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NMR STUDIES OF BRIDGED RING SYSTEMS. VII.[*1] ANISOTROPIC LONG-RANGE SHIELDING EFFECT OF AN AZIRIDINE RING

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IT has been revealed in recent years that a three-membered ring, a cyclopropane (1-4) and an epoxide ring (5, 6), has an anisotropic long-range shielding effect on neighboring protons. Although it appears to be a disputable interpretation (4) that this effect arises from a ring current (1-6), the observed phenomenon has evoked much interest. In order to add a new example to this subject, we report here the anisotropic long-range shielding effect exerted by an aziridine ring, which is quite similar to that of an epoxide ring (5, 6).

The NMR spectra of 3-azatricyclo[3.2.1.0$^{2,4\text{-}\underline{\text{exo}}}$]octane (I), 3-azatricyclo-[3.2.1.0$^{2,4\text{-}\underline{\text{exo}}}$]oct-6-ene (II), benzo-3-azatricyclo[3.2.1.0$^{2,4\text{-}\underline{\text{exo}}}$]octene (III),[*2] and benzo-3-azatricyclo[3.2.2.0^{2,4}]nonenes (IV and V)[*3] were compared with those of their parent compounds, norbornane, norbornene, benzonorbornene, and benzo-

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[*1] Part VI, Ref. (4).

[*2] 1,3-Dipolar addition of ethyl azidoformate to norbornene, norbornadiene, and benzonorbornadiene afforded the corresponding triazole derivatives which transformed into the aziridine derivatives by pyrolysis followed by hydrolysis. The detailed procedures and the structure proof will be reported elsewhere.

[*3] Prepared from benzobicyclo[2.2.2]octen-2-one oxime. The procedure of preparation and the structure proof will be published elsewhere.

bicyclo[2.2.2]octene,*[4] respectively, to evaluate the values of additional signal shifts due to the long-range shielding effect of an aziridine ring introduced. Table I shows the spectral data on the compounds I-V and the values of additional signal shifts due to an aziridine ring (shown in parentheses). Assignments of the C-8 bridge protons, anti(a) or syn(s) to an aziridine ring, were effected by the following way. The C-8 bridge-methylene signals in III appear as an AB-type quartet. The two peaks of the lower field half of this quartet are further split into clear triplets by the two bridgehead protons, whereas the two peaks of the higher field half are split into unresolved multiplets by the couplings to the bridgehead C-1 and C-5 protons and by the long-range spin-couplings to the C-2 and C-4 protons. This fact obviously indicates that the doublet of triplets arises from the C-8s proton (6, 8, 9). Signals of the bridge protons in the spectra of the other compounds were similarly assigned.*[5] For comparison, in Table I are also listed additional shift values due to introduction of an epoxide ring into the same parent compounds (6) (shown in square brackets).*[6]

The anisotropic long-range shielding effect of an aziridine ring is thus disclosed in Table I. The C-8a (C-9a) proton in IV which lies directly above the plain of the aziridine ring is fairly shielded by the ring. On the other hand, the C-8s (C-9s) proton

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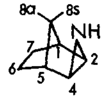
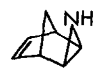
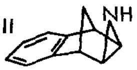
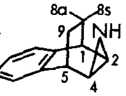
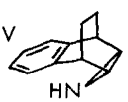
*[4] The spectral assignment procedures were described in Refs. (6-8).

*[5] Detailed spectral data and more elaborate discussions will appear in our full paper.

[6] We previously reported the presence of the anisotropic effect of an epoxide ring based only on the data obtained from the spectra of deuteriochloroform solutions (6). Recently, laszlo has published a suggestive comment on the unsuitable use of chloroform as a solvent for organic molecules containing such a proton-accepting atom as oxygen in NMR spectroscopy (10). We do have some data concerning the solvent effects on the spectra of epoxides reported previously (6) and of aziridine derivatives examined in this paper.[5] However, we report here only the data obtained from the spectra in carbon tetrachloride which is probably the most suitable solvent for the molecules under discussion. Values of additional signal shifts observed in carbon disulfide are quite similar to those observed in carbon tetrachloride shown in Table I.

