

# The Crystal and Molecular Structure of Sodium *p*-Nitrosophenolate Trihydrate

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The crystal structure of sodium *p*-nitrosophenolate trihydrate has been determined from X-ray diffraction data collected at  $-162^\circ\text{C}$  and refined by least squares methods. The space group is  $P\bar{1}$ , with cell dimensions  $a = 6.106(2)$  Å,  $b = 6.706(2)$  Å,  $c = 11.529(3)$  Å,  $\alpha = 100.76(2)^\circ$ ,  $\beta = 92.73(2)^\circ$  and  $\gamma = 110.14(2)^\circ$  at  $-162^\circ\text{C}$ . The final  $R$  factor was 3.2 % and the estimated deviations in bond lengths are about 0.001 Å and in angles  $0.1^\circ$ . The nitroso group atoms are acceptors in four hydrogen bonds. The C–N bond length (1.340 Å) is among the shortest and the N–O bond length (1.303 Å) the longest observed for *C*-nitroso compounds. The conjugation in the anion is compared with that in the corresponding acid. The “double” bonds are 0.02–0.04 Å longer and the “single” bonds 0.01–0.07 Å shorter in the anion than in the acid.

The present structure determination of sodium *p*-nitrosophenolate trihydrate (I) is part of a series of structural investigations of monomeric *C*-nitroso compounds and the oximes which are derived from these by protonation or tautomeric proton exchange. So far the crystal structure of *N,N*-dimethyl *p*-nitrosoaniline (II), its hydrochloride (III), potassium *p*-nitrosophenolate monohydrate (IV) and quinone 4-oxime (V) have been investigated.<sup>1–4</sup>

In marked contrast to (IV) forming green crystals the title compound forms pale red crystals indicating that the quinonoid character

in the anion is more pronounced in (I) than in (IV).

## EXPERIMENTAL

Pale red needle-shaped crystals were grown by slow evaporation of an alkaline ethanolic solution of quinone 4-oxime. A preliminary film investigation showed that they were triclinic. In  $\text{MoK}\alpha$  radiation at  $18^\circ\text{C}$  they decomposed after 24 h.

Unit cell constants at  $18^\circ\text{C}$  were calculated using measurements of seven reflections on a Picker diffractometer with  $\text{MoK}\alpha$  radiation.

Three-dimensional data were collected and unit cell constants were determined at low temperature using a crystal of dimensions  $0.6 \times 0.2 \times 0.1$  mm. The measurements were made on a Syntex *PI* diffractometer with graphite monochromatized  $\text{MoK}\alpha$  radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). The temperature at the crystal site was  $-162^\circ\text{C}$ . Cell constants were determined by least squares treatment of measurements of twelve reflections. Intensity data were collected using the variable  $\omega - 2\theta$ :scan technique. Prior to each scan the intensity was measured with stationary crystal and counter, and the scan speed accordingly adjusted. The scan speed varied between 2.0 and  $6.0^\circ/\text{min}$ , and the total time for background counts at the scan limits  $2\theta(\alpha_1) - 1.2^\circ$  and  $2\theta(\alpha_2) + 1.2^\circ$  was 0.7 of the time of integration. A hemisphere of reciprocal space was examined. All reflections having  $2\theta$  less than  $45^\circ$  were measured; between  $45$  and  $70^\circ$  only reflections having integrated counts of more 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 measurement. Out of 3076 unique reflections 2419 had intensities larger than  $2.5 \times \sigma(I)$ . They were regarded as observed.  $\sigma(I)$  is the estimated standard deviations of the

