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# MOLECULAR AND CRYSTAL STRUCTURE OF ACETONE N-METHYL-N-(4-CHLORO-1-PHTHALAZINYL)HYDRAZONE AND ITS BISULFATE

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UDC 547.852.7.9:548.737

Acetone N-methyl-N-(4-chloro-1-phthalazinyl)hydrazone and its bisulfate salt were subjected to x-ray diffraction study. Rotation of the fragments about the C—N (23.5°) and N—N (59.4°) bonds occurs in the hydrazone. The amino nitrogen atom is pyramidal. Protonation of the hydrazone leads to the formation of a three-ring cation, viz., the 1,3,3-trimethyl-2,3-dihydro-1,2,4-triazolo[3,4-a]-phthalazinium cation.

Data from the UV and PMR spectra constitute evidence that acetone N-methyl-N-(4-chloro-1-phthalazinyl)hydrazone (I) has a nonplanar structure (rotation about the $C_{ring}$—N and N—N bonds) [1] and behaves anomalously upon protonation, during which the amidrazone fragment undergoes ring closure to give the 1,3,3-trimethyl-2,3-dihydro-1,2,4-trazolo[3,4-a]phthalazinium cation [2]. In order to determine the precise geometry of hydrazone I and its bisulfate II we subjected them to x-ray diffraction study.

The general form of the molecule and the bond lengths and angles in hydrazone I are presented in Fig. 1.

The phthalazine system is planar within the limits of 0.050 Å. The Cl, $N_3$, and $C_9$ atoms virtually lie in the same plane, but the $N_4$ and $C_{10}$—$C_{12}$ atoms deviate considerably from it (Table 1), and, upon the whole, the molecule is not planar.

The pyridazine (P2) and benzene (P3) rings are planar within the limits of 0.020 Å, and the P2/P3 dihedral angle is 3.5° (P1/P2 1.83°), which is somewhat less than the bending of the phthalazine system in 1-dimethylamino-4-chlorophthalazine (III) (5.02°) [3] but greater than in salts of phthalazine derivatives that are protonated at the ring $N_2$ atom (1.4 and 1.6°) [4, 5].

The endocyclic bond angles are the same as in amine III [3] and with the same differences from unsubstituted phthalazine [6]. The exocyclic $N_1C_1Cl$ and $C_1C_1Cl$ angles are unequal because of short intramolecular nonvalence $Cl\cdots H_3$ [2.73(4) Å] and $Cl\cdots C_3$ [3.09(1) Å] contacts, whereas the $N_2C_8N_3$ and $C_7C_8N_3$ angles are unequal because of $N_3\cdots H_6$ (2.71 Å), $N_3\cdots C_6$ (2.97 Å), and $N_2\cdots C_9$ (2.62 Å) contacts (the peri effect). This factor also explains the certain increase in the $C_6C_7C_8$ angle as compared with the analogous angle in amine III and phthalazine [3, 6].

The $N_3$ atom has a compact trigonal-pyramidal conformation. The sum of the bond angles at $N_3$ is 340.2°, and the degree of pyramidal character [3] $C_P^N = 0.495$, which is higher than in amine III ($C_P^N = 0.327$). The $N_3$ atom deviates 0.375 Å from the $C_8C_9N_4$ plane.

The deviations of the $C_9$ and $N_4$ atoms from the P2 plane (Table 1) and the torsion angles (Table 2) constitute evidence for an angle of rotation of the hydrazone fragment about the $C_8$—$N_3$ bond from the position that is optimal for conjugation of the $N_3$ atom with the ring. A θ value of −25.8° is obtained from an analysis of the torsion angles from the Newman pro-

