STRUCTURAL EXAMINATION OF 1-VINYLPHENOTHIAZINE, 10-VINYLPHENOTHIAZINE S-OXIDE, 10-VINYLCARBAZOLE, 9-VINYLCARBAZOLE, AND 9-VINYL-β-CARBOLINE BY ^{1}H AND ^{13}C NMR

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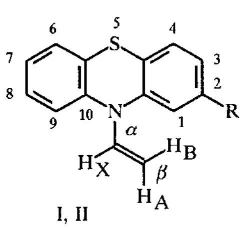
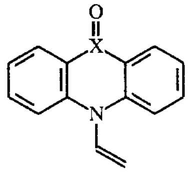
According to ^{1}H and ^{13}C NMR, the vinyl group in 10-vinylphenothiazine is coplanar with the plane orthogonal to the axis of the lone pair on nitrogen, as a result of bending of the ring along the S—N axis. In 10-vinylphenothiazine S-oxide, this bending does not occur, and as a result of the steric influence of the heterocycle the vinyl group is located nearly orthogonally to the heterocycle, and is analogous to the spatial structure of 10-vinylacridone. In 9-vinylcarbazole, the N—Cα torsion angle is 60°, increasing to 75° in 9-vinyl-1-methyl-β-carboline.

In the course of an examination of the steric and electronic structures of N-vinylheterocycles, systematic studies have been carried out of the ^{1}H and ^{13}C NMR spectra of N-vinylpyrroles [1, 2], N-vinylazoles (the azole ring being varied from pyrazole to tetrazole) [3-6], N-vinylpyridones [7, 8], and N-vinyluraciles [9, 10]. Among N-vinylheterocycles, N-vinylphenothiazine and its derivatives occupy a special place by virtue of the unusual structure of the phenothiazine ring. We have now examined the steric and electronic structures of 10-vinylphenothiazine (I), its 2-chloro derivative (II), and its S-oxide (III) by ^{1}H and ^{13}C NMR as compared with 10-vinylacridone (IV), 9-vinylcarbazole (V), 9-vinyl-1-methyl-β-carboline (VI), N-vinyldiphenylamine (VII), 1-vinylimidazole (VIII) and its hydrochloride (IX), N-vinylpyrrole (X), 1-vinylindole (XI), 1-vinyl-4-pyridone (XII), and 1-vinyl-4-quinolone (XIII).

The ^{1}H and ^{13}C NMR data for (I-XIII) are shown in Tables 1 and 2. The steric structure of 10-vinylphenothiazine may be defined in terms of three parameters, viz., the dihedral angle ξ between the planes of the two benzene rings, and the angle η between the N—S axis and the N—Cα bond, and the torsion angle φ between the plane of the vinyl group and the plane δ orthogonal to the axis of the lone pair on the nitrogen (A). The electronic structure of 10-vinylphenothiazine is dependent on the mode of hybridization of the lone pair of electrons at nitrogen.



I, II



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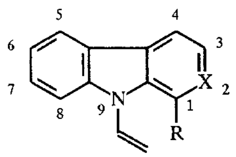
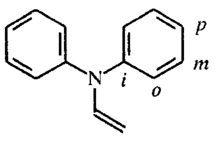
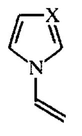


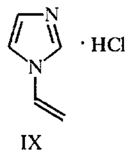
V, VI



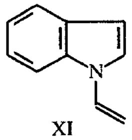
VII



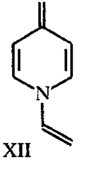
VIII, X



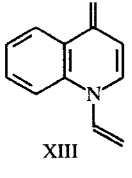
IX



XI



XII



XIII

I R=H; II R=Cl; III X=S; IV X=C; V R=H, X=CH; VI R=CH$_3$, X=N; VIII X=H; X X=CH

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TABLE 1. ^1H and ^{13}C Spectral Parameters for the Vinyl Group in (I-XIII)