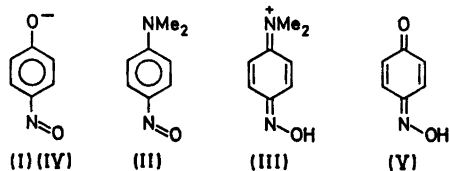


Table 1. Fractional atomic coordinates and thermal parameters ( $\times 10^5$ ) for nonhydrogen atoms. Estimated standard deviations in parentheses. The temperature factors are expressed as:  $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$ .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Na	25717(7)	53612(7)	42925(4)	720(12)	896(11)	158(3)	702(19)	76(9)	110(9)
OW1	32090(14)	24807(14)	50470(7)	1110(23)	905(20)	160(5)	805(34)	133(17)	133(17)
OW2	72663(15)	15592(14)	65646(7)	810(22)	1160(21)	206(5)	881(35)	26(18)	222(17)
OW3	83571(14)	34790(14)	37325(7)	841(22)	937(21)	224(6)	800(35)	-17(17)	5(17)
O1	42561(14)	38546(13)	26725(7)	968(22)	1228(21)	134(5)	1053(35)	24(17)	66(16)
O4	26023(14)	9835(13)	-28257(6)	937(21)	978(20)	153(5)	796(33)	184(16)	53(16)
N4	13081(15)	15973(14)	-20756(8)	740(23)	763(21)	157(6)	517(36)	78(18)	72(17)
C1	35871(18)	33209(17)	15724(9)	696(25)	693(23)	160(6)	526(40)	64(20)	110(19)
C2	50131(18)	26370(18)	7300(9)	676(26)	1043(26)	175(7)	956(43)	43(21)	121(21)
C3	43214(18)	20695(17)	-4558(9)	635(25)	901(25)	172(7)	769(41)	117(20)	101(20)
C4	21338(17)	21213(16)	-9185(9)	573(24)	689(23)	150(6)	492(39)	51(20)	98(19)
C5	6897(18)	27658(17)	-1018(9)	569(25)	895(25)	192(7)	652(41)	50(20)	131(20)
C6	13728(18)	33550(18)	10885(9)	669(26)	980(25)	174(7)	801(42)	166(21)	107(20)

net intensity based on counting statistics. A 2% uncertainty due to experimental fluctuations were included in the estimated standard deviations of the net intensity. The atomic scattering factors for the heavy atoms were those of Doyle and Turner<sup>5</sup> and for hydrogen those of Stewart *et al.*<sup>6</sup> All programs except for the ORTEP program<sup>7</sup> applied during the structure investigation are described in Ref. 8.

## CRYSTAL DATA

Sodium *p*-nitrosophenolate trihydrate, NaC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>N.3H<sub>2</sub>O, triclinic, space group *P* $\bar{1}$ . Dimension of the unit cell at 18°C: *a* = 6.144(5) Å, *b* = 6.776(5) Å, *c* = 11.56(1) Å,  $\alpha$  = 100.87(3)°,  $\beta$  = 93.08(3)°,  $\gamma$  = 109.91(4)°, *V* = 440.8 Å<sup>3</sup>. At -162°C: *a* = 6.106(2) Å, *b* = 6.706(2) Å, *c* = 11.529(3) Å,  $\alpha$  = 100.76(2)°,  $\beta$  = 92.73(2)°,  $\gamma$  = 110.14(2)°, *V* = 432.3 Å<sup>3</sup>.  $D_{\text{calc}}$  (18°C) = 1.500 g/cm<sup>3</sup>.  $D_{\text{calc}}$  (-162°C) = 1.530 g/cm<sup>3</sup>.

## STRUCTURE DETERMINATION

The structure was determined by the use of a sharpened Patterson synthesis. Positions of peaks forming a hexagon around the third highest peak in the Patterson map gave input parameters to a computer program which translated an anion model in steps and calculated *R*-values after each step using 91 low order reflections. The resulting *R*-map showed only one minimum position, reasonable from packing considerations. Subsequent Fourier and least squares refinements reduced the conventional *R* factor to 0.06. At this stage positional param-

eters for all hydrogen atoms were calculated from stereochemical considerations. Least squares full matrix refinements of positional and thermal parameters of all atoms converged with a conventional *R* factor of 0.032, a weighted *R<sub>w</sub>* factor of 0.037 and a goodness of fit *S* of 1.92. Using 2008 reflections with  $\sin \theta/\lambda > 0.45$  the refinement yielded *R* = 0.035, *R<sub>w</sub>* = 0.034, and *S* = 1.45. The difference between the scale factors is insignificant (0.140(1) and 0.143(3), respectively.) The only significant difference appears in the NO bond length which is shortened by 0.004 Å or 2.9 $\sigma$  disregarding valence electron scattering. The nitrogen atom is shifted towards the O4 oxygen atom which

