STRUCTURE OF HUGERSHOFF'S AND HECTOR'S BASES, AND ACETYLATED HECTOR'S BASE

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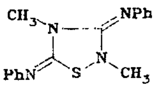
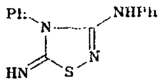
X-Ray structural analysis has been used to establish the structures of the heterocyclic oxidation products of N-arylthioureas. The oxidation product of N,N'-diphenylthiourea (Hugershoff's base) is 2-[N-phenyl-N-(phenylamino-phenylimino-methyl)]aminobenzothiazole. The oxidation product of N-phenylthiorea (Hector's base) has been confirmed to be 5-imino-4-phenyl-3-phenylamino-4H-1,2,4-thiodiazoline. The acetyl group in its acetyl derivative has been shown to be attached to the imine nitrogen atom.

The structures of the compounds obtained by the oxidation of thiourea and its N-substituted derivatives has been the subject to discussion for nearly a hundred years. First described by German chemists [1-3], these compounds have been subsequently studied by a variety of chemical and physical methods (see, for example, reviews [4-6]). It was found that many of these compounds are derivatives of the heterocycles benzothiazole and thiadiazolidine. As more recent studies have shown, however, many of the structures proposed for these compounds were erroneous, largely because in determining the structures no account was taken of the fact that most of these heterocyclic compounds readily isomerize in solution, undergoing interconversion.

Among these compounds, much controversy has been aroused by the so-called Hector and Hugershoff bases, obtained by the oxidation of 1-phenylthiourea [1] and 1,3-diphenylthiourea [2], respectively, and also the Dost base, obtained by heating Hector's base with alcoholic ammonia [3]. In view of the contradictory data on the structure of these compounds, workers have used x-ray structural analysis to establish their structures, and have found that oxidation of 1-alkyl-3-arylthioureas with nitrous acid in aqueous ethanol affords 2,4-dialkyl-3,5-bis(arylimino)-1,2,4-thiadiazolidines (I), termed by the authors Dost-type bases [7]. The structure of one of these compounds (Ia, alkyl = CH_3, aryl = Ph) was proved by x-ray structural analysis.



Ia



II

It was later shown that the product of oxidation of 1-methyl-3-phenylthiourea with benzoyl peroxide in methylene chloride has the same structure (Ia) [8].

In 1978, the product of oxidation of 1-phenylthiourea with hydrogen peroxide (Hector's base) was shown to be 5-imino-4-phenyl-3-phenylamino-4H-1,2,4-thiadiazoline (II) [9].

In a study of the radical arylation of N-arylthioureas with N-nitrosoacetoanilide (III), we observed that (III) can function in these reactions both as a source of phenyl radicals and as an oxidant [10]. Thus, reaction of 1-phenylthiourea with (III) in acetone affords (IV), which has the same empirical formula and melting point as the known [1] acetyl derivative of Hector's base.

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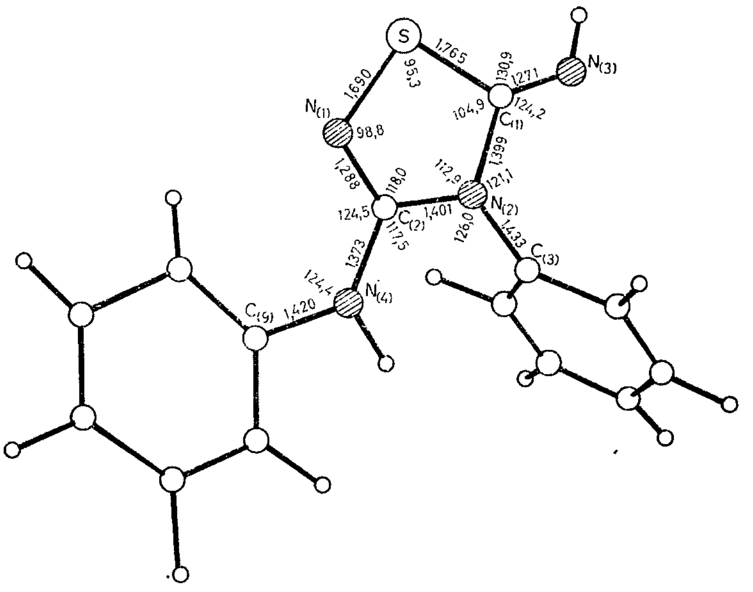
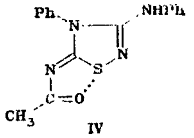
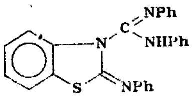


Fig. 1. Conformation of (II) (Hector's base).

