

The Crystal and Molecular Structure of 5-Nitrososalicylic Acid

H. J. TALBERG

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal and molecular structure of 5-nitrososalicylic acid has been determined from X-ray diffraction data collected at -165°C and refined by least squares methods. The space group is $P2_1/n$ with cell dimensions $a = 22.829(2)$ Å, $b = 8.028(1)$ Å, $c = 3.6696(4)$ Å and $\beta = 91.07(1)^{\circ}$ at -165°C . The final R factor was 5.1% and the estimated standard deviations in bond lengths are in the range 0.002–0.003 Å and in angles 0.2° . The C–NO and the N–O bond lengths are found to be, respectively, much longer (0.067 Å) and much shorter (0.059 Å) than those of the *p*-nitrosophenolate anion. Other bond lengths and angles resemble closely those of salicylic acid and 5-sulfosalicylic acid di- and trihydrate. The slight deviations found seem to be consistent with a less pronounced *ortho* quinonoid structure in 5-nitrososalicylic acid than in these compounds.

The present structure investigation of 5-nitrososalicylic acid (I) is part of a series of investigations of *C*-nitroso compounds. Previously the oxime tautomer of *p*-nitrosophenol (II) and three of its salts¹ and the compound *N,N*-dimethyl-*p*-nitrosoaniline and *N,N,N',N'*-tetramethyl-1,5-diamino-4-nitrosobenzene (III)² have been investigated.

The title compound forms crystals having the characteristic blue colour of *C*-nitroso compounds. This indicates that it is one of the few *para* nitrosophenols which can be isolated.³ In solution these compounds participate in a rapid equilibrium with their oxime tautomer and in most cases only the oxime tautomer crystallizes from the solution. Probably stabilization by internal hydrogen bonding causes (I) and not its oxime tautomer to form crystals (see Ref. 3 and references therein).

The investigation of the *p*-nitrosophenolate anion and (III) confirmed previous IR-studies which indicated that the ω_{NO} wave number

is much lower than that of a "pure" NO double bond. The bond number has been found to be as low as 1.5–1.7 in both compounds, and extended conjugation gives the molecules a very pronounced quinonoid appearance. As to (I) however, the IR-KBr- ω_{NO} wave number (1480 cm^{-1}) seems to be in the normal range ($1560\text{--}1480\text{ cm}^{-1}$). It was therefore decided to carry out a structure determination of (I) in order to compare the degree of conjugation in this molecule with that of the other compounds investigated.

EXPERIMENTAL

The title compound was derived from salicylic acid by nitrosation.⁴ Recrystallization from toluene gave green needle shaped crystals suited for X-ray work. Also some azur coloured tabular monoclinic crystals were obtained ($V = 830\text{ Å}^3$), probably a monohydrate of (I). All the data were collected and the unit cell constants determined using a crystal of dimensions $0.60 \times 0.16 \times 0.08\text{ mm}$. Apart from the following details the experimental conditions were as those described in Ref. 2. The temperature at the crystal site was -165°C . The scan limits were $2\theta(\alpha_1) - 1.2^{\circ}$ and $2\theta(\alpha_2) + 1.2^{\circ}$ and a quadrant of reciprocal space was examined. Out of 2272 unique reflections measured 1448 had intensities larger than $2.5\sigma(I)$ where $\sigma(I)$ 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 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 program (Ref. 8 in Ref. 1) and the MULTAN program⁶ applied during the structure investigation are described in Ref. 9.

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factors are expressed as: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. Estimated standard deviations in parentheses.

