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Crystal and Molecular Structure of 2-Diazonium-4-phenolsulfonate Monohydrate, $C_6H_3.N_2^+.SO_3^-.OH.H_2O$

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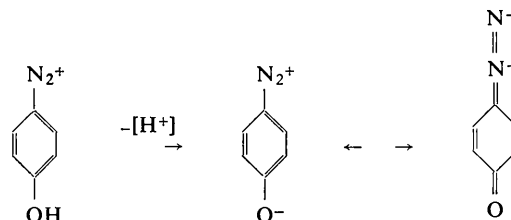
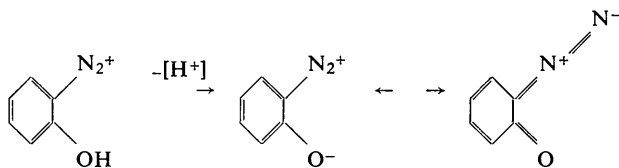
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The absorption spectra of a stable product of diazotization of 2-amino-4-phenolsulfonic acid exhibit characteristics of a diazonium salt; this is an exception to the generally established rule that a diazo-oxide structure is more stable than the corresponding diazonium salt. The monohydrate of the compound was therefore studied by the X-ray diffraction method. The crystal belongs to the monoclinic system with $a = 8.97 \pm 0.02$, $b = 11.63 \pm 0.02$, $c = 8.62 \pm 0.02$ Å, $\beta = 102.5^\circ$; the space group is $P2_1/n$. The structure was determined from three-dimensional intensity data obtained with Cu $K\alpha$ radiation. The observed bond distances and angles in the molecule established that the molecule possesses a zwitterion configuration, 2-diazonium-4-phenolsulfonate monohydrate, $C_6H_3N_2^+SO_3^- \cdot OH \cdot H_2O$. The crystal structure is essentially ionic with short intermolecular N—O electrostatic attraction (2.88 Å) between the diazonium groups and the sulfonate groups. The water molecules connect the zwitterions by forming a three-dimensional network of O—H \cdots O hydrogen bonds. The unusual stability of the diazonium structure is explained in terms of the zwitterion configuration and the crystal structure of the compound.

Introduction

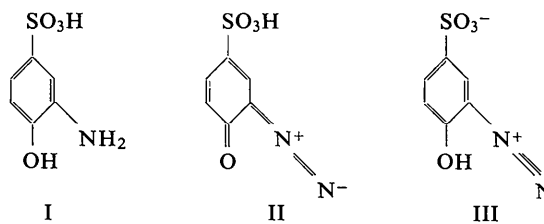
The diazo-oxides are stable compounds derived from *ortho*- and *para*-hydroxy substituted aromatic diazonium salts, sometimes through the action of alkali.



The structure of these compounds, once thought to be cyclic, is now generally accepted to be resonance hybrid of the type shown above, and the resultant reson-

ance energy is held to be responsible for the stability of these compounds. Generally, whenever the diazonium salt and the diazo-oxide from a particular amine are isolable, the diazo-oxide is by far the more stable compound.

Morgan & Porter (1915) first diazotized 2-amino-4-phenolsulfonic acid, I, and isolated an extremely stable product which they classified as a diazo-oxide, II, owing to its lack of the characteristic lability of diazonium compounds. The present X-ray work on the monohydrate crystal of this compound which was thought to be 2-diazo-1-oxide-4-benzenesulfonic acid monohydrate, the monohydrate of II, was undertaken when it was found that the visible and infrared absorption spectra of the crystal were characteristic of a diazonium salt and not of a diazo-oxide.



For example, a typical N-N absorption peak for a diazonium compound lies near 4.40μ and the corresponding peak for a diazo-oxide lies near 4.75μ (Whetzel, Hawkins & Johnson, 1956); the N-N peak for the present substance taken in KBr lies at 4.44μ . If the substance is indeed a diazonium compound, it must exhibit a rather interesting zwitterion configuration, III.

