

The Crystal Structure of Magnesium *p*-Nitrosophenolate Hexahydrate. The Influence of Hydrogen Bonding on Conjugation in the *p*-Nitrosophenolate Ion

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The crystal structure of magnesium *p*-nitrosophenolate hexahydrate, $\text{Mg}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$, has been determined from X-ray diffraction data collected at -165°C and refined by least squares methods.

The space group is $P2_1/c$ with cell dimensions $a = 10.579(1) \text{ \AA}$, $b = 6.242(1) \text{ \AA}$, $c = 13.198(3) \text{ \AA}$ and $\beta = 106.97(1)^\circ$ at -165°C . The final R factor was 3.7 % and the estimated standard deviations in bond lengths are about 0.001 \AA and in angles 0.1° .

In the anion the C-N, C-O and N-O bond lengths differ about 0.020 \AA and the C-C bond lengths differ from 0.005 to 0.012 \AA from corresponding bonds in the sodium salt. The anion has a less pronounced *p*-quinonoid character in the present structure than in the sodium salt. This is probably due to a greater, respectively lesser, ability of the crystal field in stabilizing charge in the phenoxide-oxygen atom than in the nitroso-oxygen atom in the title compound and the sodium salt.

The anions in the two salts are compared as to gross atomic populations determined from both INDO calculations and by *L*-shell refinement. Also, the two anions are compared by difference syntheses. Finally, some features of the UV and UV-KCl spectra of the title compound, the sodium and the potassium salt are discussed.

The present structure determination of magnesium *p*-nitrosophenolate hexahydrate (I) is part of a series of structural investigations of *C*-nitroso compounds and oximes derived from these. Previously the tautomeric isomer of *p*-nitrosophenol, *p*-benzoquinone monoxime (II), and the salts potassium *p*-nitrosophenolate monohydrate (III) and sodium *p*-nitrosophenolate trihydrate (IV) have been investigated.¹⁻³

A characteristic feature of oximidoketones like (II) is the diversity in colour shown by the salts obtained from alkaline solutions.⁴ In the present case (III) is green, (IV) is red while (I) is reddish green. Seventy years ago Hantzsch attributed the diversity in colour to structural differences in the anion;⁴ salts having the characteristic blue or green colour of *C*-nitroso compounds should comprise anions having a "nitroso-phenoxide" structure $\text{O}=\text{N}-\text{C}=\text{CH}-\text{CH}=\text{C}-\text{O}^-$, colourless salts should comprise anions having an "oxime-ketone" structure $^- \text{O}-\text{N}=\text{C}-\text{CH}=\text{CH}-\text{C}=\text{O}$ while red salts should comprise anions having the formal charge delocalized to both oxygen atoms.

Unfortunately the poor crystal quality prevented high accuracy in the structure investigation of (III);³ consequently the question whether the anion has a less predominant *p*-quinonoid (or "oxime-ketone") structure in the green potassium salt than in the red sodium salt could not be answered. However, the differences in hydrogen bonding to and coordination about the phenoxide oxygen atom and the nitroso group atoms in the two salts indicate that this is actually the case.

As the reddish green magnesium salt forms crystals of high quality and shows characteristic differences from both the potassium and the sodium salt in the UV, UV-KCl, and IR-KBr spectra it was decided to determine the structure of this salt in order to compare the anion structure with that found in (IV).

EXPERIMENTAL

Well-formed tabular crystals were grown by evaporation of an aqueous solution prepared by adding *p*-benzoquinone monoxime (purified by sublimation) to 0.004 M magnesium carbonate. Traces of unsolved magnesium carbonate were present during the evaporation. A preliminary film investigation showed systematic absences consistent with the space group $P2_1/c$. Determination of unit cell parameters and intensity measurements were done using a crystal of dimensions $0.55 \times 0.40 \times 0.08$ mm. The crystal was mounted with the *b* axis tilted somewhat away from the goniometer spindle axis.

All measurements were made on a SYNTEX $P\bar{1}$ diffractometer with graphite monochromatized $MoK\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). The temperature at the crystal site was -165°C . Cell constants were determined by least squares treatment of measurements of 15 general reflections. Three-dimensional data were collected using the $\omega-2\theta$ scan technique. The scan speed varied between 2.0 and $6.0^\circ/\text{min}$, and the total time for background counts at the scan limits $2\theta(\alpha_1) - 0.8^\circ$ and $2\theta(\alpha_2) + 1.0^\circ$ was 0.7 of the time of integration. A quadrant 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 2 s scan over the peak were measured. The intensity of three test reflections measured for every 50 reflections showed no significant change during the measurements. Out of 3254 unique reflections 2884 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 1% uncertainty due to experimental fluctuations. The atomic scattering factors for the heavy atoms were those of Doyle and Turner⁵ and for hydrogen those of Stewart *et al.*⁶ Core and valence electron scattering factors used in an *L*-shell refinement were those given by Stewart.⁷ All programs except for the ORTEP program⁸ and the MULTAN program⁹ applied during the structure investigation are described in Ref. 10. The UV spectra were recorded on a CARY MODEL 14 spectrophotometer with variable slit and a scan speed of 7 \AA s^{-1} .

