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THE INFLUENCE OF N-SUBSTITUENTS ON THE RING PROTON SHIFTS IN AZIRIDINES[1]

THE ROLE OF MAGNETIC ANISOTROPY AND INTRAMOLECULAR DISPERSION EFFECTS:

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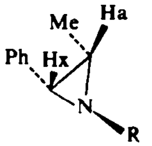
Abstract—The effect of N-alkyl substituents on the ring proton shifts in aziridines is reported. We have found that ring protons *cis* to the magnetically anisotropic N-alkyl bond show a chemical shift to higher field. The magnitude of the shielding effect tends to decrease with the steric requirements of the N-substituent, i.e., Me > Et > i-Pr ≫ t-Bu. The observed trend in deshielding has been ascribed to intramolecular van der Waals (dispersion) interactions between the N-alkyl and *cis* ring protons. A dispersion-induced deshielding *and* shielding (DIDS) effect has been invoked to account for the ring proton shifts in sterically crowded aziridines such as 1-t-butylstyrenimine and 1-t-butylaziridine.

In a recent study[2] of vicinal proton couplings in the configurationally pure *cis* isomers, A and B, we found that the benzylic proton (H_x) in B was shifted ca. 0·75 ppm upfield relative to H_x in A.

Initially, we proposed* that the magnetically anistropic N-methyl C—N bond shielded the *cis* protons, i.e., H_a and H_x, in the more stable *trans* conformation shown below.



	R
A	H
B	Me

In contrast to our proposal, however, Turner *et al.*[4] had recently suggested that the lower field absorptions in the ring proton spectra of 1-alkyl-2,3-dibenzoylaziridines were due to the ring protons *cis* rather than *trans* to the substituent on nitrogen.

In view of these conflicting claims, we undertook a more thorough investigation to elucidate the role that N-substituents played in determining ring proton shifts in aziridines. The present communication describes the remarkable effect that N-alkyl groups exert on ring proton shifts in styrenimines (2-phenylaziridines) and ethylenimines (aziridines).

RESULTS AND DISCUSSION

The 1-Me, 1-Et, 1-i-Pr, and 1-t-Bu analogs of styrenimine and aziridine were prepared according to the Wenker procedure.[5,6] The proton spectra of styrenimines

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* After completion of our work,[1] Bystrov *et al.*[3] reported in harmony with our proposal, that the diamagnetic anistropy of the N—R bond exerts a stronger effect on the cis ring protons.

I–V and aziridines VI–X were recorded at room temperature as 10 and 50% (w/w) CCl_4 solutions, and as a 50% cyclohexane-d_{12} (w/w) solution. The ring proton spectra for the five styrenimines (I–V) as 50% CCl_4 solutions are illustrated in Fig. 1. In the spectrum of III, the second line of the H_x signal is masked by the outer line of the N-methylene signal. Solvent and concentration effects did not appear to significantly alter the relative chemical shifts attributed to intramolecular contributions.

In general, first order spectra are observed for these unsymmetrical 3-spin systems and accordingly, each case was treated as a simple ABX system as previously described.[7] The assignment of bands was based on the assumption that $J_{cis} > J_{trans}$ in harmony with our earlier studies.[2] Ring proton coupling constants for the styrenimines are recorded in Table 1. Within the framework of current theory,[8] the similarity of the geminal and vicinal proton coupling constants for I–V suggests that any substituent-induced changes in the ring geometry of these molecules are essentially negligible.

Table 1. Geminal and vicinal proton coupling constants for styrenimines[a]

	J_{ax}	J_{bx}	J_{ab} (c/s)
I	6·2	3·3	0·9
II	6·4	3·2	1·3
III	6·4	3·2	1·2
IV	6·4	3·2	1·2
V	6·3	2·8	1·4

[a] As 50% CCl_4 solns at room temp.

A careful inspection of Fig. 1 and Table 2 reveals the remarkable effect that N-substituents exert on the chemical shifts of the ring protons in aziridines II–V.

Contrary to an earlier claim,[4] we find that the ring protons cis to N-alkyl substituents show a chemical shift to higher field. Moreover, the magnitude of the shielding effect tends to decrease with the steric requirements of the N-substituent, i.e., Me > Et > i-Pr ≫ t-Bu.

The observed trend in the ring proton shifts is surprising since one would have

Table 2. Chemical shift values[a] for ring protons in styrenimines

Styrenimine	H_x		H_a		H_b	
	CCl_4[b]	C_6D_{12}[c]	CCl_4	C_6D_{12}	CCl_4	C_6D_{12}
I	163·8	162·3	112·4	110·8	87·4	84·9
II	123·2	122·3	80·8	78·7	99·4	97·3
III	127·2	125·8	83·8	81·8	99·4	97·2
IV	130·5	130·0	86·8	85·2	99·4	97·2
V	149·6	149·6	104·3	103·4	86·9	84·3

[a] In c/s from internal TMS.