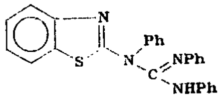


IV

When this reaction was carried out in glacial acetic acid, a compound was isolated from the products which was identical in composition and melting point to Hector's base (II). Reaction of 1,3-diphenylthiourea with (III) under the same conditions gave (V), which was identical from its composition, melting point, and IR spectrum with the known Hugershoff base [2, 11], for which the structure (Va) has recently been suggested (from chemical considerations [12]), and also (Vc) (on the basis of its IR and UV spectra [13]).



Va



Vc

The necessity therefore arose to determine the structures of these compounds (IV and V) and also to confirm independently the structure of (II), since it is known that the structures of the oxidation products of thioureas are highly dependent on the oxidant used [7].

Figures 1-3 show the conformations found for (II), (IV), and (V), together with the more important interatomic distances and angles.

The results of the structural examination of the compound (II) obtained by us are virtually identical with those reported in [9] for Hector's base, showing that these compounds, obtained by different methods, are identical. The intermolecular hydrogen bond between the amino and iminonitrogens noted in [9] is clearly located. Its parameters are: $N_{(4)}$—H 0.98(4) Å; H···$N_{(3)}$ 2.22(4) Å; $N_{(4)}\cdots N_{(3)}$ 3.179(5) Å ($x-1/2, 1/2-y, 1-z$) ; NHN angle 165(3)°.

The structure of (IV) was very interesting. Despite the suggestion of Hector [1], it has been shown clearly that this compound is 5-N-acetylimino-4-phenyl-3-phenylamino-4H-1,2,4-thiadiazoline.

A characteristic feature of the molecule of (IV) (Fig. 2) is the specific spatial location of the acetyl group due to an additional nonvalent S···O interaction (2.471 Å). A

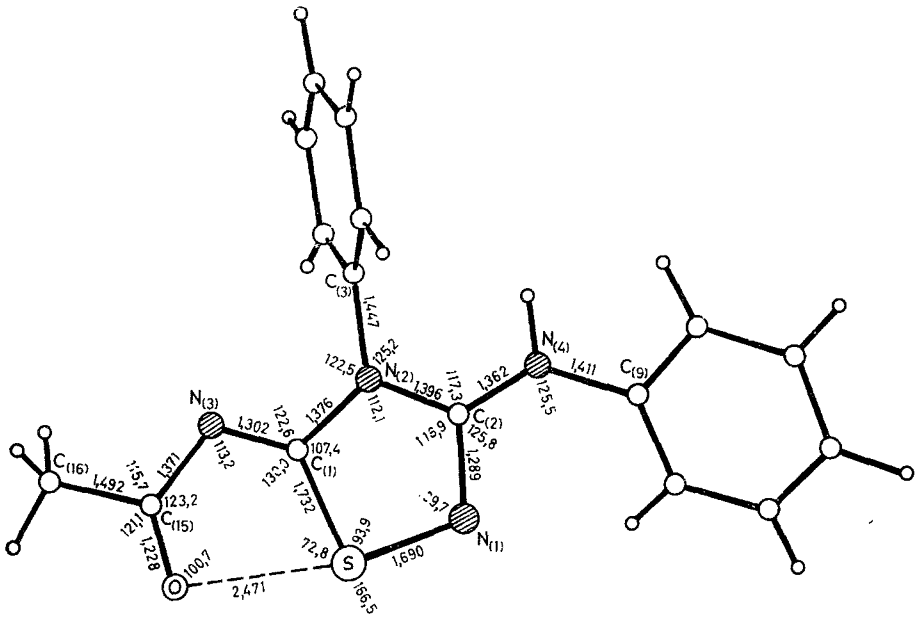


Fig. 2. Conformation of (IV) (acetylated Hector's base).