Compound	Chemical shift, ppm						Coupling constant, Hz				
	H_A	H_B	H_X	$\Delta\delta$	$C\alpha$	C_β	$^2J_{AB}$	$^1J_{C_\beta H_A}$	$^1J_{C_\beta H_B}$	$^1J_{C\alpha H_X}$	ΔJ
I	4,12	4,76	6,77	0,64	136,75	87,85	-0,8	162,2	157,8	169,4	4,4
II	4,25	4,85	6,78	0,60	136,23	90,10	-1,0	162,4	157,8	170,3	4,6
III	5,58	5,56	6,76	-0,02	132,87	116,81	-0,45	161,0	159,6	177,6	1,4
IV	5,94	5,60	6,62	-0,34	132,37	122,87	-0,4	160,8	159,4	180,2	1,4
V	5,02	5,43	7,16	0,41	129,43	101,83	-0,9	162,4	158,1	172,3	4,3
VI	5,40	5,42	7,23	0,02	129,10	110,20	-0,5	161,6	158,4	177,1	3,2
VII	4,11	4,02	6,90	-0,09	138,14	90,45	<0,3	162,4	158,0	169,1	4,4
VIII	4,78	5,19	6,83	0,41	129,51	101,72	-1,6	164,9	157,5	178,0	7,4
IX	5,39	5,82	7,48	0,43	128,36	109,02	-2,9	166,0	159,3	187,4	6,7
X	4,57	5,04	6,76	0,47	133,28	96,94	-1,3	164,0	156,6	173,3	7,4
XI	4,73	5,16	7,20	0,43	129,92	96,25	-1,2	164,1	156,8	173,0	7,3
XII	4,97	5,24	6,71	0,27	135,56	101,90	-2,7	165,8	158,1	180,7	7,7
XIII	5,34	5,47	7,21	0,13	134,35	109,94	-1,7	164,2	158,3	181,0	5,9

TABLE 2. ^{13}C NMR Spectral Data for (I), (III), (IV), (V), and (VII)*

Compound	Chemical shift, ppm					
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(11)}$	$C_{(12)}$
I	121,54	127,81	124,59	127,16	142,28	129,59
III	117,63	132,53**	122,78	130,85**	142,06	138,10
IV	116,37	133,49	121,87	127,49	141,51	***
V	110,16	126,22	120,58	120,21	139,33	123,98
	C_o	C_m	C_p	C_i		
VII	123,54	129,45	123,60	145,28	—	—

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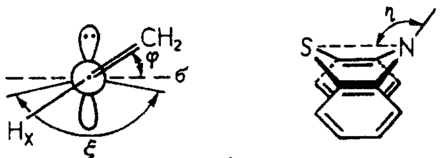
*Signals assigned as in [26].

**Signals assigned ambiguously.

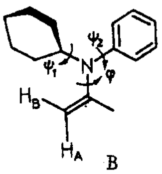
***Signal not recorded as a result of the low solubility of the sample.



A

According to x-ray crystallography, in N-alkyl- and N-phenylphenothiazines the three carbon atoms bonded to nitrogen, and the nitrogen atom itself, lie nearly in the same plane, indicating that the endocyclic nitrogen is nearly sp^2-hybridized [11, 12]. The same data indicate that the value of the angle ξ in 10-vinylphenothiazine should lie between 135 and 140°, and η around 160° [13, 14]. The torsion angle φ in 10-vinylphenothiazine can be calculated from the ^1H and ^{13}C spectra of its vinyl group. The chemical shift of the β-carbon of the vinyl group, which is a measure of the p—π interaction of the lone pair on nitrogen with the vinyl group, is 87.85 ppm in (I). Such strong screening of Cβ is not seen in any of the previously-studied N-vinylheterocycles [1-10]. It is due to particularly effective p—π conjugation with the vinyl group in 10-vinylphenothiazine (I). This requires that the torsion angle φ be close to zero, which is possible as a result of the reduction in the steric effect of the nonplanar phenothiazine ring on the vinyl group. Furthermore, the nonplanarity of the phenothiazine ring disrupts p—π conjugation of the nitrogen lone pair with the heterocycles, resulting in even stronger p—π conjugation with the vinyl group. The occurrence of effective p—π conjugation with the vinyl group bonded to the phenothiazine ring is also shown by the substantial low-field shift of the Cβ signal (2.25 ppm, see Table 1) in the 2-chloro-compound (II) as compared with (I) as a result of the transmission of the electron acceptor effect of the chlorine atom to the vinyl group.

We now compare the steric structure of 10-vinylphenothiazine with that of its structural analog lacking a sulfide bridge between the benzene rings, namely N-vinyldiphenylamine (VII). In (VII), as in the analogous phenothiazine, the nitrogen is nearly sp^2-hybridized [15]. The steric structure of N-vinyldiphenylamine may be defined in terms of three torsion angles, namely those along N—Ph (ψ_1 and ψ_2), and along N—Cα(φ) (B).



B

The chemical shift of the vinyl β-carbon in N-vinyldiphenylamine (VII) is similar to that in 10-vinylphenothiazine (I) (90.45 and 87.85 ppm, respectively), indicating that p—π conjugation with the vinyl group is similar in these molecules. The difference in the direct ^{13}C—^{1}H coupling constants for the β-carbon of the vinyl group ($\Delta J = {}^{1}J_{C\beta H_A} - {}^{1}J_{C\beta H_B}$, see Table 1) in (VII) and (I) is the same (4.4 Hz). The parameter ΔJ is functionally related to the torsion angle φ [8, 16]. The equality of the ΔJ values in (I) and (VII) indicates that the torsion angle φ remains unchanged.

