

The Crystal and Molecular Structures of Five Nitrophenolates: Potassium 4-Nitrophenolate Monohydrate, Potassium 2-Chloro-4-Nitrophenolate Monohydrate, Potassium 4-Chloro-2-Nitrophenolate Monohydrate, Ammonium 2-Chloro-4,6-Dinitrophenolate Sesquihydrate and Potassium 2,6-Dinitrophenolate

E. Krogh Andersen, I. G. Krogh Andersen and G. Ploug-Sørensen

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

Andersen, E. K., Andersen, I. G. K. and Ploug-Sørensen, G., 1989. The Crystal and Molecular Structures of Five Nitrophenolates: Potassium 4-Nitrophenolate Monohydrate, Potassium 2-Chloro-4-Nitrophenolate Monohydrate, Potassium 4-Chloro-2-Nitrophenolate Monohydrate, Ammonium 2-Chloro-4,6-Dinitrophenolate Sesquihydrate and Potassium 2,6-Dinitrophenolate. – Acta Chem. Scand. 43: 624–635.

The structures of five nitrophenolates were determined from single-crystal diffractometer data: Potassium 4-nitrophenolate monohydrate, monoclinic, space group $P2_1c$, with $a = 10.566(4)$, $b = 7.371(1)$, $c = 11.316(5)$ Å, $\beta = 117.80(1)^\circ$ and $Z = 4$; full-matrix least-squares refinement of 127 parameters gave $R = 0.028$ for 1983 observed reflections. Potassium 2-chloro-4-nitrophenolate monohydrate, monoclinic, space group $P2_1/c$, with $a = 3.795(1)$, $b = 11.501(1)$, $c = 19.727(2)$ Å, $\beta = 91.38(1)^\circ$ and $Z = 4$; full-matrix least-squares refinement of 133 parameters gave $R = 0.033$ for 2349 observed reflections. Potassium 4-chloro-2-nitrophenolate monohydrate, monoclinic, space group $P2_1/c$, $a = 15.487(2)$, $b = 3.840(1)$, $c = 16.581(2)$ Å, $\beta = 116.44(1)^\circ$ and $Z = 4$; full-matrix least-squares refinement of 133 parameters gave $R = 0.035$ for 1300 observed reflections. Ammonium 2-chloro-4,6-dinitrophenolate sesquihydrate, orthorhombic, space group $Pn2b$, with $a = 6.501(1)$, $b = 7.728(1)$, $c = 20.744(2)$ Å and $Z = 4$; full-matrix least-squares refinement of 164 parameters gave $R = 0.038$ for 1480 observed reflections. Potassium 2,6-dinitrophenolate, triclinic, space group $P\bar{1}$, with $a = 9.122(3)$, $b = 10.757(3)$, $c = 4.141(1)$ Å, $\alpha = 89.26(2)$, $\beta = 102.12(2)$, $\gamma = 96.46(2)^\circ$ and $Z = 2$; full-matrix least-squares refinement of 136 parameters gave $R = 0.033$ for 2080 observed reflections. The structures of phenolates and relevant phenols are reviewed and the changes in the structure of phenols on ionization are discussed.

Structural information on phenolates is scarce. There are many reports concerning the structure of the picrate ion, few determinations of the 2-nitrophenolate ion and one determination of the structure of the 2-bromo-4,6-dinitrophenolate ion. These determinations of nitrophenolate structures are, as far as we know, the only published structures of phenolates.

Acids undergo considerable structural change on ionization. It is the aim of this paper to shed light upon the modifications of structure occurring when phenols and their acidic protons are separated.

Experimental

Crystals of the potassium phenolates were obtained by slow evaporation of solutions of the salts in mixtures of water and ethanol. These solutions were prepared by adding 1 M aqueous potassium hydroxide to solutions of the phenols in ethanol until pH was 11. Crystals of ammonium

2-chloro-4,6-dinitrophenolate sesquihydrate were prepared in a similar manner, but in this preparation the alcoholic solution was saturated with ammonia prior to the free evaporation of solvent.

Density measurements (by flotation), lattice constants determination (from indexed quartz-calibrated Guinier Hagg diagrams), and single-crystal rotation and Weissenberg photographs provided the data reported in Table 1. For the hydrates, the observed lattice constants and densities indicated the hydration state reported at the top of Table 1. Confirmation of the hydration state was obtained by determination of the loss of mass on dehydration. In all four compounds this agreed to within 2% (relative) with the calculated value. Space group determination for potassium 2,6-dinitrophenolate ($P\bar{1}$ or $P1$) and ammonium 2-chloro-4,6-dinitrophenolate ($Pn2b$ or $Pnmb$) was decided by statistical tests. In the former case these favoured a centric, and in the latter case an acentric distribution.

Crystal data and experimental conditions for intensity data collection are given in Table 1.

e 1. Crystal and other experimental data for five nitrophenolates.