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H2	645(3)	254(2)	106(1)	1.8(3)
H3	526(3)	163(2)	-99(1)	1.4(3)
H5	-84(3)	274(2)	-45(1)	1.7(3)
H6	41(3)	380(2)	163(1)	1.3(3)
H1W1	276(3)	200(3)	567(2)	2.8(4)
H2W1	306(3)	135(3)	457(1)	2.3(3)
H1W2	610(3)	142(3)	693(2)	3.0(4)
H2W2	832(4)	154(3)	705(2)	4.4(5)
H1W3	729(4)	364(3)	339(2)	4.5(5)
H2W3	820(3)	214(3)	348(2)	2.9(4)

Table 3. Bond lengths (Å) and angles (°). Estimated standard deviations in parentheses. Bond lengths in quinone 4-oxime are also given. Libration corrected bond lengths from the refinement with all observed reflections are given on the second line.

	Anion	Acid		Anion	Acid
O1—C1	1.2586(12)	1.243(3)	C3—C4	1.4286(14)	1.441(4)
	1.2595	1.245		1.4317	1.450
O4—N4	1.3031(11)	1.371(3)	C4—C5	1.4284(14)	1.450(4)
	1.3052	1.377		1.4308	1.460
N4—C4	1.3402(13)	1.302(3)	C5—C6	1.3576(14)	1.330(4)
	1.3412	1.305		1.3586	1.332
C1—C2	1.4494(14)	1.466(4)	C6—C1	1.4471(14)	1.452(4)
	1.4519	1.473		1.4501	1.460
C2—C3	1.3536(14)	1.329(4)			
	1.3547	1.332			
Bond angles in the anion			Distances in the polyhedron surrounding the sodium ion		
O1—C1—C2	121.1(1)		Na··OW1(a)	2.3983(9)	
O1—C1—C6	122.0(1)		Na··OW1(b)	2.4791(9)	
C6—C1—C2	116.9(1)		Na··OW2(b)	2.4253(9)	
C1—C2—C3	121.8(1)		Na··OW3(c)	2.4358(9)	
C2—C3—C4	120.6(1)		Na··OW3(b)	2.4241(9)	
C3—C4—C5	118.5(1)		Na··O1(a)	2.4002(9)	
C4—C5—C6	121.5(1)		OW1··O1(a)	3.0749	
C5—C6—C1	120.8(1)		OW1··O1(b)	3.1510	
C3—C4—N4	124.8(1)				
C5—C4—N4	116.7(1)				
C4—N4—O4	117.1(1)				
Distances and angles involving hydrogen atoms.					
	O—H	H···O, H···N	O···O, O···N	O—H···O(N)	H—O—H
OW1—H1···O4(d)	0.86(2)	1.97(2)	2.812(1)	164.9(1.6)	101.7(1.5)
OW1—H2···OW2(e)	0.82(2)	2.08(2)	2.899(1)	177.1(1.5)	
OW2—H1···O4(d)	0.83(2)	2.09(2)	2.879(1)	163.6(1.3)	105.7(1.7)
OW2—H2···N4(f)	0.84(2)	2.03(2)	2.850(1)	167.2(2.0)	
OW3—H1···O4(g)	0.86(2)	1.97(2)	2.821(1)	172.1(1.7)	106.0(1.7)
OW3—H2···O1(a)	0.80(2)	2.05(2)	2.844(1)	172.0(2.1)	
	C—H		C—C—H		C—C—H
C2—H	0.97(2)	C1—C2—H	116.6(9)	C4—C5—H	116.4(8)
C3—H	0.94(1)	C3—C2—H	121.6(9)	C6—C5—H	122.2(8)
C5—H	0.99(2)	C2—C3—H	120.6(8)	C5—C6—H	120.9(8)
C6—H	0.95(1)	C4—C3—H	118.9(8)	C1—C6—H	118.3(8)
Other intermolecular contacts			Dihedral angles in the anion		
O1···O4(a)	3.296	C3—C4—N4—O4	0.5(2)		
C2···C3(g)	3.279	C5—C4—N4—O4	-179.2(1)		
		C4—N4—O4···OW1	-137.6(1)		
		C4—N4—O4···OW2	-37.4(2)		
		C4—N4—O4···OW3	98.0(1)		
		C5—C4—N4···OW2	2.8(2)		
Symmetry codes					
(a):	<i>x</i>	<i>y</i>	<i>z</i>	(b):	- <i>x</i> +1 - <i>y</i> +1 - <i>z</i> +1
(d):	<i>x</i>	<i>y</i>	<i>z</i> +1	(e):	- <i>x</i> +1 - <i>y</i> - <i>z</i> +1
(g):	- <i>x</i> +1	- <i>y</i>	- <i>z</i>	(f):	<i>x</i> +1 <i>y</i> <i>z</i> +1

