

The Crystal and Molecular Structure of the *meso*-Ionic Sydnone, Anhydro-5-mercapto-2,3-diphenyltetrazolium Hydroxide

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Abstract: The crystal and molecular structure of the sydnone, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide, has been determined by single-crystal, three-dimensional X-ray crystallographic techniques. The results show that there is extensive electron delocalization in the tetrazole ring which is coplanar with the exocyclic sulfur atom and confirm the aromatic character of the sydnone. The sandwich-type packing of the tetrazole rings between sulfur atoms in the crystal lattice provides evidence for a dipolar *meso*-ionic structure.

Many substituted tetrazoles show a variety of interesting properties. For instance, they exhibit certain types of physiological activity by affecting the nervous system in a number of ways.¹ They are, in general, good π -electron donors and form complexes with transition metal ions.² Several tetrazoles with appropriate substituents are also examples of a group of compounds called sydnones, which have aromatic character but cannot be represented satisfactorily by a conventional covalent structure; the term *meso*-ionic was used to describe the structure of such sydnones.³

A sydnone with a tetrazole ring system which has been known for a very long time is the orange-colored compound, dehydrodithizone, which is one of the oxidation products of dithizone.^{4,5} Although initially, there has been some controversy about the exact manner in which to formulate this compound,^{4,6} sufficient evidence has accumulated recently from a study of its physical and chemical properties to indicate that it is most probably a *meso*-ionic sydnone.⁷ We have prepared this oxidation product of dithizone by a novel method⁸ and have carried out a complete X-ray structure determination of the compound. The results are reported below.

Experimental Section

Orange-colored crystals were obtained by the slow evaporation of an ethanol solution containing a mixture of the nickel(II) chelate of 1,5-diphenylthiocarbazono, (dithizone), and 1,10-phenanthroline. The orange compound was identical with dehydrodithizone (C₁₃H₁₀N₄S), an oxidation product of dithizone that has been reported by several workers.⁴⁻⁷ Presumably, the ligand dithizone was displaced from its nickel(II) chelate by the ligand 1,10-phenanthroline, and the oxidation of the free dithizonate ion occurred on slow evaporation of the solution.

The orange crystals were found to be monoclinic and the cell dimensions, determined from oscillation and Weissenberg photographs (calibrated with aluminum wire) obtained with Cu K α radiation (λ 1.5418 Å) and precession photographs obtained with

Mo K α radiation (λ 0.7107 Å), were found to be: $a = 15.49 \pm 0.02$ Å; $b = 12.12 \pm 0.02$ Å; $c = 6.98 \pm 0.01$ Å; $\beta = 109.0 \pm 0.3^\circ$; $V = 1239.0$ Å³; $d_{\text{obsd}} = 1.37 \pm 0.01$ g cm⁻³ (by flotation in ZnCl₂ solution); $d_{\text{caled}} = 1.36$ g cm⁻³ and $Z = 4$. The systematic absences (hkl , $h + k + l = 2n + 1$; and $h0l$, $h = 2n + 1$) indicated that the space group was either Ic or I2/c. The latter space group, I2/c, was confirmed by the structure analysis.

A crystal 0.48-mm long with a cross-sectional area of (0.20 \times 0.13) mm² was selected for recording the $hk0$ - $hk4$ intensity data with Cu K α radiation, using the multiple-film equinclination Weissenberg technique. A second crystal, 0.48-mm long and with (0.39 \times 0.43) mm² cross-sectional area, was used to record the intensity data from $0kl$ to $9kl$. The intensities were estimated visually with a calibrated density strip. The range of relative intensities was 1-65,000. The data were scaled by means of the common reflections and a total of 1121 independent reflections was obtained, of which 1051 were nonzero reflections. Lorentz, polarization, and spot-shape corrections were applied in the usual manner and no corrections for absorption were made since the value of the linear absorption coefficient, μ (Cu K α), was 22.3 cm⁻¹. The atomic scattering factors from the "International Tables" were used.⁹

Normalized structure factors (E values) were calculated and the experimental as well as the theoretical values (for centric and noncentric systems), for several functions of E are shown in Table I. These results show that the structure is probably centric, but the ambiguity in the choice between the space groups I2/c and Ic is not completely resolved. Hence the initial stages of the structure analysis were carried out in the acentric space group Ic.