	Potassium 4-nitro-phenolate monohydrate	Potassium 2-chloro-4-nitrophenolate monohydrate	Potassium 4-chloro-2-nitrophenolate monohydrate	Ammonium 2-chloro-4,6-dinitrophenolate sesquihydrate	Potassium 2,6-dinitrophenolate
M_r	C ₆ H ₄ NO ₃ , K·H ₂ O, 195.22	C ₆ H ₃ NO ₃ Cl, K·H ₂ O, 229.66	C ₆ H ₃ NO ₃ Cl, K·H ₂ O, 229.66	C ₆ H ₂ N ₂ O ₅ Cl, NH ₄ ·1.5H ₂ O, 262.61	C ₆ H ₃ N ₂ O ₅ , 222.20
cell dimensions/Å or °	$a = 10.566(4)$ $b = 7.371(1)$ $c = 11.316(5)$ $\alpha = 90$ $\beta = 117.80(2)$ $\gamma = 90$	$a = 3.795(1)$ $b = 11.501(1)$ $c = 19.727(2)$ $\alpha = 90$ $\beta = 91.38(1)$ $\gamma = 90$	$a = 15.487(2)$ $b = 3.840(1)$ $c = 16.581(2)$ $\alpha = 90$ $\beta = 116.44$ $\gamma = 90$	$a = 6.501(1)$ $b = 7.728(1)$ $c = 20.744(2)$ $\alpha = 90$ $\beta = 90$ $\gamma = 90$	$a = 9.122(3)$ $b = 10.757(3)$ $c = 4.141(1)$ $\alpha = 89.26(2)$ $\beta = 102.12(2)$ $\gamma = 96.46(2)$
radiation	Monochromated CuK α_1 ($\lambda = 1.54051$ Å)	Monochromated CuK α_1 ($\lambda = 1.54051$ Å)	Monochromated CuK α_1 ($\lambda = 1.54051$ Å)	Monochromated CuK α_1 ($\lambda = 1.54051$ Å)	Monochromated CuK α_1 ($\lambda = 1.54051$ Å)
systematic absences	$h0l: l=2n+1$ $0k0: k=2n+1$	$h0l: l=2n+1$ $0k0: k=2n+1$	$h0l: l=2n+1$ $0k0: k=2n+1$	$0kl: k+l=2n+1, hk0: k=2n+1$ $0k0: k=2n+1, 00l: l=2n+1$	None
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pn2b$	$P\bar{1}$
Z	4	4	4	4	2
D cm ⁻³	1.678(4)	1.776(1)	1.729(1)	1.671	1.870(2)
ρ cm ⁻³	1.663	1.772	1.728	1.674	1.870
density (meas.)	9.1	7.9	7.72	10.0	0
density (calc.)	9.23	7.84	7.84	10.3	0
crystal size/mm	0.33×0.29×0.20	0.16×0.33×0.36	0.10×0.175×0.425	0.16×0.33×0.57	0.10×0.16×0.26
temperature/°C	22	22	22	22	22
θ °	30	30	30	30	30
diffraction technique	$\omega/2\theta$	$\omega/2\theta$	ω	$\omega/2\theta$	$\omega/2\theta$
diffraction angle/°	1–1.58	1–1.58	1–1.20	1–1.58	1–1.58
scan time/scan	600	600	240	600	600
diffraction condition	Graphite-monochromated, discriminated	Graphite-monochromated, discriminated	Graphite-monochromated, discriminated	Graphite-monochromated, discriminated	Graphite-monochromated, discriminated
radiation	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)
largest reflection	142, max correction for decrease 9 %	127, max correction for decrease 10 %	831, max correction for decrease 0	241, max correction for decrease 6 %	161, max correction for decrease 7 %
number of reflections measured	2365	2843	2631	1601	2586
number of reflections used in calculations	1983 [$>2.5\sigma(I)$]	2349 [$>2.5\sigma(I)$]	1300 [$>2.5\sigma(I)$]	1480 [$>2.5\sigma(I)$]	2080 [$>2.5\sigma(I)$]
correction for absorption	0.65, no correction	0.90, no correction	0.88, no correction	0.39, no correction	0.67, no correction
correction for Lorentz and polarisation effects	Lorentz and polarisation effects	Lorentz and polarisation effects	Lorentz and polarisation effects	Lorentz and polarisation effects	Lorentz and polarisation effect
structure determination method	Direct methods	Direct methods	Direct methods	Patterson methods	Patterson methods
structure refinement method	By CRYLSQ ¹	By CRYLSQ ¹	By CRYLSQ ¹	By CRYLSQ ¹	By CRYLSQ ¹
number of parameters	127	133	133	164	136
weights calculated from	$w = (2.48 + F_0 + 0.023 F_0 ^2)^{-1}$	$w = (3.68 + F_0 + 0.016 F_0 ^2)^{-1}$	$w = (\sigma(F_0))^{-2}$	$w = (3.10 + F_0 + 0.01 F_0 ^2)^{-1}$	$w = (2.02 + F_0 + 0.023 F_0 ^2)^{-1}$
R	0.028	0.033	0.035	0.038	0.033
R_w	0.042	0.049	0.036	0.052	0.048
S	0.002	0.05	0.01	0.04	0.002

Structure determination and refinement

The structures were determined and refined using programmes included in the X-RAY 76 system.¹

Trial structures of the 2,6-dinitrophenolate and the 2-chloro-4,6-dinitrophenolate were found from Patterson syntheses, and for the three other phenolates trial structures were found by direct methods. The trial structures were initially refined by alternating structure-factor and electron-density calculations and later by full-matrix least-squares calculations (CRYLSQ).¹ All hydrogen atoms (except those of the ammonium ion in the 2-chloro-4,6-dinitrophenolate) were included in the calculations (positions from difference Fourier maps). In the final cycles they were included with fixed parameters; however, the position parameters for hydrogen atoms had, prior to the final least-squares cycles, been refined with limited data sets (out to $\sin\Theta/\lambda = 0.4$). R values for the final cycles, in which position and anisotropic temperature parameters were refined, are given in Table 1 together with other details of the calculations. Atomic scattering factors were taken from Ref. 2. Atomic coordinates and equivalent isotropic temperature parameters are given in Tables 2–6. A list of structure factors, hydrogen atom positions, anisotropic

thermal parameters and deviations from least-squares molecular planes may be obtained from the authors on request.

Table 2. Final atomic coordinates with standard deviations ($\times 10^4$) and equivalent isotropic temperature factors (Å^2) for potassium 4-nitrophenolate monohydrate.

$$B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij}(a_i a_j).$$

	x	y	z	B_{eq}
K	4506(0)	4881(0)	7943(0)	2.78(2)
C(1)	-2251(1)	3456(1)	7622(1)	2.14(7)
C(2)	-1384(1)	4377(2)	7155(1)	2.62(7)
C(3)	79(1)	4423(2)	7894(1)	2.67(7)
C(4)	740(1)	3526(2)	9122(1)	2.23(7)
C(5)	-65(1)	2608(2)	9622(1)	2.46(7)
C(6)	-1531(1)	2580(2)	8890(1)	2.50(7)
N	2253(1)	3603(2)	9891(1)	2.86(7)
O(1)	-3626(1)	3424(1)	6935(1)	2.69(6)
O(2)	2957(1)	4546(2)	9492(1)	4.23(9)
O(3)	2856(1)	2762(2)	10963(1)	4.15(8)
O(4)	5219(1)	3380(1)	4140(1)	3.62(7)

Table 3. Final atomic coordinates with standard deviations ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for potassium 2-chloro-4-nitrophenolate monohydrate.

$$B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij}(a_i a_j).$$

	x	y	z	B_{eq}
K	-312(1)	3735(0)	2423(0)	2.68(3)
Cl	8049(1)	363(0)	8948(0)	2.59(3)
O(1)	4817(4)	2369(1)	8220(1)	2.72(9)
O(2)	3988(7)	3706(2)	11277(1)	5.46(17)
O(3)	7047(7)	2117(2)	11353(1)	4.99(16)
O(4)	4601(5)	5550(1)	2485(1)	3.72(11)
N	5361(6)	2845(2)	11006(1)	3.64(13)
C(1)	4817(4)	2472(1)	8865(1)	2.04(9)
C(2)	6299(5)	1606(1)	9309(1)	2.02(9)
C(3)	6448(5)	1711(1)	10002(1)	2.40(10)
C(4)	5050(5)	2711(2)	10292(1)	2.64(11)
C(5)	3478(6)	3579(2)	9892(1)	2.81(12)
C(6)	3362(5)	3463(2)	9198(1)	2.71(12)

Table 4. Final atomic coordinates with standard deviations ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for potassium 4-chloro-2-nitrophenolate monohydrate.

$$B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij}(a_i a_j).$$

	x	y	z	B_{eq}
K	5148(1)	996(2)	1310(1)	4.45(5)
Cl	9599(1)	3682(2)	868(1)	4.42(6)
O(1)	3597(1)	1001(6)	3494(1)	4.21(15)
O(2)	3891(1)	-421(8)	2067(1)	7.02(26)
O(3)	2677(1)	-705(8)	773(1)	7.68(27)
O(4)	6007(1)	1004(7)	4826(1)	5.05(18)
N	3015(2)	-69(7)	1580(2)	4.79(22)
C(1)	2737(2)	1644(7)	2891(2)	3.38(18)
C(2)	2396(2)	1122(7)	1947(2)	3.45(18)
C(3)	1425(2)	1722(7)	1318(2)	3.48(20)
C(4)	802(2)	2934(7)	1623(2)	3.32(19)
C(5)	1104(2)	3606(8)	2537(2)	3.87(20)
C(6)	2032(2)	2972(7)	3143(2)	3.89(21)