Table 1. Atomic coordinates in fraction of cell edges their standard deviations in 10^{-3} \AA and anisotropic temperature factors, β_{11} to β_{23} as used in the expression:

$$\exp[-\{h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}\}]$$

(a) Atomic coordinates

	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$
C(1)	0.3672	7	0.5500	7	0.1660	6
C(2)	0.3049	5	0.4666	6	0.2490	6
C(3)	0.3933	5	0.3814	7	0.3460	6
C(4)	0.5946	5	0.3861	4	0.3608	6
C(5)	0.6130	6	0.4732	7	0.2763	6
C(6)	0.5239	5	0.5532	6	0.1818	7
N(I)	0.1472	5	0.4698	6	0.2404	6
N(II)	0.0249	7	0.4708	7	0.2347	9
O(p)	0.2687	4	0.6225	5	0.0728	4
O(I)	0.8116	5	0.3430	6	0.5350	5
O(II)	0.6848	6	0.1876	6	0.3680	5
O(III)	0.5915	6	0.2460	6	0.5968	5
S	0.6688	1	0.2823	1	0.4750	1
O(w)	0.7127	5	0.2039	5	0.0400	5

(b) Thermal parameters

The standard deviations are of the order of 0.001.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0141	0.0066	0.0136	0.0035	0.0007	0.0027
C(2)	0.0098	0.0060	0.0169	-0.0002	-0.0003	-0.0019
C(3)	0.0105	0.0068	0.0169	-0.0027	-0.0036	0.0003
C(4)	0.0112	0.0061	0.0167	0.0007	0.0037	0.0011
C(5)	0.0112	0.0065	0.0168	0.0022	0.0009	0.0010
C(6)	0.0107	0.0072	0.0188	-0.0021	0.0018	-0.0023
N(I)	0.0097	0.0061	0.0245	0.0016	-0.0009	-0.0026
N(II)	0.0138	0.0096	0.0365	-0.0038	0.0056	-0.0031
O(p)	0.0130	0.0071	0.0211	0.0020	-0.0009	0.0044
O(I)	0.0092	0.0092	0.0240	0.0002	-0.0066	0.0038
O(II)	0.0174	0.0073	0.0214	0.0078	-0.0069	-0.0004
O(III)	0.0188	0.0082	0.0222	0.0029	0.0036	0.0069
S	0.0121	0.0060	0.0166	0.0031	-0.0023	0.0004
O(w)	0.0162	0.0075	0.0204	-0.0003	0.0035	0.0017

was started by the use of the full-matrix method on an IBM 7094 at the IBM Research Center, Yorktown Heights, New York; the number of parameters to be refined was 127. The weighting factor for the least-squares method was $\omega = 1.0/|F_{\text{obs}}|$ when $|F_{\text{obs}}| \geq 35$; $\omega = 2.0/|F_{\text{obs}}|$ when $10 \leq |F_{\text{obs}}| < 35$; and $\omega = 1.5/|F_{\text{obs}}|$ when $|F_{\text{obs}}| < 10$; the non-observed reflections were given zero weights. After the introduction of anisotropic thermal factors, the structure refined rather smoothly, and after five cycles the convergence was observed through smallness of the improvement in the residuals (less than one-tenth of the standard deviations), the final R value being 0.128. At no time was the contribution of hydrogen atoms included in the computation since the intensity data, collected photographically, were not considered to be of sufficient quality. The atomic scattering factors used in the computation were those for neutral atoms listed in *International Tables for X-ray Crystallography* (1962).

The positional and thermal parameters for all non-hydrogen atoms are given in Table 1; the designation of the atoms to be used hereafter is shown in Fig. 1. The estimated standard deviations of the atomic coordinates are calculated in the usual manner and are also in Table 1. The observed and calculated structure factors are listed in Table 2.

