Tetrahedron Vol. 25, pp 5255 to 5265 Pergamon Press 1969. Printed in Great Britain

PROTON MAGNETIC RESONANCE STUDY OF HELIOTRIDENE

A PYRROLIZIDINE DERIVATIVE

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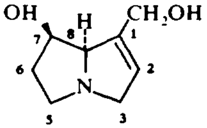
(*Received in the UK* 12 *June* 1969; *Accepted for publication* 15 *July* 1969)

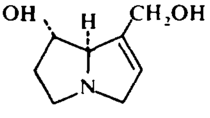
Abstract—The 100 MHz NMR spectrum of heliotridene (IV) in $CDCl_3$ solution has been analysed. The conformation of the title compound has been derived from the vicinal and allylic coupling constants. The pyrrolizidine nucleus of heliotridene (IV) consists of a planar pyrroline ring joined to a pyrrolidine ring existing in two rapidly interconverting *exo*- and *endo*-buckled C_1 conformers of approximately equal populations. On acidification the ratio of the two conformers is changed in favour of the *endo*-buckled form (3:1). Unusually large homallylic coupling of 3·6 and 5·0 Hz have been observed.

INTRODUCTION

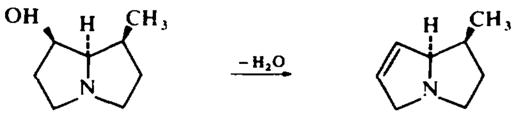
SINCE Karplus[1] proposed a relationship between the vicinal coupling constants in saturated systems and the dihedral angle, considerable attention has been given to the correlation of the signs and magnitudes of coupling constants with molecular structure.[2] Although less systematic knowledge is available on the long-range couplings, it is clear from theoretical[3,4] and abundant experimental data[5] that long-range couplings are also highly stereo-specific.



Retronecine (I)



Heliotridine (II)



Rectronecanol (III)

Heliotridine (IV)

The NMR spectra of pyrrolizidine derivatives usually consist of complex overlapping multiplets, and the amount of information which can be obtained is therefore limited. Detailed NMR studies have been reported only on retronecine (I) and heliotridine (II).[6] The NMR signals of all protons of heliotridene (IV),* a dehydration product of

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* The authors are indebted to Dr. W. E. Campbell for generously supplying a sample of heliotridene.

retronecanol (III), are well separated in a 100 MHz spectrum and a complete analysis is easily performed including the determination of allylic and homoallylic coupling constants.

RESULTS AND ASSIGNMENTS

The spectrum of heliotridene in $CDCl_3$ is depicted in Fig. 1 and may be briefly explained as follows: The sharp doublet at highest field is due to the Me group. Strong irradiation of the 7-line pattern at $\delta = 2{\cdot}27$ collapsed the Me signal, thus identifying the H-1 proton resonance. Only the H-2 protons are not subject to any strong deshielding influences. The ring-proton resonances at highest field ($\delta = 1{\cdot}34$ and $1{\cdot}81$) are therefore attributed to these protons. The two absorption patterns at $\delta = 2{\cdot}58$ and $3{\cdot}04$ are assigned to the H-3 protons as these are only deshielded by the adjacent N atom, while the multiplets at $\delta = 3{\cdot}35$ and $3{\cdot}88$ are associated with the H-5 protons which are affected by both the N atom and the double bond. The values of the geminal couplings, being relatively large in comparison to the vicinal splittings, confirmed the assignment of the various methylene groups. The complex pattern at $\delta = 4{\cdot}21$ is due to the only remaining aliphatic proton H-8. The patterns at lowest field are assigned to the two olefinic protons. Comparing the chemical shifts of these protons with the corresponding values reported by Culvenor *et al.*[6] for heliotridine leads to the conclusion that H-6 in heliotridene is at lowest field ($\delta = 5{\cdot}77$).