CRYSTAL DATA

Magnesium *p*-nitrosophenolate hexahydrate, $Mg(C_6H_4O_2N)_2 \cdot 6H_2O$, space group $P2_1/c$ (No. 14). Dimensions of the unit cell at -165°C : $a = 10.579(1) \text{ \AA}$, $b = 6.242(1) \text{ \AA}$, $c = 13.198(3) \text{ \AA}$ and $\beta = 106.97(1)^\circ$. $V = 834.1 \text{ \AA}^3$, $M = 376.61$,

$$F(000) = 396, D_{\text{calc}}(-165^\circ\text{C}) = 1.499 \text{ g cm}^{-3} \\ \mu = 0.175 \text{ mm}^{-1}.$$

STRUCTURE DETERMINATION

The structure was solved by direct methods^{9,10} and refined by full-matrix least-squares technique. Initial positional parameters for all hydrogen atoms were calculated from stereochemical considerations. The final refinement including all atoms and all the observed reflections converged with a conventional *R* factor of 0.037, a weighted R_w factor of 0.039 and a goodness of fit *S* of 2.9. Using 2266 reflections with $\sin \theta/\lambda$ greater than 0.45 the refinement yielded $R = 0.034$, $R_w = 0.032$ and $S = 1.9$. The scale factor increased from 0.138(1) to 0.144(2) and the e.s.d.'s in the bond lengths changed from 0.0012–0.0015 to 0.0010–0.0012 \AA . Further, and as with the sodium salt, (IV), all the C–C bonds and the C–N bond lengthened while the C–O and the N–O bond shortened. The change was 2.5σ in the

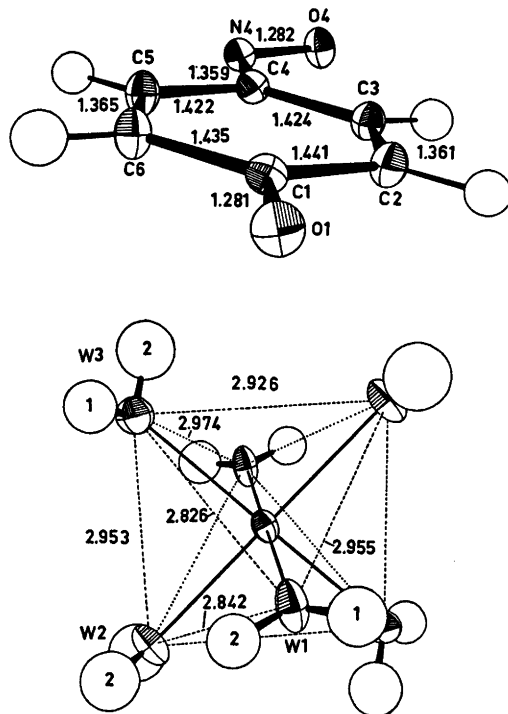


Fig. 1. 50% probability ellipsoids and numbering of atoms. a, anion; b, cation.

Table 1. Fractional atomic coordinates and thermal parameters ($\times 10^5$) for nonhydrogen and ($\times 10^3$) for hydrogen atoms. 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	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	0	0	0	101(2)	107(2)	177(2)	-7(2)	40(2)	-2(2)
OW1	2664(08)	29248(14)	6881(07)	148(4)	146(4)	332(5)	-33(3)	120(3)	-65(3)
OW2	19964(08)	-5706(15)	7140(07)	121(3)	146(4)	324(5)	-1(3)	20(3)	-4(3)
OW3	4430(08)	10932(14)	-13459(07)	194(4)	194(4)	194(4)	-70(3)	42(3)	5(3)
O1	13302(07)	-196(13)	33154(06)	124(3)	184(4)	202(3)	8(3)	57(3)	-2(3)
O4	73858(07)	215(13)	39652(07)	134(3)	171(4)	320(4)	-12(3)	65(3)	-12(4)
N4	65944(09)	-15194(15)	39917(07)	136(4)	161(4)	197(4)	8(3)	46(3)	-7(3)
C1	25619(10)	-3547(16)	34462(08)	133(4)	150(5)	137(4)	0(3)	41(3)	-9(3)
C2	34171(10)	13652(17)	33306(09)	152(4)	136(4)	207(5)	15(4)	58(4)	22(4)
C3	47353(10)	10402(18)	35045(08)	137(4)	141(4)	189(5)	-1(4)	50(4)	11(4)
C4	52935(10)	-10264(17)	37921(08)	122(4)	141(4)	156(4)	14(3)	41(3)	-6(4)
C5	44497(11)	-27516(18)	38709(09)	169(5)	128(4)	247(5)	18(4)	72(4)	10(4)
C6	31267(11)	-24470(18)	37035(09)	162(4)	134(4)	250(5)	-7(4)	81(4)	7(4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H2	301(1)	279(2)	316(1)	1.5(2)	H3	529(1)	217(2)	342(1)	1.8(2)
H6	257(1)	-358(2)	378(1)	2.1(3)	H5	488(1)	-415(2)	404(1)	1.8(2)
H1W1	-20(2)	343(3)	92(1)	2.9(3)	H2W1	92(2)	358(3)	77(1)	2.4(3)
H1W2	231(2)	-175(3)	78(1)	4.6(4)	H2W2	253(2)	48(3)	87(1)	4.0(4)
H1W3	-10(2)	87(3)	-189(1)	3.7(4)	H2W3	74(2)	231(3)	-146(1)	2.6(3)