As shown from Table 1, there exists a marked anisotropy in the thermal motion of each atom. In order to interpret the thermal motion, the temperature factors $\beta_{11} \dots \beta_{23}$ were decoded into the amplitudes and directions of thermal vibration ellipsoids by a program on the 7094; some typical examples are listed in Table 3. Since no absorption correction was made to the observed intensity data, the values of amplitudes in Table 3 have only relative significance. Even so, it is quite clear that the nitrogen atoms of the diazonium group, especially the terminal nitrogen, N(II), show marked anisotropy, the latter with amplitudes of 10.7, 5.6 and $3.7 \times 10^{-16} \text{ cm}^2$ * for the three principal axes of the ellipsoid. Since the molecules are connected to each other by a complicated combination of forces, no quan-

titative analysis of the thermal motion was made other than the evaluation of the principal directions of the ellipsoids.

Discussion of the results

The atomic coordinates and their standard deviations thus determined were used in the calculation of all interatomic distances shorter than 5.0 Å. Important bond angles as well as the equation of the least-squares plane passing through the benzene ring are obtained in the normal fashion. These values will be used in the discussions of the structure.

(a) The molecular configuration

The bond distances and angles in the molecule are shown in Figs. 2, 3 and 4; their standard deviations are also listed in these Figures.

The purpose of this study was to substantiate the results of the infrared and visible spectroscopic examinations and to seek a possible explanation of this apparently anomalous circumstance, *i. e.* that the supposedly unstable modification is, in reality, the only stable form. Translated into crystallographic terms, this means that, first, it had to be shown that the molecular structure of the compound was a diazonium-benzenoid structure, III, with little or no contribution of the imino-quinoid structure such as II, and second that some plausible mechanism existed which stabilized the normally unstable diazonium-benzenoid structure. A systematic study of the observed bond lengths in Fig. 2 reveals that it has a diazonium-benzenoid structure. Therefore, the molecule is a zwitter-ion in the crystal containing a negatively charged sulfonate group and a positively charged diazonium group. The apparent contradiction arising out of the stability of the diazotized product of 2-aminophenol-4-sulfonic acid is reconciled with existing ideas on molecular structure when one considers the existence of the strongly acidic sulfonate group and the intermolecular interactions within the monohydrate crystal, which are described in the following section.

The benzene ring is a slightly distorted hexagon with C-C distances varying from 1.37 to 1.43 Å (average, 1.39 Å) and the bond angles are all around the expected value of 120° (117 to 124°). The observed C(3)-C(4)

* These values are expressed in the same unit as the conventional isotropic temperature factor to facilitate the comparison between the two different schemes.

Table 3. Interpretation of the anisotropic thermal parameters for C(2) and the diazonium nitrogen atoms

	Temperature factor in 10^{-16} cm^2	Direction cosines with respect to		
		<i>a</i>	<i>b</i>	<i>c</i>
C(2)	5.59	-0.299	-0.142	0.833
	2.63	0.970	0.257	0.553
	3.22	0.288	-0.956	0.025
N(I)	7.83	-0.191	-0.145	0.887
	2.67	0.932	-0.337	0.372
	3.28	0.308	0.931	0.273
N(II)	10.74	-0.035	-0.069	0.953
	3.70	0.880	0.471	0.291
	5.58	0.473	-0.880	0.082

and C(5)–C(6) distances discourage the conclusion that the molecule exists as a resonance hybrid of the diazonium-benzenoid and imino-quinoid forms; this can be substantiated by the bond distances in chloranil (Chu, Jeffrey & Sakurai, 1962), a typical structure where single and double bonds exhibit separations of 1.49 and 1.29 Å respectively. The planar part of the molecule is studied by evaluating the best plane through the six carbon atoms of the ring; the equation of the plane obtained by the least-squares method is:

$$0.0851X + 0.6124Y + 0.7860Z = 4.7618,$$

where $X = ax + cz \cos \beta$, $Y = by$, and $Z = cz \sin \beta$. The shifts of the atoms from this plane are shown in Fig. 5; a negative value of the shift means that the atom and the origin of the coordinate system lie on the same side of the plane. The atoms in the ring are coplanar within experimental error; however, the shifts of C(2), N(I) and N(II) indicate that the linear diazonium group is inclined from the plane by about 3.4° . The inclination of the diazonium group as a whole from the plane bears some relationship to the thermal vibration of those three atoms; comparison of the three ellipsoids in Table 3 reveals that from C(2) to N(II), the amplitudes of the vibration increase regularly, while the directions of the maximum amplitude remain almost the same.