[b] As 50% CCl_4 solns (w/w).

[c] As 50% C_6D_{12} solns (w/w).

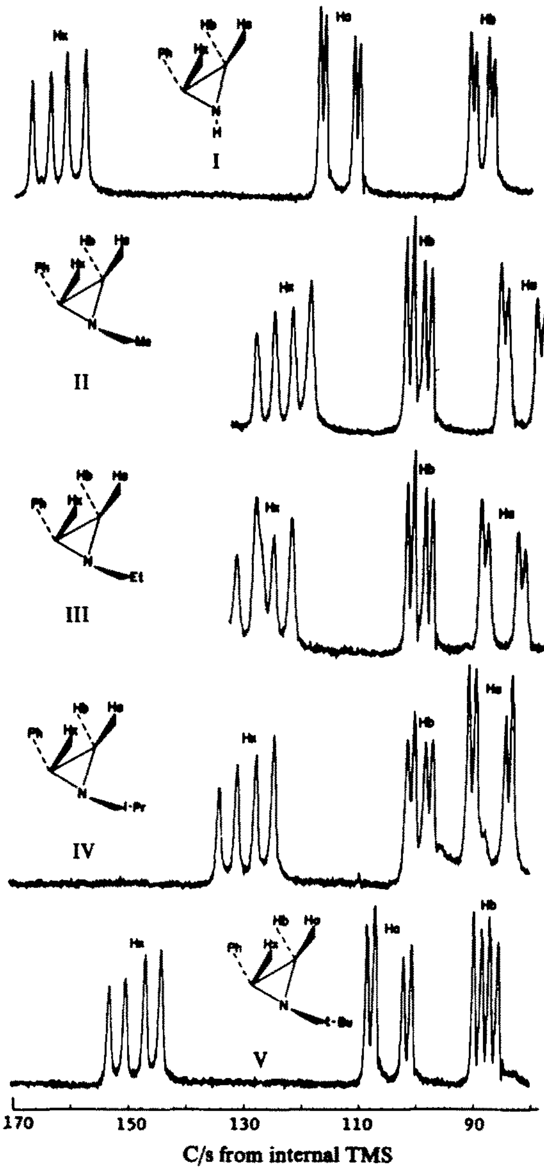

Fig. 1 Ring proton spectra of styrenimines as 50% CCl_4 solutions (100 c/s sweep width).

expected *increased* shielding from the anisotropy of the N-alkyl C—C single bonds.[9] At present, we theorize that such deshielding is ascribable to intramolecular Van der Waals (dispersion) interactions[10] between the N-alkyl and ring (H_a and H_x) protons. It appears that the inverting N-alkyl and ring protons come into such close proximity that strong dispersion interactions occur.

Presumably, the nonbonded interactions between the ring and N-alkyl hydrogens cause a distortion of the electron cloud around the compressed ring protons and

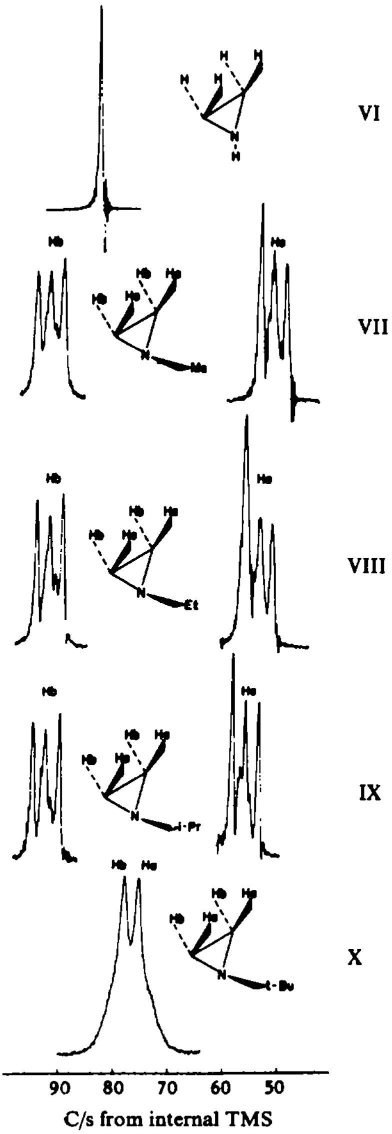

Fig. 2 Ring proton spectra of 1-alkylaziridines as 50% CCl_4 solutions. The assignment of peaks in X is provisional.

deshielding of the latter occurs. As indicated above, such dispersion effects become especially important as the steric requirements of the N-alkyl group increase. Thus the Van der Waals contribution to δ H_a and δ H_x in the 1-ethyl and 1-isopropylstyrenimine relative to the 1-Me analog is as expected, rather small. On the other hand, the steric deshielding effect on H_a and H_x due to the bulky t-Bu group in V is remarkable.