The chemical shifts of the β-trans-proton of the vinyl group (H_A) in (I) and (VII) are nearly the same (4.12 and 4.11 ppm, respectively). Further, the signal for the β-cis-proton of the vinyl group in (VII) (H_B) is strongly shifted to higher field (0.74 ppm) as compared with that in (I). For this reason, the relative chemical shift of the vinyl group β-protons ($\Delta\delta = \delta_{H_A} - \delta_{H_B}$), which is frequently used in structural studies [3-10], acquires a negative value in (VII) (—0.09 ppm, see Table 1). In all previously examined N-vinyl compounds, $\Delta\delta$ is positive, except in those cases in which the vinyl group and the unsaturated cyclic moiety are nearly orthogonally stereooriented ($\varphi \sim$ 80-90°) [1-10]. The H_B proton falls within the screening influence of the magnetic anisotropy of the ring, and its resonance is strongly shifted to higher field [7, 8]. Hence, the torsion angle ψ_1 clearly lies in the range 80-90°.

At such a value of the torsion angle ψ_1, p—π conjugation between the lone pair on nitrogen and the corresponding benzene ring must be totally absent [17]. However, the averaged resonance signal for the para-carbon in both rings in (VII) is shifted to higher field relative to the signal for benzene (123.6 and 128.8 ppm, respectively [18], see Table 2). This shows that there must be appreciable p—π conjugation between the lone pair on nitrogen and the second benzene ring. It must therefore be displaced from the plane C_i'—N—C_i'' in (VII) at a relatively small angle. In unsubstituted diphenylamine, the signal for the para-carbon is seen at 10.5 ppm higher field than in benzene [19], which is some twice as great as the shift in the vinyldiophenylamine (VII). According to reported calculations [15], the angles ψ_1 and ψ_2 in diphenylamine itself are around 35°. This suggests that ψ_2 in N-vinyldiphenylamine is likewise around 35°.

Phenothiazine (I) differs from diphenylamine (VII) in that there is a sulfide bridge between the benzene rings. This requires ψ_1 and ψ_2 to be similar, and causes bending of the plane of the heterocycle along the N—S axis. The torsion angle φ between the plane orthogonal to the lone pair on nitrogen and the vinyl group, however, remains unchanged (as shown by the equivalence of ΔJ for (I) and (VII) and the small differences between the chemical shifts of Cβ), but the mutual stereoorientation of the vinyl group and the benzene rings is changed [as shown by the sharp increase in ΔJ in (I) as compared with that in (VII), from —0.09 to 0.64 ppm].

The increase in the coordination number of the sulfur in 10-vinylphenothiazine sulfoxide (III) over that in 10-vinylphenothiazine (I) results in a marked change in the ^{1}H and ^{13}C NMR spectral parameters of the vinyl group (Table 1). First, there is a considerable downfield shift in the signal for Cβ (28.96 ppm), indicating almost complete loss of p—π conjugation with the vinyl group [the chemical shift of Cβ (116.8 ppm) in (III)] is close to that of the carbon atoms in ethylene (123.2 ppm [18]). Second, in the S-oxide (III) there are substantial downfield shifts of the signals for H_A and H_B as compared with (I) (1.46 and 0.80 ppm, respectively; Table 1), and $\Delta\delta$ becomes negative (—0.02 ppm). These marked shifts in the positions of the signals may arise from two factors in (VII), namely the electron acceptor effect of the S=O group, or the change in the torsion angle φ as a result of the change in the dihedral angle ξ (which is extremely sensitive to substitution in the phenothiazine ring [14]). In order to assess the relative significance of these factors, we may consider the changes in the ^{1}H and ^{13}C NMR parameters of the vinyl group as the coordination number of the nitrogen in the "rigid" imidazole ring is increased [1-vinylimidazole (VIII) and its hydrochloride (IX)].

In the hydrochloride (IX), the signal for Cβ is shifted to lower field by 7.3 ppm as compared with the free base (VIII) (Table 1), a value which is only a quarter of the analogous shift in the phenothiazine S-oxide (III) as compared with phenothiazine itself (I). The values of $\Delta\delta$ in (VIII) and (IX) are nearly the same (0.41 and 0.43 ppm, respectively), which is very different from the behavior of this parameter in phenothiazines (I) and (III). This suggests that the changes in the spectral data in the

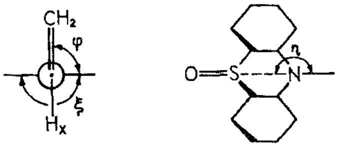
10-vinylphenothiazine S-oxide (III) as compared with 10-vinylphenothiazine (I) are due both to the electronic effect of the S=O group, and to a change in the torsion angle φ.