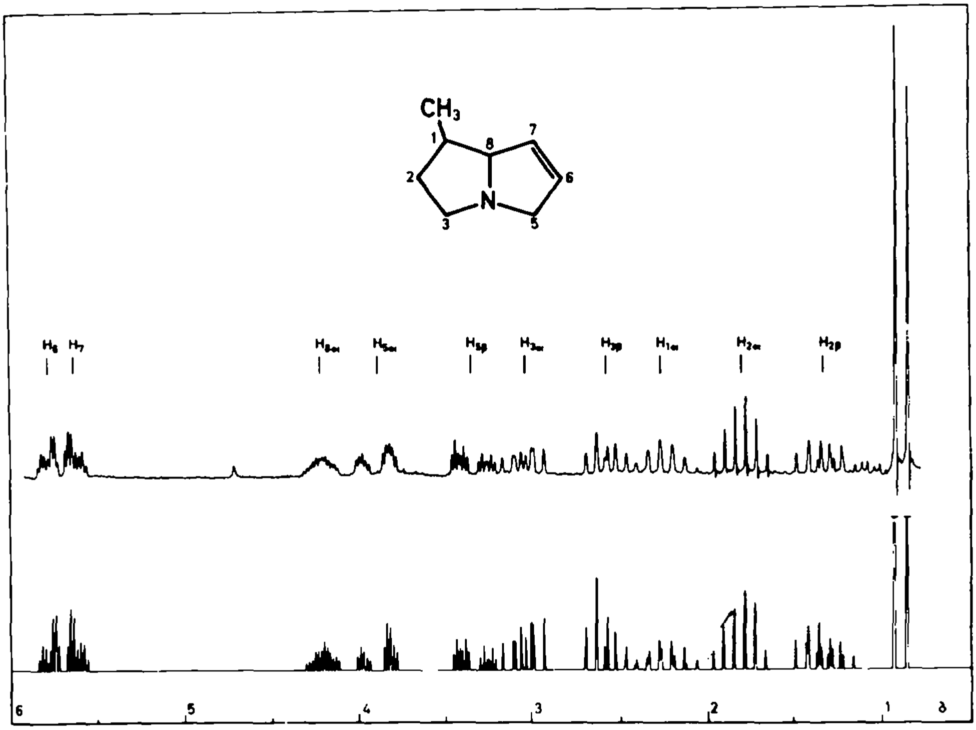

Fig. 1 Experimental and calculated NMR spectrum of heliotridene at 100 MHz.

Due to the favourable J/δ ratios, a set of coupling constants and chemical shifts could be derived from a first order analysis. Only the olefinic protons were analysed on an AB approximation. The complete spectrum was then calculated and plotted with an electronic computer. After minor adjustments to some chemical shifts and coupling constants, excellent agreement between experimental and calculated spectrum was obtained as demonstrated by Fig. 1. All the spectral parameters of heliotridene are given in Tables 1 and 2.

A uniform downfield shift of all the protons of heliotridene is observed upon acidification (see $\Delta\delta$ values in Table 1). The magnitude of these shifts allowed the identification of the individual proton resonances of the C-3 and C-5 methylene protons. The H-8 proton of heliotridene is known to be in an α-position from its relationship to retronecanol (III). H-8α, H-3α and H-5α are symmetrically disposed relative to the N atom, and protonation should influence the chemical shifts of these protons to the same extent. Inspection of Table 1 reveals that the lowfield patterns of the H-3 and H-5 proton pairs exhibit a downfield shift of the same order of magnitude as the H-8α proton. These are therefore assigned to H-3α and H-5α, respectively. The assignment of the individual H-2 proton signals will only follow from a detailed discussion of the conformation (next chapter).

The signs of the geminal (−), vicinal (+) and allylic (−) couplings in Table 2 have been assumed on the basis of the present knowledge on these coupling constants.[3, 8, 9] The relative signs of the homoallylic couplings constants $J_{5\alpha,8\alpha}$ and $J_{5\beta,8\alpha}$ have been determined by spin decoupling experiments. Saturation of the upfield half of the H-5α resonance and the lowfield part of the H-5β signal changed the H-8α pattern as shown in Fig. 2a. The calculated spectra, assuming positive and negative signs for the homoallylic coupling constants are reproduced in Fig. 2b and 2c, respectively. Comparison of these traces proves that the homoallylic couplings are of opposite sign to the geminal coupling constant $J_{5\alpha,5\beta}$ which is assumed to be negative. This is not quite as obvious in the case where H-5α is irradiated, possibly due to incomplete decoupling. However, the coincidence of the position of the strongest lines, as indicated in Fig. 2, and the observation that changes occurred at the lowfield part of the H-8α pattern while the highfield part of the H-5α was irradiated, establishes the positive sign of $J_{5\alpha,8\alpha}$ unambiguously.