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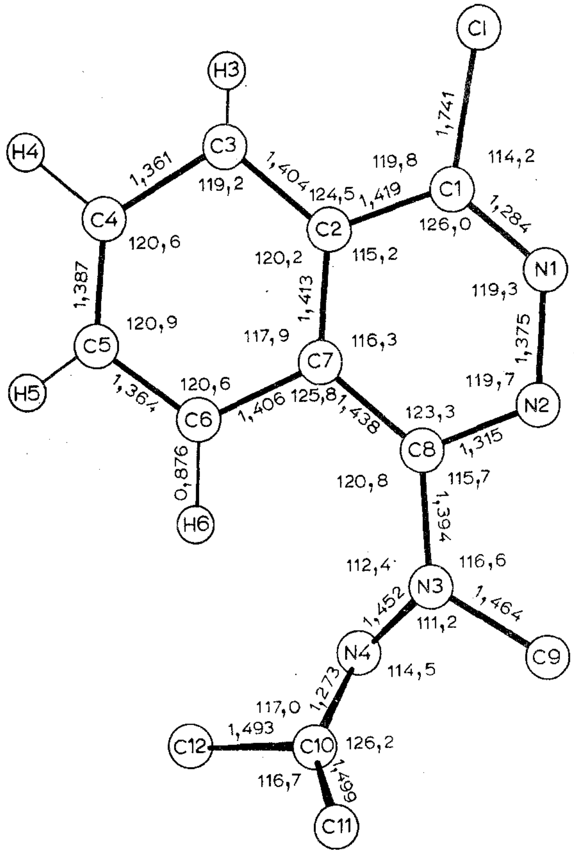

Fig. 1. General form and bond lengths (Å) and angles (in degrees in hydrazone I).

TABLE 1. Deviation of Some Atoms in Hydrazone I and Bisulfate II from the Mean-Square Planes

| Plane | Deviation of the atoms, Å |
|---|---|
| P1<br>($C_{(1)}$—$C_{(8)}$, $N_{(1)}$, $N_{(2)}$) | Cl −0,060, $N_{(1)}$ −0,055, $N_{(2)}$ 0,010, $N_{(3)}$ 0,046, $N_{(4)}$ 1,087, $C_{(3)}$ 0,031, $C_{(6)}$ −0,045, $C_{(8)}$ 0,056, $C_{(9)}$ 0,014, $C_{(10)}$ 0,754, $C_{(11)}$ −0,594, $C_{(12)}$ 1,791 |
| P2<br>($C_{(1)}$, $C_{(2)}$, $C_{(7)}$, $C_{(9)}$, $N_{(1)}$, $N_{(2)}$) | $N_{(1)}$ −0,021, $N_{(2)}$ 0,007, $N_{(3)}$ −0,031, $N_{(4)}$ 0,978, $C_{(9)}$ −0,055 |
| P7<br>($N_{(1)}$, $N_{(2)}$, $C_{(1)}$, $C_{(2)}$, $C_{(7)}$, $C_{(8)}$) | $N_{(3)}$ −0,026, $N_{(4)}$ −0,169, $C_{(9)}$ −0,015, $C_{(10)}$ 0,200, $C_{(11)}$ 1,665, $C_{(12)}$ −0,716, $H_{(N4)}$ −1,095, Cl 0,036 |

jection along the $C_8$—$N_3$ bond as in [3].* If plane P4 is drawn through the $C_8$ and $N_3$ atoms and the midpoint on the $C_9 \cdots N_4$ line, it forms an angle of 66.5° with the P2 plane, and consequently $\theta = -23.5°$. The two methods for the determination of θ give close values, which are smaller than the angle of rotation of the dimethylamino group in amine III [3]. Dihedral angle P2/P5 ($C_9N_3N_4$) is 47.7°, while angle P4/P5 is 93.0°.

Pyramidal character of the amine nitrogen atom is also present in other sterically hindered hydrazones. In the N-methyl-N-(2,4-dinitrophenyl)hydrazones of pyruvyl bromide (IV) and N,N-dimethyl-O-benzoylcarbamic acid (V) the sum of the angles at the amino nitrogen atom are 350.3° and 352.7° [7, 8], while the $C_p^N$ values are 0.242 and 0.183, respectively.