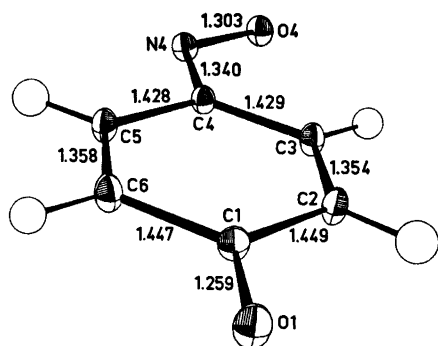


Fig. 1. 50 % probability ellipsoids, bond lengths (Å) and numbering of atoms in the anion.

is not affected. Probably asphericity of the valence electron density causes some of the differences observed.<sup>9</sup> However, only the parameters dependent upon all reflections will be considered in the following, as they are more directly comparable with those of quinone 4-oxime.

A list of structure amplitudes is available from the author upon request. Final parameters are listed in Tables 1 and 2.

An analysis of the thermal parameters in the anion was carried out. 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 Å<sup>2</sup>. The translational r.m.s. amplitudes of vibration along the principal axes are 0.11, 0.10 and 0.09 Å<sup>2</sup>. The r.m.s. librational amplitudes are 3.8, 1.8, and 1.4°. The largest increase in bond lengths was 2.2σ when adjusting the coordinates according to this libration.

Bond lengths and angles with their estimated standard deviations are given in Table 3. Fig. 1 shows numbering of atoms and distances in the anion. The estimated standard deviations were calculated from the correlation matrix. Deviations from least squares planes are given in Table 4.

## DISCUSSION

*Interionic structural features.* A general view of the structure is shown in Fig. 2. This figure

also shows a stereo plot of the structure of the potassium salt, *i.e.* (IV).

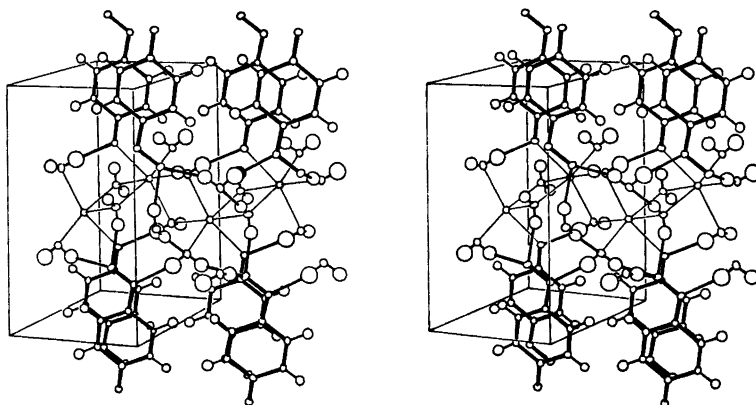
The present structure has several features which differ markedly from those of the potassium salt. While in the latter the cation coordinates four anions, the sodium ion in (I) has only one anion contact. The most important difference is, however, in the coordination about the anion terminal atoms. Fig. 3 shows this coordination. As may be seen, the nitroso group atoms are acceptors in four hydrogen bonds in the sodium salt. In the potassium salt the only hydrogen bond is between the water oxygen atom and the *phenoxide* oxygen atom. The latter is also an acceptor in the sodium salt. The coordination around O4 is tetrahedral in (I) and threefold pyramidal in (IV), while O1 has a threefold planar coordination in (I) and a tetrahedral coordination in (IV).

