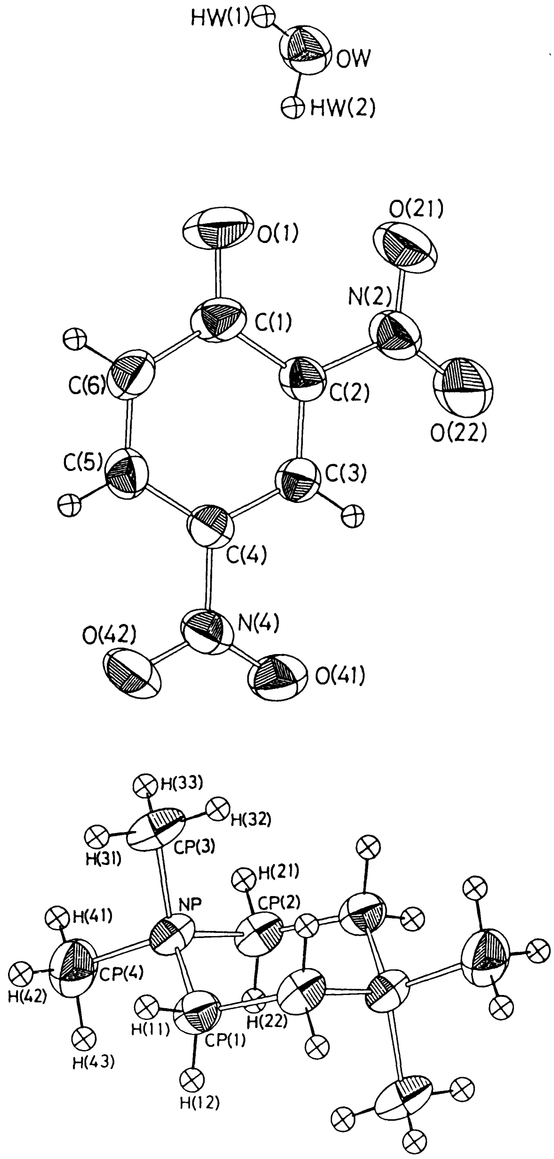

Fig. 1. Atomic numbering of the crystal chemical unit. Each non-H atom is represented as a thermal ellipsoid with a 50% probability.

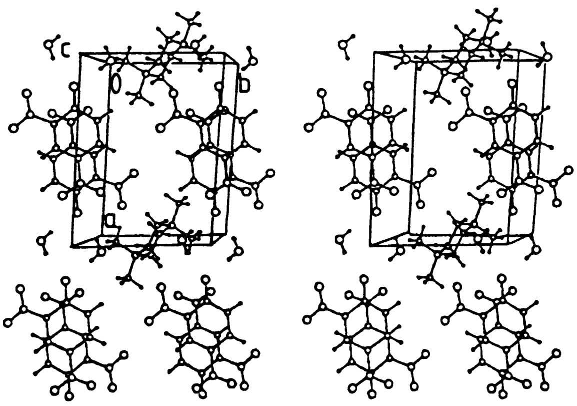

Fig. 2. Stereoscopic view of the crystal structure.

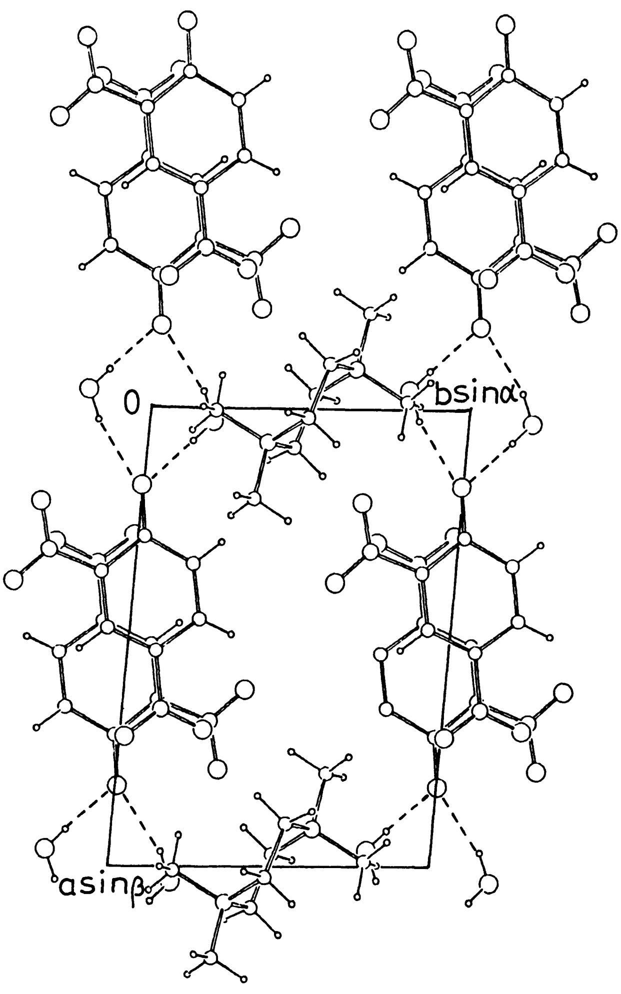

Fig. 3. Projection of the structure along the c axis.