C—O bond length and 3.5σ in the C2—C3 bond length. A list of structure amplitudes is available from the author. Final parameters from the refinement with all the observed reflections are given in Table 1.

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 0.0006 Å² in the anion. The translational r.m.s. amplitudes of vibration along the principal axes are 0.12, 0.11, and 0.11 Å and the r.m.s. librational amplitudes are 4.7, 2.0, and 1.4°. The largest increase in bond lengths was 2.7σ when adjusting the coordinates according to this libration.

Bond lengths and angles with their estimated standard deviations calculated from the correlation matrix are given in Table 2. Deviations from a least-squares plane through the benzene ring atoms are given in Table 3.

The final difference Fourier or X—X map of the anion in the benzene ring plane is shown

in Fig. 7. A similar map for the sodium salt is also shown.

In both cases the synthesis was calculated using the reflections having $\sin \theta/\lambda$ less than 0.45 and positional and temperature parameters from the refinement with the reflections having $\sin \theta/\lambda$ greater than 0.45. The scale factor used was from a refinement with reflections at $\sin \theta/\lambda$ less than 0.45 and with the other parameters fixed at their "high" angle values. This choice of scale factor is justified *a posteriori* by the reasonable appearance of the maps.^{11a}

Both the electron density in (0.15–0.50 e Å⁻³) and the position of (in the middle of the bonds and in lone pair positions) the well defined and sharp residual peaks are in good conformity with what has been found in very accurate work with other organic compounds.^{11a}

Thus, it seems reasonable to assume only small systematic errors in the intensities. A normal probability plot using observed and calculated structure factors shows absence of systematic errors not absorbed by the models.^{11b}

An *L*-shell refinement⁷ of the anionic atoms

Table 2. Bond lengths (Å) and angles (°). Estimated standard deviations in parentheses. Differences in length and angle value between corresponding bonds and angles in (I) and (IV) are also given. Bond lengths in the anion. Values obtained in refinement with all observed reflections are given on the first line and libration corrected bond lengths from the same refinement are given on the second line, while values obtained in a refinement using only reflections with $\sin \theta/\lambda$ greater than 0.45 are given on the third line.

	(I)	(I)–(IV)		(I)	(I)–(IV)
O1–C1	1.2807(12)	0.0221(17)	C3–C4	1.4235(15)	–0.0051(21)
	1.2816	0.0221		1.4273	–0.0044
	1.2770(10)	0.0216(16)		1.4247(11)	–0.0064(16)
O4–N4	1.2823(12)	–0.0208(16)	C4–C5	1.4218(15)	–0.0066(21)
	1.2856	–0.0196		1.4256	–0.0052
	1.2811(11)	–0.0176(15)		1.4240(12)	–0.0053(18)
N4–C4	1.3589(13)	0.0187(18)	C5–C6	1.3651(15)	0.0075(21)
	1.3600	0.0188		1.3662	0.0076
	1.3594(11)	0.0184(16)		1.3681(12)	0.0085(18)
C1–C2	1.4405(15)	–0.0089(21)	C6–C1	1.4351(15)	–0.0120(21)
	1.4445	–0.0074		1.4388	–0.0113
	1.4449(12)	–0.0067(18)		1.4378(12)	–0.0133(18)
C2–C3	1.3608(15)	0.0072(21)	sum of differences:		0.0021(59)
	1.3619	0.0072			0.0078
	1.3675(12)	0.0098(18)			0.0090(49)

Bond angles in the anion

	(I)	(I)–(IV)
O1–C1–C2	120.7(1)	–0.4(1)
O1–C1–C6	121.1(1)	–0.8(1)
C6–C1–C2	118.2(1)	1.3(1)
C1–C2–C3	121.0(1)	–0.8(1)
C2–C3–C4	120.3(1)	–0.3(1)
C3–C4–C5	119.0(1)	0.5(1)
C4–C5–C6	121.2(1)	–0.3(1)
C5–C6–C1	120.1(1)	–0.7(1)
C3–C4–N4	125.1(1)	0.3(1)
C5–C4–N4	115.9(1)	–0.8(1)
C4–N4–O4	117.2(1)	0.1(1)

