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

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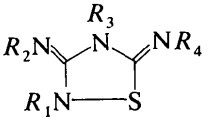
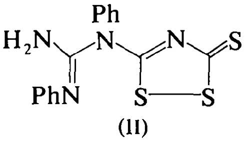
Hector's base, $C_{14}H_{12}N_4S$, is orthorhombic, space group $P2_12_12_1$, $a = 12 \cdot 196$ (2), $b = 11 \cdot 027$ (2), $c = 9 \cdot 519$ (2) Å; $Z = 4$. The structure was solved by direct methods using 2086 diffractometer data and refined by the full-matrix least-squares method to $R = 0 \cdot 0790$. The 89-year controversy concerning the constitution of Hector's base has been resolved: it has been shown to be 5-imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline.

Introduction

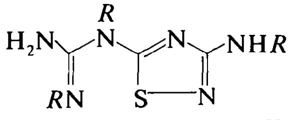
The oxidation of 1-phenylthiourea with H_2O_2 yields a heterocyclic base, $C_{14}H_{12}N_4S$ (Hector, 1889), generally known as Hector's base. Despite considerable recent interest in its chemistry (Kurzer, 1965; Akiba, Tsuchiya & Inamoto, 1976; Butler, 1978), the constitution of this base has never been definitively determined. Six structures, the six possible permutations of two phenyl groups amongst the four distinct N atoms of the 3,5-diimino-1,2,4-thiadiazolidine skeleton (I*a*–*f*) have been suggested by different authors (Kurzer, 1965): of these structures, (I*c*) has been adopted in the most recent work (Akiba, Tsuchiya & Inamoto, 1976; Butler, 1978), although (I*e*) has also been widely employed (Kurzer, 1965). The reaction of Hector's base with carbon disulphide yields an adduct $C_{15}H_{12}N_4S_3$ (Fromm & Heyder, 1909), whose constitution is (II) (Butler, Glidewell & Liles, 1978) [rather than those suggested earlier (Butler, 1978)]; similarly the bis(4-bromophenyl) analogue of Hector's base forms an adduct with 4-bromophenylcyanamide (Akiba, Tsuchiya, Ochiumi & Inamoto, 1975), whose constitution is (III) (Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura, 1976). If (I*c*) properly represents Hector's base, then the formation of both (II) and (III) requires, after ring-opening, a rotation about the C—N(1) bond of the guanidine 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 (I*e*).



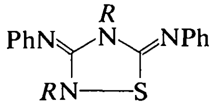
(I*a*)	$R_1 = R_2 = H$	$R_3 = R_4 = Ph$
(I*b*)	$R_1 = R_3 = H$	$R_2 = R_4 = Ph$
(I*c*)	$R_1 = R_4 = H$	$R_2 = R_3 = Ph$
(I*d*)	$R_2 = R_3 = H$	$R_1 = R_4 = Ph$
(I*e*)	$R_2 = R_4 = H$	$R_1 = R_3 = Ph$
(I*f*)	$R_3 = R_4 = H$	$R_1 = R_2 = Ph$



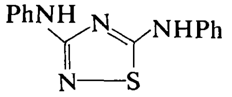
(II)



(III) $R = BrC_6H_4$



(IV*a*) $R = H$
(IV*b*) $R = Me$



(V)

In ethanolic ammonia at 150°C Hector's base forms an isomer (Dost, 1906) usually called Dost's base, for which the constitutions (IV*a*) (Christopherson, Øttersen, Seff & Treppendahl, 1975), (V) (Kurzer & Sanderson, 1963) and (VI) (*Beilstein*, 1937) have been suggested. The molecular structure of (IV*b*) has been

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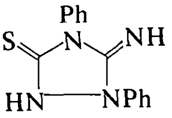
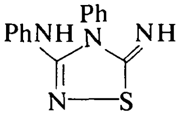
determined by X-ray analysis (Christopherson *et al.*, 1975), and was described as a Dost-type base. It was claimed that this structure provided 'conclusive evidence' on the structure of Hector's and Dost's bases, which were taken to be (I*c*) and (IV*a*) respectively. This evidence is neither conclusive nor even suggestive for the following reasons: (i) (IV*b*) was prepared by the action of nitrous acid on 1-methyl-3-phenylthiourea, although this oxidant with 1-phenylthiourea yields Hector's base rather than Dost's base (Hector, 1889); (ii) (IV*b*) cannot, because of its lack of mobile H atoms, be prepared by isomerization of a Hector-type base. Consequently, the identification of compound (IV*b*) as a Dost-type base is unsound: most importantly, the structure of (IV*b*) gives no information about the structure of Hector's base.