Discussion of the crystal structures

Potassium 4-nitrophenolate monohydrate. The crystal structure is shown in Fig. 1, where the content of one unit cell is shown. The structure is composed of layers of 4-nitrophenolate ions parallel to the (100) plane. The potassium ions and water molecules are located between these layers and hold them together by ionic forces and hydrogen bonds. The planes of the anions are roughly parallel to the (010) plane. Within one layer the anions are related by two-fold screw axes and centers of inversion. The potas-

Table 5. Final atomic coordinates with standard deviations ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for ammonium 2-chloro-4-dinitrophenolate sesquihydrate.

$$B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij}(a_i a_j).$$

	x	y	z	B_{eq}
Cl	2317(1)	0	1750(1)	3.00(5)
O(1)	5426(3)	1468(3)	924(1)	2.57(13)
O(2)	5000	4009(4)	0	3.00(21)
O(3)	1893(4)	6291(4)	341(1)	3.56(17)
O(41)	8527(4)	3090(5)	3717(1)	3.84(19)
O(42)	5934(5)	1440(6)	3916(1)	5.25(27)
O(61)	9185(4)	2842(5)	772(1)	4.14(20)
O(62)	10387(4)	4317(4)	1561(1)	3.85(18)
N(1)	2266(4)	-89(4)	107(1)	2.99(16)
N(4)	7065(4)	2202(4)	3540(1)	2.81(17)
N(6)	9168(4)	3269(4)	1338(1)	2.44(14)
C(1)	5854(4)	1665(4)	1515(1)	1.95(14)
C(2)	4504(4)	1016(4)	2011(1)	2.12(16)
C(3)	4865(4)	1178(4)	2658(1)	2.33(15)
C(4)	6651(4)	2031(4)	2859(1)	2.20(15)
C(5)	8035(4)	2704(4)	2422(1)	2.16(15)
C(6)	7647(4)	2516(4)	1768(1)	2.04(15)

Table 6. Final atomic coordinates with standard deviations ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for potassium 2,6-dinitrophenolate.

$$B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij}(a_i a_j).$$

	x	y	z	B_{eq}
K	2846(1)	4383(1)	2104(1)	3.07(3)
O(1)	6920(1)	3966(1)	2921(3)	3.40(9)
C(1)	7246(2)	2927(1)	2161(4)	2.35(9)
C(2)	8643(2)	2424(1)	3641(4)	2.59(9)
C(3)	9003(2)	1262(2)	2850(5)	3.24(11)
C(4)	8007(2)	479(2)	610(5)	3.67(13)
C(5)	6669(2)	900(1)	-1023(5)	3.16(11)
C(6)	6323(2)	2083(1)	-356(4)	2.48(9)
N(2)	9762(2)	3159(1)	6053(4)	3.10(10)
N(6)	4976(1)	2470(1)	-2413(4)	2.91(9)
O(21)	11078(2)	2908(2)	6516(5)	5.34(14)
O(22)	9426(2)	4003(1)	7592(4)	4.50(11)
O(61)	4229(2)	1769(2)	-4606(5)	5.18(13)
O(62)	4624(1)	3530(1)	-2064(4)	4.08(10)

sium ions have eight oxygen atoms as nearest neighbours (*viz.* two of each of the four different oxygen atoms in the compound), one at a distance of 3.017 \AA and seven at distances from 2.688 to 2.921 \AA . The hydrogen bonds from the water molecules have phenoxy groups as acceptors at distances of 2.809 and 2.820 \AA . The water molecules are regular with O-H bond lengths of 0.83(7), 0.87(6) \AA and an H-O-H angle of 110(7) $^\circ$. The contact distances are shown in Fig. 1. No other intermolecular distances than those shown in Fig. 1 are shorter than 3 \AA .

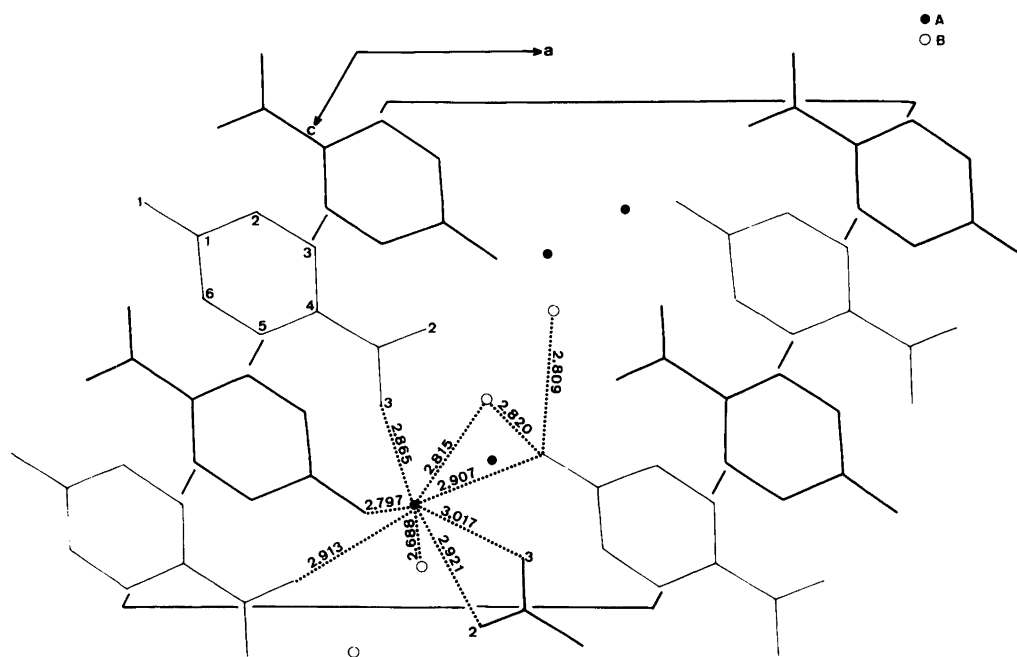


Fig. 1. Intermolecular distances in the crystal structure of potassium 4-nitrophenolate monohydrate. A designates potassium ions, B oxygen atoms in water molecules.

Potassium 2-chloro-4-nitrophenolate. A projection of the structure along the [100] direction is shown in Fig. 2. The structure is composed of layers of 2-chloro-4-nitrophenolate ions parallel to the (001) plane. The potassium ions and water molecules are located between the layers, and hold them together by ionic forces and hydrogen bonds. The anions within one layer are related by centers of inversion. The potassium ions have seven oxygens as nearest neighbours, one at a distance of 3.092 Å and six at distances from

2.764 to 2.969 Å. The water molecules form two hydrogen bonds, one to a phenoxide oxygen ($O\cdots O$ distance 2.780 Å) the other to an oxygen in the nitro group ($O\cdots O$ distance 2.993 Å). The water molecules are fairly regular, with $O-H$ bond lengths of 0.88(1) and 0.97(1) Å and an $H-O-H$ angle of $117(1)^\circ$. The contact distances are shown in Fig. 2. No other intermolecular distances than those shown in Fig. 2 are shorter than 3.0 Å.