CONFORMATION OF HELIOTRIDENE

Pyrroline ring. Vicinal coupling constants in a system incorporating a sp^2 hydridized C atom (CH—CH═) are a function of the dihedral angle, similar to the Karplus equation for a saturated ethane fragment, and vary between 1·5 and 3·0 Hz in 5-membered ring compounds.[9] The $J_{5\alpha,6}$, $J_{5\beta,6}$ and $J_{7,8\alpha}$ couplings being equal within experimental accuracy (1·8–2·0 Hz), therefore suggest a planar pyrroline ring in heliotridene.

This is supported by the magnitude of the three allylic coupling constants. Values for allylic coupling constants reported in the literature vary between 0 and 3·0 Hz,[5] having a maximum value when the angle θ, i.e. the angle between the plane of the double bond and the C—H bond direction of the tetrahedral carbon, is 90°.[4, 5] The allylic couplings $J_{5\alpha,7}$, $J_{5\beta,7}$ and $J_{6,8\alpha}$ are almost equal, indicating angles θ of similar magnitude, and therefore a planar ring.

The planarity of the unsaturated ring of heliotridene is in accord with energy

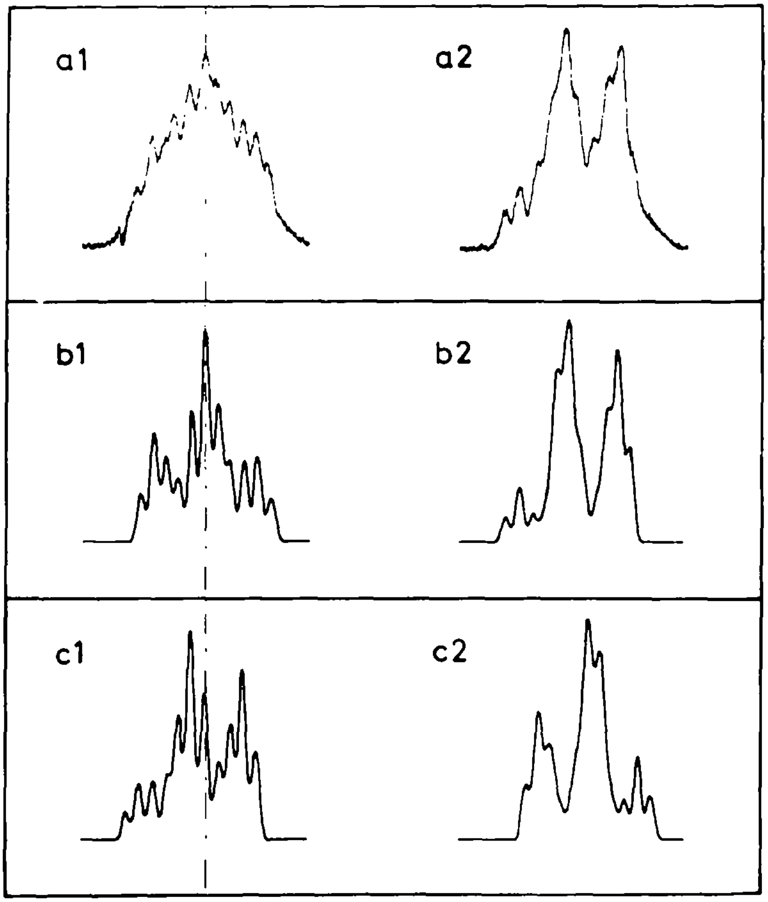

FIG. 2 Experimental and calculated NMR signal of the H-8 proton with simultaneous irradiation of the H-5 protons.

(a1) highfield part of H-5α irradiated
(a2) lowfield part of H-5α irradiated
(b1) calculated for positive sign of $J_{5\alpha,\,8\alpha}$
(b2) calculated for positive sign of $J_{5\beta,\,8\alpha}$
(c1) calculated for negative sign of $J_{5\alpha,\,8\alpha}$
(c2) calculated for negative sign of $J_{5\beta,\,8\alpha}$

considerations since bending the C-5, C-6, C-7, C-8 plane would be energetically unfavourable.

Pyrrolidine ring. The conformational stability of alicyclic organic compounds is determined by bond angle and torsional strain and non-bonded interactions. The preponderance of the last two contributions over the bond angle strain leads to a staggering of the C—H bonds in 5-membered rings with tetrahedral atoms.[10] Pitzer and Donath[11] predicted that two equally stable conformations of different symmetry (C_s or "envelope" and C_2 or "twist" form) exist for cyclopentane. This was confirmed by Hendrickson,[12] whose calculations also showed that for all asymmetric modes between the C_s and C_2 limits, conformations can be found with the same energy minimum.