Distances in the $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ ion

Mg···OW1(a)	2.0218
Mg···OW2(a)	2.0770
Mg···OW3(a)	2.0801
OW1(a)···OW2(a)	2.8416(12)
OW1(a)···OW2(b)	2.9546(12)
OW1(a)···OW3(a)	2.9735(12)
OW1(a)···OW3(b)	2.8262(12)
OW2(a)···OW3(a)	2.9264(12)
OW2(a)···OW3(b)	2.9526(12)

Distances and angles involving hydrogen atoms

	O–H	H···O(N)	O···O(N)	O–H···O(N)	H–O–H
OW1–H1···O1(c)	0.73(2)	2.02(2)	2.743(1)	173.6(1.8)	113.7(1.7)
OW1–H2···O4(d)	0.79(2)	1.94(2)	2.726(1)	175.3(1.6)	
OW2–H1···O4(e)	0.80(2)	2.05(2)	2.831(1)	156.2(1.3)	117.7(1.7)
OW2–H2···N4(d)	0.85(2)	2.08(2)	2.904(1)	165.1(1.7)	
OW3–H1···O1(f)	0.79(2)	2.02(2)	2.807(1)	172.8(1.9)	101.8(1.6)
OW3–H2···O1(g)	0.85(2)	1.86(2)	2.708(1)	178.1(1.5)	
	C–H		C–C–H		C–C–H
C2–H	0.98(1)	C1–C2–H	116.9(8)	C4–C5–H	115.3(8)
C3–H	0.95(1)	C3–C2–H	122.0(8)	C6–C5–H	123.5(8)
C5–H	0.98(1)	C2–C3–H	120.7(8)	C5–C6–H	121.3(9)
C6–H	0.95(1)	C4–C3–H	118.9(8)	C1–C6–H	118.5(9)

Table 2. Continued.

Other intermolecular contacts		Dihedral angles in the anion	
OW1...OW1(f)	3.120	C3-C4-N4-O4	3.4(2)
		C5-C4-N4-O4	-177.5(1)
		C2-C1-O1(f)...OW3	98.6(1)
		C2-C1-O1(g)...OW3	-26.6(1)
		C2-C1-O1...OW1	-148.6(1)
		C5-C4-N4...OW2	-9.6(1)
		C4-N4-O4...OW2	-13.9(1)
		C4-N4-O4...OW1	-167.1(1)
Symmetry codes			
(a): x	y	z	(b): $-x$
(d): $-x+1$	$y-\frac{1}{2}$	$\frac{1}{2}-z$	(e): $-x+1$
(g): x	$-y+\frac{1}{2}z-\frac{1}{2}$		(f): $-x-y+1$
			$-z$

Table 3. Atomic coordinates, l, m , and deviations, n , of atoms from a least-squares plane through the benzene ring atoms C1, C2, C3, C4, C5, and C6. The coordinate system is orthogonal and its unitary vectors L, M, and N (with a length of 1 Å) are defined by the following equations:

$$\begin{aligned} \mathbf{L} &= -0.0271\mathbf{a} - 0.1486\mathbf{b} + 0.0128\mathbf{c} \\ \mathbf{M} &= -0.0936\mathbf{a} + 0.0490\mathbf{b} - 0.0147\mathbf{c} \\ \mathbf{N} &= 0.0164\mathbf{a} + 0.0342\mathbf{b} + 0.0768\mathbf{c} \end{aligned}$$

The origo, which is the center of gravity, has coordinates $x=0.3931$, $y=0.9304$ and $z=0.3608$. N is normal to the plane.

	l	m	n
C1	0.2348	1.3972	0.0171
C2	-1.1038	0.8657	-0.0111
C3	-1.3258	-0.4768	-0.0041
C4	-0.2311	-1.3864	0.0135
C5	1.0942	-0.8720	-0.0073
C6	1.3318	0.4723	-0.0080
O1	0.4346	2.6616	0.0550
O4	-1.5236	-3.2321	0.1024
N4	-0.3411	-2.7408	0.0330
H2	-1.842	1.516	0.013
H3	-2.208	-0.822	-0.038
H5	1.805	-1.547	-0.039
H6	2.213	0.816	0.008

using the reflections having $\sin \theta/\lambda$ less than 0.65 \AA^{-1} yielded $R=0.041$ and $R_w=0.042$ for the present structure and $R=0.037$ and $R_w=0.040$ for the sodium salt structure. The R factors from a normal refinement on the same data sets were not different from those of the refinement with all data. The adjusted 7 gross atomic populations are listed in Table 4 together with results from INDO 12 calculations.

