7-Acetylamino-3-ethoxycarbonylbenzo[b]thiophene (VI). To a suspension of 3 g (11 mmole) compound V in 60 ml dioxane, 40 ml EtOH and 9 ml concentrated HCl, cooled to −10°C, was added a solution of 2 g (29 mmole) sodium nitrite in 6 ml water, maintaining the reaction mixture at −10°C and holding it as this temperature for a further 20 min. The diazo solution was then added to a solution of 0.05 g copper acetate in 25 ml EtOH and the mixture held at 70°C for 30 min and then poured into water. The solution was extracted with $CHCl_3$, the chloroform evaporated, alcohol added to the residue and the solid filtered off. Yield 1 g (35.2%), mp 194-195°C (from EtOH). IR spectrum, cm^{-1}: 1645, 1710 (CO); 3240 (NH). PMR spectrum (in acetone-d_6), ppm: 9.26 (str. s, NH), 8.55 (s, 2-CH), 8.40 (d, J_{45} = 7.5 Hz, 4-CH), 7.70 (str. d, J_{45} = 7.5 Hz, 6-H), 7.49 (t, J_{45} = J_{56} = 7.5 Hz, 5-H), 4.39, 1.70 (t, d, $COOCH_2CH_3$), 2.20 (str. s, $COCH_3$). Found, %: C 59.2, H 5.0, N 5.2, S 12.3; M^+ 263. $C_{13}H_{13}NO_3S$. Calculated, %: C 59.3, H 5.0, N 5.3, S 12.2; M 263.

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^{13}C AND ^{15}N NMR SPECTRA OF 2,3-SUBSTITUTED 2H-AZIRINES

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The ^{13}C and ^{15}N NMR spectra of a series of 2,3-substituted 2H-azirines have been studied. The ^{15}N chemical shift for the nitrogen in the azirine ring is found at much higher field than in acyclic imines with a considerable electronic effect for the substituents on the double bond. Cooperative steric and electronic effects associated with substituents on the unsaturated carbon atom of the ring were found to influence the shielding of the ^{13}C and ^{15}N nuclei. Reaction constants have been calculated for 2-alkyl(aryl)-3-phenylazirines. It has been shown that the azirine ring has a powerful −I effect (when compared with the phenyl ring) that exceeds the analogous value for the cyano group.

The ^{13}C and ^{15}N NMR spectra of a series of 2,3-substituted 2H-azirines have been examined in order to study the factors influencing ^{13}C and ^{15}N nuclear shielding in 2H-azirines and the effect of the azirine ring on adjacent bonds.

The ^{13}C and ^{15}N NMR spectral parameters are given in Tables 1 and 2. In the literature [1, 2] only the ^{13}C spectra of II and III have been reported and our results are in good agreement. Assignment of ^{13}C signals were carried out using long range $^{13}C-^{1}H$ spin-spin coupling constants as described in [2].

The ^{15}N signal for the nitrogen of the azirine ring was shifted to high field of the cyclic analogues of azirines — the imines [3, 4]. This is apparently due to steric strain in the three membered ring. Analogous shifts have been reported [5] for aziridines when compared with acyclic amines. High field shifts for the azirines (~40-50 ppm) were larger than for the aziridines (~35-45 ppm) [5]. This is possibly connected with the higher ring strain at the nitrogen atom in the azirines than the aziridines. ^{15}N chemical shifts (CS) depend significantly on the properties of the substituents on the double bond, the basic influence on this shift being the mesomeric effect. This is a consequence of the correlation of ^{15}N CS with the reaction constants for the 3-substituents. The ^{15}N resonance was shifted to higher field with increasing donor ability of this substituent (COOEt < Ph < NH_2) and is in agreement with observations on imines [3, 4]. The effect of the C_2 substituent on the ^{15}N shift was also observed. Notable symbate shifts for both ^{15}N and C_3 resonances were observed

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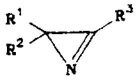
TABLE 1. ^{15}N NMR Spectral Data for Azirines I-VII



Compound*	R^1	R^2	R^3	^{15}N chemical shift, ppm			$^1J_{^{15}N-^1H}$, Hz	
				$N_{(1)}$	$N(R^1)$	$N(R^3)$	$N(R^1)$	$N(R^3)$
I [10]	CH_3	CH_3	C_6H_5	−83,5	—	—	—	—
II [11]	CH_3	H	C_6H_5	−98,0	—	—	—	—
III [11]	C_6H_5	H	C_6H_5	−104,3	—	—	—	—
IV [12]	C_6H_5	H	$COOC_2H_5$	−63,2	—	—	—	—
V [13]	C_6H_5NHCO	H	NH_2	−200,0	−249,8	−319,8	91,0	92,3
VI [13]	$4\text{-}CH_3C_6H_4NHCO$	H	NH_2	−199,7	−250,7	−319,9	89,9	91,7
VII [13]	$4\text{-}CH_3OC_6H_4NHCO$	H	NH_2	−199,9	−252,2	−319,9	90,1	91,3

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*Synthetic method in brackets.

