

Structure of 1,4-Dihydrazinophthalazinium Sulfate 2·64-Hydrate

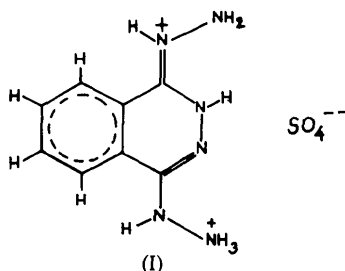
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Abstract. $C_8H_{12}N_6^+ \cdot SO_4^{2-} \cdot 2 \cdot 64H_2O$, monoclinic, $P2_1/c$, $a = 6.939$ (2), $b = 11.063$ (2), $c = 18.976$ (3) Å, $\beta = 104.72$ (2)°, $U = 1409$ Å³, $D_m = 1.59$ (1), $D_x = 1.583$ Mg m⁻³, $Z = 4$. The structure was solved by the Patterson method and refined to $R = 0.057$ for 2410 diffractometer-measured independent reflections. The crystal structure is stabilized by three-dimensional hydrogen bonding and by ring stacking, with a separation of 3.34 Å between centrosymmetrically related molecules.

Introduction. The title compound (I) is a hypotensive and antihypertensive agent used as dihydralazine or Nepresol (Druey & Tripod, 1967). This analysis was carried out to compare its molecular geometry with those of other phthalazine derivatives having similar activity: hydralazine (Stadnicka & Lebioda, 1978) and ethoxycarbonylhedralazine (Stadnicka & Lebioda, 1979).



Pale-yellow needle-shaped crystals, elongated along the a axis, were obtained by recrystallization from an aqueous solution. The space group was established from the systematic absences observed on the Weissenberg photographs. A crystal with dimensions $0.12 \times 0.10 \times 0.08$ mm was used to collect intensity data with a CAD-4 diffractometer (graphite-monochromated Cu $K\alpha$ radiation). Reflections were measured in the range $2^\circ \leq \theta \leq 60^\circ$ with a $\theta/2\theta$ scan mode and a $(0.65 + 0.2 \tan \theta)^\circ$ scan range. The fluctuation in the intensity of a standard reflection was less than 2.5%. The intensities were corrected for Lorentz and polarization effects but not for absorption [$\mu(\text{Cu } K\alpha) = 2.370$ mm⁻¹]. Of the 2731 measured independent reflections, 2410 with $|F_o| > \sigma(F_o)$ were used in the structure deter-

mination. The Patterson synthesis was solved using a fourth-order minimum image-seeking function (Buerger, 1959). In the Fourier refinement all non-hydrogen atoms of the sulfate anion, the organic cation and one water molecule were revealed. After isotropic refinement, two peaks of about $5 e \text{ \AA}^{-3}$ appeared on the difference map, one of them elongated. The models with two and three positions for the water molecules with partial occupancy factors were tested. The best convergence in the refinement was obtained for a model with only one additional variable. It was assumed that

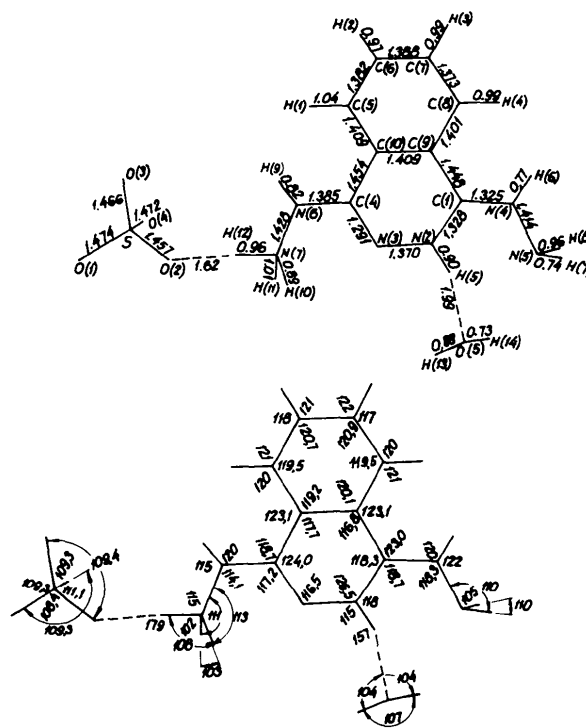


Fig. 1. Bond lengths (Å) and angles (°). Estimated standard deviations are 0.004 Å and 0.2° for bonds involving non-hydrogen atoms only and 0.03 Å and 2° for those involving H. Bond lengths and angles for water molecules not marked in the figure are: O(6)–H(15) 0.76, O(6)–H(16) 0.98 Å, H(15)–O(6)–H(16) 100°; O(7)–H(17) 1.01, O(7)–H(18) 0.70 Å, H(17)–O(7)–H(18) 111°; O(8)–H(17) 0.66, O(8)–H(18) 1.03 Å, H(17)–O(8)–H(18) 112°.