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DISCUSSION

Interionic structural features. A general view of the structure is shown in Fig. 2. The structure comprises separate $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ ions with the magnesium atom located in the inversion centres at $x=0$. Consequently, there are only three independent water molecules (as in (IV)). The cation structure resembles closely that usually found in the magnesium aquo ions; *i.e.* a regular octahedral coordination and an average length of the coordination contacts of 2.05 \AA .¹³ The W1 and W2 water molecules belong to Class 1, type D of Ferraris and Franchini-Angela (see Ref. 13) having e_1 values *i.e.* values of the angle between the coordination contact direction and the plane of the water molecule, of 3 and 7°, respectively. Probably

Table 4. Gross atomic populations. Estimated standard deviations are given in parentheses. The INDO calculations were performed using the l and m coordinates in Table 3 as input parameters ($n=0$). INDO calculations using coordinates for the anion in (IV) as input parameters yielded nearly identical results.

Atom	(I)	(IV)	INDO
O1	8.39(3)	8.36(3)	8.55
O4	8.31(3)	8.33(3)	8.38
N4	7.27(3)	7.20(3)	6.98
C1	5.90(3)	5.91(4)	5.70
C2	6.05(4)	6.01(4)	6.15
C3	5.84(4)	5.92(4)	5.94
C4	6.06(4)	6.02(4)	6.06
C5	5.95(4)	5.94(4)	5.95
C6	5.97(4)	5.93(4)	6.16

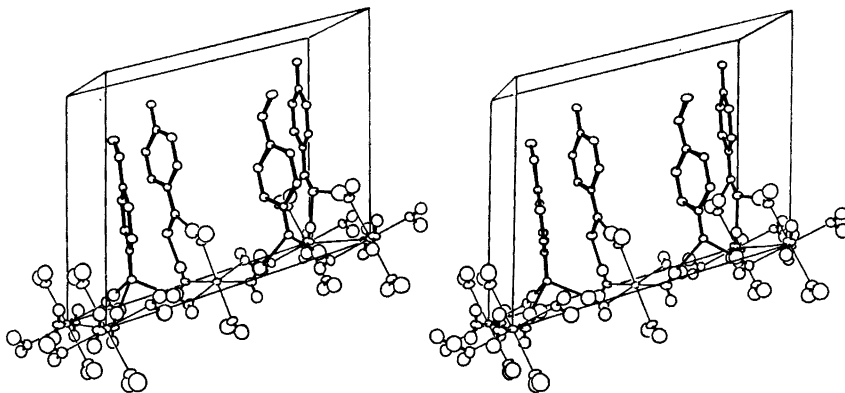


Fig. 2. A stereoscopic illustration of the structure. Anion hydrogen atoms are not shown for clarity.

the $W3$ molecule is a Class 1', type J water molecule as e_1 is 32° in this case.

All the six water protons are engaged in hydrogen bonding to anion atoms. The length of the $O \cdots H - OW$ bonds are in the usual range,¹³ the average value being 2.76 Å.

Fig. 3 shows the coordination about the anion terminal atoms in (I) and (IV).³ In both structures there are six contacts to the anion; *i.e.* one for each lone pair. The nitroso group atoms are acceptors in four hydrogen bonds in (IV)³ and three in the present structure. However, the nitrogen atom is an acceptor in both structures. On the other hand the phenoxide oxygen atom accepts only one hydrogen atom in (IV) and even three in (I). The coordination around $O4$ is tetrahedral in (IV) and trigonal in (I) whereas the opposite is the case for $O1$. Apparently the ability of the crystal field to stabilize negative charge is greater at $O1$ than at $O4$ as to the title compound and less so at $O1$ than at $O4$ as to the sodium salt. Thus, the contribution of the "oxime-ketone" or *p*-quinonoid VB structure to resonance in the anion should be expected to be less in (I) than in (IV).

The p-nitrosophenolate ion. A comparison between bond lengths in (I) and (IV) clearly shows that the above expectation is realized. The C–O and the C–N bond is about 0.020 Å longer and the N–O bond 0.021 Å shorter in (I) than in (IV). Accordingly, the C–C "double" bonds are 0.007 Å longer and the C–C "single" bonds from 0.005 to 0.012 Å shorter in (I) than

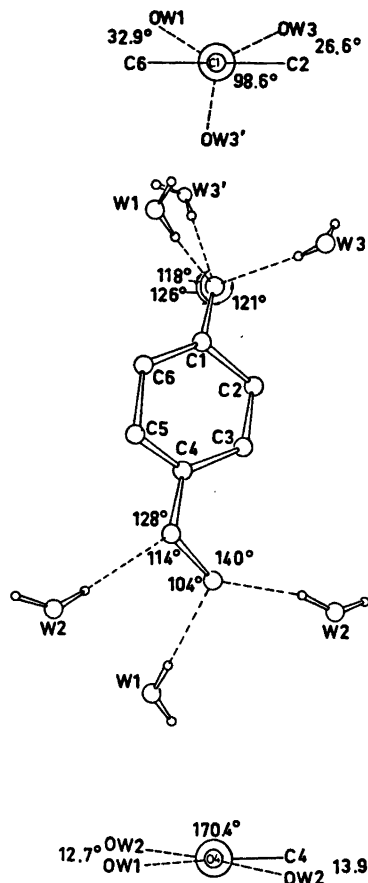


Fig. 3. The coordination about the anion.