Four hydrogen bonds involving the *W2* and the *W3* water molecules are linking together anions while two hydrogen bonds involving the *W1* water molecule constitute a bridge between the organic layers in (I). Five of six acidic protons are engaged in hydrogen bonds to the anion while the last one is donated from OW1 to OW2. The hydrogen bond lengths are normal.

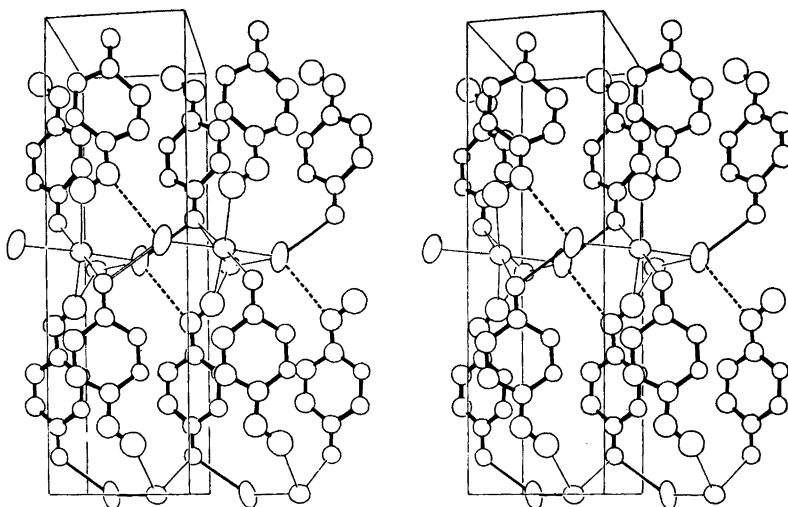
*The p-nitrosophenolate ion.* The anion has the same weakly expressed boat form as its corresponding acid, *i.e.* (V). Furthermore, bond angles not involving the N4 and the O4

Table 4. Atomic coordinates and deviations (Å) of atoms from a least-squares plane through the benzene ring atoms C1, C2, C3, C4, C5, and C6.

C1	1.4074	-0.2578	0.0026
C2	0.8776	1.0913	-0.0034
C3	-0.4540	1.3342	-0.0002
C4	-1.3894	0.2543	0.0047
C5	-0.8874	-1.0829	-0.0056
C6	0.4457	-1.3391	0.0019
O1	2.6480	-0.4698	0.0061
O4	-3.1885	1.6131	0.0069
N4	-2.7220	0.3964	0.0130
H2	1.523	1.809	-0.056
H3	-0.778	2.214	-0.008
H5	-1.564	-1.808	-0.027
H6	0.772	-2.234	0.008



(I)



(IV)

Fig. 2. A stereoscopic illustration of the structure of sodium *p*-nitrosophenolate trihydrate (I) and potassium *p*-nitrosophenolate monohydrate (IV). Thermal ellipsoids and spheres are scaled to 50 % probability.

atom are very similar to corresponding angles in (V).

The angle at N4 is, however, 4.5° wider, the exocyclic angles at C4 are more equal and the nonbonded O4···C3 distance is 0.04 Å longer in (I) than in (V). These differences are probably a result of forming four hydrogen bonds to the nitroso group atoms.

In Table 3 anion bond lengths are compared with those of (V). All differences except that between the C1–C6 bond lengths are highly significant. As expected an increase in conjuga-

tion expressed by lengthening of “double” bonds and shortening of “single” bonds appears upon ionization.

A comparison of the CN and the NO bond length values listed in Table 5 shows that the CN bond in (I) is among the shortest observed and that the NO bond in (I) is the longest observed for *C*-nitroso compounds. The distances resembles those of the violurates<sup>15,16</sup> and are nearly identical to those of the dicyano-nitrosomethanidide anion.<sup>17</sup> The CN bond is 0.11 Å shorter and the NO bond 0.03 Å longer than