The observed distances in the C(2)–N(I)–N(II) grouping further preclude the resonance hybrid of the diazonium-benzenoid and the imino-quinoid structures. The C(2)–N(I) distance of 1.41 Å can be compared with those of 1.47 and 1.27 Å which are the expected pure single and double bond distances, respectively. The corresponding distance in benzenediazonium chloride as determined by a three-dimensional crystal structure analysis is 1.39 Å (Romming, 1962). It is then rather obvious that the C(1)–O(*p*) bond should be close to a single bond. The observed separation of 1.35 Å is again compared with similar aromatic C–O bond distances, e.g. 1.35 Å in resorcinol (Bacon & Curry, 1956) and others, whereas C=O bond distances are around 1.2 Å [1.195 Å for chloranil (Chu, Jeffrey & Sakurai, 1962)]. The N(I)–N(II) distance of 1.08 Å compares with that of 1.10 Å for benzene diazonium chloride (Rømming, 1962) and a figure of 1.10 Å for the pure triple bond (Pauling, 1960).

The sulfonate group is a distorted tetrahedron and the C(4)–S distance of 1.76 Å can be compared with those of 1.74 Å in magnesium and zinc *p*-toluenesulfonates (Hargreaves, 1960) and of 1.76 Å in similar benzenesulfonates (Broomhead & Nicol, 1948). The S–O distances, as shown in Fig. 2, are all normal and comparable with the values in other substances: 1.47 to 1.41 Å in the above mentioned sulfonates; 1.43 to 1.45 Å in sulfamic acid (Osaki, Tadokoro & Nitta, 1955); 1.448 to 1.465 Å in taurine, $\text{NH}_3^+\text{--CH}_2\text{--CH}_2\text{--SO}_3^-$ (Okaya, 1966). The average C–S–O and O–S–O angles for the present structure are 105 and 113° , respectively. It has been well established that the C–S–O angles in sulfonate groups are always smaller than the

tetrahedral angles whereas the oxygen atoms tend to have larger separations with each other by making O–S–O angles of 110° or more. [See for an example of aromatic sulfonates, recent accurate data (Okaya, 1967) on ammonium acid *o*-carboxybenzenesulfonate,

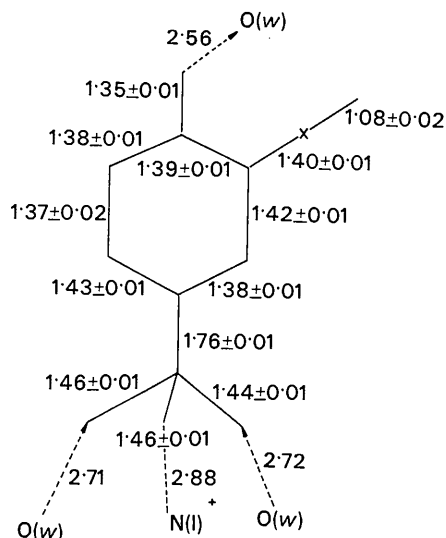


Fig. 2. Bond distances in the zwitterion molecule. Separations for the ionic contact and the hydrogen bond approaches are also shown.

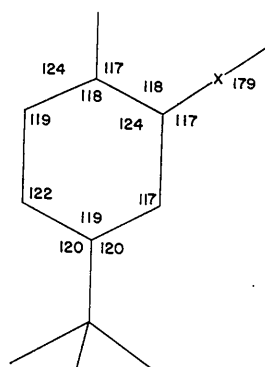


Fig. 3. Bond angles in degrees.

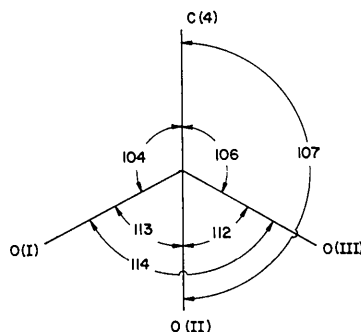


Fig. 4. Bond angles in the sulfonate group in degrees.

