

# Investigation of the Solution Phase and Solid State Structures of Hector's and Dost's Bases by $^{13}\text{C}$ NMR Spectroscopy

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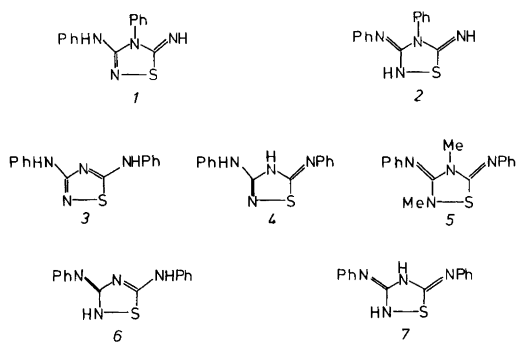
Butler, A., Edlund, V., Glidewell, C. and Nordén, B., 1986. Investigation of the Solution Phase and Solid State Structures of Hector's and Dost's Bases by  $^{13}\text{C}$  NMR Spectroscopy. – Acta Chem. Scand. B 40: 779–781.

The solid state and solution  $^{13}\text{C}$  NMR spectra of two heterocyclic compounds, Hector's Base and Dost's Base, have been compared. It was concluded that the solution and solid state structures of the former are similar but, for the latter, crystallisation causes greater coplanarity and parallel stacking of the molecules.

Oxidation of phenylthiourea by hydrogen peroxide yields a nitrogen/sulfur heterocyclic compound,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ , known as Hector's Base.<sup>1</sup> The structure of this compound was for many years not known with certainty, but an X-ray crystallographic study<sup>2</sup> established it unambiguously as *1*. A further study<sup>3</sup> of its  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra in solution showed that although tautomerism to give *2* is possible, structure *1* is retained in solution.

By heating an ethanolic solution of Hector's Base with ammonia in a sealed tube, isomerisation to Dost's Base occurs.<sup>4</sup> From  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR studies,<sup>3</sup> we concluded that the structure of Dost's Base in solution is *3* rather than any tautomeric structure such as *4*. The assignments of the solution structures of Hector's and Dost's Bases were established by comparison of their spectra with those of related compounds, such as *5*, where tautomerism is not possible.

Information concerning the solid state structure of Dost's Base was difficult to obtain. Crystals of Dost's Base are monoclinic with two molecules of  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$  in the asymmetric unit.\* Two independent data sets (STADI-2 diffractometer, SHELX-76/MULTAN, and Syntex  $\text{P}_1$ , SHELX-



82) both failed to provide a crystal structure: from each data set, the best E maps provided only a small part of the asymmetric unit and these could never be developed satisfactorily. Comparison of the solution and solid state NMR spectra was therefore of importance in establishing the constitution of Dost's Base in the solid state.

Completely new sets of solution  $^{13}\text{C}$  NMR data for *1*, *3*, and *5* were obtained and the probable assignments are given in Table 1. The CH and  $\text{CH}_3$  groups were separated from the quaternary carbons by the DEPT  $3\pi/4$  pulse sequence. The nomenclature is that used in a previous paper<sup>3</sup> and assignments were made in the manner described therein; but there are inevitably some uncertainties. However, it is clear that when the aromatic

\*Crystal data:  $a = 29.18(1)$ ,  $b = 11.746(8)$ ,  $c = 7.828(5)$  Å;  $\beta = 108.24(3)^\circ$ ; space group  $\text{P2}_1/c$ ;  $Z = 8$  for  $\rho = 1.398 \text{ g cm}^{-3}$  (cf. Hector's Base,  $\rho = 1.393 \text{ g cm}^{-3}$ ).

rings are in similar chemical environments, as in 3 and 5, the resonances from the aromatic carbons appear as four distinct pairs and, within each pair, the chemical shifts are rather similar (cf. C(g) with C(k), etc.); where the aromatic ring is attached to a nitrogen bound by an exocyclic double bond, as in 5, the resonances of the quaternary carbons C(g) and C(k) move to much higher chemical shifts.

The solid state  $^{13}\text{C}$  NMR spectrum of Hector's Base was expected, the aromatic carbons appearing between 119.8 and 137.7 ppm and the spectrum had the same appearance as the solution spectrum, except that the aromatic resonances were not resolved. C(e) and C(f) probably resonated at 144.6 and 166.1 ppm although the poor signal-to-noise ratio due to interaction with the quadrupolar  $^{14}\text{N}$  made assignment uncertain. The similarity of the solid state and solution spectra of Hector's Base confirmed our view<sup>3</sup> that Hector's Base undergoes no significant structural changes

Table 1. Assignment of the  $^{13}\text{C}$  NMR of compounds 1, 3 and 5 in DMSO solution.

