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# COMPARISON OF CRYSTAL STRUCTURES OF THE TETRAMETHYLAMMONIUM AND SODIUM SALTS OF 3-NITROPHENOLATE

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## ABSTRACT

The addition of either sodium hydroxide or tetramethylammonium hydroxide to 3-nitrophenol led to orange-red crystals of sodium 3-nitrophenolate dihydrate or a complex of 3-nitrophenol and tetramethylammonium 3-nitrophenolate. For the sodium salt, 11707 Mo-Kα reflections were measured at 150 K via Bruker *SMART* 1-K CCD diffractometer. For the tetramethylammonium salt, 12664 Mo-Kα reflections were measured at 173 K via Bruker *SMART* 2-K CCD diffractometer. The unit cell of the sodium salt has: $a$ = 6.814(1) Å, $b$ = 6.5437(8) Å, $c$ = 18.206(4) Å, $\beta$ = 94.46(3)°, $V$ = 809.4(3) $Å^3$, space group = $P2_1/n$. The unit cell of the tetramethylammonium salt has: $a$ = 23.543(4) Å, $b$ = 5.636(1) Å, $c$ = 16.387(3) Å, $\beta$ = 128.513(3)°, $V$ = 1701.4(9) $Å^3$, space group = $C2/c$. The bond lengths of the 3-nitrophenolate moiety were statistically the same in the two crystal structures, showing that it is not affected by the cation.

## INTRODUCTION

A crystallographic study of phenolates is underway in an attempt to determine whether or not the alpha effect is an electrostatic phenomenon. In the determination of the alpha effect of N-methylbenzohydroxamates, phenolates are often chosen as the non-alpha-nucleophiles (1). In order to study the alpha effect, a high-precision data set must be collected along with specific conditions including the reduction of the crystal temperature and the correction of the data for absorption of the X-rays by heavy atoms. Then one's data may be used to reliably determine the distribution of electron density of the compound (2,3). However, first the compound must be successfully synthesized, and then the crystal structure must be solved in order to confirm that the crystal is in fact what it was intended to be without any impurities or disorder.

In 2000, the strong base sodium hydroxide was combined with 3-nitrophenol and crystals were formed. The solved crystal structure of the synthesized compound sodium 3-nitrophenolate dihydrate resulted in a phenolate of reasonable geometry. The results were shared at the annual meeting of the Georgia Academy of Science, but due to a large *R*-factor the results were never published.

The crystal structure of sodium 3-nitrophenolate dihydrate had already been solved by Krygowski *et al* (4). However, that study was conducted at 298 K. In order to perform a charge density analysis, the X-ray data set must be collected at reduced temperature. The unit cell parameters of sodium 3-nitrophenolate dihydrate at 150 K agree very well with those measured at 298 K [compare: $a$ = 6.814(1) Å, $b$ = 6.5437(8) Å, $c$ = 18.206(4) Å, $\beta$ = 94.46(3)° at 150 K; $a$ = 18.192(3) Å, $b$ = 6.579(1) Å, $c$ = 6.842(2) Å, and $\beta$ = 94.11(2)° at 298 K]. The differences can be attributed to a unit cell transformation in which the a and c axes were switched and the difference in temperature. The volume of the unit cell at 298 K is 816.8 Å$^3$ and that at 150 K is 809.4 Å$^3$, demonstrating that at lower temperatures the atoms do not vibrate as much, allowing the molecules to draw closer together.

Figures 1 and 2 show the determined bond lengths and angles of the solved structure of 3-nitrophenolate at 150 K, respectively. Table I gives the typical values for the lengths of bonds found within the 3-nitrophenolate moiety. It is noted that the accepted and experimentally-determined bond lengths are in agreement. Also the bond angles calculated for the 3-nitrophenolate structure are very reasonable.