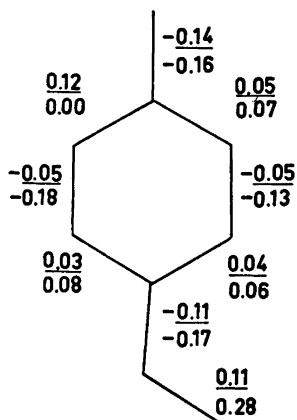


Fig. 4. Differences between "observed" bond orders. The underlined figures are the differences between the anion in (I) and the anion in (IV), while the other figures are the differences between (IV) and the acid (II).

in (IV). All the differences but that of the C3 - C4 bond are significant.

Craven *et al.*¹⁴ have found that when the exocyclic C-O bonds in the barbiturates are engaged in a hydrogen bond, this bond is lengthened by approximately 0.010 Å. A shift in the C-O bond in the *p*-nitrosophenolate ion about twice this value may be caused by

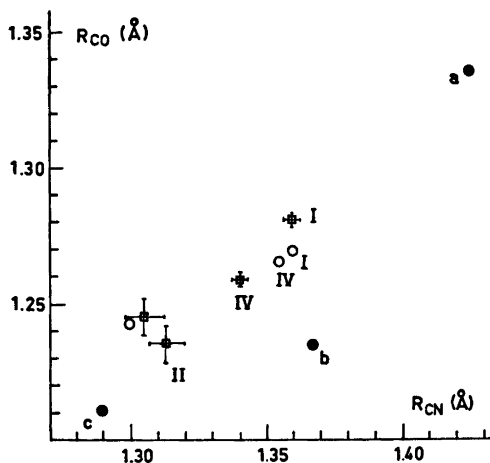


Fig. 5. A plot of the C-O bond length against the C-N bond length in (I), (II), (IV), *p*-nitrosophenol (a), anion (b), and *p*-benzoquinone monoxime (c). □, observed point (2.5σ indicated with bars); ○, calculated point (CNDO/2); ●, calculated point (MINDO/3).

several factors. First, and perhaps most important, is the fact that the nitroso oxygen atom is less engaged in hydrogen bonding in (I) than in (IV). This has probably a similar, but of course smaller, lengthening effect on the C-O bond as that caused by ionization. Further, a sodium ion contact has been replaced by a hydrogen bond. A sodium ion contact may probably be considered less effective in lengthening the bond than hydrogen bonding, as a lithium ion contact is considered about as effective as a hydrogen bond in this respect.¹⁵ Finally, the change from a trigonal to a tetrahedral coordination may induce a slight shift in the hybridization of the phenoxide oxygen atom. The minor changes in conjugation in the ring is probably mainly caused by the transfer of charge between the oxygen atoms.

This analysis indicates that the change in the N-O bond length is about the same as

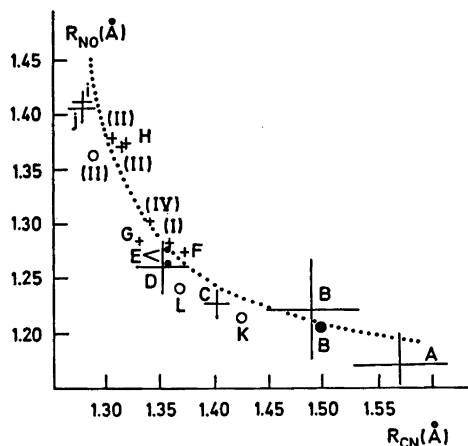


Fig. 6. A plot of the N-O bond length against the C-N bond length in the *C*-nitroso compounds whose structure is determined with some accuracy and in some selected oximes. Names and references for the compounds A, B, C, D, and G are given in Table 5 in Ref. 3, E is tetramethylammonium benzonitrosolate;²¹ F, *N,N,N',N'*-tetramethyl-4-nitroso-1,3-phenylenediamine;²² H, i, and j are the references 3, 14 and 13 in Ref. 1; K, *p*-nitrosophenol and L, *p*-nitrosophenolate. The graph is for $R_{NO} - R_{NO}^{\circ} = k / (R_{CN}^{\circ} - R_{CN}^{\circ})$ with $R_{NO}^{\circ} = 1.150$ Å, $R_{CN}^{\circ} = 1.233$ Å and $k = 0.016$ Å². CNO angles (°): A, 121(2); B, 113(1) and 113.0; C, 115(1); D, 116; E, 117; F, 116.3(2); (I), 117.2(1); (IV), 117.1(1); G, 116.4(1); H, 111.7(2); (II), 112.3(2); (II), 112.8(2) and 112.3; i, 112.0(2); j, 110.2(2) and 110.7(2); K, 113.0; L, 117.1.