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*Here and subsequently, the sign of the angles of rotation along the bonds are presented from the condition that the fragment with the atom indicated first rotates relative to the fragment with the atom indicated second, which is arbitrarily assumed to be stationary.

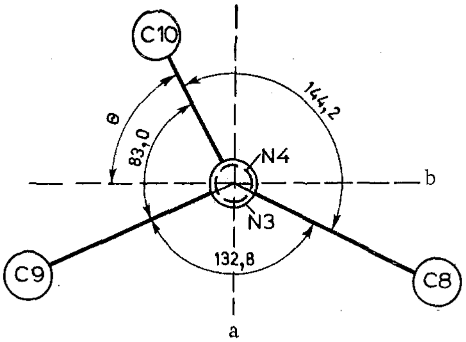

Fig. 2. Newman projection along the $N_3$—$N_4$ bond in hydrazone I: a) median of angle $N_4C_9C_8$; b) perpendicular to (a).

TABLE 2. Torsion Angles τ (in degrees, ±0.2-0.4) in Hydrazone I and Bisulfate II

| Angle | τ | Angle | τ |
|---|---|---|---|
| Hydrazone I | | Bisulfate II | |
| $N_{(2)}—C_{(8)}—N_{(3)}—C_{(9)}$ | −1,2 | $C_{(1)}—C_{(2)}—C_{(7)}—C_{(8)}$ | −3,5 |
| $N_{(2)}—C_{(8)}—N_{(3)}—N_{(4)}$ | −131 | $C_{(1)}—C_{(2)}—C_{(7)}—C_{(6)}$ | 177,3 |
| $C_{(7)}—C_{(8)}—N_{(3)}—C_{(9)}$ | −177,0 | $C_{(3)}—C_{(2)}—C_{(7)}—C_{(8)}$ | 178,5 |
| $C_{(7)}—C_{(8)}—N_{(3)}—N_{(4)}$ | 52,9 | $C_{(3)}—C_{(2)}—C_{(7)}—C_{(6)}$ | −0,8 |
| $N_{(3)}—N_{(4)}—C_{(10)}—C_{(11)}$ | 3,0 | $N_{(1)}—N_{(2)}—C_{(8)}—N_{(3)}$ | −178,3 |
| $N_{(3)}—N_{(4)}—C_{(10)}—C_{(12)}$ | −178,8 | $N_{(2)}—C_{(8)}—N_{(3)}—N_{(4)}$ | −5,6 |
| $C_{(9)}—N_{(3)}—N_{(4)}—C_{(10)}$ | 83,0 | $C_{(8)}—N_{(3)}—N_{(4)}—C_{(10)}$ | 18,1 |
| $C_{(8)}—N_{(3)}—N_{(4)}—C_{(10)}$ | −144,2 | $N_{(3)}—N_{(4)}—C_{(10)}—N_{(2)}$ | −21,1 |
| $C_{(1)}—C_{(2)}—C_{(7)}—C_{(6)}$ | 175,2 | $N_{(4)}—C_{(10)}—N_{(2)}—C_{(8)}$ | 19,5 |
| $C_{(8)}—C_{(7)}—C_{(2)}—C_{(3)}$ | 177,9 | $C_{(10)}—N_{(2)}—C_{(8)}—N_{(3)}$ | −9,4 |
| $C_{(1)}—C_{(2)}—C_{(3)}—C_{(4)}$ | −177,4 | | |
| $C_{(1)}—C_{(2)}—C_{(7)}—C_{(8)}$ | −3,1 | | |
| $C_{(3)}—C_{(2)}—C_{(7)}—C_{(6)}$ | −3,9 | | |