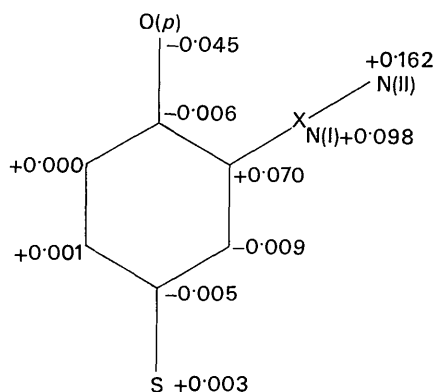


Fig. 5. Planarity of the molecule. The deviations of atoms from the least-squares plane are indicated (\AA).

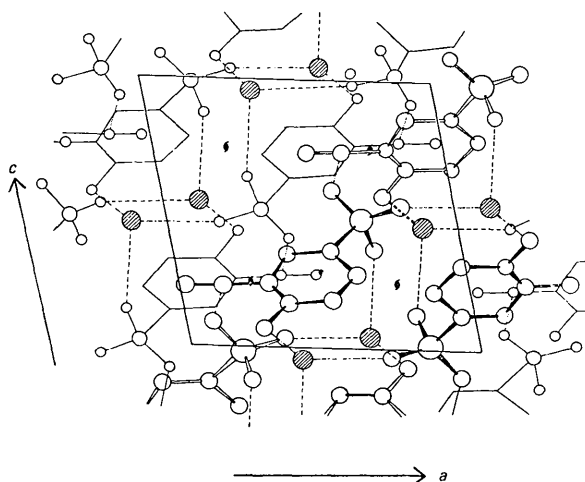


Fig. 6. Projection of the structure along the b axis. Short intermolecular approaches are given by broken lines. Shaded circles represent water molecules.

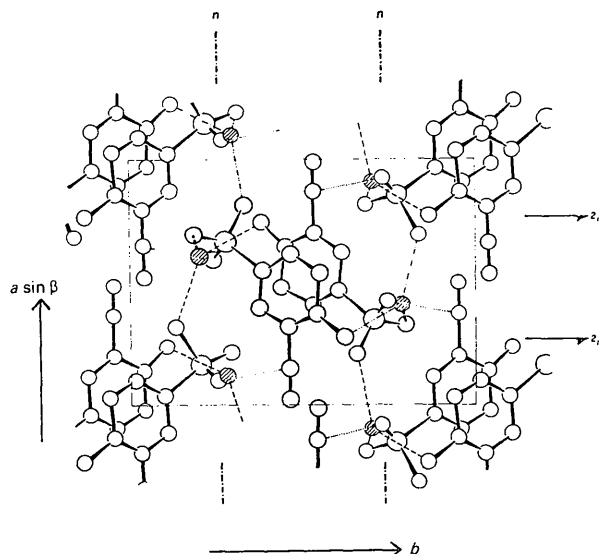


Fig. 7. Drawing of the structure projected down the c axis.

$\text{NH}_4\text{C}_6\text{H}_4\text{COOHSO}_3$: C-S, 1.775 \AA C-S-O, 106.3° and O-S-O, 112.3°.