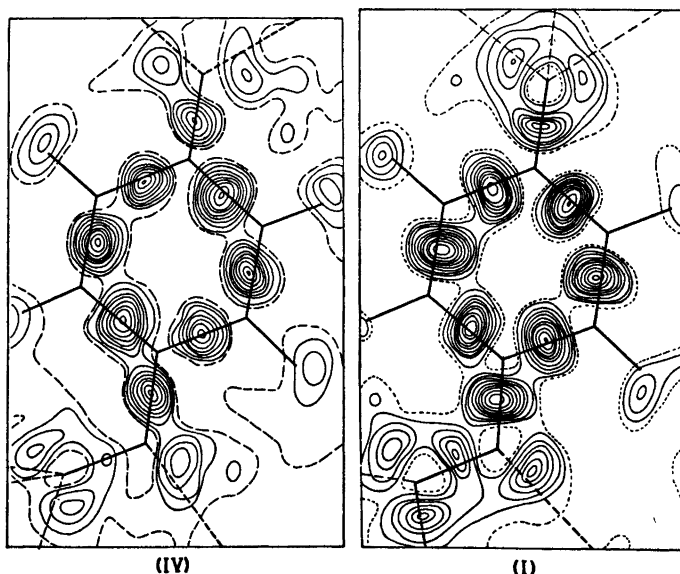


Fig. 7. Final difference Fourier syntheses in the least-squares plane through the benzene ring atoms in (I) and (IV). The dotted line runs through points of $0.0 \text{ e } \text{Å}^{-3}$, and the differences between the contours are $0.05 \text{ e } \text{Å}^{-3}$.

Table 5. Wave length ($m\mu$) of some transitions in the UV and UV-KCl absorption spectra of (I), (II), (III) and (IV) and the number of hydrogen bonds to the nitroso group atoms, n , and to the phenoxide oxygen atom, m . Molecular extinction coefficients are shown in parentheses.

Compound in the solid state	Nitroso band ($n_{\text{NO}^- - \pi^*}$)		2nd band (charge transfer band, $\pi - \pi^*$)		3rd band ($\pi - \pi^*$)	
	λ_{max} (e)	n	λ_{max} (KCl) (log e)	m	λ_{max} (KCl) (log e)	
(II)			305 (strong) or 360 (weak)	1		
(IV)	535	4	354	1	260	
(I)	560	3	387	3	255	
(III)	610	1?	337	1	265	
Compound in solution						
(II) in water			310	(3.9)		
(I), (III), (IV) in water	500	(100)	400	(4.2)	255	(3.7)
(III) in acetone	610	(35)	410	(4.2)		
<i>p</i> -nitrosophenol in water	735	(35)				

in the C-O bond length towards a similar change in the environment.

A shift in the resonance equilibrium between the two main VB structures is more directly expressed by changes in bond orders than by

changes in bond lengths. Fig. 4 shows the bond order differences between (I) and (IV). The bond orders are calculated using a linear bond order-bond length relationship.¹⁶ The differences between (IV) and the acid (II) is shown

for comparison. The differences are fairly consistent with a decrease in the weight of the *p*-quinonoid VB structure from 83 % in the acid (II) to 55 % in (IV) to 44 % in (I).

In Fig. 5 the C–O bond length is plotted against the C–N bond length in (II), (IV) and (I). Some calculated points are also shown; both CNDO/2¹⁷ calculations using the *l* and *m* coordinates in Table 3 as input parameters ($n=0$), and MINDO/3¹⁸ calculations with bond length and angle optimization (fixing the CNO angle at the observed value and the C–H bond length at 1.0 Å) have been performed. The plot indicates roughly a linear relationship between the two bond lengths. Evidently the change in conjugation caused by a slight change in the environment is comparable with that caused by ionization.

A plot of C–N bond lengths against N–O bond lengths is shown in Fig. 6. Apparently a hyperbola having asymptotes at $R_{\text{NO}}=1.150$ Å and $R_{\text{CN}}=1.233$ Å might pass through nearly all the indicated areas formed by an 2.5σ uncertainty allowance in the bond lengths. Thus, in those compounds having the largest conjugation over the CNO fragment the sum of the C–N and the N–O bond lengths appears to be less than elsewhere along the curve. According to VSEPR theory¹⁹ this should promote larger CNO angles in these compounds than in the other. The values observed seem to indicate that this expectation is realized to some extent.