The strong acceptor effect of the S=O group in (III) should result in a considerable decrease in the geminal coupling constant $^2J_{AB}$ as compared with (I) [20], as in the imidazole hydrochloride (IX) as compared with imidazole (VIII) (—2.9 and —1.6 Hz, respectively). In the S-oxide (III), however, the $^2J_{AB}$ value is 0.35 Hz greater than in the phenothiazine (III), possibly due to a considerable increase in the torsion angle φ in the first instance. For example, in N-vinylpyrroles a change in the torsion angle from 0 to 90° gives rise to an additional contribution to $^2J_{AB}$ of more than 1 Hz [1].

The value of ΔJ, which is independent of electronic effects of ring substituents [4, 5, 8], is 3.0 Hz less in the S-oxide (III) than in (I) (Table 1). This is 4.5 times greater than the analogous changes in ΔJ in imidazole (VIII) as compared with its hydrochloride (IX). In (IX), the decrease in ΔJ relative to imidazole (VIII) is due to an increase in the angle φ, mean weighted with respect to the torsion vibration equations, as a result of increases in the amplitudes of the torsional vibrations with lowering of the barrier to internal rotation, caused by the acceptor effect of HCl coordinated with the vinylimidazole [21]. In 10-vinylphenothiazine S-oxide (III), the marked increase in the torsion angle φ as compared with that in (I) (to judge from the value of ΔJ) could be due to an increase in the dihedral angle ξ when the coordination number of the sulfur is changed, resulting in enhancement of the steric effects of the condensed rings on the vinyl group. That the dihedral angle ξ is greater in the S-oxide (III) than in (I) is confirmed by the high-field shift of the signals for the carbon atoms peri- (C1) and para- (C3) to the nitrogen by 3.9 and 1.8 ppm, respectively (Table 2). This is in spite of the acceptor effect of the sulfoxide group, and results from enhancement of the p—π conjugation of the lone pair on nitrogen with the S-oxide (III) as the angle ξ is increased.

The ^1H and ^{13}C NMR spectral parameters for the S-oxide (III) are very different from those for (I), but are quite close to those for the isostructural compound 10-vinylacridone (IV). In (IV), $\Delta\delta$ is also negative (—0.34 ppm), the Cβ nucleus is strongly descreened (122.87 ppm), and the values for ΔJ and $^2J_{AB}$ are similar to those for 10-vinylphenothiazine S-oxide (I) (1.4 and 1.4; —0.40 and —0.45 Hz, respectively) (Table 1). This indicates that the vinyl group and the vinyl group are stereooriented similarly in (III) and (IV). By analogy with the pyridone ring, the acridone ring may be regarded as planar [8, 22]. The steric effects of the two condensed rings in (IV) on the vinyl group favor the orthogonal disposition of the planes of the rings relative to the vinyl group [8]. A similar situation could occur with the S-oxide (III), assuming that the phenothiazine ring therein becomes planar.

Thus, conversion of 10-vinylphenothiazine (I) into its S-oxide (III) results in an increase in the dihedral angle ξ from 135-140° to ~180°. As a result of the (near) sp^2-hybridization of the nitrogen, this should result in a simultaneous increase in η from ~160° to ~180°, with a consequent marked increase in the steric effect of the heterocycle on the vinyl group, which is forced to move from the position with torsion angle φ close to 0° to one in which the torsion angle is close to 90° (A and B).



C

In 9-vinylcarbazole (V), the chemical shift of Cβ is intermediate between that in (I) and its S-oxide (III) (101.83, 87.85, and 116.81 ppm, respectively). Likewise, the value of ΔJ in (V) is intermediate between those for (I) and (III) (0.41, 0.64, and —0.02, respectively). This suggests that the vinyl group in (V) stands out to some extent from the plane of the heterocycle (the planar structure of the carbazole ring has been shown by crystallography) [23].

An empirical relationship has been found between ΔJ values for N-vinyl-heterocycles and the torsion angle φ [8, 16, 24]:

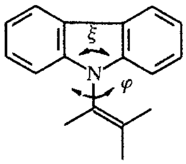
$$\Delta J = A \cdot \cos\varphi + B, \tag{1}$$

where A = 5.5-6.3, B = 1.4-2.0 [8, 16, 24].