In carrying the argument from cyclopentane to the pyrrolidine ring of heliotridene, bond angles and bond lengths around the ring are expected to be more or less uniform as both C and N atoms have tetrahedral symmetry. Therefore, the conformational behaviour of the pyrrolidine ring should be similar unless it is altered by substituent effects. The two 5-membered rings of heliotridene are *cis*-joined as a *trans*-junction would impose too much strain on the ring system. Because of the planarity and rigidity of the unsaturated ring, the pyrrolidine ring in heliotridene will most probably take up a C_s conformation, the "envelope form", in which the N atom, C-8, C-1 and C-3 are coplanar and C-2 forms the tip of the "envelope". Fig. 3 shows the two possible *exo*- and *endo*-buckled forms of the pyrrolizidine ring system.

FIG. 3 Conformations of the pyrrolizidine nucleus with exo- and endo-buckled pyrrolidine rings.

There is ample experimental support for the assumption of a C_s conformation of the pyrrolidine ring. X-ray crystallographic investigations of three pyrrolizidine alkaloids[13, 14] showed that all these compounds have the pyrrolidine ring basically in an "envelope" form, the angle of buckle* varying between 30° and 50°. Furthermore, Donohue and Trueblood[15] found that *trans*-hydroxy proline in the crystalline state, takes up a C_s conformation. Abraham *et al.*[16, 17] concluded from NMR evidence that *cis*- and *trans*-hydroxyproline in their zwitterionic and cationic forms in D_2O solution also exist in C_s conformations with angles of buckle of 53° and 75°, while the conformation of the anionic species is more complex though still related to the "envelope".[17] Culvenor *et al.*[6] using the original Karplus equation in a NMR study of heliotridine and retronecine, suggested C_s conformations for these compounds with angles of buckle near 40°.

The experimental vicinal coupling constants of heliotridene have been analysed using a Karplus equation in the form[18]

$$J_{\text{vic}} = a + b\cos\phi + c\cos 2\phi, \tag{1}$$

a, *b* and *c* being empirical constants. It is easily shown that *a* is numerically equal to J_{av}, the average vicinal coupling constant of an ethane-like CH—CH fragment, given by[19]

$$J_{\text{av}} = 18{\cdot}0 - 0{\cdot}8\Sigma E, \tag{2}$$

with Σ E the sum of the electronegativities of the atoms bonded directly to the two central C atoms. The constant *b* is relatively small and has been set equal to $-1{\cdot}0$ Hz, a value proposed by Bothner-By.[9] In order to determine *c*, a second equation relating

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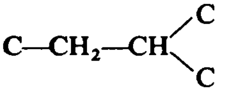
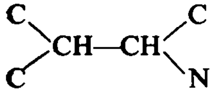
* The angle of buckle is the angle between the planes formed by C_1—C_8—N—C_3 and C_1—C_2—C_3 in heliotridene or the corresponding planes in retronecine and heliotridine.

the vicinal coupling constant to the dihedral angle ϕ is required. From the study of substituted ethanes it was found[20] that the *trans* proton–proton coupling J_{180} (dihedral angle 180°), is a function of the electronegativity of the substituents attached to the CH—CH fragment, similar to J_{av}. This relationship can be expressed as follows:

$$J_{180} = 28{\cdot}4 - 1{\cdot}04\Sigma E \qquad (3)$$

Substituting the value of J_{180} thus derived into the Karplus equation yields *c*. The appropriate equations for the various fragments in heliotridene are:

Fragment	*Equation*	
$N{-}CH_2{-}CH_2{-}C$	$J_{2,3} = 6{\cdot}7 - 1{\cdot}0\cos\phi + 6{\cdot}0\cos 2\phi$	(4)
 $\mathrm{C{-}CH_2{-}CH}\!\begin{array}{l}\diagup\mathrm{C}\\ \diagdown\mathrm{C}\end{array}$	$J_{1,2} = 6{\cdot}7 - 1{\cdot}0\cos\phi + 6{\cdot}0\cos 2\phi$	(5)
 $\begin{array}{r}\mathrm{C}\diagdown\\ \mathrm{C}\diagup\end{array}\!\mathrm{CH{-}CH}\!\begin{array}{l}\diagup\mathrm{C}\\ \diagdown\mathrm{N}\end{array}$	$J_{1,8} = 6{\cdot}0 - 1{\cdot}0\cos\phi + 5{\cdot}9\cos 2\phi$	(6)