In view of the unsatisfactory nature of the foregoing evidence, and of the unexpected rearrangement required for the formation of compounds (II) and (III) [if (I*c*) does indeed properly represent Hector's base], we have determined the crystal and molecular structure of Hector's base. The structure analysis shows that it adopts none of the suggested structures (I*a*–*f*) but is in fact 5-imino-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline (VII).



(VI)



(VII)

Experimental

Hector's base was prepared by oxidizing 1-phenylthiourea with hydrogen peroxide in aqueous ethanol (Hector, 1889), and was recrystallized from ethanol. Crystals suitable for X-ray examination were grown from ethanol–acetone solution.

Data collection

The intensities of 2151 unique reflections with $3 \leq \theta \leq 30°$ in the octant $+h$ $+k$ $+l$ were measured using a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation in the ω–2θ scan mode, with a scan speed of 0·05° s^{-1} in ω and a scan width of $(0{\cdot}64 + 0{\cdot}05 \tan \theta)°$ in ω. Backgrounds were measured at each end of the scan range for a time equal to (scan time)/2. Three standard reflections were measured every six hours during data collection, and showed only small random deviations about their mean intensities. Lorentz and polarization corrections were applied, but no corrections for absorption were made.

Crystal data

$C_{14}H_{12}N_4S$, M_r = 268·34, orthorhombic, space group $P2_12_12_1$; a = 12·196 (2), b = 11·027 (2), c = 9·519 (2) Å; U = 1280·2 Å^3; Z = 4; D_c = 1·392 g cm^{-3}; $F(000)$ = 560. Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 1·99 cm^{-1}.

The space group was determined uniquely from the systematic absences: $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$. Unit-cell dimensions were obtained by a least-squares fit to the angular positions of 25 reflections measured on the diffractometer.

Structure solution and refinement

The structure was solved by direct methods and refined using the *SHELX* 76 program system (Sheldrick, 1976). 252 reflections with normalized structure factors E > 1·40 giving 5284 triple-phase relations were used to calculate a convergence map. The origin was defined by assigning phases of 90° to the reflections 019, 201 and 1,11,0. Reflection 395 was assigned a phase of 45 or 135° to fix the enantiomorph and reflections 321 and 218 were each assigned phases of 45, 135, 225 or 315° to give 32 starting phase permutations. The best solution from the multi-solution tangent refinement yielded an E synthesis from which positions for all non-hydrogen atoms in the molecule were found.

Three cycles of full-matrix least-squares refinement using 2086 observed reflections with individual isotropic temperature factors for C, N and S atoms and a weighting scheme $w = [\sigma(F_o)]^{-2}$ gave R = 0·1354 and a generalized index R_G $[= (\sum w\Delta^2/\sum wF_o^2)^{1/2}]$ of 0·1210. The introduction of anisotropic temperature factors reduced R_G to 0·0857. At this stage a difference synthesis gave the positions of all H atoms except H(2). Three cycles of refinement of the parameters for all atoms except H(2), with an individual isotropic temperature factor (U) for H(1) and a common U value for all of the phenyl H atoms reduced R_G to 0·0592. A further difference synthesis gave the position of H(2) and three cycles with an individual U value for H(2), and other parameters as before, yielded final agreement indices of R = 0·0790, R_w $(= \sum w^{1/2}\Delta/\sum w^{1/2}F_o)$ = 0·0642 and R_G = 0·0592. At each stage of refinement the reduction in R_G was significant at the 99·5% level (Hamilton, 1965). Refinement of the alternative enantiomorph yielded indices of R = 0·0792 and R_G = 0·0594. The difference in R_G was significant at the 99·5% level (Hamilton, 1965).

Complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) were employed for all atoms. In the final refinement a total of 211 parameters were varied, comprising 93 positional coordinates, 114 anisotropic temperature factor components, three isotropic temperature factors, and one overall scale factor. In the final cycle all parameter shifts were less than 0·53σ. A final difference synthesis revealed no residual electron density >0·40 e Å^{-3}.

The final fractional coordinates are given in Table 1.* These, together with the full covariance matrix, were used to calculate the bond lengths, bond angles and e.s.d.'s which are given in Tables 2 and 3. Least-squares planes calculated for selected parts of the molecule are given in Table 4. Fig. 1 shows the molecule and the numbering scheme for atoms and bonds: H atoms bonded to C are given the numbers of the corresponding C atoms. Fig. 2 shows the unit-cell contents.