Table 1. The final atomic coordinates ($\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms) with e.s.d.'s in parentheses

	x	y	z
S	10151 (1)	10532 (1)	3261.3 (4)
O(1)	10198 (3)	11563 (2)	2774 (1)
O(2)	8566 (4)	9714 (2)	2895 (1)
O(3)	9735 (4)	10974 (2)	3936 (1)
O(4)	12098 (4)	9920 (2)	3435 (1)
O(5)	6753 (4)	2939 (2)	2232 (1)
O(6)*	1895 (8)	4296 (4)	330 (2)
O(7)†	4772 (11)	3743 (6)	483 (4)
O(8)*	5800 (10)	3982 (6)	367 (3)
N(2)	6512 (4)	4106 (2)	3537 (1)
N(3)	6889 (4)	5284 (2)	3394 (1)
N(4)	6034 (4)	2488 (3)	4220 (1)
N(5)	5435 (5)	1827 (3)	3563 (2)
N(6)	7905 (4)	7172 (2)	3818 (1)
N(7)	7416 (4)	7494 (3)	3065 (1)
C(1)	6532 (4)	3639 (3)	4183 (2)
C(4)	7406 (4)	5996 (3)	3949 (2)
C(5)	8263 (5)	6395 (3)	5299 (2)
C(6)	8384 (5)	5968 (3)	5993 (2)
C(7)	7897 (5)	4779 (3)	6105 (2)
C(8)	7295 (5)	3995 (3)	5529 (2)
C(9)	7138 (4)	4408 (3)	4819 (2)
C(10)	7610 (4)	5616 (3)	4698 (2)
H(1)	866 (4)	728 (3)	522 (2)
H(2)	892 (4)	650 (3)	640 (2)
H(3)	794 (4)	446 (3)	659 (2)
H(4)	697 (4)	315 (3)	562 (2)
H(5)	635 (4)	360 (3)	316 (2)
H(6)	604 (4)	220 (3)	459 (2)
H(7)	451 (4)	149 (3)	356 (2)
H(8)	651 (5)	128 (3)	358 (2)
H(9)	776 (5)	772 (3)	410 (2)
H(10)	799 (4)	702 (3)	280 (2)
H(11)	785 (4)	835 (3)	300 (2)
H(12)	601 (4)	753 (3)	283 (2)
H(13)	718 (4)	356 (3)	203 (2)
H(14)	760 (5)	253 (3)	235 (2)
H(15)*	156 (6)	451 (5)	994 (3)
H(16)*	149 (6)	499 (5)	58 (3)
H(17)	615 (5)	405 (4)	73 (2)
H(18)	429 (5)	414 (4)	20 (2)

* Denotes position with site-occupancy factor $k = 0.64$.

† Denotes position with site-occupancy factor $1 - k = 0.36$.

there can be two water molecules, O(6) and O(8), with an equal occupancy factor k or one molecule O(7) with an occupancy of $1 - k$. The final k of 0.64 agrees very well with the $2.64\text{H}_2\text{O}$ per molecule found in the thermogravimetric measurement. After anisotropic refinement the difference map revealed all the expected H-atom positions. The positions of the H atoms for water O(6) were also observed, together with two peaks which were attributed to the overlapping positions of the H atoms for water molecules O(7) and O(8). The full-matrix least-squares refinement was carried out with neutral-atom scattering functions and anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974). In the final least-squares cycle,

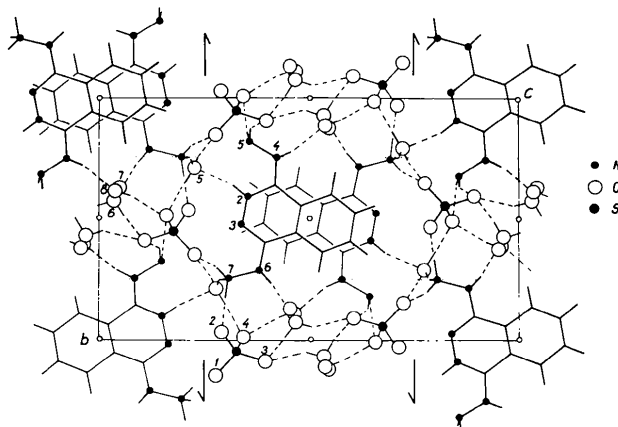


Fig. 2. Packing in the structure viewed along *a*. Hydrogen bonds are drawn with broken lines. For clarity some of molecules at the vertices of the unit-cell projection were omitted. The numbering refers to Table 1.

the maximum shift to e.s.d. ratio was less than 0.3 for non-hydrogen atoms and 0.8 for H atoms. The highest peak of $0.39 \text{ e } \text{Å}^{-3}$ on the final difference map was without chemical significance. Discrepancy factors were $R = 0.057$ and $R_G = 0.047$ where $R = \sum |\Delta F| / \sum |F|$ and $R_G = [\sum w \Delta F^2 / \sum w F^2]^{1/2}$.* The weighting scheme $w = k[\sigma^2(F_o)]^{-1}$ was used; k refined and converged to 0.253. The final positional parameters of the atoms are given in Table 1. Computations were performed with the program system *SHELX* (Sheldrick, 1975).