The isopropylideneimine fragment $N_4C_{10}C_{11}C_{12}$ is planar (P6) within the limits of 0.009 Å. The angle is turned about the $N_4=C_{10}$ bond to a very small extent (2.1° from the Newman projection, Table 2). The $N_3$ atom virtually lies in the P6 plane with a deviation of 0.037 Å, but the isopropylidenehydrazone fragment is turned about the $N_3=N_4$ bond from the position that is optimal for conjugation of $N_3$ with $N_4=C_{10}$ $\varphi = -59.4°$ (from the Newman projection along the $N_3$—$N_4$ bond and Table 2 and Fig. 2). Close angle φ values were obtained from data from the UV spectra for acetone N-methyl-N-phenylhydrazone (64°) [9] and acetophenone N-methyl-N-phenylhydrazone (60°), but according to the UV spectra for hydrazone I, angles θ and φ should be minimal for the crystalline state and should increase as they pass into solution [1]. From x-ray diffraction data for hydrazones IV and V [7, 8] we determined that $\theta_{C—N}$ = 9.1 and 16.3° and $\varphi_{N-N} = -28.7$ and 65.6°, respectively (from the Newman projection and the torsion angles along the corresponding bonds).

Thus in sterically hindered hydrazones, as in aryl(hetaryl)dimethylamines [3], disruption of the conjugation of the amino nitrogen atoms leads to its pyramidal character, the degree of which depends on the degree of conjugation with both the aryl (hetaryl) and azomethine bonds.

As a consequence of rotation about the $C_8$—$N_3$ and $N_3$—$N_4$ bonds, conjugation is disrupted, and this is reflected in the lengths of the bonds of the hydrazone fragment. The $C_8$—$N_3$ bond is longer than the analogous bond in amine III [1.376(6) Å] and the corresponding bonds in hydrazones IV (1.35 Å) and V (1.366 Å) [7, 8] and in acetone 4- and 3-nitrophenylhydrazones VI and VII (1.350 and 1.351 Å) [10]. The length of the $N_3$—$N_4$ bond [1.452(3) Å] is virtually equal to the length of the N—N bond in hydrazine [11] [1.453(5) Å]. It is longer than in ordinary arylhydrazones (1.31-1.41 Å; see [12] for a compilation of data for 17 representatives) and in most sterically hindered hydrazones (for example, 1.41 and 1.42 Å in IV and V