TABLE I

NMR Spectral Data on 3-Azatricyclo[3.2.1.$0^{2,4}$]octane and 3-Azatricyclo-[3.2.2.$0^{2,4}$]nonane Derivatives,[a] and Additional Shift Values Due to Introduction of an Aziridine or an Epoxide Ring[b]

Compound	Proton chemical shift (τ)[c]					
	Olefinic or phenyl	Bridgehead C-1, C-5	Bridgehead C-2, C-4	Bridge anti(a) to an aziridine ring	Bridge syn(s) to an aziridine ring	NH[d]
I 	-	7.72(m)[e] (-0.09) [-0.21]	8.17(s)[e]	9.42(d-m)[f] (+0.68) [+0.63]	~8.78[g] (~+0.04) [-0.06]	10.20
II 	3.70(t)[h] (-0.36)	7.30(m) (+0.08)	7.82(s)[e]	9.07(d-m)[f] (+0.20)	8.38(d-t-d)[f] (-0.32)	9.23
III 	i	6.82(m)[e] (+0.12) [-0.01]	7.82(s)[e]	8.73(d-m)[f] (+0.21) [+0.01]	8.07(d-t)[f] (-0.20) [-0.20]	9.42
IV 	2.96(s)	6.85(m) (-0.21) [-0.28]	7.73(m)[h]	~9.09[j] (~+0.38) [~+0.37]	~8.02[j] (~-0.23) [~-0.28]	9.15
V 	i	6.67(m) (-0.39) [-0.41]	7.93(m)[h]	~8.62[j] (~+0.01) [~+0.05]	~8.25[j] (~ 0.00) [~+0.03]	10.75

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a The spectra were taken with a Varian A-60 spectrometer in carbon tetrachloride solutions (infinite dilutions) containing tetramethylsilane as an internal reference at room temperature. Calibration of the spectrometer was checked by the usual side-band method. Accuracies of chemical shifts are within about ±0.02τ.

b Values in parentheses are additional shift values due to the introduction of an aziridine ring in comparison with the corresponding parent compounds bicyclo-[2.2.1]heptanes and bicyclo[2.2.2]octanes. Values in square brackets are additional shift values due to the introduction of an epoxide ring instead of an aziridine ring into the same parent compounds.*[6]

c Peak multiplicities are represented by s (singlet), d(doublet), t (triplet), q (quartet), and m (multiplet).

d Assigned by an addition of a small amount of deuterium oxide to the examined solution.

e Not well-resolved peaks.

f The A-part of an ABX_2 system.

g Obscured by other signals.

h An A_2X_2-type pattern.

i A complex multiplet of an A_2B_2 type.

j The A_2-part of an $A_2B_2X_2$ system. See Refs. (6-8).

in IV, though also situated above the aziridine ring, is fairly deshielded by this moiety. This deshielding can be ascribed to van der Waals interaction between the proton and the NH group (6, 11) owing to their close proximity; and in addition, the influence of lone-pair electrons of the nitrogen atom in the ring may be included (12). The signals of the bridgehead C-1 (C-5) protons in IV and V which are nearly situated by the sides of the aziridine ring are shifted downfield. Difference in the additional shift values between IV and V might bear some relation to a transannular interaction of the aziridine ring with the benzene ring in V[*7] (7). The bridge C-8 (C-9) protons in V appear to be situated at such positions as the aziridine ring does not have marked effects. It should be emphasized that the shielding effects of aziridine rings introduced into benzobicyclo[2.2.2]octene are quite similar to those of epoxide rings introduced into the same skeleton. Introduction of a three-membered ring or an additional unsaturation into a bridge of the bicyclo[2.2.2]octene skeleton would not cause a significant alteration in the molecular geometries, as also conjectured in a previous paper (4).

On the other hand, shielding effects upon the protons at the same position due to an aziridine ring as well as an epoxide ring vary immensely in magnitude and sometimes in sign when they are introduced into the bicyclo[2.2.1]heptane skeleton, as shown in Table I. Among factors entangled in these observed effects, it appears most significant that a geometrical alteration in the skeleton due to introduction of a three-membered ring causes changes in the shielding effects of the three-membered ring, and the double bond or the fused benzene ring. Nevertheless, it should be noted that even in the bicyclo[2.2.1]heptane skeleton the bridge C-8a proton is at any rate shielded by a

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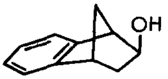
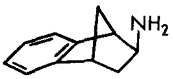
[*7] The ultraviolet absorption spectrum of V shows apparent hypsochromic shifts in its E- and B-bands in comparison with those of IV and benzobicyclo[2.2.2]octene.[*5] Similar results were obtained in the spectra of the corresponding epoxides.[*5] We thank Mr. M. Yamakawa of this laboratory for the measurements of the spectra and discussions.

three-membered ring introduced. Even though it may be argued that the observed effects arise only from the hetero-atom in a three-membered ring, the findings that the both bridge-methylene protons in 2-*exo*-hydroxy- and 2-*exo*-aminobenzobicyclo-[2.2.1]heptenes (VI and VII) are fairly deshielded[*5] have been considered as evidence that the observed effects arise from magnetic properties of the ring. Furthermore, the fact that the spectrum of 3,3-dichlorotricyclo[3.2.1.$0^{2,4}$-*exo*]octane (VIII) (13) is quite analogous to those of I and its corresponding epoxide would support the above discussion.



VI



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