Table I. Statistical Distribution of Normalized Structure Factors (E Values)

	Experimental	Theoretical	
		Centro-symmetric	Noncentro-symmetric
$ E > 3.0$, %	0.27	0.30	0.01
$ E > 2.0$, %	3.48	5.00	1.80
$ E > 1.0$, %	34.46	32.00	37.00
$\langle E \rangle$	0.820	0.798	0.886
$\langle E ^2 - 1 \rangle$	0.906	0.968	0.736

The two-dimensional Patterson synthesis, $P(UV)$, $P(VW)$, $P(UW)$, and the three-dimensional Patterson synthesis, $P(UVW)$, were calculated. The positional parameters of the sulfur atom were determined first. In the space group Ic, there are no restrictions on the x and z parameters of the sulfur atom. Therefore the values $x = 1/2$ and $z = 1/8$ were selected, and the y parameter of the sulfur atom was found to be 0.640 from the Patterson synthesis. The initial value of R , $R = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$, was 56% with the positional parameters of only the sulfur atom. The calculated

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electron density map however, had pseudo-symmetry. A comparison of this map with the $P(UW)$ and $P(UVW)$ maps suggested four possible orientations of the phenyl groups. Structure-factor calculations for each of the four independent models were carried out and the best R value obtained was 29%. The electron density map calculated for the latter case clearly showed the presence of a twofold axis in the molecule. Three cycles of full-matrix least-squares refinement¹⁰ with isotropic temperature factors for all the atoms (excluding the hydrogen atoms) reduced the R value to 14%. These results confirmed the presence of a twofold axis in the molecule and the space group was changed from Ic to $I2/c$. The positions of the hydrogen atoms in the phenyl ring were calculated on the basis that the C-H distance was 1.08 Å. The refinement was continued with anisotropic temperature factors; after three cycles (in which the hydrogen atom positions were not refined) a final R value of 7.8% was obtained for the 1051 observed reflections, and 8.2% for all the 1121 reflections. The quantity minimized was $\sqrt{\sum w(F_o - F_c)^2}$. Cruickshank's weighting scheme¹¹ was used where $w = 1/(A + B|F_o| + C|F_c|^2)$, and $A = 5.0$, $B = 1.0$, and $C = 0.014$. In the final refinement cycle the maximum shift was 0.005 Å in the z parameter of atom C_6 . The final atomic parameters and the anisotropic thermal parameters, together with their estimated standard deviations, are shown in Tables II and III, respectively.

Table II. Final Atomic Parameters

Atom	x	y	z	$B, \text{Å}^2$
S	0.5000 (—)	0.6421 (1)	0.5000 (—)	
C ₁	0.5000 (—)	0.5029 (3)	0.5000 (—)	
N ₁	0.4235 (2)	0.4395 (2)	0.4556 (4)	
N ₂	0.4553 (2)	0.3378 (2)	0.4747 (4)	
C ₂	0.3962 (2)	0.2438 (2)	0.4587 (5)	
C ₃	0.3158 (2)	0.2423 (3)	0.3001 (6)	
C ₄	0.2554 (3)	0.1562 (4)	0.2866 (7)	
C ₅	0.2796 (3)	0.0736 (3)	0.4320 (7)	
C ₆	0.3607 (3)	0.0763 (3)	0.5870 (6)	
C ₇	0.4214 (3)	0.1635 (3)	0.6054 (6)	
H ₁	0.298	0.308	0.183	4.0
H ₂	0.191	0.153	0.162	4.0
H ₃	0.234	0.006	0.421	4.0
H ₄	0.378	0.012	0.704	4.0
H ₅	0.487	0.167	0.731	4.0