ATOM	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O2	0.17728(6)	0.86428(18)	1.23519(48)	0.0122(7)	0.0144(7)	0.0323(10)	0.0014(6)	-0.0032(7)	-0.0080(7)
O5	0.15285(6)	0.15579(19)	0.59201(52)	0.0225(7)	0.0176(8)	0.0421(11)	0.0038(6)	-0.0018(8)	-0.0111(8)
O71	0.00595(6)	0.77907(19)	0.83405(51)	0.0113(6)	0.0158(7)	0.0358(10)	0.0034(6)	-0.0061(7)	-0.0070(7)
O72	0.06644(6)	0.95502(17)	1.13367(45)	0.0149(6)	0.0135(7)	0.0303(9)	0.0022(5)	-0.0028(7)	-0.0057(7)
H5	0.11344(7)	0.25982(22)	0.62185(57)	0.0191(8)	0.0153(9)	0.0255(10)	0.0007(7)	0.0003(8)	-0.0049(8)
C1	0.10188(8)	0.68968(24)	0.95744(57)	0.0111(8)	0.0117(9)	0.0156(11)	0.0009(6)	-0.0014(8)	-0.0007(8)
C2	0.15994(8)	0.72085(23)	1.08051(61)	0.0144(9)	0.0128(9)	0.0142(10)	-0.0010(7)	-0.0018(8)	-0.0019(8)
C3	0.20328(8)	0.59799(25)	1.04711(63)	0.0112(8)	0.0169(9)	0.0186(11)	0.0005(7)	-0.0003(8)	-0.0023(9)
C4	0.18981(8)	0.44687(25)	0.89693(60)	0.0122(8)	0.0150(9)	0.0181(11)	0.0038(7)	-0.0005(8)	-0.0014(9)
C5	0.13193(8)	0.41361(24)	0.78057(59)	0.0150(8)	0.0110(9)	0.0156(11)	0.0004(7)	-0.0017(8)	-0.0012(9)
C6	0.08883(8)	0.53350(24)	0.81013(61)	0.0113(8)	0.0144(9)	0.0173(11)	-0.0005(7)	-0.0013(8)	-0.0010(9)
C7	0.05683(8)	0.81979(24)	0.98513(62)	0.0136(9)	0.0153(9)	0.0178(11)	0.0014(7)	0.0011(8)	-0.0003(9)

ATOM	x	y	z	B	ATOM	x	y	z	B
H2	0.1506(9)	0.9218(29)	1.2640(70)	1.8(5)	H3	0.2417(8)	0.6231(25)	1.1280(61)	1.1(4)
H4	0.2184(8)	0.3564(25)	0.8706(62)	1.1(4)	H6	0.0501(8)	0.5106(23)	0.7301(63)	1.1(4)
H71	-0.0152(10)	0.8552(32)	0.8512(86)	3.2(6)					

CRYSTAL DATA

5-Nitrososalicylic acid or 1-carboxy-2-hydroxy-5-nitrosobenzene, $C_7H_5O_4N$, monoclinic, space group $P2_1/n$ (No. 14). Dimensions of the unit cell at -165°C : $a = 22.829(2)$ Å, $b = 8.028(1)$ Å, $c = 3.6696(4)$ Å, $\beta = 91.07(1)^\circ$, $V = 672.4$ Å³, $M = 167.12$, $F(000) = 344$, $D_{\text{calc}}(-165^\circ\text{C}) = 1.651$ g cm⁻³, $Z = 4$.

STRUCTURE DETERMINATION

The structure was determined by direct methods^{8,9} and refined by full matrix least squares techniques. Including only heavy atoms anisotropic refinement yielded a conventional R factor of 0.069. 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 [with I greater than $2.5\sigma(I)$] converged with $R = 0.051$, a weighted R_w factor of 0.046 and a goodness of fit S of 1.73. Using 1018 reflections with $\sin \theta/\lambda$ greater than 0.45 the refinement yielded $R = 0.055$, $R_w = 0.049$ and $S = 1.26$. Disregarding valence electron scattering the C-N, C-O bonds and the N-O bond became shorter while the C-C bonds became longer. The shifts were in the range 0.001–0.007 Å. Apart from the C-N bond similar shifts have been observed previ-

ously for the *p*-nitrosophenolate ion¹ and for (III).² Only parameters obtained from the refinement with all the observed reflections will be discussed in the following as this enables a direct comparison of (I) with the previously investigated compounds in this series.