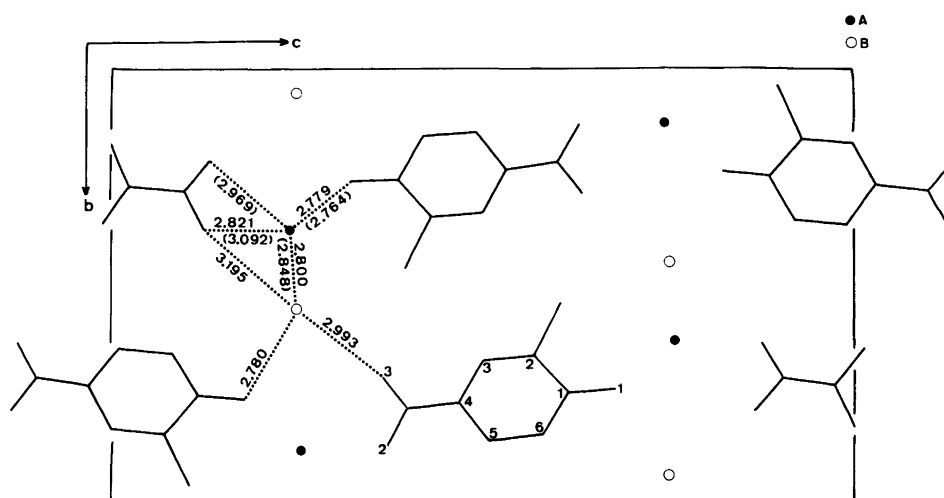


Fig. 2. Intermolecular distances in the crystal structure of potassium 2-chloro-4-nitrophenolate monohydrate. A designates potassium ions, B oxygen atoms in water molecules.

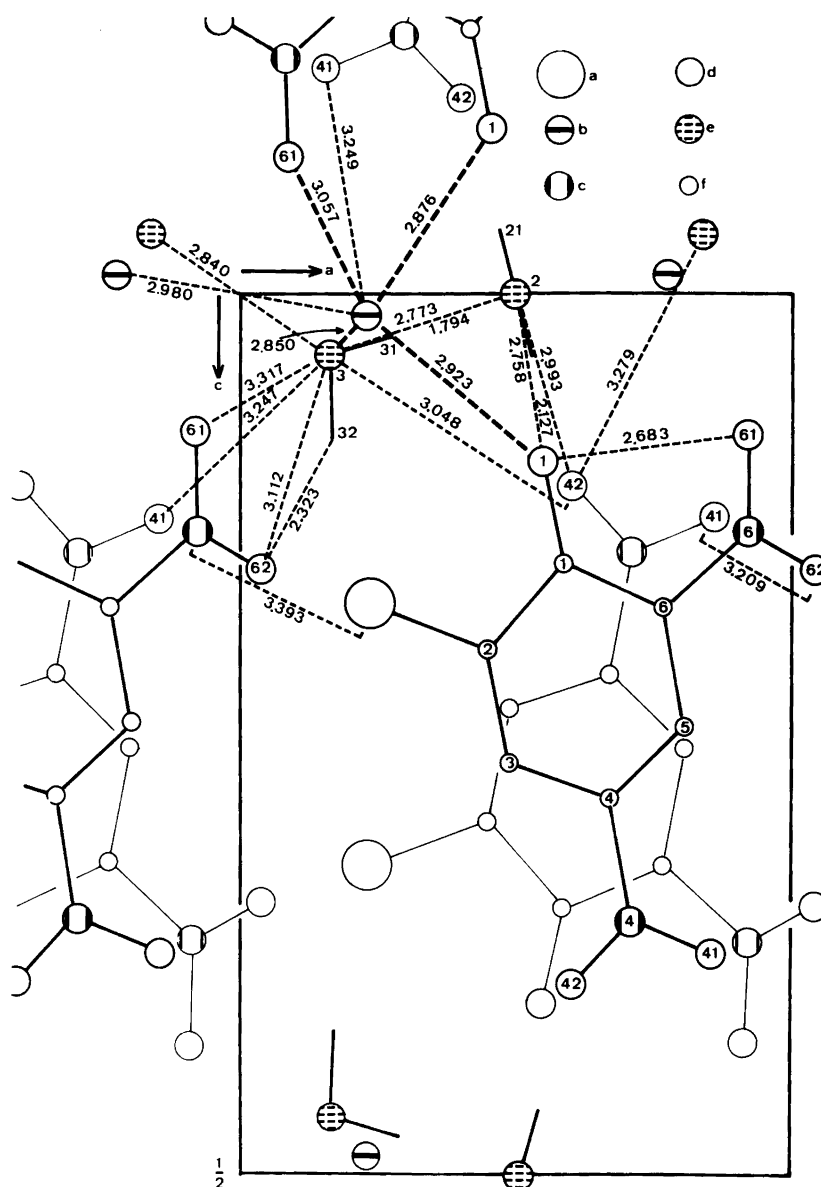


Fig. 4. Intermolecular distances in the crystal structure of ammonium 2-chloro-4,6-dinitrophenolate sesquihydrate. The symbols are: (a) chlorine atoms, (b) nitrogen atoms in ammonium ions, (c) nitrogen atoms in nitro groups, (d) oxygen atoms, (e) oxygen atoms in water molecules and (f) carbon atoms.

Potassium 2,6-dinitrophenolate. The boundary lines of Fig. 5 delineate the content of one unit cell. The molecules are stacked in layers along the (010) direction. There are a few short contact distances between neighbour anions belonging to the same layer. The shortest of these distances, viz. between the C(1) atom in one anion and the O(22) atom in the ion above, is 3.14 Å. The columns are held together by van der Waals and ionic forces.

The potassium ions have nine oxygen atoms as nearest neighbours, six at distances from 2.696 Å to 2.903 Å, and three at distances of 3.035, 3.008 and 3.268 Å. These distances and the closest contact between oxygen atoms are shown in Fig. 5.

The molecular structures of nitrophenols and nitrophenolates

The molecular structures of nine nitrophenols and seven nitrophenolates are known from crystal structure determinations. In this section we attempt an analysis of the structural information obtained by these structure determinations. One part of this analysis concerns the carbon ring system. The change in structure of these rings on separation of the phenolic proton is particularly worth noting. Another part concerns the nitro group. Finally, the C-(OH) and C-O⁻ bond distances are examined in relation to the acid strength of the phenols.

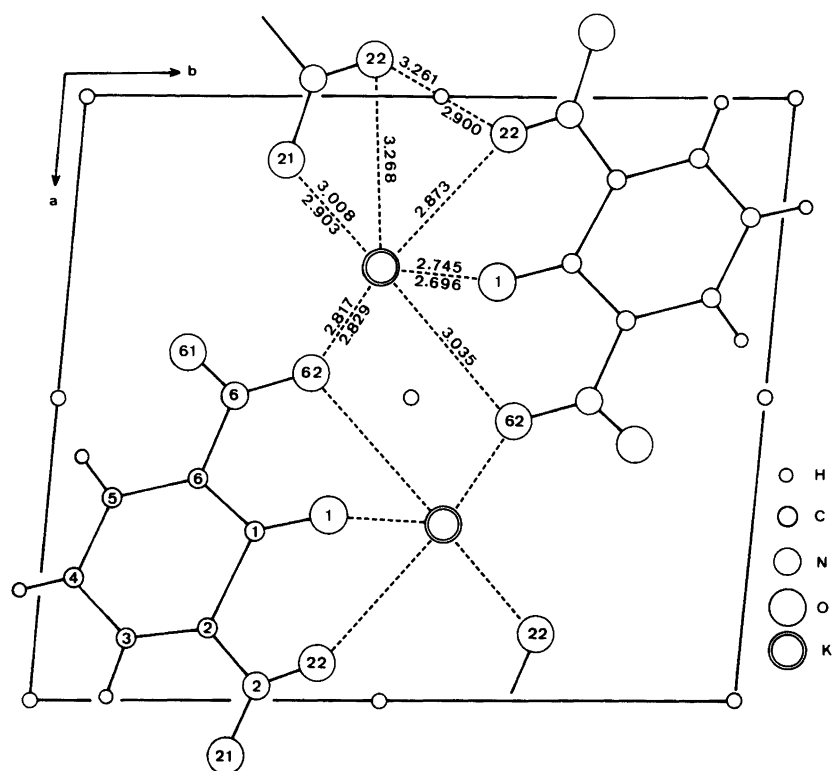


Fig. 5. Intermolecular distances in the crystal structure of potassium 2,6-dinitrophenolate. The structure is viewed along the c axis.