***Figure 1.*** 3-nitrophenolate bond lengths from the crystal structure of sodium 3-nitrophenolate dihydrate at 150 K.

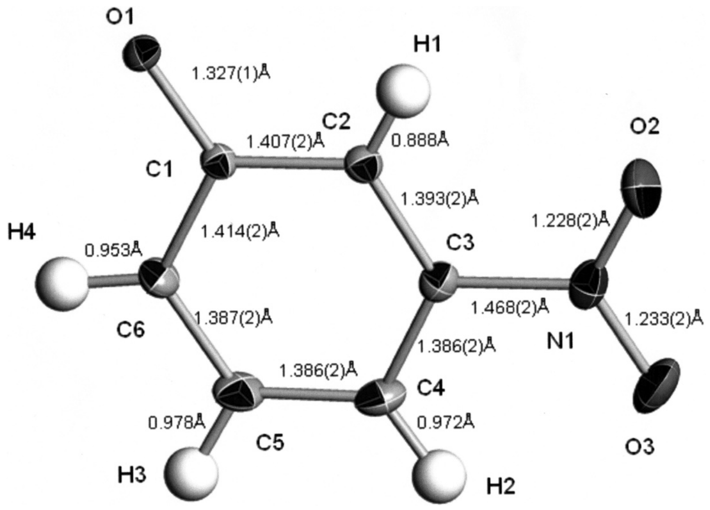


***Figure 2.*** 3-nitrophenolate bond angles from the crystal structure of sodium 3-nitrophenolate dihydrate at 150 K.

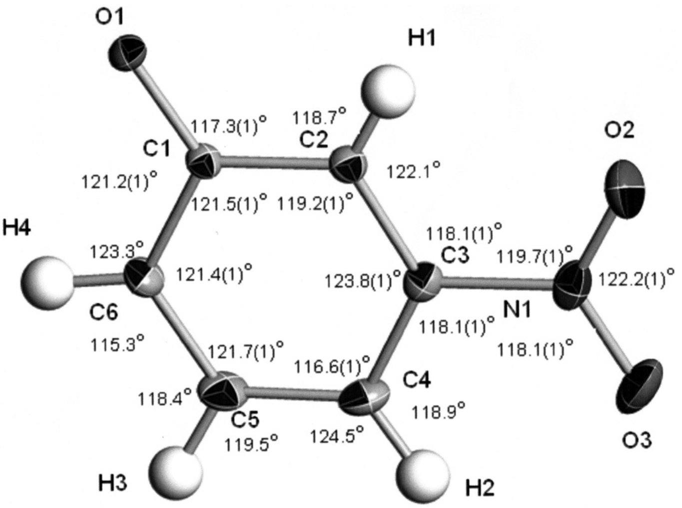


***Table I.*** Typical lengths of various bonds, as reported in the **CRC Handbook for Chemistry and Physics** (5).

| Bond Type | Bond length (Å) |
|---|---|
| Aromatic carbon-carbon | 1.395 |
| Aromatic carbon-hydrogen | 1.010 |
| Carbon-oxygen | 1.361 |
| Oxygen-hydrogen | 1.0289 |
| Aromatic carbon-nitrogen | 1.426 |
| Nitrogen-oxygen | 1.210 |

Of interest was the geometry around the sodium atom, around which there are seven oxygen atoms. Based on the bond angles between the central sodium atom and the surrounding oxygen atoms, the geometry was determined to be a monocapped octahedron. O4, O5, O4A, and O5A (from four water molecules) all essentially lie on a central plane with the sodium atom. The plane was found to be slightly bent toward O3A, which is due to the steric hindrance of the two oxygen atoms (O2 and O3 from the same nitro group) above the central plane. O2 and O3A (nitro oxygens of symmetry-related phenolates) were found above and below the central plane with a bond angle of 178.43(5) degrees. Also O3 (the second nitro oxygen of the phenolate in the asymmetric unit) was determined to have a bond angle of 134.86(5) degrees with O3A, therefore revealing the presence of the monocapped octahedron geometry. The monocapped octahedron is shown in Figure 3 and can also be seen in the packing diagram of the unit cell (Figure 4).