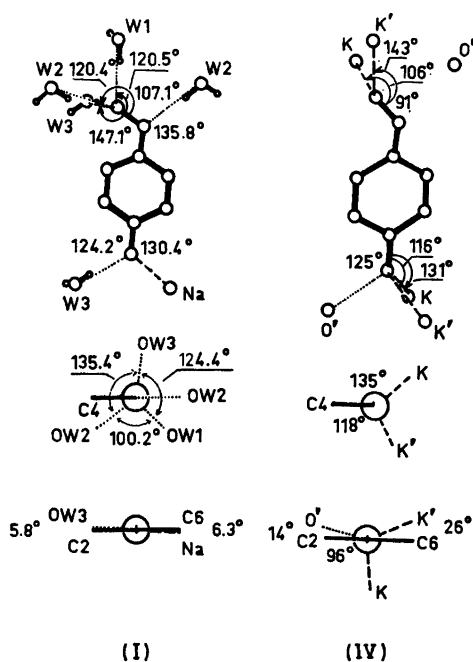


Fig 3. The coordination about the anion in (I) and (IV).

the corresponding bond in the nitrosobenzene dimer [1.454(5) Å and 1.268(4) Å, respectively].<sup>18</sup>

*The charge distribution in the anion.* The charge distribution in the anion is of considerable interest as it is a transition state when

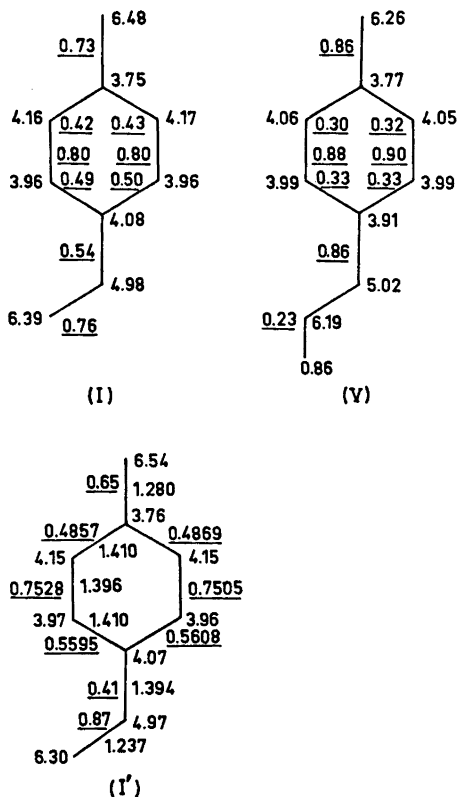


Fig. 4. Results from the CNDO/2 calculations. Underlined figures are the  $\pi$ -bond orders, while the other figures denote the total charge densities. In the anion with *mm* symmetry, (I'), also the "input" bond lengths are shown.

Table 5. Structural parameters in monomeric nitrosocompounds.

Compound <sup>a</sup>	Method <sup>b</sup>	R value in X-ray invest.	Bond lengths C-N	(Å) N-O	Bond angle (°) CNO	Ref.
A	e.d.		1.57(2)	1.171(8)	121(2)	10
B	e.d.		1.49(3)	1.22(3)	113(1)	11
	( <i>ab initio</i> calculations)		(1.499)	(1.208)	(113.0)	12
C	m.w.		1.401(5)	1.228(5)	115(1)	13
D	x.,c.	0.116	1.358(9)	1.265(8)	116	14
E	x.,f.		1.34(2)	1.26(2)	119	15
F	x.,f.	0.118	1.34(2)	1.27(2)	122	16
G	x.,c.	0.035	1.330(1)	1.285(1)	116.4(1)	17
(I)	x.,c.	0.037	1.340(1)	1.303(1)	117.1(1)	

<sup>a</sup> A, Trifluoro nitrosomethane; B, Nitrosomethane; C, Nitrosyl cyanide; D, 4-Nitroso-5-triphenyl-phosphoranylidene-aminobenzo(1,2-c:3,4-c)difurazan; E, Potassium violurate dihydrate; F, Cupric violurate tetrahydrate; G, Potassium dicyanonitrosomethanide. <sup>b</sup> e.d., electron diffraction; m.w., microwave; x., X-ray diffraction; c., counting; f., film.