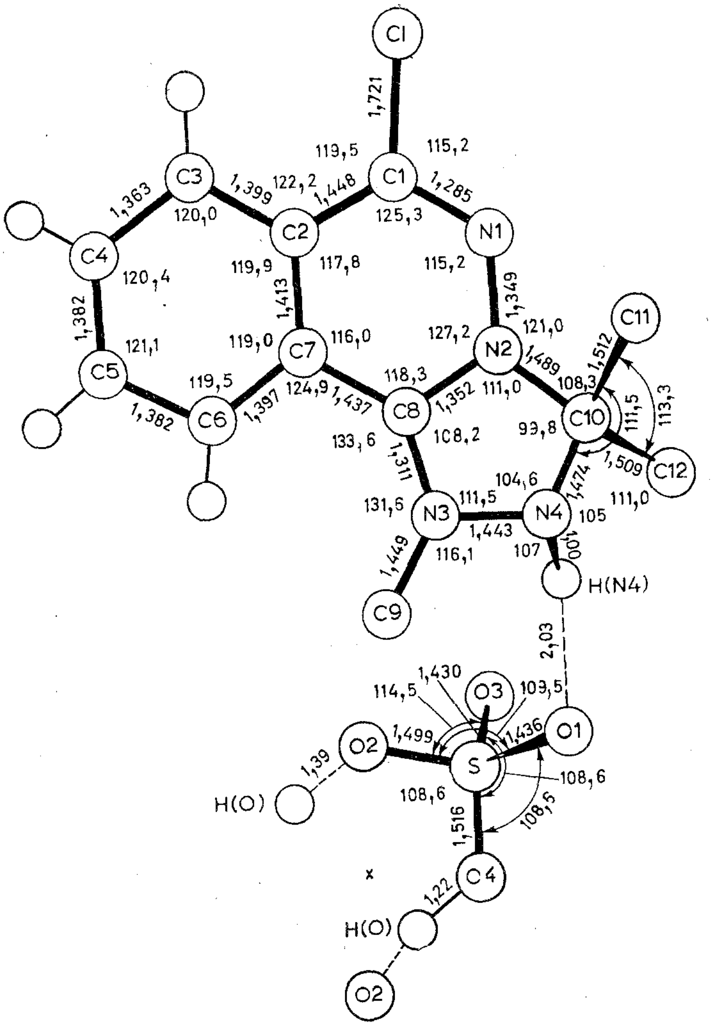

Fig. 3. General form and bond lengths (Å) and angles (in degrees) in bisulfate II.

[7, 8]) and is still comparable only with the length of the N—N bond in 3,6-dimethoxy-5,19-cycloandrostan-17-one N-acetyl-N-(4-bromophenylsulfonyl)hydrazone [13].

With respect to its length [1.273(3) Å] and order (1.90), the $N_4{=}C_{10}$ bond is similar to the C=N bond of aryl- and acylhydrazones of aliphatic aldehydes and ketones [10, 12, 14-16].

The possibility that the smaller angle of rotation about the $C_8{-}N_3$ bond in hydrazone I as compared with amine III and the direction or rotation about the $N_3{-}N_4$ bond are due to a donor—acceptor interaction between $N_4\cdots H_6$ is not excluded. The $N_4\cdots H_6$ contact is 2.454 Å, the $N_4\cdots C_6$ contact is 2.45 Å, and $\angle N_4H_6C_6$ is 115.7°; the conformation of the hydrazone fragment is favorable for an $H_6\cdots\pi$ (N=C) interaction rather than with the unshared pair of $N_4$. The ability of the $sp^2$-hybridized N atom to form an intramolecular hydrogen bond with the proton of the =CH group has already been noted [17].

The packing in the crystal of hydrazone I is determined by the usual van der Waals contacts.

The general form of the molecule and the bond lengths and angles in the bisulfate of hydrazone I (salt II) are presented in Fig. 3.

It is apparent from Fig. 3 that cation II actually has a three-ring structure, and the added proton is localized on $N_4$, which is an imino nitrogen atom in hydrazone I. Not only the length of the $N_2{-}C_{10}$ bond, which is close to that in methylamine [18] [1.474(15) Å], but also the change in the hybridization of the $C_{10}$ atom (the sum of the angles at $C_{10}$ is 544.9° and is close to the value for the tetrahedral C atom, viz., 547.33°) and the increase in the length of the $C_4{-}C_{10}$ bond to 1.474(3) Å constitute evidence that the amidrazone fragment

TABLE 3. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$) and the Hydrogen Atoms ($\cdot 10^3$) of Hydrazone I