**Figure 3.** Monocapped octahedron in crystals of sodium 3-nitrophenolate dihydrate.

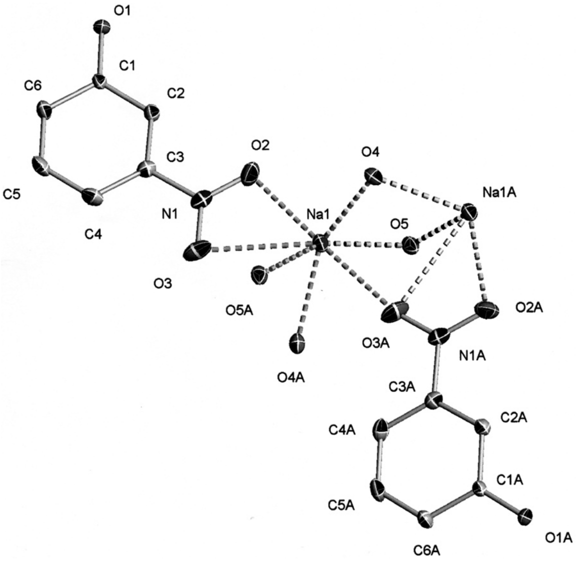
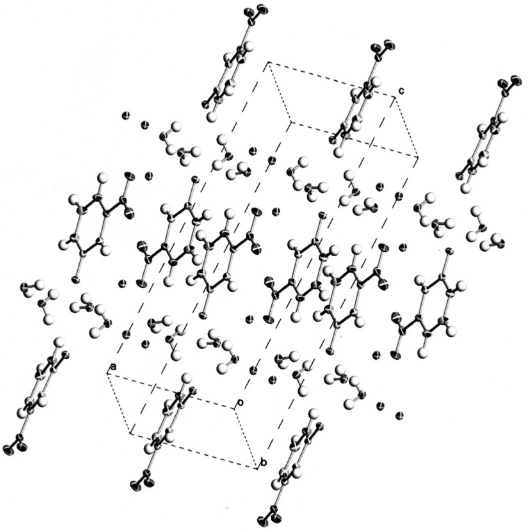


**Figure 4.** Packing diagram in crystals of sodium 3-nitrophenolate dihydrate.



The problem with the solved structure of sodium 3-nitrophenolate dihydrate arose in the *R* factor of 0.0740 (Table II). The high *R* factor is attributed to the possibility that an unknown and disordered impurity was present in the crystal structure. The impurity could have been due to the method that the crystal was synthesized and/or recrystallized. The synthesis by volumetrically adding a solution of sodium hydroxide to a solution of 3-nitrophenol resulted in a powder. This powder was dissolved in hot acetonitrile and oiled out. But from the oil grew an orange needle, which was analyzed via X-ray diffraction. In addition to a high *R* factor, the electron density difference map involved a largest peak value of 1.18 $e/Å^3$ and a deepest hole value of -0.78 $e/Å^3$ (Table II). Values closer to zero are desired in order to confirm that the structure determined is in fact what it is said to be.

***Table II.*** Data collected for the crystal structure of sodium 3-nitrophenolate dihydrate.

| | | |
|---|---|---|
| Empirical Formula | $NaC_6H_8NO_5$ | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | monoclinic, $P2_1/n$ | |
| Unit cell dimensions | $a$ = 6.824(1) Å | $\alpha$ = 90° |
| | $b$ = 6.544(1) Å | $\beta$ = 94.46(3)° |
| | $c$ = 18.206(4) Å | $\gamma$ = 90° |
| Volume | 809.4(3) $Å^3$ | |
| Z, Calculated density | 4, 1.618 g $cm^{-3}$ | |
| Absorption Coefficient | 0.23 $mm^{-1}$ | |
| $F$(000) | 500.0 | |
| Max 2-theta | 116.93° | |
| Limiting indices | $-15 \leq h \leq 15$, $0 \leq k \leq 15$, $0 \leq l \leq 43$ | |
| Reflection collection/rejected/unique | 11707/497/11210 | |
| Refinement Method | Full-matrix least-squares on $F^2$ | |
| Data/ restraints/ parameters | 11210/ 0/ 150 | |
| Goodness of fit on $F^2$ | 0.936 | |
| Final $R$ indices [3269 data $I>4\sigma(I)$] | $R_1$ = 0.0740, w$R_2$ = 0.2467 | |
| $R$ index for all data | $R_1$ = 0.1468 | |
| Largest difference peak and hole | 1.18 and -0.78 $e$ $Å^{-3}$ | |