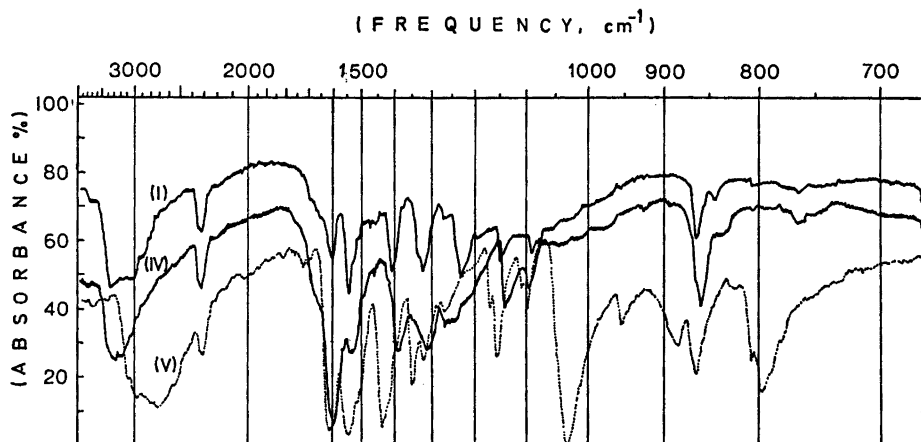


Fig. 5. The IR spectra of (I), (IV) and (V) in KBr recorded on a Perkin-Elmer 137 spectrophotometer. Peak positions:

(IV):	1590	1525	1380	1310	1260	1135	1090			
(I):	1600	1545	1400	1330	1230	1150	1090			
(V):	1620	1550	1440	1350	1325	1170	1155	1100	1030	( $\omega$ NO) <sup>22</sup>

quinone 4-oxime converts to *p*-nitrosophenol.<sup>19</sup>

In order to obtain information on this distribution both CNDO/2<sup>20</sup> and INDO<sup>21</sup> calculations were performed. The atomic coordinates used were those given in Table 4. Also an isolated ion having hypothetical structural parameters expressing a strong benzenoid character and *mm* symmetry in the benzene ring were treated. The results from the CNDO/2 calculations are shown in Fig. 4. The INDO results were nearly identical. The negative charge (*i.e.* 87 %) is predicted to be nearly equally distributed between the two oxygen atoms, and the O1 atom to be slightly more negative than the O4 atom. This is also the case in the  $\pi$ -electron system. These results are rather surprising as the UV studies of the tautomeric equilibrium indicate that 85 % of the species exists as oxime.<sup>19</sup> Simple VB calculations indicate that the O4 atom has twice the charge situated at the O1 atom.

The CNDO/2 calculations indicate that the benzene ring symmetry is less than *mm* as the C1–C2 bond is predicted to be longer than the C1–C6 bond, the C2–C3 bond shorter than the C6–C5 bond and the C3–C4 bond longer than the C5–C4 bond. Actually all these trends are seen in the experiment. The measured differences are, however, not significant (2 $\sigma$  between C2–C3 and C5–C6).

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*The influence of hydrogen bonding on the quinonoid character.* Unfortunately the low accuracy of the molecular structure in (IV) does not allow a discussion of this question by a comparison of anions in (I) and (IV). Owing to the differences in the hydrogen bonding it seems, however, reasonable to expect a measurable difference between the two ions as to the quinonoid character.

Two observations indicate that (IV) has less quinonoid character than (I): the green colour of the potassium salt and the red colour of the sodium salt, and the fact that the potassium salt becomes red upon dehydration by heating to 100 °C. Probably the introduction of four hydrogen bonds to the nitroso group or the removal of one hydrogen bond from the phenoxide oxygen atom causes a red shift of a  $\pi \rightarrow \pi^*$  transition into the visible region.

The IR spectrum of (IV) in KBr has features which make it markedly different from that of (I). The two spectra are shown in Fig. 5. The band at 1230 cm<sup>-1</sup> in (I) has previously been assigned to a  $\omega$ NO frequency by Hadzi.<sup>22</sup> This band is missing in the spectrum of (IV). On the other hand a band at 1260 cm<sup>-1</sup> in the spectrum of (IV) is missing in the spectrum of (I). This may possibly indicate that the NO bond is shorter in (IV) than in (I).

The IR spectra of (I) and (IV) in nujol mull were also recorded. No differences in peak positions were observed between these spectra and those from the KBr tablets.

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