Discussion. The molecular dimensions and atomic notation of the cation of 1,4-dihydrizinophthalazine protonated at N(2) and N(7) together with the sulfate anion and one water molecule are shown in Fig. 1. There is no significant difference between the molecular dimensions of the phthalazine system in dihydralazine and those in hydralazine (Stadnicka & Lebioda, 1978) and ethoxycarbonylhydralazine (Stadnicka & Lebioda, 1979). The phthalazine system is almost planar but the deviations of the atoms from the best planes are statistically significant. The $\chi^2_{n-3} = \sum_n \Delta^2 / \sigma^2$ statistics (Hamilton, 1964) were 247 for the phthalazine system ($n - 3 = 7$), and 93 and 13 for the pyridazine ($n - 3 = 3$) and benzene ($n - 3 = 3$) rings respectively. The angle between the best planes through the benzene ring and the pyridazine ring is 1.59° . The equations of the best planes are $6.6585x - 2.9783y - 3.1206z = 1.9359$ and $6.6872x - 2.7414y - 2.8256z = 2.2059$ respectively.* The $-\text{NH}-\text{NH}_2$ substituent at C(1) is in

* Lists of structure factors, thermal parameters and deviations of the atoms from the best planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34053 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å) and angles (°) in the hydrogen-bonding system

$D-H \cdots A$	Acceptor position	$D \cdots A$	$H \cdots A$	$\angle DHA$
N(2)—H(5)···O(5)	x, y, z	2.835 (4)	1.99 (3)	157 (3)
N(4)—H(6)···O(8)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.756 (6)	2.01 (4)	163 (5)
[N(4)—H(6)···O(7)]	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.072 (6)	2.34 (4)	158 (4)]
N(5)—H(7)···O(4)	$-1 + x, -1 + y, z$	3.096 (5)	2.39 (3)	164 (4)
N(5)—H(8)···O(3)	$x, -1 + y, z$	3.037 (4)	2.20 (3)	146 (3)
N(6)—H(9)···O(6)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	2.836 (5)	2.04 (4)	162 (3)
[N(6)—H(9)···O(7)]	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	3.079 (5)	2.39 (4)	141 (4)]
N(7)—H(10)···O(1)	$2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.770 (4)	1.93 (3)	158 (3)
N(7)—H(11)···O(2)	x, y, z	2.627 (4)	1.62 (3)	179 (2)
N(7)—H(12)···O(5)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	2.846 (4)	1.95 (3)	154 (3)
O(5)—H(13)···O(4)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.749 (4)	1.87 (3)	177 (3)
O(5)—H(14)···O(1)	$x, -1 + y, z$	2.800 (3)	2.07 (3)	172 (4)
O(6)—H(15)···O(3)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	2.704 (6)	2.07 (5)	142 (4)
O(6)—H(16)···O(3)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.733 (6)	1.78 (6)	164 (5)
O(8)—H(17)···O(4)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.585 (6)	1.99 (6)	150 (5)
O(8)—H(18)···O(6)	x, y, z	2.714 (7)	1.75 (6)	155 (5)
[O(7)—H(17)···O(4)]	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.891 (7)	1.99 (4)	147 (4)]

the plane of the rings and there is a double bond with the phthalazine system, as in the structures mentioned above. The $-\text{NH}-\text{NH}_3^+$ substituent at C(4) has an additional H atom at N(7); the bonds at N(6) are not planar and a much weaker conjugation with the phthalazine system can be inferred. The hydrogen-bond geometry of the structure is described in Table 2 and illustrated in Fig. 2. The dihydralazine cation is the donor in the hydrogen bonds to the O atoms of four different sulfate anions and to the water molecules. All available H atoms are involved in the hydrogen-bonding system, which forms a three-dimensional net. Additional cohesive forces in the crystals are from the stacking of the molecules along **a**. The distance between molecules related by two different inversion centers is the same and has the expected value of 3.34 Å.

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4,4',5,5'-Tetramethyl- $\Delta^{2,2'}$ -bis-1,3-diselenole, TMTSF*

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Abstract. TMTSF, $\text{C}_{10}\text{H}_{12}\text{Se}_4$, crystallizes from methylene chloride in the triclinic system, space group $P\bar{1}$, with the following crystal data: $a = 6.935$ (1), $b =$

A powder specimen of the title compound was obtained through the courtesy of POLFA, Pabianice.

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8.092 (2), $c = 6.314$ (1) Å, $\alpha = 105.51$ (2), $\beta = 95.39$ (1), $\gamma = 108.90$ (2)°, $V = 316.6$ Å³, $Z = 1$, $D_m = 2.34$ (1), $D_c = 2.35$ Mg m⁻³. Full-matrix, least-squares refinement (non-hydrogen atoms anisotropic, H atoms included but not refined) based on 1327 counter-collected F_o 's led to final R and weighted R

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