Assuming an angle of buckle of 45° for the *exo*- and *endo*-buckled forms, the 1,2 and 2,3 dihedral angles are approximately 0° ± 45° for *cis*-couplings (α,α or β,β) and 120° ± 45° for *trans*-couplings (α,β or β,α) and the 1,8 angles become 0° ± 30°.[12, 16] The values of the vicinal coupling constants calculated with these angles using Eq. 4–6, are given in Table 3. It becomes obvious from these figures that under the assumptions made, the *cis*-couplings are only dependent on the angle of buckle, while the *trans*-couplings reflect the relative populations of the *exo*- and *endo*-buckled forms. Comparing the experimental results for neutral and acidic solutions, one notices that some of the couplings stay constant, others change drastically. This now leads to an unambiguous assignment of the individual protons in the C-2 methylene group. Of the two possibilities the one accepted in Table 1 (downfield proton at $\delta = 1{\cdot}81$ as H-2α) gives an excellent agreement between calculated and experimental vicinal couplings with a 45:55 ratio of *exo*- and *endo*-buckled conformers for the neutral solution, while the experimental results obtained after acidification, are well reproduced by only changing this ratio to 25:75.

In the other assignment (Table 4) *cis*- and *trans*-couplings are interchanged. The 2α,3α-coupling constant increases from 7·2 to 10·0 Hz, while the 2β,3β-coupling decreases from 6·1 to 3·9 Hz on acidification. The geometry of the 5-membered ring, however, requires these couplings to change in the same direction if the conformation of the ring is altered.

The average deviation of the experimental coupling constants from the calculated values as shown in Table 3 is 0·3 Hz for both the neutral and acidic solution of heliotridene. This agreement is certainly excellent and furnishes strong support for the approach chosen to derive the empirical constants of the Karplus equation. The largest deviation is encountered with the 1α,8α coupling, but this can easily be reduced by increasing the H-1,H-8 dihedral angle slightly (35° → $J_{calc} = 7{\cdot}2$ Hz). Whether minor corrections of this type are meaningful in view of the approximations inherent in the derivation of the Karplus equation and the assumptions made concerning the conformation of the pyrrolidine ring, remains doubtful. We do, however, believe that the conformation of the pyrrolidine ring of heliotridene in $CDCl_3$ solution is correctly described by an approximately 1:1 equilibrium mixture of *exo*- and *endo*-buckled conformers of the C_s mode with the C-2 atom forming the tip of an "envelope" and an angle of buckle of ca. 45°, and that this equilibrium is changed in favour of the *endo*-conformer (3:1) on addition of acid. The reason for the signifcant change of this ratio upon acidification is not easily explained. Various factors such as the effect of the positively charged N atom, the alteration of the solvent system and the solvation of the heliotridene molecule may play a role in influencing the equilibrium of the two conformers. The slight increase of the values of $J_{1\alpha,2\beta}$ and $J_{2\beta,3\alpha}$ at $-50°$ compared to the values at room temperature indicates that the *endo*-conformer is energetically favoured, as assumed in the calculations of Table 3. The vicinal $J_{NH,CH}$ couplings also obey a Karplus-type equation, as was recently established by Bystrov *et al.*[21] The values reported in this paper for $J_{NH,CH}$ (Table 2) are in fair agreement with the empirical relationship between the dihedral angle and $J_{NH,CH}$ couplings and the proposed conformation of heliotridene.

CONFORMATIONS OF HELIOTRIDINE AND RETRONECINE

A similar analysis of the experimental data of Culvenor *et al.*[6] on heliotridine(I) and retronecine(II) was performed. Eq (4) was used for the 5,6 fragment,* and the following equations for the 6,7 and 7,8 fragments, respectively:

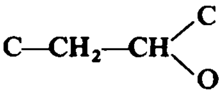
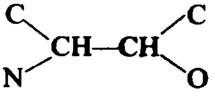
Fragment	*Equation*	
	$J_{6,7} = 6{\cdot}0 - 1{\cdot}0\cos\phi + 5{\cdot}7\cos 2\phi$	(7)
	$J_{7,8} = 5{\cdot}3 - 1{\cdot}0\cos\phi + 5{\cdot}6\cos 2\phi$	(8)