(b) *The crystal structure, hydrogen-bond system*

The crystal structure of this aromatic zwitterion compound is essentially ionic with electrostatic interaction between positive diazonium groups and negative sulfonate groups; the water molecules are involved in a hydrogen-bond system connecting these zwitterions together through sulfonate-water-hydroxyl linkages. The general feature of the structure is illustrated in Figs. 6 and 7 as its projections along the b and c axes, respectively. The ionic interaction is found between N(I) of the diazonium group of one molecule and O(II) of the sulfonate group of another molecule related to the first by an n -glide; N-O distance is 2.88 \AA . Since no proton is available from the sulfonate group, this short distance is a result of the ionic interaction and not a hydrogen bond. The interaction results in the shift of the linear diazonium group out of the plane of the benzene ring towards the indicated sulfonate oxygen atom; the exact nature of the shift was discussed earlier. The molecules are then connected by a three-dimensional hydrogen-bond system, the water molecules being active as intermediaries. As shown in Figs. 6 and 7, the water molecule connects two sulfonate groups related by an n -glide forming a sheet-like hydrogen-bond system perpendicular to the b axis. The OH group makes a hydrogen bond to the water molecule, through which two aromatic molecules related by a twofold screw axis are connected; thus infinite spiral chains along the b axis are formed. These two hydrogen-bond systems therefore form a three-dimensional network of hydrogen-bonds. The hydrogen bonds made by the water molecules are 2.71 and 2.72 \AA , respectively, and are of medium strength as compared with the O-H...O bonds in similar substances; the six hydrogen-bond distances in zinc and magnesium p -toluenesulfonate hexahydrates (Hargreaves, 1960) vary from 2.72 to 2.82 \AA , the average being 2.78 \AA . The third hydrogen-bond of 2.56 \AA formed by the OH group to the water molecule is stronger than the other two hydrogen-bonds but comparable with other hydrogen-bond distances involving hydroxyl groups and water molecules. The water molecule is surrounded by three oxygen atoms, the quartet forming a distorted pyramid with the water molecule sitting at the apex. The arrangement is quite common among the structure of various hydrates of organic compounds.

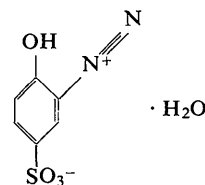
An observed red shift of the visible absorption maximum, from 388 μ in acid solution to 488 μ in basic solution, in the course of base titration favors the conclusion that the proton is associated with the phenolic oxygen and substantiates the above assignment of proton donors and acceptors in the last hydrogen bond around the water molecule. In this connection it can be safely assumed that the molecule does not make a 'double zwitterion' salt of a hydronium ion (see Fig. 8). However, it would be desirable to confirm the above

conclusion directly by the neutron diffraction method.

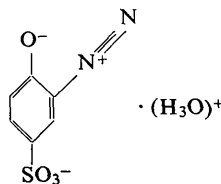
This rather fully developed system of hydrogen bonds together with the ionic interaction between positive diazonium nitrogen atoms and sulfonate oxygen atoms in all probability provides the necessary minimization of the energy to make the diazonium form so stable. Also the zwitterion character of the molecule and the electrostatic attraction in the crystal structure account for the infeasibility of preparing alkaline salts of the compound.

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(a) 2-Diazonium-4-phenolsulfonate monohydrate



(b) The less likely hydronium 2-diazonium-4-sulfophenolate

Fig. 8. Possible chemical formulas.

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Crystal and Molecular Structure of 3-Hydroxy-5-phenylisoxazole (β form)

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The crystal structure of the β form of 3-hydroxy-5-phenylisoxazole has been determined from three-dimensional X-ray data. The crystals, which are obtained either by sublimation or by slowly cooling the melt in the atmosphere, are monoclinic, space group $P2_1/c$, with four molecules in the unit cell. The cell dimensions are: $a=8.75$, $b=5.64$, $c=16.10$ Å, $\beta=95.9^\circ$. The structure was refined by the block-diagonal least-squares method to a final R value of 0.084 for 1116 observed reflexions. The molecule is present in the hydroxyl form and the values of bond distances suggest a conjugation effect between isoxazole and benzene rings. Pairs of molecules form dimers linked together by two hydrogen bonds across a centre of symmetry.

Introduction

In the course of the investigation of the crystal structure of 3-hydroxy-5-phenylisoxazole (Fig. 1), two crystalline forms were identified. One (α) is obtained when an *n*-hexane solution is allowed to crystallize; the crystals are colourless prisms, space group $P2_1/c$. The crystal

structure has already been reported in a short communication (Cannas & Mocci, 1965) and the refinement, based on three-dimensional data, is now being completed. A second type of crystallization (β) was detected during the determination of the melting point of the α form with a hot stage microscope. It was noticed that at a temperature around 140°C the compound sublimes