TABLE 2. ^{13}C NMR Spectra of Azirines I-VII

Compound	^{13}C chemical shift,* ppm				$^1J_{^{13}C_2-H}$, Hz	Solvent
	$C_{(2)}$	$C_{(3)}$	$C_{(R^1)}$	$C_{(R^3)}$		
I	35,82	178,07	25,04	126,58 (C_α), 132,95 (C_p), 129,64 (C_m), 129,38 (C_o)	—	$CDCl_3$
II	27,18	172,34	19,22	126,32 (C_α), 132,99 (C_p), 129,58 (C_m), 129,44 (C_o)	186,5	$CDCl_3$
III	34,98	164,05	141,73 (C_α), 127,67 (C_p) 128,96 (C_m), 126,75 (C_o)	124,80 (C_α), 133,73 (C_p), 130,35 (C_o), 129,90 (C_m)	186,9	$CDCl_3$
IV	39,27	163,79	139,29 (C_α), 128,63 (C_p), 129,07 (C_m), 127,14 (C_o)	159,34 (CO), 63,87 (CH_2), 14,41 (CH_3)	185,7	$CDCl_3$
V	33,82	149,00	170,23 (CO), 139,20 (C_α), 128,21 (C_m), 119,33 (C_o), 123,29 (C_p)	—	180,0	DMSO
VI	34,84	150,09	171,06 (CO), 137,75 (C_α), 130,16 (C_m), 120,35 (C_o), 133,21 (C_p), 21,47 (CH_3)	—	180,1	DMSO
VII	34,79	150,37	170,91 (CO), 133,57 (C_α), 121,97 (C_m), 115,02 (C_o), 156,45 (C_p), 56,23 (OCH_3)	—	178,5	DMSO

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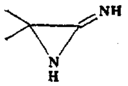
*For compound I $C_{(R^2)}$ = 25.04.

with a change in the substituent at position 2. Evidently, the joint influence of steric and electronic effects for these substituents is common to both nuclei but the sensitivity of the ^{15}N CS is some 1.5 times greater than the ^{13}C CS. This is less than in the 2-substituted aziridines [6] where the ^{15}N resonance is 2.7 times more sensitive than the $^{13}C_3$ signal.

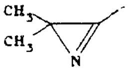
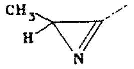
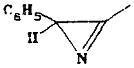
The strong shielding of the azirine ^{15}N nucleus in the 3-amino derivatives V-VII might also have been due to an increased contribution from the tautomeric structure A.



A

However, in the ^{15}N spectra obtained with proton spin-spin coupling, the signal for the amino group was a clear triplet with a coupling of ~91-92 Hz (Table 1) making such an

TABLE 3

Azirine	σ_R^0	σ_I
	0,08	0,69
	0,08	0,66
	0,10	0,78

explanation unlikely. This spin-spin coupling is characteristic of an sp^2 hybridized planar nitrogen atom; a contribution from structure A would be expected to decrease it. Increasing acceptor property in the 4-substituent of the phenyl ring (compounds V-VII) led to an increase in both the ${}^1J_{{}^{13}C_2H}$ in the ring and ${}^1J_{{}^{15}NH}$ in the amino group. This points to greater conjugation of the amino group with the C=N bond when the acceptor strength of the 2-substituent is increased. The ${}^{15}N$ CS of the amino group showed a low sensitivity to this change of conjugation whereas the ${}^{15}N$ shift of the amido nitrogen atom proved to be fairly sensitive to substituent change in the phenyl ring. In future work, it is proposed to carry out quantitative analysis of this relationship with the use of an extended series of substituted 3-aminoazirines.

The ${}^{13}C$ CS of the carbon atoms of the 3-phenyl ring in I-III have been used to calculate the reaction constant of 2-substituted azirine rings according to [7] (Table 3).

In relation to a phenyl ring the 3-azirinyl group behaves as a powerful acceptor. Indeed, the inductive effect of the 3-azirinyl fragment exceeds such strong acceptors as the cyano group ($\sigma_R = 0.56$, $\sigma_R = 0.13$ [8]).

EXPERIMENTAL

${}^{13}C$ and ${}^{15}N$ NMR spectra were obtained on WH90/DS (22.63 MHz) and WM 360 (36.5 HMz) instruments, respectively. For ${}^{13}C$ the internal standard was TMS and the precision of measurement ±0.03 ppm whereas nitromethane was used for ${}^{15}N$ with a precision of ±0.1 ppm. The pulse angle was ~30° with pulse intervals of 4 sec for carbon and 15 sec for nitrogen. About 1000 pulses were accumulated for carbon and ~ 2000 for nitrogen. ${}^{13}C-{}^{1}H$ Spin-spin couplings were measure from proton coupled spectra with a precision of ±0.2 Hz. ${}^{15}N-{}^{1}H$ Spin-spin couplings were obtained from the ${}^{15}N$ spectra using polarization transfer from protons (the INEPT method [9]) with a precision of ±0.1 Hz. Solutions were ~10% for ${}^{13}C$ and ~50% for ${}^{15}N$.

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