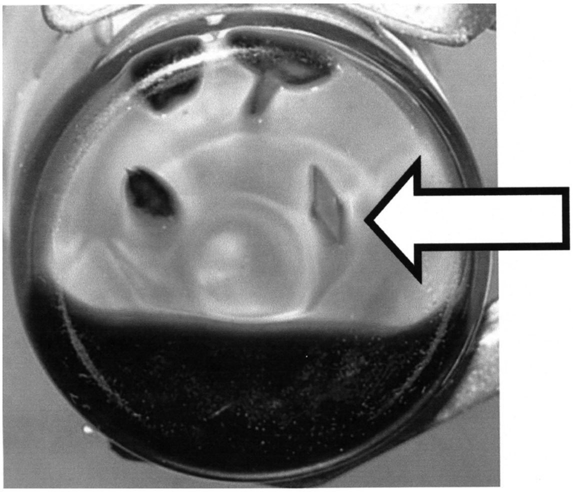
Due to the high *R* factor, the unclean difference map, and the possibility of a disordered impurity present in the crystal structure, no high-resolution X-ray data set was collected in order to precisely map out the electron density distribution of the sodium salt of 3-nitrophenolate. Upon repeated failed attempts to regrow the sodium salt, we chose to try to synthesize different salts of 3-nitrophenolate, one of which was the product of the volumetric addition of solutions of tetramethylammonium hydroxide and 3-nitrophenol.

## MATERIALS AND METHODS

The crystals of the tetramethylammonium salt of 3-nitrophenolate were formed by first dissolving the 3-nitrophenol solid in an ethanolic aqueous solution to obtain a 1.5 *M* solution. Then 25.0 mL of a 1.5 *M* aqueous solution of tetramethylammonium hydroxide were added to 25.0 mL of the dissolved phenol. The solution was covered with parafilm and allowed to slowly evaporate for three years. The solution evaporated until the appropriately-sized crystals were formed.

A crystal of the tetramethylammonium salt of 3-nitrophenolate (similar to the ones sent for data collection but larger) is shown in Figure 5. The crystals were collected and sent to Dr. Kenneth Hardcastle at Emory University X-ray Crystallography Laboratory for an X-ray diffraction data set to be collected. The instrument used to collect the X-ray diffractions was a Bruker 2K CCD diffractometer and the data were collected at a low temperature (173 ± 2 K) using the vapor of liquid nitrogen to cool the crystals. For the salt, 12664 X-ray reflections were collected, 2134 of which were unique. The Miller indices for the crystal structure were $-30 \leq h \leq 31$, $-7 \leq k \leq 7$, $-21 \leq l \leq 21$. The crystal structure was solved and refined using the programs within the SHELXTL V. 5.1 software package (6).

***Figure 5.*** Grown crystal of the tetramethylammonium salt of 3-nitrophenolate.



## RESULTS

The data collected from the solved crystal structure is summarized on Table III. The *R* factor was determined to be 0.0402. Also it is important to note the values for the deepest hole and highest peak in the electron density difference map. These values are 0.268 $e$ Å$^{-3}$ for the highest peak and -0.235 $e$ Å$^{-3}$ for the deepest hole.

***Table III.*** Data collected for tetramethylammonium salt of 3-nitrophenolate.

| | | |
|---|---|---|
| Empirical Formula | $C_{10}H_{16}N_2O_3$ | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | monoclinic, *C*2/*c* | |
| Unit cell dimensions | $a$ = 23.543(4) Å | $\alpha$ = 90° |
| | $b$ = 5.636(1) Å | $\beta$ = 128.513(3)° |
| | $c$ = 16.387(3) Å | $\gamma$ = 90° |
| Volume | 1701.16 Å$^3$ | |
| Z, Calculated density | 4, 1.243 g cm$^{-3}$ | |
| Absorption Coefficient | 0.09 mm$^{-1}$ | |
| *F*(000) | 684.0 | |
| Max 2-theta | 56.80° | |
| Limiting indices | $-30 \le h \le 31$, $-7 \le k \le 7$, $-21 \le l \le 21$ | |
| Reflection collection/rejected/unique | 12664/696/2134 | |
| Refinement Method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 2134/21/155 | |
| Goodness of fit on $F^2$ | 0.707 | |
| Final *R* indices [1368 data $I>4\sigma(I)$] | $R_1$ = 0.0402, w$R_2$ = 0.1128 | |
| *R* index for all data | $R_1$ = 0.0616 | |
| Largest diff. peak and hole | 0.268 and -0.235 $e$ Å$^{-3}$ | |