A value of $117.1(1)^\circ$ for the CNO angle in the present structure is in good conformity with the values found in the compounds having a similar degree of conjugation over the CNO fragment. In nitrosates the angles are in the range 116 – 117° . Other factors may also influence this angle and hydrogen bonding is probably of particular importance. It is therefore surprising that all anion bond angles *but* the CNO angle are significantly different from those of the anion in (IV). The differences are shown in Table 2. As to the benzene ring angles, the angle at C1 and C4 is larger while the other angles are smaller in (I) than in (IV). It appears that $\Delta C1 \sim -2\Delta C2 \sim -2\Delta C6$ and $\Delta C4 \sim -2\Delta C3 \sim -2\Delta C5$, Δ denoting the C–C–C angle differences. Whereas the average benzene ring angle differs 1.7° from 120° in (IV) it differs only

0.9° from 120° in the present structure. This is in accordance with the change in bond lengths towards a more benzenoid (or “nitroso-phenoxide”) structure when passing from (IV) to (I).

The anion has the same weakly expressed boat form as in (IV) although to a somewhat greater extent.

The charge distribution in the anion. This subject has previously been discussed to some extent.³ The *L*-shell refinement gives adjusted gross atomic populations that lend support to the result of the CNDO/2 and the INDO calculations of a nearly equal distribution of negative charge between the two oxygen atoms. Further there is a rather good accordance between theory and experiment as to the charge distribution in the benzene ring. The comparison is made in Table 4. Comparing (I) and (IV) one detects a striking resemblance between the two anions. The differences are in the range 0.01 – 0.08 e and far from significant.

The UV and UV-KCl absorption spectrum of the p-nitrosophenolate ion. The λ_{max} values for the three transitions of least energy of the anion in the three salts and in water and acetone solution are given in Table 5. Some values for the acid (II) and its tautomer are shown for comparison.

Generally the spectrum bear strong resemblance with that of other *p*-substituted nitrosobenzenes.²⁰ However, contrary to what has been found for these the weak $n_{\text{NO}^-} - \pi^*$ transition seems not to be coupled with the 2nd transition so that a blue shift in the first follows a red shift in the second. CNDO/2 calculations on *isolated* species indicate that the more the “oxime-ketone” or *p*-quinonoid structure dominates the longer the wave length of the second ($\pi - \pi^*$) transition and the shorter the wave length of the weak transition.

The two transitions are also strongly dependent upon the crystal field. It is interesting to note that the weak transition gets an increasing blue shift when the number of hydrogen bonds to the nitroso group atoms increases. The diversity in colour is then probably caused both by hydrogen bonding *per se* and the shift it induces in the resonance equilibrium between the two main VB structures.

REFERENCES

1. Talberg, H. J. *Acta Chem. Scand. A* 28 (1974) 910.
2. Talberg, H. J. *Acta Chem. Scand. A* 28 (1974) 593.
3. Talberg, H. J. *Acta Chem. Scand. A* 29 (1975) 919.
4. Hantzsch, A. *Ber. Dtsch. Chem. Ges.* 42 (1909) 966.
5. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1970) 2232.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Stewart, R. F. *J. Chem. Phys.* 53 (1970) 205.
8. Johnson, C. K. *ORTEP*, Report ORNL-3795, Oak Ridge National Laboratory, Oak Ridge 1965.
9. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
10. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
11. a. Griffin, J. F. and Coppens, P. *J. Am. Chem. Soc.* 97 (1975) 3496; b. Abrahams, S. C. and Keve, E. T. *Acta Crystallogr. A* 27 (1971) 157.
12. Pople, J. A., Beveridge, D. L. and Dobosh, P. A. *J. Chem. Phys.* 47 (1967) 2026.
13. Ferraris, G. and Franchini-Angela, M. *Acta Crystallogr. B* 28 (1972) 3572.
14. Craven, B. M., Cusack, C., Gartland, G. L. and Vizzini, E. A. *J. Mol. Struct.* 16 (1973) 331.
15. Enders-Beumer, A. and Harkema, S. *Acta Crystallogr. B* 29 (1973) 682.
16. Stals, J. *Rev. Pure Appl. Chem.* 20 (1970) 1.
17. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* 44 (1966) 3289.
18. Bingham, R. C., Dewar, M. J. S. and Lo, D. H. *J. Am. Chem. Soc.* 97 (1975) 1285.
19. Gillespie, R. J. *J. Chem. Educ.* 47 (1970) 18.
20. Nakamoto, K. and Rundle, R. E. *J. Am. Chem. Soc.* 78 (1956) 1117.
21. Vetter, G., Kopf, J. and Klar, G. *Z. Naturforsch. B* 28 (1973) 293.
22. Talberg, H. J. *Acta Chem. Scand. A* 30 (1976) 829.

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