Table III. Anisotropic Thermal Parameters

Atom	$10^6\beta_{11}$	$10^6\beta_{22}$	$10^6\beta_{33}$	$10^6\beta_{12}$	$10^6\beta_{13}$	$10^6\beta_{23}$
S	465 (8)	428 (8)	1714 (125)		340 (13)	
C ₁	346 (19)	509 (28)	1146 (154)		322 (35)	
N ₁	380 (14)	463 (18)	1743 (144)	35 (11)	466 (26)	32 (24)
N ₂	335 (13)	458 (17)	1467 (137)	7 (11)	479 (24)	68 (23)
C ₂	326 (14)	506 (20)	1820 (145)	-66 (12)	546 (27)	-228 (28)
C ₃	409 (18)	710 (26)	2391 (157)	-14 (16)	526 (36)	-330 (39)
C ₄	438 (20)	881 (31)	3346 (186)	-120 (18)	722 (42)	-749 (49)
C ₅	597 (22)	730 (29)	3826 (189)	-244 (19)	1114 (47)	-726 (47)
C ₆	652 (24)	620 (26)	2949 (177)	-126 (19)	1025 (47)	-78 (40)
C ₇	527 (19)	578 (22)	2082 (152)	-46 (16)	817 (35)	-37 (33)

Description of Structure

In the body-centered centric space group $I2/c$, the position of the origin was selected on a twofold axis and

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not at a center of symmetry. The coordinates of the equivalent positions are $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, -z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z; x, -y, \frac{1}{2} + z$. The special positions are $0, y, 0$; and $0, -y, \frac{1}{2}$, which lie on a twofold axis.¹² The sulfur atom and the carbon atom in the tetrazole ring lie on this twofold axis and two nitrogen atoms, six carbon atoms, and five hydrogen atoms occupy general positions. The remaining atoms in the molecule $C_{13}H_{10}N_4S$ are related by the twofold axis (Figures 1 and 2). Figure 1 shows a perspective view of the molecule obtained by ORTEP,¹³ in which the thermal motions of the hydrogen atoms have been arbitrarily fixed. Figure 2 shows the bond distances and bond angles in the molecule.

There are no true single or double-bond distances in the tetrazole ring. The only single-bond distance in the molecule is from the nitrogen atom in the tetrazole ring (N_2) to a carbon atom of the phenyl group (C_2). The N-N distances in the tetrazole ring are identical (1.316 Å) and the C-N distances are 1.360 Å. The ring is almost exactly planar (the maximum deviation being 0.003-Å from the least-squares plane), and is an irregular pentagon. The sulfur atom also lies on the plane formed by the tetrazole ring and the C-S distance is 1.687 Å, which is intermediate between a double-bond and a single-bond distance. These bond distances indicate that there is considerable electron delocalization in the ring and the exocyclic sulfur atom. It is of interest that in the structures of three other tetrazole ring systems that have been reported recently, the tetrazole rings are planar.¹⁴⁻¹⁶ A summary of the N-N bond distances in these three structure (Table IV) shows that the r_{23} distances are shorter than the r_{12} and r_{34} distances. In the sydnone structure, however, the r_{12} , r_{34} , and r_{23} distances are all equal within experimental error, and as a consequence there is a residual positive charge in the tetrazole ring and a similar negative charge on the exocyclic sulfur atom.

The bond distances and bond angles in the phenyl group are normal. The maximum deviation of a carbon atom from the least-squares plane of the phenyl ring

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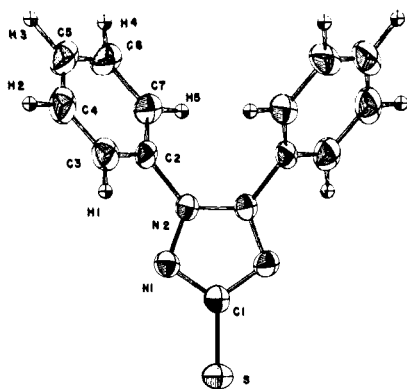


Figure 1. An ORTEP plot of a perspective view of the molecule. The thermal motions of the hydrogen atoms have been fixed arbitrarily.