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 axes of the vibrational ellipsoids are indicated in Fig. 1. A rigid body analysis of the entire

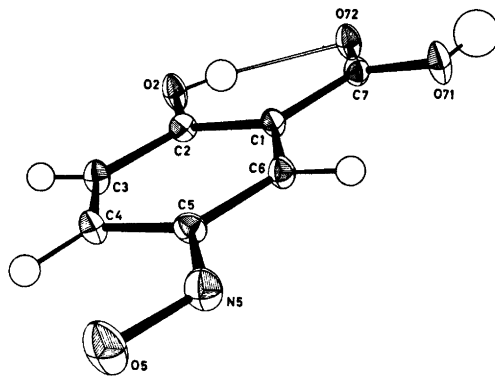


Fig. 1. 50% probability ellipsoids and numbering of atoms.

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

Bond lengths. (Libration corrected bond lengths are given in the second row).					
O5-N5	1.234(2)	1.235	C1-C2	1.415(3)	1.418
O71-C7	1.319(2)	1.321	C2-C3	1.404(3)	1.406
O72-C7	1.233(2)	1.234	C3-C4	1.365(3)	1.367
O2-C2	1.340(2)	1.342	C4-C5	1.407(3)	1.409
N5-C5	1.426(2)	1.428	C5-C6	1.382(3)	1.384
C7-C1	1.471(3)	1.473	C6-C1	1.395(3)	1.398
Bond angles					
O71-C7-O72	123.5(2)		N5-C5-C4	123.9(2)	
O72-C7-C1	122.5(2)		N5-C5-C6	115.4(2)	
O71-C7-C1	114.0(2)		C1-C2-C3	120.4(2)	
O5-N5-C5	114.3(2)		C2-C3-C4	120.4(2)	
C7-C1-C2	120.3(2)		C3-C4-C5	119.7(2)	
C7-C1-C6	121.4(2)		C4-C5-C6	120.7(2)	
O2-C2-C3	115.9(2)		C5-C6-C1	120.6(2)	
O2-C2-C1	123.7(2)		C6-C1-C2	118.3(2)	
Distances and angles involving hydrogen atoms					
	O-H	H...O	O...O	O-H...O	C-O-H
O2-H...O72	0.77(2)	1.99(2)	2.653(2)	144(2)	110.2(1.8)
O2-H...O5(2)		2.23(2)	2.744(2)	125(2)	
O71-H...O72(b)	0.78(3)	1.92(3)	2.704(2)	177(3)	108.2(1.9)
	C-H		C-C-H		C-C-H
C3-H	0.94(2)	C2-C3-H	118.4(1.3)	C4-C3-H	121.2(1.3)
C4-H	0.98(2)	C3-C4-H	123.4(1.3)	C5-C4-H	116.9(1.2)
C6-H	0.94(2)	C5-C6-H	120.3(1.2)	C1-C6-H	119.2(1.2)
Intermolecular contacts			Torsion angles		
O72...O5(a)	3.032		O72-C7-C1-C6	177.2(2)	
O71...N5(c)	3.187		O5-N5-C5-C4	-0.3(3)	
			O5-N5-C5-C6	178.7(2)	
			H-O2-C2-C3	-174(2)	
Symmetry code					
(a): $x, y+1, z+1$, (b): $-x, -y+2, -z+2$, (c): $-x, -y+1, -z+1$					

molecule shows a good agreement between observed and calculated vibration tensor elements ($\Delta U = 0.0015 \text{ \AA}^2$). The r.m.s. eigenvalues of T are 0.11, 0.11 and 0.10 Å and of L 3.6, 2.6 and 1.3°. Adjusting the coordinates according to this libration, shifts in the bond lengths from 0.001 to 0.003 Å were obtained.

Bond lengths and angles are given in Table 2. The estimated standard deviations were derived from the final correlation matrix of the least squares refinement.