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| Cl | 851 (1) | 2333 (0) | 5796 (1) | $C_{(11)}$ | 218 (5) | -2042 (2) | 10334 (4) |
| $N_{(1)}$ | 2223 (3) | 1303 (1) | 7962 (3) | $C_{(12)}$ | 534 (5) | -2963 (2) | 8282 (4) |
| $N_{(2)}$ | 2445 (2) | 568 (1) | 8789 (2) | $H_{(3)}$ | −190 (4) | 141 (2) | 427 (4) |
| $N_{(3)}$ | 1605 (2) | −727 (1) | 9323 (2) | $H_{(4)}$ | −395 (4) | 40 (2) | 359 (4) |
| $N_{(4)}$ | 1377 (3) | −1527 (1) | 8516 (2) | $H_{(5)}$ | −365 (3) | −80 (2) | 511 (3) |
| $C_{(1)}$ | 939 (4) | 1384 (2) | 6758 (3) | $H_{(6)}$ | −141 (4) | −99 (2) | 719 (4) |
| $C_{(2)}$ | −361 (3) | 792 (1) | 6204 (3) | $H_{(9.1)}$ | 313 (4) | −21 (3) | 1119 (5) |
| $C_{(3)}$ | −1763 (3) | 908 (2) | 4896 (3) | $H_{(9.2)}$ | 320 (4) | −123 (2) | 1122 (4) |
| $C_{(4)}$ | −2966 (4) | 312 (2) | 4492 (4) | $H_{(9.3)}$ | 413 (4) | −77 (2) | 1038 (3) |
| $C_{(5)}$ | −2842 (3) | −397 (2) | 5386 (4) | $H_{(11.1)}$ | 101 (6) | −230 (3) | 1120 (7) |
| $C_{(6)}$ | −1488 (3) | −529 (2) | 6656 (4) | $H_{(11.2)}$ | −82 (5) | −236 (2) | 1008 (5) |
| $C_{(7)}$ | −183 (3) | 52 (1) | 7083 (3) | $H_{(11.3)}$ | 0 (4) | −143 (3) | 1039 (4) |
| $C_{(8)}$ | 1317 (3) | −26 (1) | 8372 (3) | $H_{(12.1)}$ | 111 (4) | −337 (2) | 895 (4) |
| $C_{(9)}$ | 3133 (4) | −726 (2) | 10647 (4) | $H_{(12.2)}$ | −67 (5) | −315 (2) | 784 (4) |
| $C_{(10)}$ | 767 (3) | -2118 (2) | 9044 (3) | $H_{(12.3)}$ | 103 (4) | −297 (2) | 751 (4) |

TABLE 4. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$ for S and $\cdot 10^5$ for Cl) and Hydrogen Atoms ($\cdot 10^3$) of Bisulfate II

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| S | 57105 (4) | 15824 (6) | 59609 (7) | $C_{(10)}$ | 9124 (2) | 782 (2) | 7438 (3) |
| Cl | 98923 (7) | 31340 (7) | 118884 (8) | $C_{(11)}$ | 8460 (2) | −147 (3) | 7836 (3) |
| $O_{(1)}$ | 5265 (2) | 2557 (2) | 5039 (2) | $C_{(12)}$ | 10112 (2) | 283 (4) | 7633 (4) |
| $O_{(2)}$ | 4979 (1) | 883 (2) | 6469 (2) | $H_{(N4)}$ | 928 (2) | 149 (3) | 572 (3) |
| $O_{(3)}$ | 6424 (1) | 2012 (2) | 7117 (2) | $H_{(O)}$ | 556 (4) | −1 (6) | 442 (6) |
| $O_{(4)}$ | 6149 (1) | 648 (2) | 5172 (3) | $H_{(3)}$ | 884 (2) | 521 (3) | 1103 (3) |
| $N_{(1)}$ | 9524 (2) | 2037 (2) | 9568 (2) | $H_{(4)}$ | 790 (3) | 683 (4) | 1005 (4) |
| $N_{(2)}$ | 9103 (1) | 1965 (2) | 8216 (2) | $H_{(5)}$ | 703 (2) | 652 (3) | 773 (3) |
| $N_{(3)}$ | 8247 (1) | 2383 (2) | 6188 (2) | $H_{(6)}$ | 733 (2) | 475 (2) | 658 (3) |
| $N_{(4)}$ | 8745 (2) | 1248 (2) | 6029 (2) | $H_{(9.1)}$ | 718 (4) | 333 (4) | 510 (5) |
| $C_{(1)}$ | 9357 (2) | 3046 (2) | 10162 (3) | $H_{(9.2)}$ | 733 (3) | 247 (4) | 442 (5) |
| $C_{(2)}$ | 8746 (2) | 4055 (2) | 9505 (3) | $H_{(9.3)}$ | 787 (3) | 373 (5) | 472 (5) |
| $C_{(3)}$ | 8586 (2) | 5122 (3) | 10223 (4) | $H_{(11.1)}$ | 869 (2) | −36 (3) | 883 (4) |
| $C_{(4)}$ | 7968 (2) | 6018 (3) | 9576 (4) | $H_{(11.2)}$ | 782 (2) | 22 (3) | 757 (4) |
| $C_{(5)}$ | 7500 (2) | 5883 (3) | 8210 (4) | $H_{(11.3)}$ | 847 (2) | −98 (3) | 737 (4) |
| $C_{(6)}$ | 7656 (2) | 4853 (3) | 7463 (3) | $H_{(12.1)}$ | 1036 (2) | −15 (3) | 859 (3) |
| $C_{(7)}$ | 8281 (2) | 3919 (2) | 8108 (3) | $H_{(12.2)}$ | 1054 (2) | 91 (3) | 754 (4) |
| $C_{(8)}$ | 8507 (2) | 2809 (2) | 7447 (3) | $H_{(12.3)}$ | 1011 (2) | −33 (3) | 708 (4) |
| $C_{(9)}$ | 7691 (3) | 2947 (4) | 4935 (3) | | | | |