The carbon ring system. The carbon ring systems in nitrophenolates are essentially planar. The carbon atoms deviate typically a few hundredths of an Å from the least-squares planes. In the rings of 2,6-dinitrophenolate ions there are, however, somewhat larger deviations [0.032 and 0.029 Å for the C(6) and C(1) atoms respectively].

Table 7 gives the bond lengths and bond angles in the carbon rings of nitrophenols and nitrophenolates. The nitrophenols are listed in order of decreasing acidity (pK_a values are listed in the last column). The nitrophenolates are listed in order of decreasing acidity of their parent phenol. Where more than one structure determination of a nitrophenol or a nitrophenolate has been made, only the determination with the smallest e.s.d. is reported in Table 7.

The average carbon-carbon bond lengths are given in column VII of Table 7. The standard deviations of the mean values are large, and for the phenolates they are particularly large (up to 10 times the standard deviations of the individual bond lengths). We regard this as experimental evidence that the carbon-carbon bonds are of different length. In our treatment of these differences we have chosen to separate the compounds into three categories: one comprising substances with two *o*-nitro groups, one in which the substances have one nitro group in *o* position and finally a group comprising *p*- and *m*-nitrophenol. By this separation in groups we have also separated the substances

according to acidity. To the first group belong the most acidic phenols, to the second those of medium acidity and to the third group the most weakly acidic nitrophenols.

In nitrophenolates with two nitro groups at *o* positions (i.e. picrates and 2,6-dinitrophenolate) there are two distinct classes of bonds in the carbon rings. One class consists of the two very long bonds [C(1)-C(2) and C(6)-C(1)] adjacent to the phenoxide group. These bonds are the longest carbon-carbon bonds [average 1.451(2) Å] found in benzene compounds. The remaining four bonds in the rings are definitely shorter [average 1.381(10) Å]. In the corresponding phenols the trend is similar; however, the difference in length between the long and short bonds is less marked. The C(1)-C(2) and C(6)-C(1) bonds [average 1.402(3) Å] are in all cases found to be longer than the remaining four bonds [average 1.378(11) Å]. It is proper to remark that the scatter of the four short bonds is much larger for phenols than for phenolates [the C(3)-C(4) in the determinations of picric acid is 1.393 Å]. Nearly all angles in the carbon rings deviate from 120°. The angles facing the phenoxide (phenol) oxygen and the nitro group deviate to a marked extent. The former is in all cases much smaller than 120° [average 115.7(5)° and 111.1(1)° for phenols and phenolates, respectively], whereas the latter is much larger than 120° [average 122.6(8)° and 123.8(1.4)° for phenols and phenolates, respectively].

Our conclusion is that the benzene rings in these nitro-

7. C–C bond lengths (Å), C–C–C angles in nitrophenols and nitrophenolates (°), and pK_a values. Standard deviations in parentheses.

	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–C(6)	C(6)–C(1)	Mean C–C	C(6) C(1) C(2)	C(1) C(2) C(3)	C(2) C(3) C(4)	C(3) C(4) C(5)	C(4) C(5) C(6)	C(5) C(6) C(1)	pK _a
acid ^a	1.403(4) ⁱ	1.370(4) ^m	1.393(4) ^m	1.373(4) ^m	1.379(4) ^m	1.406(4) ^j	1.387(16)	115.3(3)	123.9(3)	117.5(3)	122.0(3)	118.6(3)	122.7(3)	0.33 ^o
ro-4,6-phenol ^b	1.402(7) ⁱ	1.370(7) ^s	1.382(7) ^m	1.376(7)	1.370(7)	1.407(7) ^j	1.385(11)	116.7(4)	122.0(4)	118.2(4)	123.0(4)	117.5(4)	122.7(4)	2.10 ^p
ro-4,6-phenol ^c	1.397(7) ⁱ	1.374(7) ^s	1.396(8) ^m	1.371(8) ^s	1.385(7) ^m	1.397(8) ^j	1.387(12)	117.2(4)	122.3(5)	117.5(5)	123.1(5)	117.4(5)	122.5(5)	
nitrophenol ^d	1.400(8) ⁱ	1.382(9) ^m	1.389(9) ^m	1.358(9)	1.391(9) ^m	1.399(8) ^j	1.387(15)	116.0(5)	121.9(5)	120.0(6)	119.9(6)	119.9(6)	122.3(5)	3.71 ^q
nitrophenol ^e	1.407(6) ⁱ	1.385(5) ^m	1.366(5) ^s	1.385(5) ^m	1.366(6) ^s	1.398(6) ^j	1.385(17)	118.6(4)	121.1(4)	117.6(4)	123.3(4)	118.8(4)	120.6(4)	4.09 ^r
ro-2-nitrophenol ^f	1.401(7) ⁱ	1.378(7) ^m	1.357(7) ^s	1.391(7) ^m	1.373(7) ^s	1.373(7)	1.379(22)	117.2(5)	121.9(5)	119.3(5)	120.4(5)	119.6(5)	121.6(5)	6.46 ^r
phenol ^g	1.392(2) ⁱ	1.373(2) ^s	1.386(2) ^m	1.386(2) ^m	1.377(2) ^s	1.388(2) ^j	1.384(7)	120.3	120.1	118.8	121.9	118.8	120.0	7.14 ^u
phenol ^h	1.396(7)	1.393(8) ^m	1.365(9) ^s	1.373(9) ^m	1.354(9) ^s	1.384(8)	1.378(16)	117.7(5)	120.7(5)	119.9(5)	119.1(6)	121.8(6)	120.8(6)	7.23 ^u
phenol ⁱ														
oclinic form A	1.390(3)	1.377(3)	1.366(3)	1.382(3)	1.381(3)	1.375(3)	1.379(8)	119.8(2)	117.7(2)	123.7(2)	117.7(2)	120.3(2)	120.8(2)	8.35 ^u
oclinic form B	1.385(2)	1.376(2)	1.371(2)	1.385(2)	1.379(2)	1.378(2)	1.379(5)	119.9(1)	118.1(1)	123.5(1)	117.4(1)	120.7(1)	120.5(1)	
s ion ^j	1.450(4) ⁱ	1.368(4) ^m	1.390(5) ^m	1.379(5) ^m	1.374(5) ^m	1.449(4) ^j	1.402(38)	111.2(2)	125.0(3)	118.7(3)	121.3(3)	119.1(3)	124.5(3)	0.33 ^o
ro-4,6-phenolate ^k	1.442(4) ^k	1.368(4) ^s	1.398(4) ^m	1.379(4) ^s	1.387(3) ^m	1.438(3) ^j	1.402(31)	113.0(2)	124.3(2)	118.6(2)	121.6(2)	119.0(2)	123.6(2)	2.10 ^p
nitrophenolate ^k	1.453(2) ⁱ	1.388(2) ^m	1.375(2) ^m	1.386(3) ^m	1.390(2) ^m	1.451(2) ^j	1.407(35)	111.0(1)	124.1(1)	118.9(2)	120.6(1)	120.6(1)	124.1(1)	3.71 ^q
ro-4-tenolate ^k	1.433(2) ⁱ	1.372(2) ^s	1.396(3) ^m	1.398(3) ^m	1.376(3) ^s	1.433(2) ^j	1.401(27)	115.0(1)	123.7(1)	118.4(2)	121.2(2)	119.8(2)	122.0(2)	5.45 ^r
ro-2-tenolate ^k	1.426(4) ⁱ	1.416(4) ^m	1.356(5) ^s	1.397(5) ^m	1.360(4) ^s	1.426(5) ^j	1.397(32)	114.5(2)	122.6(3)	118.7(3)	121.2(2)	120.1(3)	122.9(3)	6.46 ^r
phenolate ^k	1.425(2) ⁱ	1.372(2) ^s	1.396(2) ^m	1.397(2) ^m	1.374(2) ^s	1.427(2) ^j	1.399(24)	117.0(1)	121.5(1)	119.6(1)	121.0(1)	119.4(1)	121.5(1)	7.14 ^u
phenolate	1.425(7) ⁱ	1.407(6) ^m	1.375(7) ^s	1.397(9) ^m	1.360(7) ^s	1.440(6) ^j	1.401(30)	115.2(4)	122.5(4)	119.5(5)	119.6(4)	121.8(5)	121.4(4)	7.23 ^u