A final difference Fourier map of the molecule in the benzene ring plane is shown in Fig. 5. The map was calculated in the same manner as for the *p*-nitrosophenolate ions.¹ The pat-

tern of the residual peaks resembling closely that of the anions¹ (location in the middle of the bonds and at lone pair positions) indicates that only small systematic errors influence the structural results.

Using the data in the range 0.0–0.65 Å⁻¹ for $\sin \theta/\lambda$ an *L*-shell refinement⁷ gives $R = 0.045$, $R_w = 0.039$ and $S = 1.71$. The adjusted⁷ gross atomic populations are shown in Fig. 3 together with results from an INDO calculation.

DISCUSSION

The location of the hydrogen atoms in the difference Fourier map and the subsequent

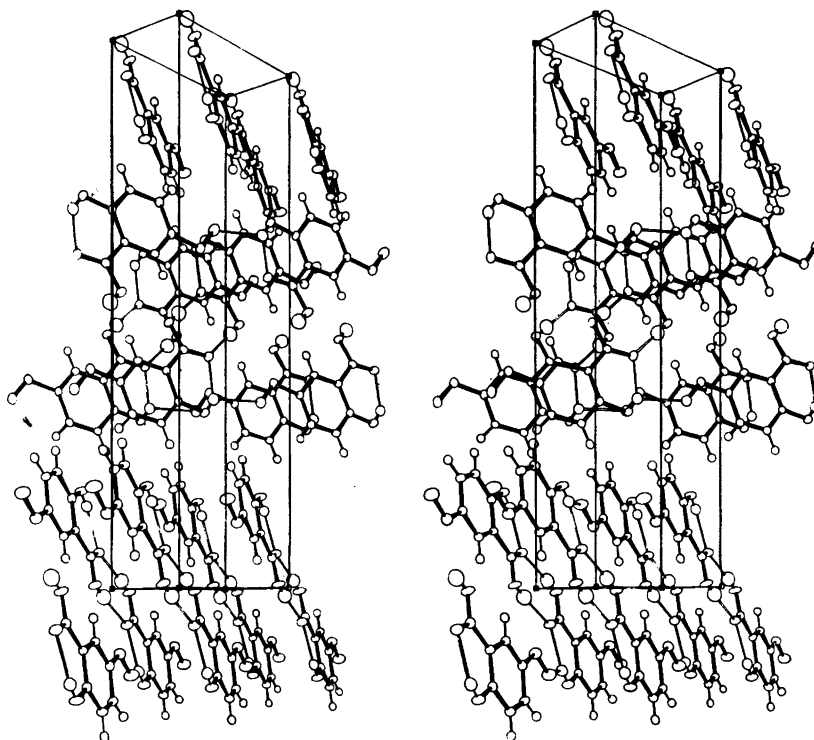


Fig. 2. A stereoscopic illustration of the structure.

refinement leave no doubt about the compound being 5-nitrososalicylic acid and not its oxime tautomer. It is further clear that, as in salicylic acid there is an intramolecular hydrogen bond. Also, and in conformity with most other carboxylic acids, (I), does form a centrosymmetric hydrogen bonded dimer. Fig. 2 shows that these dimers form layers parallel to (011). There seems to be only weak van der Waals forces between the layers. The short translation along c gives a separation between molecular planes of 3.34 Å. Fig. 3 shows the projection of a molecule onto the neighbouring molecular plane along the plane normal. Apparently the positively charged heavy atoms (C2, C4, C6, C7 and N5) are in contact with negatively charged atoms (O2, C3, C1, O72 and C5). The interplanar spacing is, however, by no means especially short considering the temperature,¹⁰ and it seems unlikely that these interactions should influence the degree of conjugation in the molecule to any appreciable extent (contrary to what apparently is the case for N,N -dimeth-

ylnitrosamine¹¹). Dimers approximately in the same plane have contact with each other through the hydroxyl group at C2 and the nitroso group. Probably the interaction is the weaker part of an asymmetric bifurcated hydrogen bond ($O\cdots O$: 2.744 Å, $O\cdots H$: 2.23 Å and $O-H\cdots O$: 125°).¹² Then 5-nitrososalicylic acid conforms with the oxime tautomer of p -nitrosophenol in that the proton involved in the tautomerism is bonded to both the nitroso and the phenoxide oxygen atom. It is tempting to relate the weaker interaction in the present case to the vanishingly small amount of the oxime form present in solution.