Table 1. *Fractional atomic coordinates* (× 10^4; *for* H × 10^3)

	x	*y*	*z*
S(1)	2306 (1)	3636 (1)	4653 (1)
N(1)	1856 (2)	2271 (2)	5222 (3)
N(2)	839 (2)	2610 (2)	3234 (2)
N(3)	546 (3)	823 (3)	4562 (3)
N(4)	1300 (3)	4500 (3)	2249 (3)
C(1)	1098 (3)	1889 (3)	4380 (3)
C(2)	1432 (3)	3699 (3)	3182 (4)
C(3)	597 (3)	81 (3)	5782 (3)
C(4)	1506 (4)	36 (4)	6652 (5)
C(5)	1487 (4)	−714 (5)	7826 (5)
C(6)	601 (4)	−1411 (4)	8120 (4)
C(7)	−300 (4)	−1388 (4)	7255 (4)
C(8)	−309 (3)	−636 (3)	6076 (4)
C(9)	25 (3)	2336 (3)	2174 (3)
C(10)	312 (3)	1603 (3)	1051 (4)
C(11)	−476 (5)	1376 (4)	22 (4)
C(12)	−1506 (4)	1856 (4)	133 (5)
C(13)	−1767 (4)	2583 (4)	1257 (5)
C(14)	−1000 (3)	2829 (4)	2288 (5)
H(1)	7 (3)	63 (3)	407 (3)
H(2)	174 (3)	506 (4)	232 (4)
H(4)	211 (3)	48 (3)	654 (4)
H(5)	213 (3)	−72 (3)	839 (4)
H(6)	59 (3)	−190 (4)	885 (4)
H(7)	−95 (3)	−201 (4)	742 (5)
H(8)	−91 (3)	−65 (4)	550 (5)
H(10)	107 (3)	121 (4)	97 (4)
H(11)	−28 (3)	95 (3)	−81 (5)
H(12)	−211 (3)	174 (3)	−57 (5)
H(13)	−250 (3)	294 (3)	137 (4)
H(14)	−115 (3)	329 (4)	324 (4)

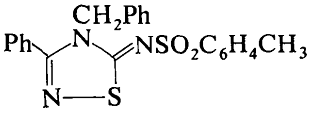
Table 2. *Bond distances* (Å)

The mean H—C(aryl) distance is 0·97 (6) Å.

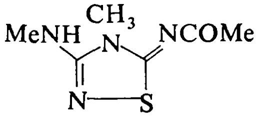
a	1·691 (3)	*g*	1·264 (5)	*m*	1·390 (6)	*s*	1·395 (5)
b	1·294 (4)	*h*	1·422 (4)	*n*	1·355 (6)	*t*	1·367 (7)
c	1·386 (4)	*i*	1·447 (4)	*o*	1·373 (6)	*u*	1·374 (6)
d	1·402 (4)	*j*	0·77 (3)	*p*	1·395 (5)	*v*	1·383 (6)
e	1·761 (4)	*k*	0·82 (4)	*q*	1·388 (5)	*w*	1·368 (5)
f	1·365 (4)	*l*	1·385 (5)	*r*	1·385 (5)		

Discussion

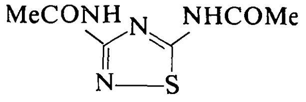
The structure determination clearly shows that in the solid state Hector's base has the constitution (VII) rather than any of those previously suggested (I*a*–*f*), and is a rare example of a 1,2,4-thiadiazoline. The dimensions of the heterocycle are similar to those reported for (VIII) (L'abbé, Verhelst, Toppet, King & Briers, 1976) and (IX) (Sato, Kinoshita, Hata & Tamura, 1972), these being the only other reported structures for 1,2,4-thiadiazolines.