$N_2C_8N_3N_4C_{10}$ upon protonation formed a triazolidine ring rather than undergoing a simple change in its conformation with random drawing together of the $N_2$ and $C_{10}$ atoms. The $N_3$ atom in cation II takes on a planar configuration (the sum of the angles is 359.2°), while the $N_4$ atom assumes a pyramidal configuration (316.6°). The participation of the imino nitrogen atom of hydrazones in the formation of a new bond, as, for example, during complexing, is usually not accompanied by any substantial change in the lengths of the bonds and the angles in the hydrazone fragment (compare [10] with [19], [15] with [20], [21] with [22], and [17] and [23] with [24]); only the angle at the imino nitrogen atom increases, whereas it decreases on passing from hydrazone I to salt II. Unfortunately, comparative crystallographic data for the hydrazone and its salt protonated at the imino nitrogen atom are not yet available.

As compared with hydrazone I, the phthalazine system in cation II undergoes small changes that are similar to those observed on passing from phthalazine to salts of phthalazine derivatives or to phthalazones (see the discussion of this problem in [3] and the data in [4-6]). Thus the $N_1N_2C_8$ angle increases only somewhat, the $N_2C_8C_7$ angle decreases, and the $N_2$—$C_8$ bond becomes only somewhat longer.

Although the phthalazine system in cation II is virtually planar (P7, within the limits of 0.075 Å), cation II, upon the whole, is not planar due to bending of the triazolidine ring along the $N_2\cdots N_4$ line (envelope, see Tables 1 and 2).

The cations and anions in the crystal are connected by $N_4H\cdots O_1$ [2.03(3) Å] and $N_4\cdots O_1$ [2.95(3) Å] hydrogen bonds, and angle $N_4HO_1$ is 17.1(2)°. The bisulfate anions are joined together to form centrosymmetric dimers by means of two hydrogen bonds, viz., $O_4{-}H\cdots O_2'$ [$H\cdots O_2'$ 1.39(6) Å, $O_4\cdots O_2'$ 2.597(3) Å, $O_4HO_2'$ 170(5)°] and $O_2\cdots H{-}O_4'$.

## EXPERIMENTAL

The crystals of hydrazone I ($C_{12}H_{13}N_4Cl$) are monoclinic; at 20°C, $a$ = 8.851(2), b = 15.731(1), c = 9.6187(8) Å, β = 112.28(1)°, $d_{calc}$ = 1.34 g/cm³, Z = 4, and space group $P2_1/a$.

The crystals of bisulfate II [$(C_{12}H_{14}N_4Cl)^+HSO_4^-$] are monoclinic; at 20°C, $a$ = 14.667(2), b = 10.6552(4), c = 10.0852(8) Å, β = 104.70(1)°, $d_{calc}$ = 1.51 g/cm³, Z = 4, and space group $P2_1/a$.

The cell parameters and intensities of 1190 reflections for hydrazone I and 1581 reflections for sulfate II with $F^2 > 3\sigma$ were measured with a Hilger-Watts automatic four-circle diffractometer (λ $CuK_\alpha$, graphite monochromator, θ/2θ scanning, $\theta \leqslant 66°$).