Table 5 gives the experimental and calculated vicinal coupling constants assuming an *exo*/*endo* ratio of 35:65 for heliotridine and 100% *exo*-form for retronecine. The mean deviation is improved from ca. 1·9 Hz obtained by Culvenor *et al.*[6] with the original Karplus equation to 0·5 Hz for heliotridine and 1·0 Hz for retronecine. Inspection of Table 5 reveals that the largest deviations for retronecine originate in the 6,7 and 7,8 fragments indicating an influence of the 7-OH group. Culvenor *et al.*[6] have already established that steric interactions between the 7-OH group, the pyrrolidine ring and the hydroxy-methylene group in position 1 rather than H-bonding effects are responsible for the deviations. A twist around the C-7, C-8 axis in retronecine reduces the non-bonded interactions of the substituents on these two C atoms, affecting the 6,7 and 7,8 dihedral angles. An increase of these angles by 10° and 15°, respectively, improves the mean deviation to 0·5 Hz. No serious steric interactions are expected for heliotridine.

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* Note that the double bond in heliotridine and retronecine is not in the same ring as in heliotridene resulting in a different numbering.

Thus the empirical determination of the parameters in the Karplus equation as suggested in this paper, significantly improves the agreement between calculated and observed vicinal coupling constants for heliotridine and retronecine.

GEMINAL COUPLING CONSTANTS

The electronegativity of substituents and neighbouring lone pairs and π-electron systems, influence the value of geminal proton–proton couplings in an additive fashion.[8,23] The value for methane (−12·4 Hz)[22] is usually taken as a reference.

The small deviation of $J_{2\alpha,2\beta}$ from the reference value may be due to the presence of the N atom in a β-position to the methylene group, the relative orientation being favourable for a slight positive shift.[9]

The N atom in an α-position with respect to a methylene group leads to a positive shift of the geminal coupling constant, which according to Antheunis[24] has a maximum value of 1·8 Hz if the nitrogen lone pair orbital is parallel to a CH bond. The C—$H_{2\beta}$ bond is more or less parallel to the lone pair orbital of the N atom in heliotridene. Addition of an increment of 1·8 Hz to the reference value of methane yields exactly the experimental value for $J_{3\alpha,3\beta}$ of −10·6 Hz.

In addition to the effect of the β-N atom discussed above, a negative contribution by the adjacent π-electron system should increase the absolute value of the geminal coupling of the C-5 methylene group. Barfield and Grant[25] calculated the maximum π-electron contribution to be 4·5 Hz for a fragment with a 30° angle between the π-electrons and the C—H bond directions which coincides with the conformation of the planar pyrroline ring. Addition of the two effects (1·8–4·5 Hz) to the reference value yields −15·1 Hz, in excellent agreement with the observed value of −15·3 Hz.

It is interesting to note that all three geminal coupling constants become more negative upon acidification, which is probably due to the reduced capability of the nitrogen atom to back-donate its electron pair.

HOMOALLYLIC COUPLING CONSTANTS

The positive sign of the homoallylic coupling constants in heliotridene agrees with theoretical considerations,[26] their magnitude, however, is exceptionally large. Only a few homoallylic couplings of similar magnitude have so far been reported,[6,27,28] normal values being less than 3·5 Hz.[5] Barfield[3] predicted a maximum value of 5·0 Hz for homoallylic couplings for a 90° angle between the C—H bond and the plane of the double bond. These steric conditions cannot be met in the pyrroline ring and therefore other factors than the σ–π overlap mechanism in the homoallylic fragment may be of importance.

All those compounds with unusually large homoallylic couplings have a common fragment in which a heteroatom with lone-pair electrons, or in the case of 1,4-cyclohexadiene[28] a π-electron system, is symmetrically opposed to the double bond transmitting the coupling. It appears as if such an arrangement is favourable for large homoallylic couplings, particularly since protonation of the N atom in heliotridene reduces these couplings to normal values (Table 2).

The fairly large difference between the *cis-* and *trans-* homoallylic couplings in heliotridene, retronecine and heliotridine is another surprising aspect in view of the planarity of the pyrroline ring. Different additional contributions to these couplings arising from an alternate pathway via the N atom seem to be ruled out, as no coupling between H-3 and J-8α is observed.