(VIII)



(IX)



(X)

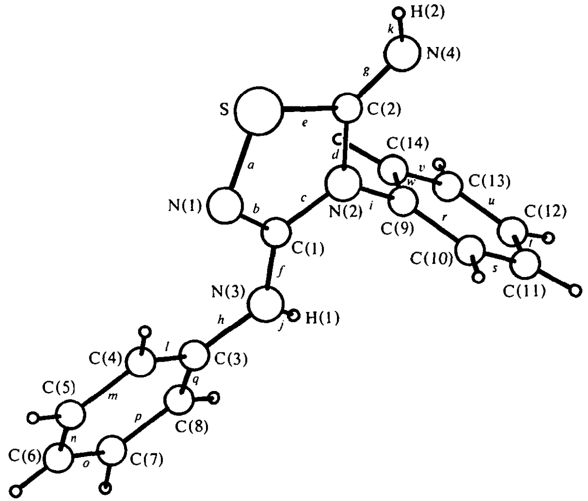


Fig. 1. The molecule showing the numbering of atoms and bonds.

Table 3. *Bond angles* (°)

ab	108·9 (2)	*fh*	125·3 (3)	*mn*	121·2 (4)
ae	95·3 (2)	*fj*	122 (2)	*no*	120·2 (4)
bc	117·6 (3)	*gk*	112 (3)	*op*	120·0 (4)
bf	123·7 (3)	*hj*	112 (2)	*pq*	119·6 (4)
cd	113·7 (3)	*hl*	123·0 (3)	*rs*	118·2 (4)
cf	118·8 (3)	*hq*	117·3 (3)	*rw*	121·6 (3)
ci	125·8 (3)	*ir*	119·1 (3)	*st*	120·6 (4)
de	104·5 (2)	*iw*	119·3 (3)	*tu*	119·9 (4)
dg	123·9 (3)	*lm*	119·2 (4)	*uv*	120·7 (4)
di	120·5 (3)	*lq*	119·8 (3)	*vw*	119·0 (4)
eg	131·6 (2)				

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33737 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Least-squares planes*

Least-squares planes are defined in orthogonal coordinates (in Å) by the equation: $Ax + By + Cz + 1 = 0$.

Plane	Atoms	*A*	*B*	*C*	Atom distances from the plane (Å × 10^{-4})
1	S(1), N(1), C(1), N(2), C(2)	0·3040	−0·1981	−0·2394	S(1), 6; N(1), 44; C(1), −86; N(2), 90; C(2), −52; N(3), −392; N(4), −311; C(9), 82
2	C(3), C(4), C(5), C(6), C(7), C(8)	0·1376	−0·2635	−0·1957	C(3), −95; C(4), 91; C(5), −21; C(6), −48; C(7), 42; C(8), 32; N(3), 78
3	C(9), C(10), C(11), C(12), C(13), C(14)	−0·2939	−0·7811	0·4941	C(9), 15; C(10), 18; C(11), −44; C(12), 37; C(13), −4; C(14), −23; N(2), −285

Dihedral angles between planes (°)

Planes	1,2	1,3	2,3
Angles	24·41	−82·79	78·53

The S—N bond distance in (VII) of 1·691 (3) Å is comparable with the distances reported for similar heterocycles where S is bonded to a two-connected N atom, *e.g.* 1·68 Å in (VIII), 1·685 Å in (IX), and 1·67 Å in (X) (Sato *et al.*, 1972), and 1·690 (9) Å in (III) (Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura, 1976), but is shorter than the distances in similar heterocycles where S is bonded to a three-connected N atom, *e.g.* 1·734 (2) Å in (IV*b*) (Christopherson *et al.*, 1975). In addition, the N(1)—C(1) bond distance is very similar to the equivalent C—N double-bond distances in (VIII) (1·30 Å), (IX) (1·29 Å), (X) (1·31 Å) and (III) [1·29 (1) Å], but is much shorter than the equivalently positioned C—N single-bond distances in (IV*b*) [1·39 (1) Å]. The amino *R*N(H)—C(heterocycle) bond distance of 1·365 (4) Å in (VII) (*R* = Ph) is comparable with those in (IX) (1·35 Å, *R* = Me) and (X) (1·39 Å, *R* = COMe) and is much longer than the imino *R*′N=C(heterocycle) bond distances in (VII) [1·264 (5) Å, *R*′ = H], (IV*b*) [1·271 (4) and 1·260 (4) Å, *R*′ = Ph], (VIII) (1·31 Å, *R*′ = $SO_2C_6H_4CH_3$) and (X) (1·31 Å, *R*′ = COMe). These observations, together with the satisfactory refinement of the H atom [H(1)] bonded to N(3), conclusively prove the identity of Hector's base as a 1,2,4-thiadiazoline rather than the 1,2,4-thiadiazolidine constitution (I*c*) proposed by, for example, Christopherson *et al.* (1975).