	1	3	5
C(e)	148.2	162.3	147.4
C(f)	165.4	176.6	153.3
C(g)	139.4	141.1	149.2
C(h)	129.7	129.2	129.5
C(i)	129.1	122.7	124.3
C(j)	122.3	117.9	121.4
C(k)	134.3	140.7	148.7
C(l)	129.2	128.5	128.8
C(m)	128.3	120.6	121.7
C(n)	119.8	117.1	120.7
C(p)	—	—	40.3
C(q)	—	—	31.4

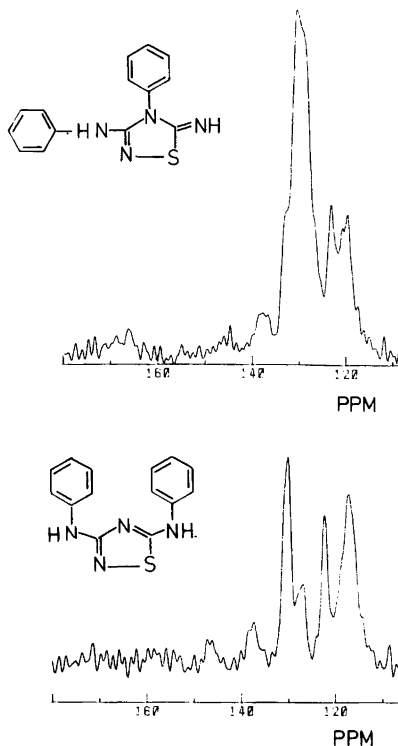
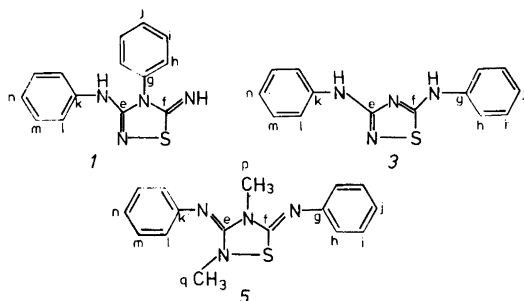


Fig. 1. Solid state  $^{13}\text{C}$  NMR spectra of Hector's and Dost's Bases. Chemical shifts are shown relative to glycine.

in solution. The phenyl groups will librate in solution but the spectra suggest that their mean positions are similar to the fixed positions in the crystal. In contrast, the solid state spectrum of Dost's Base is substantially different from the corresponding solution spectrum. The absence of resonances in the 150 ppm region eliminates the possibility of tautomerism to give 4, 6 or 7 and confirms that structure 3 is retained. Furthermore, the close pairing of the aromatic resonances, observed for 1, 3, and 5 in solution, and for 1 in the solid state also, was lost. The aromatic resonances in the solid state spectrum of Dost's Base were grouped into two clusters, one having  $\delta$  in the range 117.3–122.3, and the other with  $\delta$  127.5–137.6 ppm, with more resolvable resonances than for 1. Clearly, the close similarity of the phenyl groups observed in solution for Dost's Base 3 is lost upon crystallisation, and

in this respect, Dost's Base differs markedly from Hector's Base, *1*.

For Hector's Base, the two phenyl groups are approximately normal to the planar heterocyclic ring in the solid state,<sup>2</sup> and it would be expected that the two phenyl groups of Dost's Base would be similarly disposed towards the heterocyclic ring. If on crystallisation, however, intermolecular forces twist one of the rings away from this favoured disposition to one where it is approximately coplanar with the heterocyclic ring, then the two phenyl groups are in different chemical environments. This appears at present to be the most plausible interpretation of the solid state spectrum. At the same time, the whole molecule moves closer to total coplanarity with parallel stacking in the crystal and this may explain the E statistics and our inability to solve the crystal structure.

### Experimental

Hector's Base (*1*) was prepared by the oxidation of 1-phenylthiourea;<sup>5</sup> Dost's Base *3* by the oxidation of 1-(*N,N*-dimethylamidino)3-phenylthiourea.<sup>6</sup>

The <sup>13</sup>C CP/MAS NMR spectra of *1* and *2* were obtained on a Bruker MSL-100 wide bore instrument operating at 25.78 MHz with the standard fixed frequency high power probe for CP/MAS experiments. Rotors were made of Delrin and were of the Andrew-Beams type.

Experimental parameters were: 3 ms contact time, 20 s repetition rate, 10 kHz spectral width and 700 data points zero-filled to 4 K. Chemical shifts are given using the carbonyl carbon of glycine as reference (176.03 ppm).

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