Once the crystal structure was solved, the bond lengths and angles were determined. The geometry of the 3-nitrophenolate moiety is shown in Figures 6 and 7. The values of the average bond lengths are shown in Table IV. A packing diagram is also shown in Figure 8. One notices immediately that there is a hydrogen atom attached to the phenolic oxygen. But the bond length between this hydrogen atom and the oxygen atom is far too long. Careful examination of the packing diagram reveals that one hydrogen atom is shared between two phenolate moieties. The hydrogen atom itself sits on a center of symmetry in the *C*-centered lattice, and what has been synthesized is actually the 1:1 complex of tetramethylammonium 3-nitrophenolate and 3-nitrophenol.

***Figure 6.*** Bond lengths within the 3-nitrophenolate moiety of the tetramethylammonium salt of 3-nitrophenol. The present phenolic hydrogen (H6) is shared by the phenolic oxygen shown (O1) and the symmetry-related phenolic oxygen.

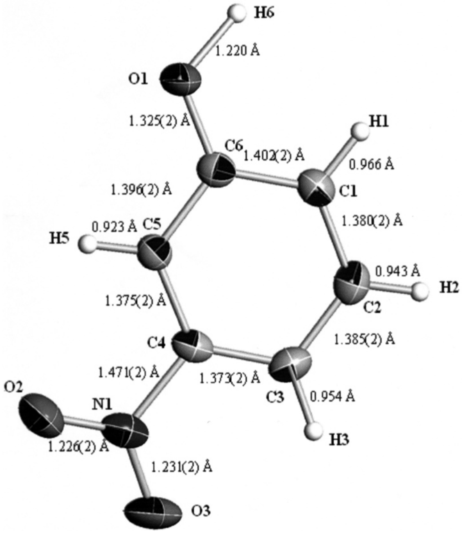


***Figure 7.*** Bond angles within the 3-nitrophenolate moiety of the tetramethylammonium salt of 3-nitrophenol. The present phenolic hydrogen (H6) is shared by the phenolic oxygen shown (O1) and the symmetry-related phenolic oxygen.

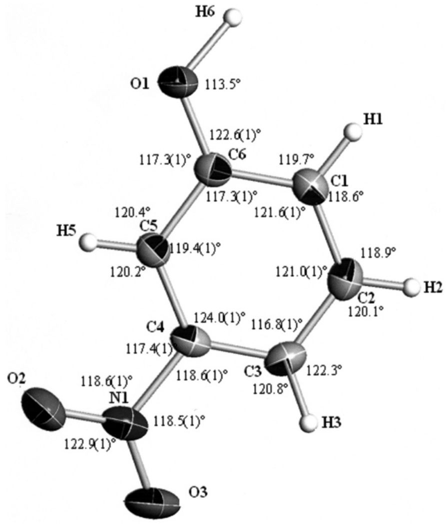
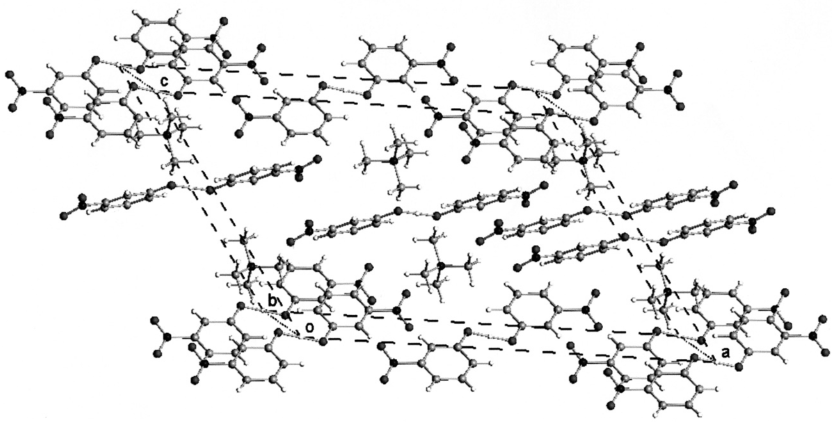