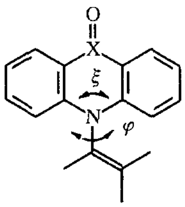
According to this relationship, the angle φ in (V) is ~60°. It is noteworthy that according to the crystallographic data, the departure of the plane of the vinyl group from that of the carbazole ring is only 14° [23]. This substantial difference between the values for φ found by NMR and crystallographic methods is apparently due to the different aggregate states of the molecule in (V) (in solution and as the solid, respectively), although there is also the possibility of systematic errors in calculation of the torsion angle using the empirical relationship.

Calculation of the torsion angle φ in (IV) and the S-oxide (III) by relationship (1) gives a value of $\sim 90°$. The considerable increase n the value of φ ($\sim 30°$) in (IV) and (III) over that in (V) has a marked effect on the conditions for p—π conjugation with the vinyl group. In the first instance, it is almost completely lost (the chemical shifts of $C\beta$ is similar to the value in ethylene), while in the second instance it remains substantial (the signal for $C\beta$ is shifted to higher field by 21 ppm relative to ethylene).

We now examine the reasons for the change in the stereoorientation of the vinyl group in (III) and (IV) as compared with (V). In N-vinylpyrrole (X), the valence angle ξ at nitrogen is, according to calculations carried out by us using the AM I method [25] with full optimization of the geometric parameters, 105.7°. According to a similar calculation for 1-vinyl-4-pyridone (XII), ξ is considerably larger (120.4°). The values of ΔJ in (X) and (XII) are nearly the same (7.4 and 7.7 Hz, respectively), and are in accordance with the vinyl and heterocyclic groups being coplanar [8, 16]. Introduction of a condensed benzene ring into N-vinylpyrrole (1-vinylindole, XI) has little effect on the torsion angle φ (ΔJ changes by only 0.1 Hz), and therefore on p—π conjugation with the vinyl group [the chemical shifts of $C\beta$ in (X) and (XIII) are the same to within 1 ppm) (Table 1). Similarly, introduction of a condensed benzene ring into 1-vinyl-4-pyridone (1-vinyl-4-quinolone, XIII) results in an increase in the torsion angle φ by 45° [ΔJ is reduced to 5.9 Hz, see relationship (1)]. Consequently, p—π conjugation with the vinyl group is much weaker in (XIII) than in (XII) (the chemical shift of $C\beta$ is increased to 8.0 ppm, see Table 1). The introduction of two condensed benzene rings into (X) (9-vinylcarbazole, V) results in partial departure of the vinyl group from the plane of the heterocycle (ΔJ changes from 7.4 to 4.3 Hz), and partial disruption of p—π conjugation with the vinyl group (the chemical shift of $C\beta$ is shifted downfield by 4.9 ppm). Similarly, introduction of two benzene rings into (XII) (10-vinylacridone, IV) results in the vinyl group becoming nearly orthogonal to the heterocycle (ΔJ decreases from 7.7 to 1.4 Hz) and in total loss of p—π conjugation with the vinyl group. Hence, the steric effects of condensed benzene rings on the vinyl group at small values of the valence angle ξ in the six-membered ring (IV and XIII) (E) are much greater than in five-membered rings (V and XII) (D), requiring it to occupy a position with a greater torsion angle φ.



D



E

In 9-vinyl-1-methyl-β-carboline (VI), the chemical shift of $C\beta$ is seen at lower field by 8.4 ppm as compared with the carbazole (V), and $\Delta\delta$ decreases from 0.43 to 0.02 ppm (Table 1). In (VI), ΔJ is 1.1 Hz less than in (V) (3.2 and 4.3 Hz, respectively). Using Eq. (1), it is possible to calculate the torsion angle φ in (VI) as being $\sim 75°$, which is some 15° greater than the value in 9-vinylcarbazole (V). This increase is due to the steric effect of the CH_3 group in the peri-position to vinyl group in (VI).

EXPERIMENTAL

^1H NMR spectra were recorded on a Tesla BS-567A (100 MHz) spectrometer, and ^{13}C NMR spectra on Tesla BS-567A (25.14 MHz) and Bruker WP 200 SY (50.33 MHz) instruments. The direct $^{13}C—^1H$ coupling constants for the α- and β-isotopomers of the vinyl group were obtained by analysis of the four-spin ABXZ system ($Z = {}^{13}C$) using the PANIC program on an Aspect 2000 minicomputer. The solvent was $CDCl_3$, internal standard HMDS. The sample concentrations were 5% for PMR, and 10-30% for ^{13}C NMR. Measurements were carried out at room temperature (25 ± 2°C).

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