Table 2. Bond lengths and angles with their estimated standard deviations

Superscript (i) $-x\ -y\ -z$ (ii) $2-x\ 1-y\ 1-z$

Distance	l/Å	Distance	l/Å
C(1)-C(2)	1.440(3)	O(1)···OW^{i}	2.753(3)
C(1)-C(6)	1.432(4)	C(3)-H(3)	0.92(3)
C(1)-O(1)	1.254(4)	C(5)-H(5)	0.91(3)
C(2)-C(3)	1.379(3)	C(6)-H(6)	0.96(3)
C(2)-N(2)	1.444(3)	OW-HW(1)	0.80(3)
C(3)-C(4)	1.373(3)	OW-HW(2)	0.81(3)
C(4)-C(5)	1.402(3)	CP(1)-H(11)	0.93(3)
C(4)-N(4)	1.436(3)	CP(1)-H(12)	0.96(2)
C(5)-C(6)	1.351(4)	CP(2)-H(21)	0.97(3)
N(2)-O(21)	1.203(4)	CP(2)-H(22)	0.96(2)
N(2)-O(22)	1.196(6)	CP(3)-H(31)	0.97(3)
N(4)-O(41)	1.218(3)	CP(3)-H(32)	1.00(3)
N(4)-O(42)	1.236(3)	CP(3)-H(33)	0.93(3)
NP-CP(1)	1.504(3)	CP(4)-H(41)	0.94(3)
NP-CP(2)	1.506(3)	CP(4)-H(42)	0.99(3)
NP-CP(3)	1.507(3)	CP(4)-H(43)	0.99(3)
NP-CP(4)	1.498(3)	O(1)···HW(2)	1.98(3)
CP(1)-CP^{ii}(2)	1.502(3)	O(1)···HW^{i}(1)	1.96(3)
O(1)···OW	2.764(3)		

Angle	θ/°	Angle	θ/°
C(2)C(1)C(6)	114.3(2)	C(6)C(5)H(5)	121(2)
C(2)C(1)O(1)	125.5(3)	C(1)C(6)H(6)	117(2)
C(6)C(1)O(1)	120.2(3)	C(5)C(6)H(6)	120(2)
C(1)C(2)C(3)	122.4(2)	HW(1)OWHW(2)	108(3)
C(1)C(2)N(2)	121.2(2)	NPCP(1)H(11)	108(2)
C(3)C(2)N(2)	116.3(2)	NPCP(1)H(12)	107(1)
C(2)C(3)C(4)	119.5(2)	CP^{ii}(2)CP(1)H(11)	108(2)
C(3)C(4)C(5)	121.1(2)	CP^{ii}(2)CP(1)H(12)	113(1)
C(3)C(4)N(4)	119.0(2)	H(11)CP(1)H(12)	108(2)
C(5)C(4)N(4)	119.9(2)	NPCP(2)H(21)	106(2)
C(4)C(5)C(6)	119.3(2)	NPCP(2)H(22)	106(1)
C(1)C(6)C(5)	123.4(3)	CP^{ii}(1)CP(2)H(21)	109(1)
C(2)N(2)O(21)	121.1(2)	CP^{ii}(1)CP(2)H(22)	114(1)
C(2)N(2)O(22)	118.8(3)	H(21)CP(2)H(22)	109(2)
O(21)N(2)O(22)	120.1(3)	NPCP(3)H(31)	105(2)
C(4)N(4)O(41)	119.7(2)	NPCP(3)H(32)	110(2)
C(4)N(4)O(42)	118.1(2)	NPCP(3)H(33)	107(2)
O(41)N(4)O(42)	122.2(2)	H(31)CP(3)H(32)	108(2)
CP(1)NPCP(2)	108.5(2)	H(31)CP(3)H(33)	114(3)
CP(1)NPCP(3)	111.2(2)	H(32)CP(3)H(33)	113(3)
CP(1)NPCP(4)	109.2(2)	NPCP(4)H(41)	109(2)
CP(2)NPCP(3)	111.3(2)	NPCP(4)H(42)	106(2)
CP(2)NPCP(4)	108.3(2)	NPCP(4)H(43)	108(2)
CP(3)NPCP(4)	108.2(2)	H(41)CP(4)H(42)	114(3)
NPCP(1)CP^{ii}(2)	112.4(2)	H(41)CP(4)H(43)	114(3)
NPCP(2)CP^{ii}(1)	112.4(2)	H(42)CP(4)H(43)	106(2)
C(2)C(3)H(3)	121(2)	O(1)HW(2)OW	162(3)
C(4)C(3)H(3)	120(2)	O(1)HW^{i}(1)OW^{i}	173(3)
C(4)C(5)H(5)	120(2)	HW(2)O(1)HW^{i}(1)	92(1)