***Table IV.*** Average bond lengths within the 3-nitrophenolate moiety.

| Bond Type | Bond length (Å) |
|---|---|
| Aromatic carbon-carbon | 1.385 |
| Aromatic carbon-hydrogen | 0.947 |
| Carbon-oxygen | 1.325 |
| Oxygen-hydrogen | 1.220 |
| Aromatic carbon-nitrogen | 1.471 |
| Nitrogen-oxygen | 1.229 |

***Figure 8.*** Packing diagram of the 1:1 complex of tetramethylammonium 3-nitrophenolate and 3-nitrophenol.



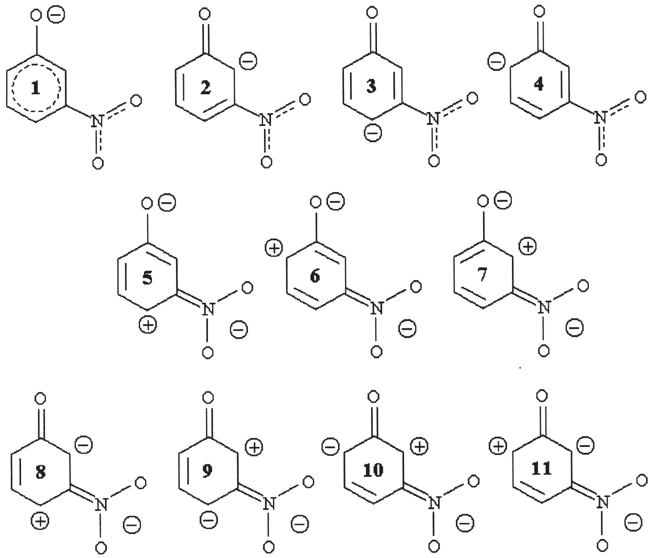
## DISCUSSION

The data collected on the tetramethylammonium salt of 3-nitrophenol resulted in a structure that is more reliable than the sodium salt. The *R* factor for the tetramethylammonium salt was much lower. The small peak height and hole values in the electron density difference map show that the structure factors calculated for the model are very similar to the structure factors based on the X-ray data.

The determined bond lengths and angles for the structure (Figures 6 and 7) reveal a very reasonable geometry. The experimentally-determined bond lengths are comparable to those shown in Table I. However, the calculated oxygen-hydrogen bond length is significantly larger than an acceptable value. It was determined that this is because the hydrogen is shared between two phenolate moieties. This can be clearly seen in the packing diagram of the unit cell (Figure 8). When the hydrogen is shared by two molecules in the unit cell, the hydrogen is considered to be of half occupancy. It was determined that the hydrogen was not completely removed from the phenol by tetramethylammonium hydroxide.

The crystal structure reveals which of the resonance structures of the 3-nitrophenolate moiety is dominant. Of the resonance structures of the 3-nitrophenolate moiety shown in Figure 9, there is a considerable difference in the bond order of the carbon-oxygen bond as well as the carbon-nitrogen bond. In some of the resonance structures the carbon-oxygen bond is a single bond, and in others it is a double bond. Also, some structures show the carbon-nitrogen bond has an order of one, while others an order of two. Therefore since the bond order is directly related to the bond length the dominant resonance structure(s) can be identified.

***Figure 9.*** Resonance structures of 3-nitrophenolate ion. Half-bonds are dashed. Only the overall charge on the nitro group is indicated if an overall charge is at all present.



