The Constitution of Hector's Base; *X*-Ray Crystal and Molecular Structure of 5-Imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline

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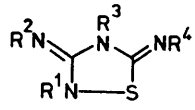
Summary The 89-year controversy concerning the constitution of Hector's Base has been resolved by *X*-ray analysis; the base is shown to be 5-imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline.

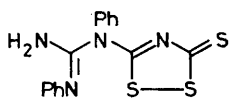
THE oxidation of 1-phenylthiourea yields a heterocyclic base $C_{14}H_{12}N_4S$,[1] generally known as Hector's Base. Although this base was first prepared in 1889, its constitution has never been definitively determined, despite considerable recent interest in its chemistry,[2–4] and six structure, the six possible permutations of two phenyl groups amongst the four distinct nitrogen atoms of the 3,5-di-imino-1,2,4-thiadiazolidine skeleton (Ia—f) have been suggested by



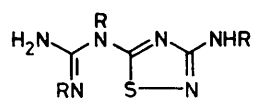
(I)

	R^1	R^2	R^3	R^4
a	H	H	Ph	Ph
b	H	Ph	H	Ph
c	H	Ph	Ph	H
d	Ph	H	H	Ph
e	Ph	H	Ph	H
f	Ph	Ph	H	H

different authors:[2] of these structures, (Ic) has been adopted in the most recent work,[3,4] although (Ie) has also been widely employed.[2] The reaction of Hector's Base with carbon disulphide yields an adduct[5] $C_{15}H_{12}N_4S_3$, whose constitution is[6] (II) (rather than those suggested earlier[4]): similarly, the bis-(4-bromophenyl) analogue of Hector's Base forms an



(II)



(III) R = 4-BrC_6H_4

adduct with 4-bromophenylcyanamide,[3a] whose constitution is (III).[3b] If (Ic) properly represents Hector's Base, then formation of both (II) and (III) requires, after ring-opening, a rotation about the C–N(1) bond of the guanidino group, the rationale of which is by no means apparent. The structures (II) and (III) raise the possibility that Hector's Base is in fact (Ie). In view of the unexpected rearrangement required for the formation of compounds (II) and (III) [if (Ic) does indeed properly represent Hector's Base], we have determined the crystal and molecular structure of Hector's Base, which shows that it adopts none of the structures (Ia—f), but rather that shown in Figure 1.

Crystal Data: $C_{14}H_{12}N_4S$, orthorhombic, $P2_12_12_1$; $a=12{\cdot}196(2)$, $b=11{\cdot}027(2)$, $c=9{\cdot}519(2)$ Å; $M=268{\cdot}34$; $U=1280$ Å^3; $F(000)=560$; $D_c=1{\cdot}392$ kg dm^{-3}; $Z=4$; μ(Mo-K_α) $=1{\cdot}99$ cm^{-1}. The structure was solved by direct methods using diffractometer data, and refined by full-matrix least squares with C, N, S anisotropic and H isotropic to $R=0{\cdot}079$ for 2086 data and 211 variables. The bond lengths and angles of the heterocycle are shown in Figure 1, and a perspective view of the whole molecule in Figure 2.†

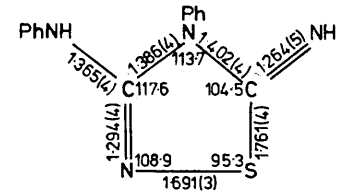


FIGURE 1. The structure of Hector's Base, showing the bond lengths and angles of the heterocyclic ring: e.s.d.s on bond angles are 0·3°.

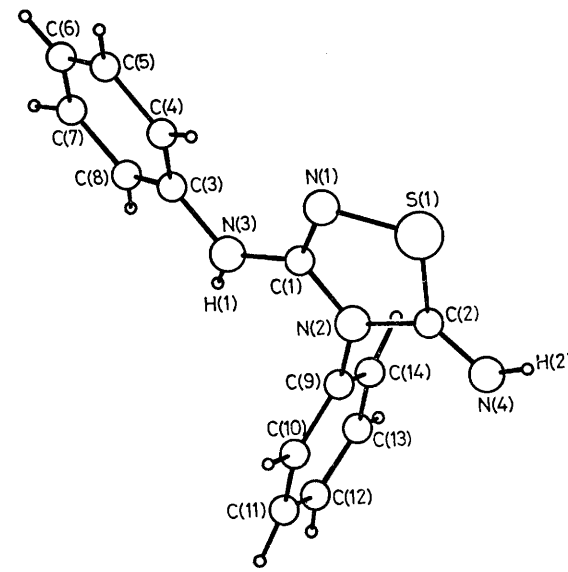


FIGURE 2. Perspective view of the molecule of Hector's Base.

Hector's Base is a rare example of a 1,2,4-thiadiazoline and the structure reported here is the first accurate determination for this ring system.[7] The S–N distance is comparable to the S–N distances in similar heterocycles containing two-co-ordinate nitrogen,[3d] but is shorter than S–N distances in heterocycles containing three-co-ordinate nitrogen.[7,8] Similarly the heterocyclic C=N double bond has a length typical of such bonds, but which is much shorter than those of C–N single bonds: the exocyclic C–N and C=N bonds are also readily distinguishable. The structure in Figure 1 shows that a bond rotation must occur in the formation of (II) and (III).

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The 89-year controversy concerning the structure of Hector's Base has now been finally resolved. However, the structure found is that in the solid state: in solution, there could be a prototropic shift.

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