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The Molecular Structure of Three Hydroxyquinones

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The crystal structures of nitranilic acid hexahydrate, chloranilic acid and ammonium chloranilate monohydrate have been determined by X-ray methods.

Table 1 gives the formulae, space groups, unit cell parameters, calculated and observed densities, and the number of formula units (Z) per unit cell for the three substances. At the bottom of the table the number of observed structure factors and the reliability index are also given.

The chemical formulae of Table 1 are all written in quinoidal form whether this is supported by our experiments or not.

The structures were determined by standard methods and refined by least squares (diagonal) with isotropic temperature factors only.

In Fig. 1 the molecular structure of the three substances are given together with the molecular structure of the nitranilate ion previously reported by Jensen and Andersen.¹ From the figure it may be seen that the ring system of three of the compounds, namely nitranilic acid, nitranilate and chloranilate are much alike. Due to the center of symmetry present in all the molecules there are only three carbon-carbon distances to be discussed.

The three compounds are clearly not quinoidal, since they have two rather short carbon-carbon distances (C_1-C_2) and (C_1-C_3) of the same length, and one very long carbon-carbon bond (C_2-C_3). Further-

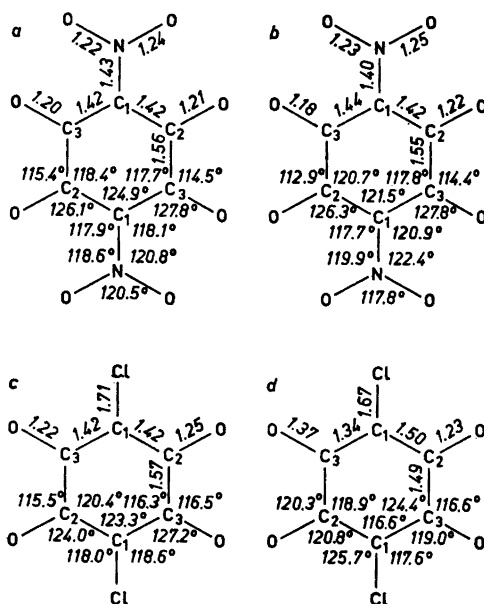
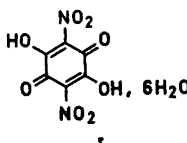
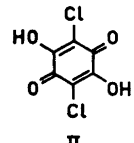
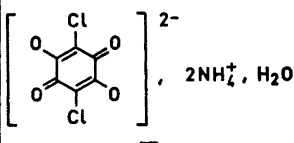


Fig. 1. Atomic distances (Å) and angles (°) in a: nitranilic acid from hexahydrate; b: nitranilate ion from ammonia salt; c: chloranilate ion from ammonia salt; d: chloranilic acid.

more the carbon-oxygen distances are equal (within our present accuracy).

Chloranilic acid, on the other hand, is in the quinoidal form. It has the same ring system as found by Robertson² and Trotter³ in benzoquinone, and it has two kinds of carbon-oxygen distances. The shorter distances correspond to two carbonyl groups and the longer ones to C—OH groups (hydrogen has not yet been located). We had expected the nitranilic acid molecule to be in the quinoidal form also, the results however do not support our expectations. The acid is very strong ($pK_I = -3.5$ and $pK_{II} = -0.5$) and it is probably dissociated into nitranilate and oxonium ions in the solid hexahydrate. This proposal needs further experimental support which we hope to gain by location of the hydrogen atoms. All the molecules are planar except for the nitro group. This is twisted around the C—N bond so that the attached oxygen atoms are out of the ring plane.

Table 1.

Name	Nitranilic acid hexahydrate, I	Chloranilic acid, II	Ammonium chloranilate monohydrate, III
Space group	$P2_1/c$	$P2_1/a$	$C2/c$
a Å	3.65 ± 0.01	10.03 ± 0.02	17.05 ± 0.02
b Å	19.40 ± 0.01	5.55 ± 0.02	4.79 ± 0.02
c Å	9.18 ± 0.01	7.59 ± 0.02	14.09 ± 0.02
β	$94.3^\circ \pm 0.1$	$123.0^\circ \pm 0.5$	$119.0^\circ \pm 0.5$
Density obs. (flotation) g/cm ³	1.729 ± 0.005	1.957 ± 0.008	1.718 ± 0.005
Density calc.	1.731	1.959	1.725
Z	2	2	4
Number of F_{obs} used in refinement	717 ($0kl \rightarrow 2kl$)	464 ($h0l \rightarrow h3l$)	495 ($h0l \rightarrow h2l$)
R index at present	0.13	0.16	0.14
			

Refinements of the structures with more complete experimental data and with anisotropic temperature factors are proceeding.

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Correction to "On the Biosynthesis of Lichen Substances. Part I. The Depside Gyrophoric Acid"*

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On p. 331 in Table 1 (last line) the value of Kuhn-Roth carbon dioxide is incorrectly stated. It should read 16.8.

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