ng, medium, short bonds respectively. ^aRef. 3. ^bRef. 4. ^cRef. 5. ^dRef. 6. ^eRef. 7. ^fRef. 8. ^gRef. 9. ^hRef. 10. ⁱRef. 11. ^jRef. 12. ^kThis work. ^lRef. 13. ^mRef. 14. ⁿRef. 15. ^oRef. 16. ^pRef. 17. ^qRef. 18. ^rRef. 19.

phenols are distorted. The benzene rings in the corresponding nitrophenolates are also distorted. The distortion is much larger for the phenolates than for the phenols but it is in the same direction for both.

In *o*-nitrophenolates with only one nitro group in *o* position (2-chloro-4,6-dinitrophenolate, 4-chloro-2-nitrophenolate and 2-nitrophenolate) there are three classes of bonds in the carbon ring. The first group consists of the two bonds adjacent to the phenoxide group [C(1)–C(2) and C(6)–C(1)]. These bonds are very long [average 1.433(8) Å], but significantly shorter than the corresponding bonds in phenolates with two nitro groups at *o* positions. The

second group is formed by the two bonds marked with m's in Table 7. They are significantly shorter [average 1.400(9) Å] than the bonds in the former group. The remaining two bonds marked with s's in Table 7 form a third group. These bonds are extremely short [1.366(9) Å]. They are the shortest carbon–carbon ring bonds we have come across in benzene compounds, and rather close in length to the carbon–carbon double bonds found in small (non-benzenoid) molecules in which the carbon atoms have trigonal surroundings (1.344 Å; Ref. 20). For phenols with only one *o*-nitro group a separation of C–C bonds into three groups is less justified. The C(1)–C(2) and C(6)–C(1) bonds [av-

Table 8. C–O⁻, C–OH and C–N bond distances (Å, standard deviations in brackets) for nitrophenols and phenolates.

	pK _a	In nitrophenolates		In nitrophenols	
		C–O ⁻	C–N	C–(OH)	C–N
Picric acid	0.33	1.237(4)	1.463(4) 1.443(5) 1.444(4)	1.327(3)	1.457(4) 1.467(4) 1.469(4)
2-Chloro-4,6-dinitrophenol	2.10	1.266(3)	1.454(4) 1.443(3)	1.333(7)	1.464(7) 1.472(7)
2,6-Dinitrophenol	3.71	1.249(2)	1.440(2) 1.441(2)	1.337(7)	1.457(9) 1.473(9)
2,4-Dinitrophenol	4.09			1.344(6)	1.452(6) 1.486(6)
2-Chloro-4-nitrophenol	5.45	1.277(2)	1.419(2)		
4-Chloro-2-nitrophenol	6.46	1.284(3)	1.421(5)	1.342(6)	1.442(7)
4-Nitrophenol	7.14	1.290(1)	1.421(2)	1.352(2)	1.446(2)
2-Nitrophenol	7.23	1.281(5)	1.422(5)	1.339(7)	1.456(7)
3-Nitrophenol A	8.35			1.366(3)	1.480(3)
3-Nitrophenol B	8.35			1.362(2)	1.474(2)

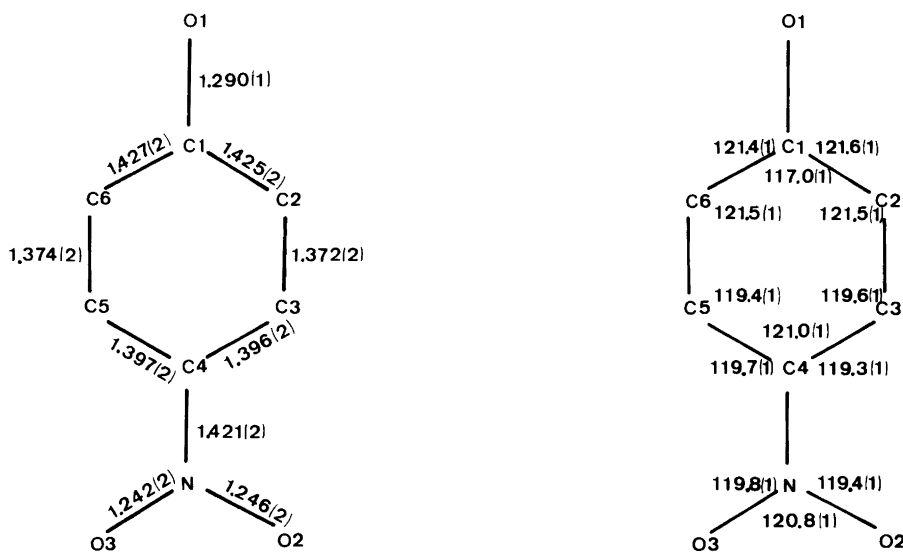


Fig. 6. Bond lengths (Å) and angles (°) in 4-nitrophenolate. Standard deviations in parentheses.

erage length 1.398(10) Å] are with one exception (4-chloro-2-nitrophenol)⁸ the longest bonds in the carbon rings. There are two short bonds [average length 1.367(7) Å], and they are with one exception (2-chloro-4,6-dinitrophenol)⁴ the shortest bonds in the rings. Finally, there are two bonds of medium length [average 1.389(8) Å]. Our conclusion is that nitrophenols and nitrophenolates with one *o*-nitro group have ring systems whose bond distances and angles deviate significantly from those in the unsubstituted benzene ring. The deviation is much larger for the phenolates than for the phenols, but they are generally in the same direction. The position of the short bonds in the rings justifies the designation *o*-quinonoidal for these ring systems. Further justification for this designation is pro-

vided by the shortness of the C–O and C–N bonds (Table 8). Most angles in the carbon rings deviate from 120°. The angles at the carbon atoms to which oxygen atoms or nitro groups are bonded show the largest deviations. The former are always much smaller, the latter much larger than 120°. These deviations are also in general larger for the phenolates than for the phenols.