The intramolecular hydrogen bond (the stronger part of the bifurcated H-bond) is found to be slightly longer than that of salicylic acid (IV)^{13,14} and nearly identical to that of 5-sulfosalicylic acid di- (V)¹⁵ and trihydrate.¹⁶ In these compounds bifurcated H-bonds are not present. As accentuation of the *ortho* quinonoid element in the π resonance hybrid probably strengthens the H-bond, 5-substitu-

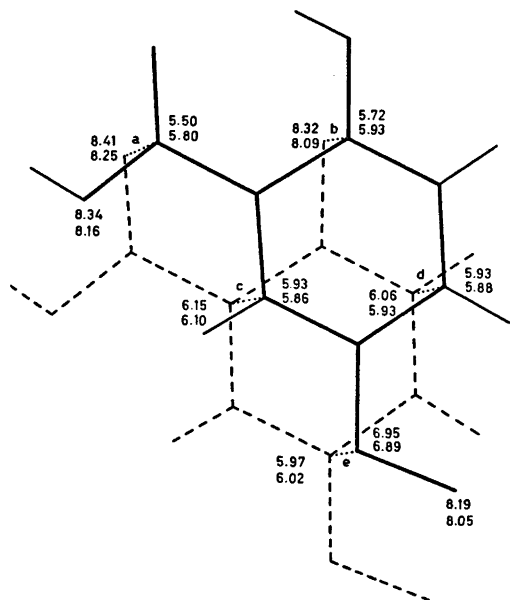


Fig. 3. The projection of a molecule onto the neighbouring molecular plane along the plane normal and the calculated (upper line) and experimental (lower line) gross atomic populations. The letters denote intermolecular contacts: $a=3.319$ Å, $b=3.339$ Å, $c=3.389$ Å, $d=3.366$ Å and $e=3.359$ Å.

ents promoting a *para* quinonoid structure to the displacement of an *ortho* quinonoid structure should weaken the H-bond. Also the forming of a bifurcated H-bond arrangement

Table 3. Deviation (Å) of atoms from least squares planes. Atoms defining the planes are marked with an asterisk.

O2	0.0319	
O5	-0.0217	
O71	-0.1547	-0.0009*
O72	0.0349	-0.0011*
N5	0.0006	
C1	-0.0081*	-0.0011*
C2	0.0056*	
C3	0.0025*	
C4	-0.0081*	
C5	0.0055*	
C6	0.0027*	
C7	-0.0351	0.0038*
H1	-0.195	-0.031
H2	0.111	
H3	-0.002	
H4	0.001	
H6	0.006	

probably weakens this bond.¹⁷ This may be the cause of a slightly longer O2...O72 separation in (I) than in (IV).

As may be seen from Table 3 the benzene ring and the carboxyl group are both planar within the accuracy of the experiment. The angle between these two fragments is 5.07° or somewhat larger than the corresponding angle in (IV)¹³ (1.1°). The phenolic hydrogen atom deviates 0.11 Å from the ring plane and to the same side as its acceptor atoms. Probably the somewhat larger torsion angle about the C-COOH bond in (I) than in (IV) may be due to the H2...O5 hydrogen bond.