The aromatic carbon-carbon, carbon-oxygen, and the carbon-nitrogen bond lengths are in good agreement with the values in Table I. The observed carbon-oxygen and carbon-nitrogen bond lengths give evidence as to the dominant resonance structure. Paraffinic carbon-oxygen bonds typically are 1.43 Å in length and carbon-oxygen bonds with “partial double bond character” are typically 1.36 Å in length. The C6–O1 bond in the 3-nitrophenolate ion is found to be 1.327 Å in length. This suggests that the carbon-oxygen bond has a bond order of slightly more than 1.5. This is reasonable since the electron-withdrawing nitro group should pull away some of O1’s lone pair electron density into the $\pi$ system of the phenyl ring. Paraffinic carbon-nitrogen bonds typically are 1.47 Å in length and carbon-nitrogen bonds with partial double bond character are typically 1.35 Å in length. The C4–N1 bond in the 3-nitrophenolate ion is found to be 1.468 Å in length. This suggests that the C4–N1 bond has a bond order of very nearly 1. While resonance structure 1 (Figure 9) most likely is the principle structure describing the observed structure of the 3-nitrophenolate ion, the experimental C6—O1 and C4–N1 bond lengths give evidence that structures 2, 3, and 4 (Figure 9) also significantly contribute to the structure that is observed. It may also be pointed out that the carbon-carbon bond length in benzene is 1.39 Å. To two decimal places, the average of the C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, and C6–C1 bond lengths is 1.39 Å. The C5–C6 and C6–C1 bonds are 1.40 Å in length, thus evidencing that they possess slightly less partial double bond character. This is in good agreement with structures 2, 3, and 4, which have a ketone-like structure in which the carbonyl carbon is bound singly to two carbon atoms.

Structures 1, 2, 3, and 4, suggest that the nitrogen-oxygen bonds that are present in the 3-nitrophenolate moiety exist with a bond order somewhere between 1 and 2. The experimental nitrogen-oxygen bond lengths are between the typical N–O single and double bond lengths. The average experimental N–O bond length (1.23 Å) is closer to the typical N–O double bond length (1.13 Å) than to the typical N–O single bond length (1.40 Å).

The experimentally-determined values for the carbon-hydrogen bonds are slightly shorter than the accepted values. This is because the crystal structure is solved using the electron density map, and the electrons of the hydrogen atom are mostly between the hydrogen and carbon atoms' nuclei in the sigma bond. Since the location of the hydrogen atom is dependent on the electron density in X-ray crystallography, the hydrogen seems closer to the carbon than it really is (7).

All of the observed bond lengths differed from the values in Table I by only their uncertainties. After the analysis of the bond lengths of the solved structure, the *R* factor, and the electron density difference map it was determined that the solved structure is a fairly accurate depiction of what it was expected to be. It was also observed that the 3-nitrophenolate structures of the sodium and tetramethylammonium salts were very similar. (See Table V.) The bond lengths and angles were found to be statistically the same (*i.e.*, most within 1 estimated standard deviation of each other). From this observation it can be concluded that the bases which reacted with the phenol did not affect the structure of 3-nitrophenolate. This is valuable and suggests that the tetramethylammonium salt may be a good candidate on which a high-precision data set would be collected in order to perform a charge density analysis of the 3-nitrophenolate ion in our investigation of the alpha effect.

***Table V.*** Comparison of the phenolate moiety for the sodium and tetramethylammonium salts.

| Bond | Sodium Salt | Tetramethylammonium Salt |
|---|---|---|
| C–O | 1.327(1) Å | 1.325(2) Å |
| C–N | 1.468(2) Å | 1.471(2) Å |
| Avg. N–O | 1.231(2) Å | 1.229(2) Å |

## ACKNOWLEDGEMENTS

We would like to thank Dr. Edwin Stevens at the University of New Orleans for collecting the data of sodium 3-nitrophenolate dihydrate and Dr. Kenneth Hardcastle at Emory University X-ray Crystallography Laboratory for collecting the data of the tetramethylammonium salt of 3-nitrophenol. We also acknowledge Berry College's Kirbo Scholarship and Faculty Development Program for providing the funds to do this research.

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