In the *p*-nitrophenolates (2-chloro-4,1-nitrophenolate and 4-nitrophenolate), three pairs of carbon–carbon bonds are discernible. The bonds adjacent to the phenoxide group are, as in the other phenolates, longer [1.429(5) Å] than the other four bonds. Two bonds [C(2)–C(3) and C(5)–C(6)] are short [1.374(2) Å]. The remaining two bonds are of medium length [1.397(1) Å]. The position of the short

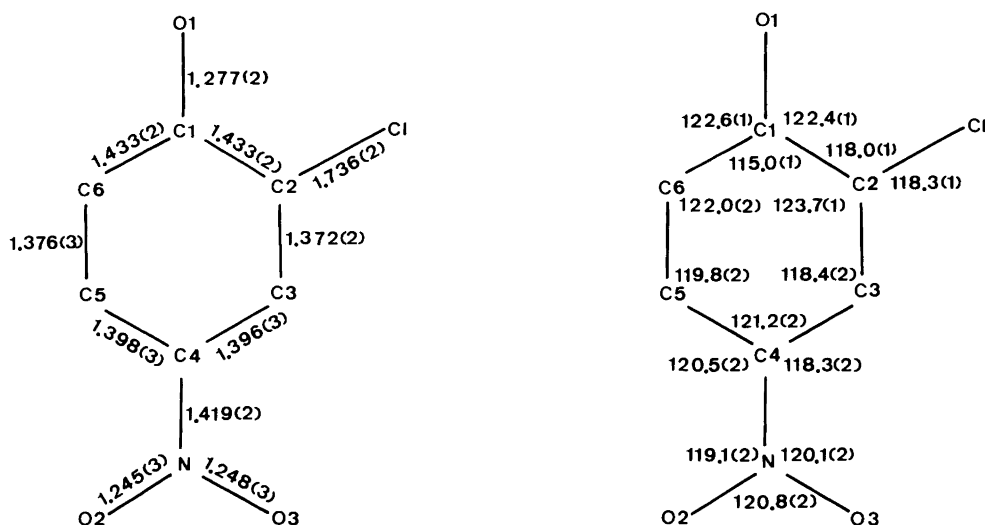


Fig. 7. Bond lengths (Å) and angles (°) in 2-chloro-4-nitrophenolate. Standard deviations in parentheses.

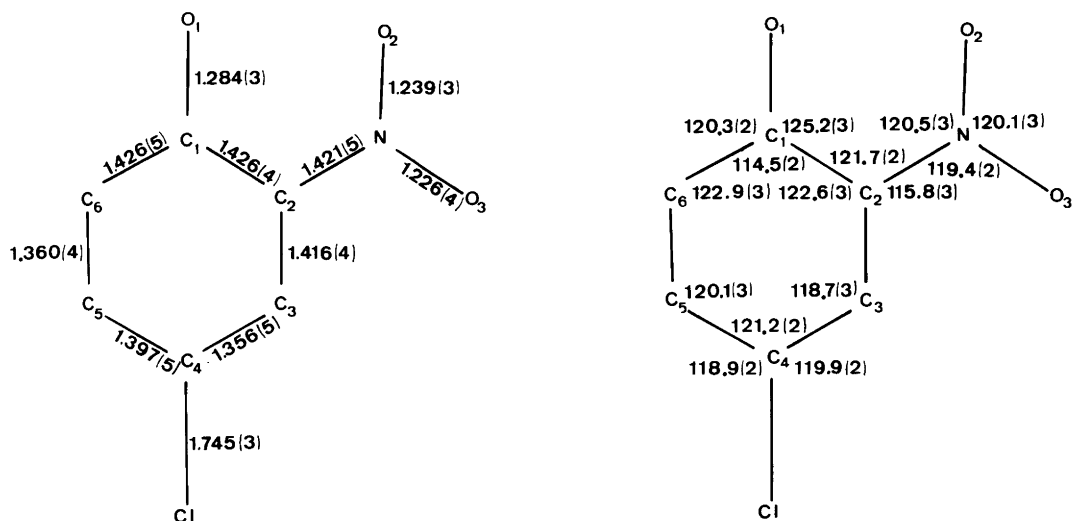


Fig. 8. Bond lengths (Å) and angles (°) in 4-chloro-2-nitrophenolate. Standard deviations in parentheses.

bonds leads to the designation *p*-quinonoidal for this structure. The substituents (oxygen and nitro group) are in *p* position and the bond distances to the substituent atoms are short (C–O 1.286 Å, C–N 1.414 Å).

Coppens and Schmidt⁹ concluded from their structure determination of *p*-nitrophenol that “the shortening of the two C–C bonds parallel to the long molecular axis ... can be attributed to contributions of quinonoid resonance structures”.

The structure of the *m*-nitrophenolate ion is not known. We have prepared many *m*-nitrophenolate salts (potassium-, sodium-, ammonium- and calciumsalts). However, we have not been able to find untwinned crystals in these preparations. The structure of *m*-nitrophenol is known

from crystal structure determinations.¹¹ There is no distinct distribution of the C–C bond distances in groups in *m*-nitrophenol.

The nitro group. In the nitrophenolates the nitrogen atoms usually deviate very little (0.006–0.009 Å) from the plane formed by the two oxygen atoms and the carbon atom to which the nitro group is attached. In two cases, however, there are larger deviations. N(6) in 2-chloro-4,6-dinitrophenolate and N(6) in 2,6-dinitrophenolate deviate 0.024 Å from the planes. The dihedral angles between the plane of the nitro groups and the plane of the benzene rings are in the range from 4.6° (in *p*-nitrophenolate) to 41.2° (one of the nitro groups in *o* position in picrate). The dihedral

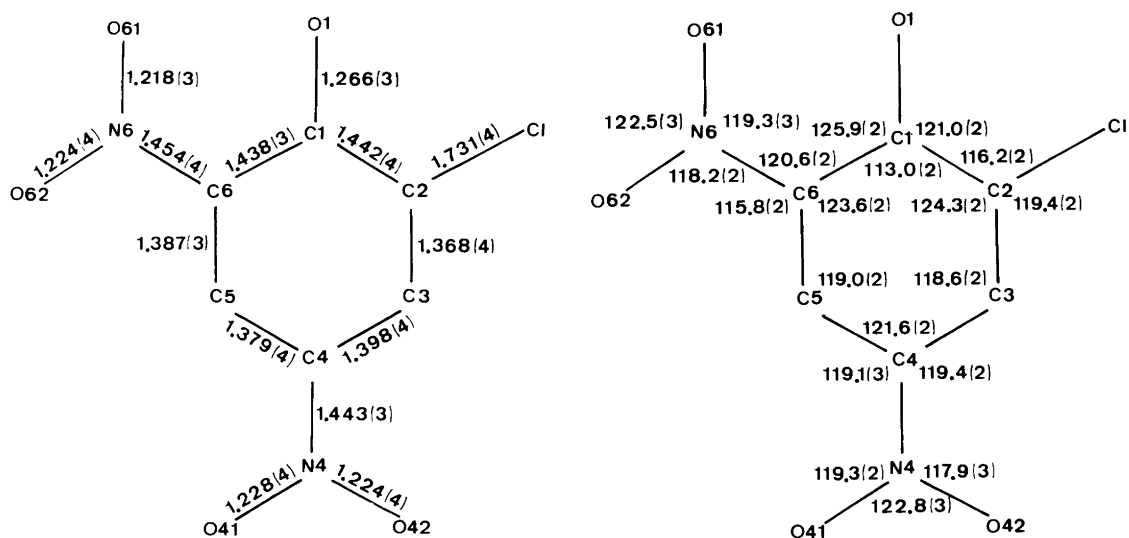


Fig. 9. Bond lengths (Å) and angles (°) in 2-chloro-4,6-dinitrophenolate. Standard deviations in parentheses.