The torsion angle about the C-NO bond is only 1.07° . Nitrosation of (IV) in the 5-position apparently introduces only a slight *para* quinonoid element as the benzene ring of (I) definitely has the same *ortho* quinonoid appearance as that of (IV). Fig. 4 shows a comparison between observed and calculated (INDO) differences in bond lengths between (I) and (IV).¹³ Only the sign of the differences are comparable since the calculations have been based on the found geometry of (I) for both compounds. In this respect there is a good correspondence between experiment and theory. Benzene ring bonds approximately parallel to the C5-X (X=H,NO) bond seem to be slightly shorter while the other C-C

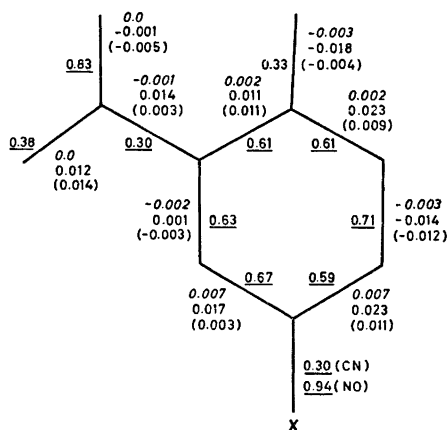


Fig. 4. Underlined figures are (INDO) π -bond orders for (I). The figures in the rows are calculated (upper line) and observed (middle line) bond length differences between (I) and (IV) and observed bond length differences between (I) and (V) (lower line).

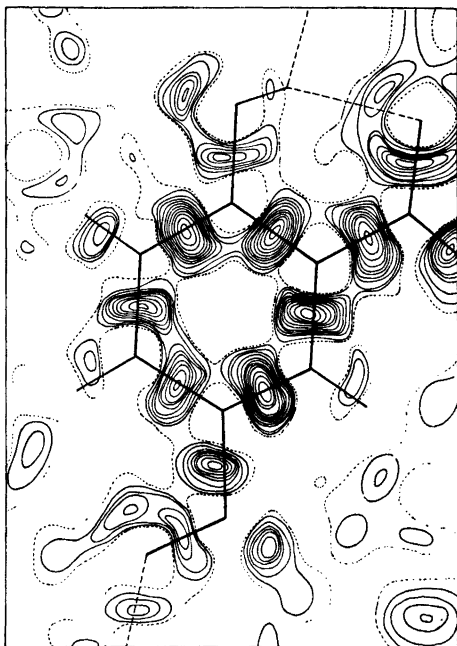


Fig. 5. Final difference Fourier synthesis in the least squares plane through the ring atoms. The zero line is dotted and the difference between the contours is $0.05 \text{ e}\text{\AA}^{-1}$.

bonds are somewhat longer in (I) than in (V). Accordingly the C2–OH bond is slightly shorter in (I) than in (IV). Then substitution at the 5-position by a nitroso group apparently introduces a *para* quinonoid element to the displacement of some of the *ortho* quinonoid element present in the π system of the benzene ring of salicylic acid. However, only some of the observed shifts are formally significant. Comparing (I) and 5-sulfosalicylic acid dihydrate (V)¹⁵ one finds four significant and one probably significant difference in the range $0.009\text{--}0.014 \text{ \AA}$. The differences are consistent with a slightly less *ortho* quinonoid structure in (I) than in (V).¹⁶

Both the C–N bond and the C2–O bond are found to be much longer than the corresponding bonds in the *p*-nitrosophenolate ions. Comparing with the anion of the magnesium salt one finds that the C–N bond is 0.067 \AA and the C–O bond 0.059 \AA longer in (I) than in the anion.¹ If one assumes that the C–O bond is slightly longer and the C–N bond

length practically unchanged after decarboxylation of (I) it is possible to estimate roughly a point for *p*-nitrosophenol in the plot of Fig. 5 in Ref. 1. From the resulting plot of the C–O bond length against the C–N bond length in *p*-nitrosophenol, its oxime tautomer and the *p*-nitrosophenolate anions one gets the impression that there is *not* a linear relationship between the two bond lengths as previously thought.¹

The C–N bond length [$1.426(2) \text{ \AA}$] is also much longer than the corresponding bond length in (III) [$1.372(2) \text{ \AA}$]. In accordance with this the N–O bond length [$1.234(2) \text{ \AA}$] is much shorter than that of the *p*-nitrosophenolate ions and (III) [$1.276(2) \text{ \AA}$]. The two nitroso group bond lengths are, however, about 0.03 \AA shorter/longer than that of a “pure” $C(sp^2)\text{--}N(sp^2)/N=O$ single/double bond.¹⁸ This then confirms the spectroscopic indication of a somewhat long although “normal” N–O bond in 5-nitrososalicylic acid.