The structures were decoded by a direct method with a MULTAN program and were refined by the method of least squares, initially within an isotropic approximation and then within an anisotropic approximation. All of the H atoms were exposed from differential synthesis and were refined isotropically in the final step. The final divergence factors were as follows: R = 0.040 and $R_W$ = 0.047 for hydrazone I, and R = 0.033 and $R_W$ = 0.040 for bisulfate II. All of the calculations were made with an Eclipse S/200 computer by means of EXTL programs, modification of which was accomplished in the laboratory of x-ray diffraction analysis of the Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR by A. I. Yanovskii and R. G. Gerr. The coordinates of the atoms are presented in Tables 3 and 4. The accuracy in the bond lengths without participation of the hydrogen atoms was ±0.003-0.005 Å, while the accuracy with participation of the H atoms was ±0.04-0.06 Å. The accuracy in the bond angles without participation of the hydrogen atoms was +0.3-0.5°, while the accuracy with participation of H was ±2°.

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# REACTION OF o-DIAMINOANTHRAQUINONES WITH ACETOACETIC ESTER AND CROTONIC ACID

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UDC 547.673.5'892.07:543.422

The reaction of 1,2 (and 2,3)-diamino-9,10-anthraquinones with acetoacetic ester and crotonic acid gave dihydro- and tetrahydroanthraquinonediazepinones, the structures of which were established on the basis of spectral data and chemical transformations.

The reaction of o-diaminoarenes with carbonyl compounds is one of the methods for the synthesis of 1,5-diazepine derivatives, many of which are of pharmacological value [1]. The first representatives of anthraquinonediazepines were recently obtained by the reaction of o-diaminoanthraquinones with mesityl oxide [2] and malonic ester [3]. In the present research in order to synthesize new representatives of this series of compounds we studied the possibility of the use of acetoacetic ester (AAE) and crotonic acid as the carbonyl components.

We found that a complex mixture of reaction products, from which we isolated acetoacetyl derivative III and diazepinones IV and V (the latter in the form of tautomeric forms Va and Vb), is formed when 1,2-diaminoanthraquinone (I) and AAE are heated in toluene by the method previously described for 2,3-diaminonaphthoquinone [4]. Diazepinone IV (55%) is the principal product, and V and III are obtained in 26 and 13% yields, respectively. The structures of the compounds obtained were established on the basis of analytical and spectral data (see Table 1).

The IR spectra of diazepinones IV and V at 1600-1700 $cm^{-1}$ contain broad absorption bands that confirm the presence of carbonyl and amido groups. The presence of absorption bands in the high-frequency region (3100-3300 $cm^{-1}$) may constitute evidence for the presence of NH groups that participate in the formation of hydrogen bonds. In addition to the absorption bands that correspond to the amido and carbonyl groups of the quinone, frequencies that belong to the vibration of ketone C=O (1720 $cm^{-1}$) and amino group N—H (3320 and 3440 $cm^{-1}$) bonds are observed in the IR spectrum of III.

In addition to the signals of aromatic protons and protons of $CH_2$ and CH groups, the PMR spectra of diazepinones IV and Va contain signals of protons of NH groups, the position of which is in good agreement with the spectral data for similarly constructed compounds [2, 3]. The chemical shifts of the protons of the NH group in IV proved to be close (8.69 and 9.17 ppm), but the position of the protons of the NH group in Va differ substantially (8.7 and 11.3 ppm). The weak-field signal in the spectrum of diazepinone Va evidently belongs to the proton of the NH group in the 1 position, since it is adjacent to the carbonyl groups of the quinone and the heteroring. The deshielding effect of the carbonyl groups is also manifested in the diazepinone Vb molecule, the PMR spectrum of which at weak field (11.76 ppm) contains one signal from the proton of the NH group in the 1 position. In addition, in contrast to tautomers IV and Va, a signal of protons of the $CH_2$ group (in addition

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0009-3122/82/1808-0848$07.50