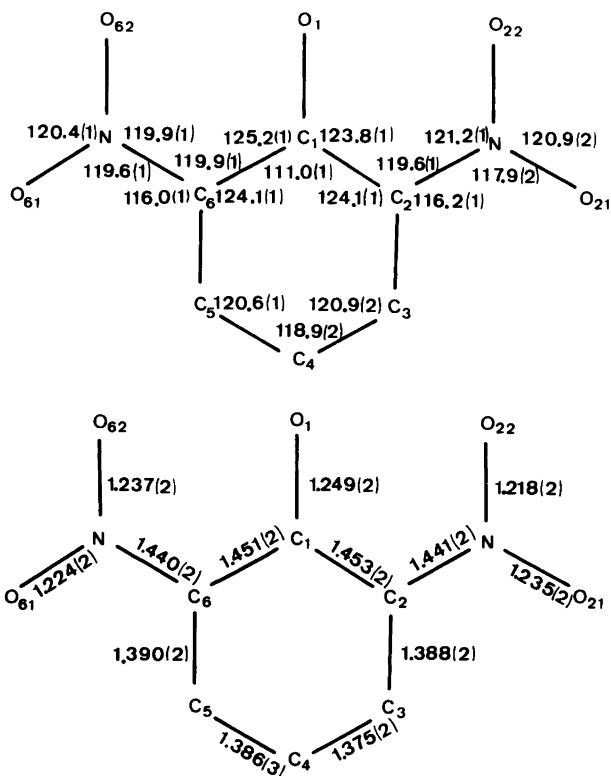


Fig. 10. Bond lengths (Å) and angles (°) in 2,6-dinitrophenolate. Standard deviations in parentheses.

angles are usually larger for nitro groups in *o* position than for nitro groups in *p* position. In Table 8 the C–N bond distances for nitrophenolates and nitrophenols are listed.

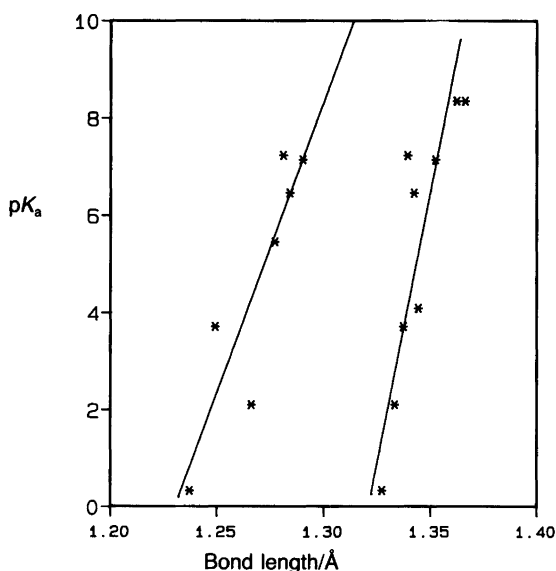


Fig. 11. pK_a values for nitrophenols vs. C–(OH) and C–O[−] (in the phenolates) bond lengths (Å). C–(OH) distances on the right-hand side, and C–O[−] on the left-hand side of the plot. For numerical data concerning pK_a values and bond lengths, see Table 8.

The latter table shows that the C–N bonds in the phenolate are generally shorter than in the corresponding phenols. Further details of the structure of nitro groups in the phenolates are shown in Figs. 6–10.

The phenoxide group. Table 8 gives the C–O and the C–(OH) bond distances for nitrophenolates and nitrophenols. It is seen that the separation of the proton from a phenol results in a drastic shortening of the C–O bond distances. It was shown⁴ for eight phenols that their C–(OH) bond lengths are linearly correlated with the acidic strength (pK values). The short C–(OH) bonds are found in strongly acidic, and the long bonds in weakly acidic compounds. In the right-hand part of Fig. 11, C–(OH) bond lengths of nitrophenols are plotted against their pK values. The left-hand part of Fig. 11 shows that the C–O bond lengths also vary with the pK values. Further information regarding the phenoxide groups can be found in Figs. 6–10.

Conclusions

The structure determinations of nitrophenols and nitrophenolates with one nitro group in an *o* position indicate that the molecules have an *o*-quinone-like structure. This conclusion is drawn from the shortness of C–O and C–N bonds, and from the distribution of short and long bonds in the carbon ring. The justification for this designation is much stronger for the phenolates than for the phenols. Similarly (and on the same premisses), *p*-nitrophenols have a *p*-quinone-like structure. Interpreted in terms of resonance, inclusion of contributions from quinonoidal structures would be predicted to lead to enhancement of acidic strength. The fact that the C–O and C–(OH) bond lengths are linearly correlated with acidic strength supports this interpretation.

References

1. Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. and Flack, H. *The X-Ray 76 System*. Technical Report TR-446, Computer Center, Univ. of Maryland, College Park, MD 1976.
2. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, Vol. III, p. 202.
3. Herbstein, F. H. and Kaftory, M. *Acta Crystallogr., Sect. B* 32 (1976) 387.
4. Andersen, E. K. and Andersen, I. G. K. *Acta Crystallogr., Sect. B* 31 (1975) 387.
5. Neustadt, R. J. and Cagle, F. W., Jr. *Acta Crystallogr., Sect. B* 31 (1975) 2727.
6. Iwasaki, F., Sato, M. and Aihara, A. *Acta Crystallogr., Sect. B* 32 (1976) 102.
7. Iwasaki, F. and Kawano, Y. *Acta Crystallogr., Sect. B* 33 (1977) 2455.
8. Kawai, R., Kashino, S. and Haisa, M. *Acta Crystallogr., Sect. B* 32 (1976) 1972.
9. Coppens, P. and Schmidt, G. M. J. *Acta Crystallogr.* 18 (1965) 654.
10. Iwasaki, F. and Kawano, Y. *Acta Crystallogr., Sect. B* 34 (1978) 1286.

11. Pandarese, F., Ungaretti, L. and Coda, A. *Acta Crystallogr., Sect. B31* (1975) 2671.
12. Jensen, B. *Acta Chem. Scand., Ser. B29* (1975) 891.
13. Andersen, E. K. and Andersen, I. G. K. *Acta Crystallogr., Sect. B31* (1975) 391.
14. Davis M. M. and Paabo, M. *J. Res. Natl. Bur. Stand., Sect. A67* (1963) 241.
15. Robinson, R. A. *J. Res. Natl. Bur. Stand., Sect. A71* (1967) 385.
16. Kortüm, G. and Wilski, H. *Z. Phys. Chem.* 2 (1954) 256.
17. Hammett, L. P. *J. Am. Chem. Soc.* 56 (1934) 2010.
18. Bower, V. E. and Robinson, R. A. *J. Phys. Chem.* 64 (1960) 1078.
19. Judson, C. M. and Kilpatrick, M. *J. Am. Chem. Soc.* 71 (1949) 3110.
20. Stoicheff, B. P. *Tetrahedron* 17 (1962) 135.

Received November 9, 1988.