TABLE 1. CHEMICAL SHIFTS OF HELIOTRIDENE IN $CDCl_3$ SOLUTIONS AND CHANGES OF SHIFTS UPON ACIDIFICATION

Proton	δ [ppm from TMS]	$\Delta\delta(\delta_{acidic} - \delta_{neutral})$
$H_{1\alpha}$	2·27	0·35
$H_{2\alpha}$	1·81	0·39
$H_{2\beta}$	1·34	0·30
$H_{3\alpha}$	3·04	0·71
$H_{3\beta}$	2·58	0·56
$H_{5\alpha}$	3·88	0·74
$H_{5\beta}$	3·35	0·30
H_6	5·77	0·14
H_7	5·62	0·12
$H_{8\alpha}$	4·21	0·84
CH_3	0·90	—

TABLE 2. COUPLING CONSTANTS OF HELIOTRIDENE IN NEUTRAL AND ACIDIFIED $CDCl_3$ SOLUTIONS AND AT − 50°

Coupling protons		Coupling constants $J_{i,j}$[Hz]		
i	j	$CDCl_3$ solution	Acidified $CDCl_3$	$CDCl_3$ at − 50°
1α	2α	6·0	6·1	6·0
1α	2β	7·3	10·0	7·5
1α	8α	6·9	7·0	6·5
1α	Me	7·1	7·0	7·0
2α	2β	− 12·2	− 12·9	− 11·8
2α	3α	6·1	6·1	6·0
2α	3β	6·1	3·9	6·0
2β	3α	7·2	10·0	7·5
2β	3β	6·1	6·7	6·5
3α	3β	− 10·6	− 11·9	− 10·6
5α	5β	− 15·3	− 16·0	− 15·4
5α	6	1·8	1·8	1·7
5α	7	− 2·0	− 2·0	− 2·0
5α	8α	3·6	2·2	3·3
5β	6	2·0	1·8	1·7
5β	7	− 2·0	− 2·0	− 2·0
5β	8α	5·0	≤ 3·9	5·1
6	7	6·0	6·5	6·0
6	8α	− 1·7	− 1·8	− 1·7
7	8α	1·8	2·0	2·0
NH	3α	—	6·8	—
NH	5α	—	11·0	—
NH	5β	—	2·9	—
NH	8α	—	~ 6	—

Table 3. Observed and calculated vicinal coupling constants for heliotridene in neutral and acidic $CDCl_3$ solutions

Protons		ϕ_{exo}	ϕ_{endo}	J_{exo}	J_{endo}	Neutral Solution J_{calc} [45 exo: 55 endo]	Neutral Solution J_{obs}	Acidic Solution J_{calc} [25 exo: 75 endo]	Acidic Solution J_{obs}
1α	2α	45°	45°	6·0	6·0	6·0	6·0	6·0	6·1
1α	2β	75°	165°	1·2	12·9	7·6	7·3	10·0	10·0
1α	8α	30°	30°	8·1	8·1	8·1	6·9	8·1	7·0
2α	3α	45°	45°	6·0	6·0	6·0	6·1	6·0	6·1
2α	3β	165°	75°	12·9	1·2	6·5	6·1	4·1	3·9
2β	3α	75°	165°	1·2	12·9	7·6	7·2	10·0	10·0
2β	3β	45°	45°	6·0	6·0	6·0	6·1	6·0	6·7

Table 4. Observed chemical shifts and coupling constants for the alternate assignment of the H-2 protons

Chemical shifts Proton	Chemical shifts δ[ppm]	Protons		Vicinal coupling constants [Hz] Solutions Neutral	Vicinal coupling constants [Hz] Solutions Acidic
2α	1·34	1α	2α	7·3	10·0
2β	1·81	1α	2β	6·0	6·1
		2α	3α	7·2	10·0
		2α	3β	6·1	6·7
		2β	3α	6·1	6·1
		2β	3β	6·1	3·9

Table 5. Observed and calculated vicinal coupling constants for the pyrrolidine ring in heliotridine and retronecine

Protons		ϕ_{exo}	ϕ_{endo}	J_{exo}	J_{endo}	J_{calc} [35 exo: 65 endo]	Helio-tridine	Retro-necine
5α	6α	45°	45°	6·0	6·0	6·0	5·7	7·2
5α	6β	75°	165°	1·2	12·9	8·8	8·4	1·2
5β	6α	165°	75°	12·9	1·2	5·3	5·7	12·0
5β	6β	45°	45°	6·0	6·0	6·0	5·7	6·0
6α	7α	45°	45°	5·3	5·3	—	—	3·6
6α	7β	165°	75°	11·9	0·8	4·7	4·2	—
6β	7α	75°	165°	0·8	11·9	—	—	1·3
6β	7β	45°	45°	5·3	5·3	5·3	6·2	—
7α	8α	30°	30°	7·2	7·2	—	—	3·9
7β	8α	150°	90°	9·0	−0·3	3·0	3·4	—