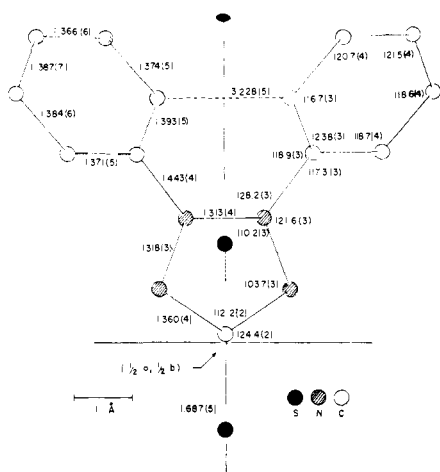


Figure 2. Bond distances and bond angles in the molecule.

is 0.01 Å for C₆. The dihedral angle between the plane of the tetrazole ring and the plane of the phenyl ring is 45.0°. Hence there is little or no conjugation between

Table IV. Bond Distances in Tetrazole Ring Systems

Molecule	Structure	Bond length, Å
Anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide		$r_{12} = 1.318 (3)$ $r_{23} = 1.313 (4)$ $r_{15} = 1.360 (4)$
Hydrazine salt of 5-aminotetrazole ¹⁴		$r_{12} = 1.356 (8)$ $r_{23} = 1.295 (7)$ $r_{34} = 1.346 (6)$ $r_{45} = 1.302 (8)$ $r_{15} = 1.318 (6)$
Sodium tetrazole monohydrate ¹⁵		$r_{12} = 1.348 (2)$ $r_{23} = 1.310 (2)$ $r_{15} = 1.329 (3)$
5-Aminotetrazole monohydrate ¹⁶		$r_{12} = 1.381 (15)$ $r_{23} = 1.255 (15)$ $r_{34} = 1.373 (15)$ $r_{45} = 1.321 (15)$ $r_{15} = 1.329 (15)$

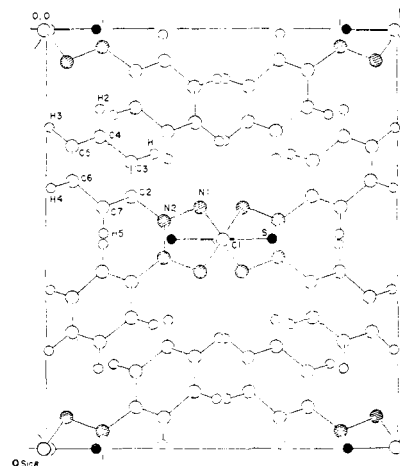


Figure 3. Projection of the contents of the unit cell down the *c* axis.

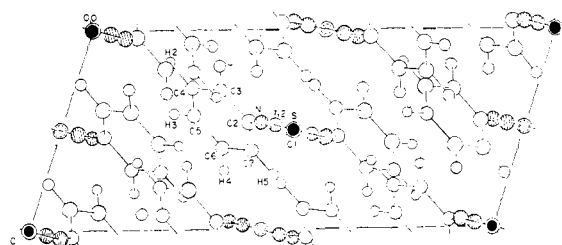
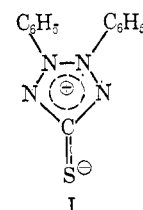


Figure 4. Projection of the contents of the unit cell down the *b* axis.

the two ring systems. This is confirmed further by the C₂-N₂ distance, which is clearly a single-bond distance.

The two phenyl groups in the molecule are related by a twofold axis. The dihedral angle between the planes of the two phenyl groups is 61.2°. The shortest intramolecular nonbonded C-C distance is 3.228 Å between C₇ and C₇'.

There are several unusual features in the crystal structure of this sydnone containing a tetrazole ring. Figures 3 and 4 show the packing of molecules in the crystal. Each sulfur atom is sandwiched between the planes of two tetrazole rings which are at a distance of 3.482 Å on either side of the sulfur atom. The tetrazole rings are also sandwiched between the two sulfur atoms, although the sulfur atoms are not directly above and below the center of the tetrazole ring. The nonbonded contact S...N₁ = 3.727 Å and S...N₂ = 3.512 Å. Therefore the crystal consists of alternating tetrazole rings and sulfur atoms in infinite chains along the crystallographic *c* axis. The crystal habit also reflects this tendency because the *c* axis is elongated. The reason for this type of crystal packing can be attributed to a residual positive charge in the tetrazole ring and a residual negative charge on the sulfur atom. This confirms the *meso-ionic* formulation of the sydnone as shown in structure I.



The minimum intermolecular C-C distance between

phenyl rings is 3.529 Å, which suggests that there is no extensive intermolecular interaction between phenyl rings. The intense orange color of the compound must be ascribed, therefore, to the tetrazole ring system conjugated with the exocyclic sulfur atom.

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