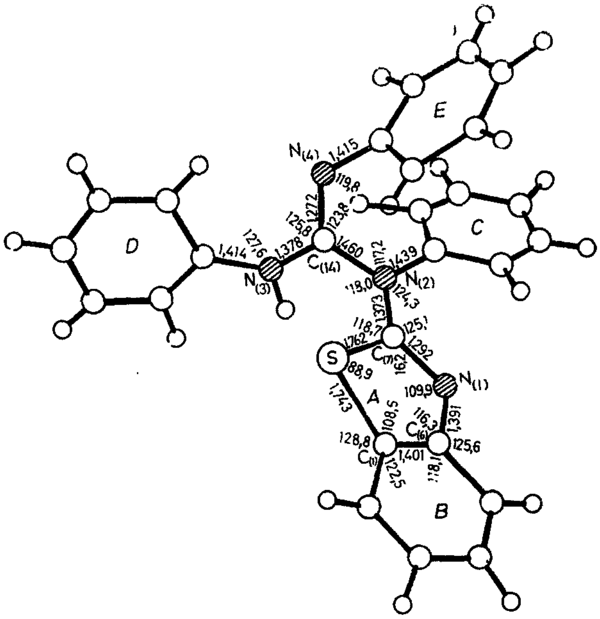


Fig. 3. Conformation of (V) (Hugershoff's base).

similar situation has been reported in several cases, particularly in N-acetyl- and N-thioacetylimino-1,3-thiadiazolidines [14] and 1,2,4-thiazolines [15]. The formation of this bond gives rise to a bicyclic system in which there is a clear redistribution of electron density. Comparison of the geometrical characteristics of (IV) and (II) shows that in (IV) the NSC valence angle is reduced (93.9 and 95.3°) together with the exocyclic N–C=N angle (122.6 and 124.2°), with a simultaneous increase in the endocyclic SCN angle (107.4 and 104.9°). The S–C bond is markedly shortened (1.732 and 1.765 Å), and the C=N bond is lengthened (1.302 and 1.271 Å). The bicyclic system becomes nearly planar (the maximum departure of the atoms from the mean plane is 0.035 Å, and the angle between the planes of the five-membered rings is 2°). The amide nitrogen N($_4$) is clearly pyramidally coordinates, this atom departing from the plane C($_2$)HC($_9$) by 0.116 Å.

TABLE 1. Main Crystallographic Data for (II), (IV), and (V)

Compound	a, Å	b, Å	c, Å	γ, deg	ρ (meas.), g/cm^3	Structural class (z = 4)	N (no. of reflections)	R factor
II	11,021 (2)	9,513 (2)	12,198 (2)	90	1,40	$P2_12_12_1$	803	0,028
IV	19,677 (5)	10,504 (2)	7,420 (2)	102,05 (2)	1,37	$P2_1/a$	1413	0,032
V	9,770 (1)	18,447 (2)	12,116 (1)	98,03 (1)	1,29	$P2_1/n$	1068	0,030

X-Ray structural analysis of (V) showed unambiguously that its structural formula is given by (Vc), and consequently Hugershoff's base is 2-N-phenyl-N-(phenylamino-phenyliminomethyl)aminobenzothiazole. The interatomic distances (Fig. 3) clearly show that $N_{(2)}$ and $N_{(3)}$ are present in the amino form, and $N_{(4)}$ in the imino form, and also that the bond $C_{(7)}$—$N_{(1)}$ possesses double bond character. The geometrical characteristics of the benzothiazole system are in good agreement with those found for similar compounds [16, 17]. The bicyclic AB system (Fig. 3) is nearly planar (the angle between planes A and B is 2.4°). The central four atoms $C_{(14)}$, $N_{(2)}$, $N_{(3)}$, and $N_{(4)}$ lie in the same plane to within 0.003 Å (plane F). The molecular conformation is determined by the angles between the planes of the fragments AB—C 31.8; AB—E 68.4; AB—D 79.3; AB—F 73.0°. Also seen is an $N_{(3)}H\ldots N_{(1)}$ hydrogen bond with the parameters $N_{(3)}$—H 1.13(5); H···$N_{(1)}$ 1.92; $N_{(3)}$—$N_{(1)}$ 3.023(5) Å ; NHN angle 165(4)°.

EXPERIMENTAL

Monocrystals suitable for x-ray structural analysis were obtained by slow evaporation of the ethanol solutions (II, IV, V). Determinations were carried out using Nicolet P3 (IV, II) and Sintax PT (V) automatic diffractometers, $\lambda_{Mo\text{-}K_\alpha}$ irradiation, graphite monochromator, θ/2θ scanning. The main crystal parameters are given in Table 1. Structures were calculated by the direct method, the H atom coordinates being located by difference synthesis of electron density. Refinement of the positional and thermal parameters was carried out by least squares in anisotropic (nonhydrogen atoms) and isotropic (H atoms) approximations. In the case of (IV), in order to correct for extinction [K_{ext} = 0.0113 (6)], weighting was introduced during refinement, given by $\omega = 1/\sigma^2(F) + 0.0005F^2$ (tables of the positional and thermal factors may be obtained from the authors).

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