Significantly, van der Waals shifts of similar magnitude have also been observed[11] for the ring protons in 1-alkylaziridines (VIII-X). The proton spectra (Figure 2) and ν_{AB} values (Table 3) for the 1-alkylaziridines clearly illustrate this point. In addition,

TABLE 3. ν_{AB} VALUES FOR 1-ALKYLAZIRIDINES[a]

R	ν_{AB} c/s
Me	42
Et	39
i-Pr	36
t-Bu	3[b]

[a] 60-Mc/s spectra recorded as 50% CCl_4 solutions.
[b] Peak separation.

note that the strong dispersion forces associated with the bulky t-Bu group in X appear to alter the magnetic environment of the cis (H_a) *and* (H_b) protons.

The dispersion-induced deshielding and shielding (*DIDS*) *effect.* Especially germane to the mechanism of dispersion effects in aziridines is the observation that H_b in 1-t-butylstyrenimine (V) and 1-t-butylaziridine (X) is shifted over 0·2 ppm to *higher* field relative to H_b in the corresponding N-Me, N-Et and N-i-Pr analogs. We conjecture that this diamagnetic shift reflects further distortion of the ring proton electron cloud by the sterically demanding t-Bu group. Apparently, the distorted electron cloud of the ring protons is shifted away from the *cis* protons towards the other plane of the ring, thus accounting for the deshielding of the compressed protons and higher shielding of H_b in aziridines V and X.

At present, we propose that the NMR spectral data for such sterically crowded aziridines as typified by 1-t-butylaziridine and 1-t-butylstyrenimine can be most easily rationalized in terms of a dispersion-induced deshielding and shielding (DIDS) effect. We are currently seeking to magnify the DIDS effect in model aziridines with more sterically-demanding substituents of varying electronegativities (12).

EXPERIMENTAL†

Aziridine synthesis. The styrenimines I–V and aziridines VI–X were prepared according to the procedure described by Brois.[5] Physical, yield and analytical data for the styrenimines are depicted in Table 4. The aziridines VI–X were previously reported.[5b]

NMR spectra. The proton spectra of styrenimines I–V and aziridines VI–X as 10 and 50% CCl_4 solns (w/w) and as 50% cyclohexane-d_{12} solution (w/w) were determined at room temp employing a Varian A-60 spectrometer. Chemical shift values were obtained in each case from replicate spectra run at a sweep width of 100 c/s.

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[*] The remarkable chemical shift trend recently observed[10f] for the ring protons in sterically crowded half-cage molecules represents a classic example of the DIDS effect.

[†] B.ps are uncorrected. IR spectra of neat liquid samples were determined with a Perkin–Elmer Model 21 spectrophotometer with NaCl optics. The NMR spectra were run at room temp employing a Varian Model A-60 spectrometer. Gas chromatographic analyses were obtained with an F & M Scientific Corp. Model 500 linear programmed temp gas chromatograph. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

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TABLE 4. YIELDS AND PHYSICAL DATA FOR STYRENIMINES

Aziridine	Yield %	B.p. °C (mm)	n_D^{20}	Analyses		
				C	H	N
I	90	94–95 (10)	1·5588	80·62	7·61	11·76 Theory
				80·75	7·79	11·50 Found
II[a]	76	39–40 (0·5)	1·5327	81·16	8·33	10·52
				81·36	8·00	10·44
III[b]	82	41–42 (0·1)	1·5220	81·58	8·90	9·52
				81·58	8·93	9·55
IV[c]	87	31·5–32 (0·05)	1·5087	81·93	9·38	8·69
				81·88	9·75	8·75
V	75	65–66 (0·65)	1·5070	82·23	9·78	7·99
				82·01	9·93	8·00

[a] Ref. 7 reports b.p. 35–37° (0·3 mm), n_D^{20} 1·5321.

[b] Ref. 7 reports b.p. 68–70° (2·5 mm), n_D^{20} 1·5220.

[c] Ref. 7 reports b.p. 68–70° (2·4 mm), n_D^{20} 1·5090.