EXPERIMENTAL DETAILS

The NMR spectra of heliotridene in $CDCl_3$ soln were recorded on a Varian HA-100 spectrometer at a probe temp of 32°. TMS was used as an internal reference. Chemical shifts are quoted as δ values and are considered to be accurate to 0·01 ppm. The calibration of the instrument was checked with a Hewlett-Packard electronic counter, model 5512 A. The line frequencies used in the analysis of the spectra are the average values of four measurements recorded on a 250 Hz sweep width, with alternate directions of the magnetic sweep.

In order to facilitate the assignment of the individual protons of the methylene pairs, a spectrum of heliotridene at −50° in $CDCl_3$ was recorded. The temp was measured using a Varian V-4343 variable temp controller calibrated with a MeOH sample. Further information regarding the geminal protons was obtained by progressively adding conc HCl to the $CDCl_3$ soln until no further changes in the chemical shifts and coupling constants could be detected. Coupling constants are expressed in Hertz with an estimated accuracy of 0·2 Hz in the case of the neutral soln and of 0·3 Hz for the acidic soln and the low temp run.

The relative signs of the homoallylic coupling constants were determined by means of the spin decoupling echnique involving irradiation at the H-5 protons and observing the collapse of certain lines in the H-8 esonance pattern. A Hewlett-Packard audiofrequency oscillator (200 CD) was used and the decoupling experiment was performed in the frequency-sweep mode.

The theoretical spectrum was calculated with the LAOCN3 programme of Bothner-By and Castellano[7].

REFERENCES

[1] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959).

[2] W. A. Thomas, *Annual Review of NMR Spectroscopy* Vol. 1. Academic Press, London and New York (1968).

[3] M. Barfield, *J. Chem. Phys.* **48**, 4458, 4463 (1968).

[4] M. Barfield, *Ibid.* **41**, 3825 (1964).

[5] S. Sternhell, *Rev. Pure Appl. Chem.* **14**, 15 (1964).

[6] C. C. J. Culvenor, M. L. Heffernan and W. G. Woods, *Austral. J. Chem.* **18**, 1605 (1965).

[7] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.* **41**, 3863 (1964).

[8] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron* Suppl. 7,335 (1966).

[9] A. A. Bothner-By, *Advances in Magnetic Resonance* Vol. 1. Academic Press, New York and London (1965).

[10] E. L. Eliel, *Stereochemistry of Carbon Compounds.* McGraw-Hill, New York (1962).

[11] K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.* **81**, 3213 (1959).

[12] J. B. Hendrickson, *Ibid.* **83**, 4537 (1961).

[13] J. Fredrichsons, A. McL. Mathieson, and D. J. Sutor, *Acta Crystallogr.* **16**, 1075 (1963).

[14] J. Fredrichsons and A. McL.Mathieson, *Ibid.*, **16**, 206 (1963).

[15] J. Donohue and K. N. Trueblood, *Ibid.*, **5**, 419 (1952).

[16] R. J. Abraham and K. A. McLauchlan, *Mol. Phys.* **5**, 195 (1962).

[17] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.* 3739 (1964).

[18] M. Karplus, *J. Am. Chem. Soc.* **85**, 2870 (1963).

[19] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.* **7**, 165 (1964).

[20] K. G. R. Pachler and P. L. Wessels, *J. Mol. Structure* **3**, 207 (1969).

[21] V. F. Bystrov, S. L. Portnova, V. I. Tsetlin, V. T. Ivanov and Yu A. Ovchinnikov, *Tetrahedron* **25**, 493 (1969).

[22] M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.* **27**, 597 (1957).

[23] J. A. Pople and A. A. Bothner-By, *Ibid.* **42**, 1339 (1965).

[24] M. Antheunis, *Bull. Soc. Chim. Belges* **75**, 413 (1966).

[25] M. Barfield and D. Grant, *J. Am. Chem. Soc.* **85**, 1899 (1963).

[26] M. Karplus, *J. Chem. Phys.* **33**, 1842 (1960).

[27] H. Appel, R. P. Bond and K. H. Overton, *Tetrahedron* **19**, 635 (1963).

[28] E. W. Garbisch and M. Griffith, *J. Am. Chem. Soc.* **90**, 3590 (1968).