It is interesting to note that the point for (I) in the plot of N–O bond lengths against C–N bond lengths in Fig. 6, Ref. 1 lies nearly exactly on the graph of $R_{NO} = R_{NO}^\circ + k/(R_{CO} - R_{CO}^\circ)$ where $R_{NO} = 1.150 \text{ \AA}$, $R_{CN}^\circ = 1.233 \text{ \AA}$ and $k = 0.016 \text{ \AA}^2$. This is also the case for a new point for trifluoronitrosomethane (VI) which has recently been investigated by microwave spectroscopy.¹⁹ Inserting the values observed for R_{CN} [$= 1.512(16) \text{ \AA}$ in (VI)] one gets $R_{NO}^{\text{calc}} = 1.233 \text{ \AA}$ for (I) and $R_{NO}^{\text{calc}} = 1.207 \text{ \AA}$ for (VI). These values are not different from those observed [$R_{NO} = 1.198(4) \text{ \AA}$ in (VI)].

It is further noteworthy that (I) and (VI) which both have less conjugation over the C–N–O fragment than the nitrosates¹ and (III) also have substantially smaller CNO angles than those latter compounds; $114.3(2)^\circ$ for (I) and $112.4(3)^\circ$ for (VI) compared with values in the range $116\text{--}117^\circ$.¹

The exocyclic angles at the carbon atom bonded to the NO group resemble closely those of the *p*-nitrosophenolate ions and those of *p*-benzoquinone monoxime. As to the ring angles and the other exocyclic angles they resemble closely those of (V). Probably the minor deviations found (less than 1.5°) may be attributed to the crowded situation arising when substituting a NO group for a SO_3^- group.

The *trans* conformation about the C-N bond with respect to the *meta* position (to C5) carrying the carboxyl group is possibly adopted because it gives less crowding than the corresponding *cis* conformation.

REFERENCES

1. Talberg, H. J. *Acta Chem. Scand. A* 31 (1977) 37.
2. Talberg, H. J. *Acta Chem. Scand. A* 30 (1976) 829.
3. Uffman, H. *Z. Naturforsch. Teil B* 22 (1967) 491.
4. Gulinov, V. G. *J. Chem. Ind. (Moscow)* 5 (1923) 225; see *Chem. Abstr.* 22 (1928) 3648.
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. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
9. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
10. Semmingsen, D. *Acta Chem. Scand. A* 30 (1976) 808.
11. Krebs, B. and Mandt, J. *Chem. Ber.* 108 (1975) 1130.
12. Olovsson, I. and Jönsson, P. G. In Schuster, P., Zundel, G. and Sandorty, C., Eds., *The Hydrogen Bond*, Nort-Holland Publishing Company, Amsterdam, New York and Oxford 1976, Vol. II, p. 408.
13. Sundaralingam, M. and Jensen, L. H. *Acta Crystallogr.* 18 (1965) 1053.
14. Bacon, G. E. and Jude, R. J. *Z. Kristallogr.* 138 (1973) 19.
15. Attig, R. *Cryst. Struct. Commun.* 5 (1976) 223.
16. Mootz, D. and Fayos, J. *Acta Crystallogr. B* 26 (1970) 2046.
17. Furberg, S. and Schwitters, B. *Acta Chem. Scand. B* 31 (1977) 313.
18. Fischer-Hjalmars, I. and Sundbom, M. *Acta Chem. Scand.* 22 (1968) 2237.
19. Turner, P. H. and Cox, A. P. *Chem. Phys. Lett.* 39 (1976) 585.

Received March 15, 1977.