benzene ring is planar, deviations being within 0.002 Å. Deviations of O(1), N(2), and N(4) from this plane are 0.006, 0.02, and 0.03 Å respectively. The two nitro groups are tilted only slightly from the mean plane of the benzene ring by 4.5 and 6.1° for the groups of N(2) and N(4) respectively. Some shortenings for the N-C lengths are found; N(2)-C(2) (1.444 Å) has the same value of the corresponding N-C bond in 2,4-DNP. The N(4)-C(4) length (1.436 Å) is significantly shorter than that of 2,4-DNP, but close to those in picrates. These shortenings of N-C bonds are due to the quinonoidal character of the anion.

The dimensions of $O^-\cdots H$-O hydrogen bonds between 2,4-DNP$^-$ and H_2O are also listed in Table 2. The normal to the mean plane of the benzene ring of 2,4-DNP$^-$ is almost parallel to the c axis and the average length between the ring planes of two 2,4-DNP$^-$ related by the center of symmtry at (1/2,0,0) is 3.351 Å.

The piperazinediium ring exhibits the space-group imposed $\bar{1}$ (Ci) symmetry, and also shows the 2/m symmetry with a good approximation. The endocyclic C-N length is 1.505 Å and exocyclic C-N bonds are 1.507 and 1.498 Å. These values are longer than those usually found in C-N single bonds (1.47—1.49 Å), but similar values are reported for $C(sp_3)$-$N^+(alkyl)_3$ bonds in 1,1-dimethyl-4-phenylpiperazinium iodide,[9] (+)-*N*-2-(benzylmethylamino)propyl propionanilide hydrobromide,[10] and *trans*-2,5-dimethylpiperazine dihydrochloride.[11] The C-C length is 1.502 Å, which is significantly shorter than that in cyclohexane (1.520 Å). One of the reasons for the long C-N bond may be a nonbonding repulsion between ring hydrogens and methyl hydrogens. There are some short contacts between the axial hydrogens and the axial methyl

Table 3. Some intermolecular contacts with their estimated standard deviations

Superscript (none) x y z (iii) x $1+y$ z
(iv) $1+x$ $1+y$ z (v) $1-x$ $-y$ $-z$
(vi) $1-x$ $-y$ $1-z$

Distance	l/Å	Distance	l/Å
O(42)···CP(1)	3.297(3)	C(1)···O^{v}(42)	3.423(3)
O(42)···CP(4)	3.287(3)	C(2)···O^{v}(42)	3.355(3)
O(21)···OW	3.020(3)	C(3)···C^{v}(5)	3.385(3)
CP(4)···O^{iii}(41)	3.156(4)	OW···CP^{v}(2)	3.292(3)
CP(2)···OW^{iv}	3.264(3)	O(21)···CP^{v}(2)	3.401(3)
CP(3)···OW^{iv}	3.321(3)	O(21)···CP^{vi}(1)	3.279(3)
CP(4)···OW^{iv}	3.464(3)	O(41)···C^{vi}(2)	3.350(3)
C(1)···N^{v}(4)	3.357(3)	N(2)···N^{vi}(4)	3.444(3)

group; H(12)···H(43) and H(22)···H(43) are 2.29 and 2.27 Å respectively. The mean endocyclic CCN angle is 112.4° and the CNC angle is 108.5°. The exocyclic CNC angles average to 109.6°. The mean value of the ring torsion angle is 55.7° (min. 55.0—max. 57.2°). For cyclohexane derivatives and heterocyclic compounds in the chair conformation a correlation exists between the average torsion angle, ϕ, and the average ring bond angle, θ: $\cos\phi=-\cos\theta/(1+\cos\theta)$.[11] In the present case $\phi_{\mathrm{calcd}}=55.8°$ for $\theta_{\mathrm{obsd}}=111.1°$, which is compared with the observed value of 55.7°. This value shows that the ring in TMP^{2+} is more flat than the perfect chair model of cyclohexane with tetrahedral bond angles and torsion angles of 60°.

Some of the shorter intermolecular contacts are listed in Table 3. There are distinctly short C–H···O contacts between O(42)···CP(1), O(42)···CP(4), CP(4)···O^{iii}(41), CP(2)···OW^{iv}, OW···CP^{v}(2), and O(21)···CP^{vi}(1).

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