The 89-year controversy concerning the structure of Hector's base has now been finally resolved. However, the structure reported here is that in the solid state; the possibility of a prototropic shift occurring in solution cannot be ruled out.

The intermolecular distance between the imino N(4) and the amino H(1^{i})* is 2·44 Å and may represent a weak hydrogen bond. No other significant short inter- or intramolecular contacts occur.

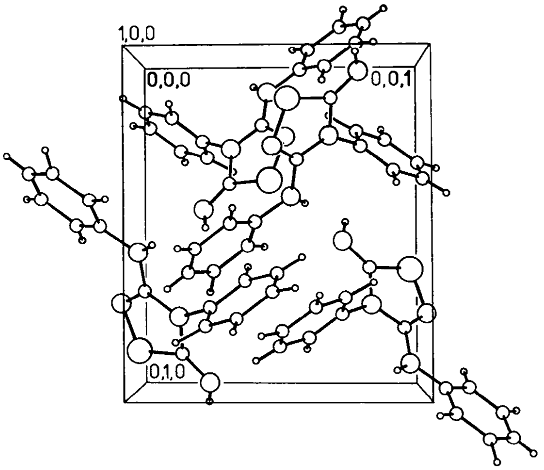

Fig. 2. The unit-cell contents.

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* The superscript (i) refers to the symmetry position $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$.

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Low-Temperature Refinement of the Structure of 11-Methyl-11-azabicyclo[5.3.1]undecan-4-one

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The structure of $C_{11}H_{19}NO$ has been refined with new X-ray diffraction data collected at 98 K. Crystals are monoclinic, $P2_1/n$; $a = 6{\cdot}940\,(1)$, $b = 13{\cdot}819\,(3)$, $c = 10{\cdot}561\,(2)$ Å, $\beta = 93{\cdot}04\,(2)°$. Comparison of the results with those of the room-temperature analysis reveals systematic differences in bond lengths. When rigid-body libration corrections are applied these differences disappear and virtually identical molecular geometries are obtained for the two temperatures, except that the pyramidality at the N atom appears to be slightly less pronounced at the higher temperature. The N lone-pair density is clearly visible in a difference map based on the low-temperature data.

Introduction

A room-temperature (RT) analysis of the title compound (Kaftory & Dunitz, 1975) has shown that the molecular conformation is characterized by a short, transannular, non-bonded N···C=O distance of 2·46 Å, corresponding to a strong intramoecular donor-acceptor interaction. From the marked solvent dependence of the carbonyl absorption (from 1666 cm^{-1} in C_6H_{12} to 1613 cm^{-1} in $CHCl_3$) the strength of this interaction would appear to be sensitive to small, external perturbations, with the implication that the potential-energy variation along the N···C distance coordinate might exhibit only a rather shallow minimum with pronounced anharmonicity. Since interatomic separations derived from diffraction methods do not correspond to equilibrium distances (r_e) but rather to the centroids of distributions obtained by averaging over the intra- and intermolecular vibrations (r_g), any pronounced anharmonicity in the potential would lead to slightly different r_g values being observed at different temperatures.

In this paper we describe results of a low-temperature (LT, 98 K) analysis of the title compound and compare them with those of the earlier RT study.

Details of analysis

A single crystal with dimensions 0·50 × 0·40 × 0·35 mm was taken from the original sample and sealed in Araldite as protection against moisture. Cell dimensions (Table 1) and intensities were measured on an Enraf–Nonius CAD-4 diffractometer (graphite-monochromatized Mo $K\alpha$ radiation) equipped with a low-temperature device. During the measurements the crystal was maintained at 98 ± 1 K and no detectable loss of intensity occurred. Of the 2424 independent reflexions recorded ($\theta \leq 24°$), 1670 were regarded as significantly above background ($I > 3\sigma I$).

Table 1. *Crystal data*

11-Methyl-11-azabicyclo[5.3.1]undecan-4-one. Molecular formula:* $C_{11}H_{19}NO$, FW = 181·28.

	RT	98 K
a (Å)	7·033	6·940 (1)
b (Å)	13·980	13·819 (3)
c (Å)	10·656	10·561 (2)
β (°)	93·26	93·04 (2)
Z	4	
V (Å^3)	1046·0	1011·4
Space group	$P2_1/n$	
D_x (g cm^{-3})	1·15	1·19

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* Erroneously given as $C_{11}H_{16}NO$ (FW = 178·26) in Kaftory & Dunitz (1975).