ing with 4 × 20 ml aliquots of methylene chloride. After concentration and tlc on silica P-254 (chloroform), a material containing a yellow impurity (λ_m 430) was obtained. Vpc on a 5 ft × 0.25 in. 15% XF 1150 on 60–80 mesh Chromosorb column at 125–135° removed the impurity, giving **1** as a colorless oil which melts below −30°. Attempts to prepare the picrate of **1** led to nitrogen evolution: high-resolution mass spectroscopy, obsd mass 114.0905, calcd for $C_4H_{10}N_4$ 114.09054; ir (CCl_4) 1450 (br), compared to 1480 (br) for **2**.

Esr spectroscopy was performed using Varian E15 equipment and Varian electrolysis cells.

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The Stereochemical Dependence of ^{15}NCH and ^{13}CH Coupling Constants in Oxaziridines[1]

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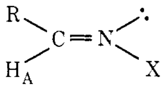
Abstract: The stereochemical dependence of ^{13}CH and ^{15}NCH coupling constants has been investigated in a series of diastereomeric (*Z*)- (cis) and (*E*)- (trans) oxaziridines. In both cases the reduced coupling constant (*K*) has been found to be more positive in the *Z* isomer where the nitrogen lone pair of electrons is cis to the ring proton. The absolute sign of $^2K(^{15}NCH)$ in a representative (*Z*)-oxaziridine was shown to be positive, while that of $^1K(^{15}N\text{-}^{13}C)$ was found to be negative, the first demonstrated negative one-bond C–N reduced coupling constant. It is suggested that a cis lone pair of electrons may make a positive contribution to *K* by direct (*i.e.*, "through space") orbital overlap.

There is considerable evidence that the magnitude of nuclear spin coupling constants can be affected by the presence of proximate lone pairs of electrons. The influence of lone pairs of electrons on indirect coupling between two nuclei may be divided into two types: (I) the lone pair formally situated on either of the coupled atoms, or (II) the lone pair formally situated on a third atom.



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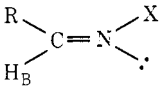

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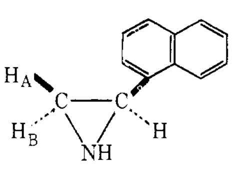

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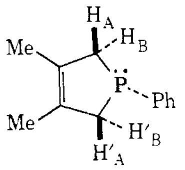

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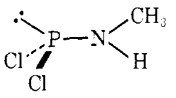

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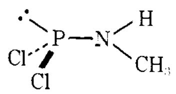

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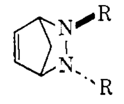

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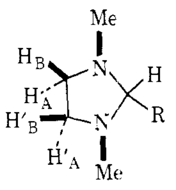

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Several examples of type I effects that have been recently reported involve PH or NH coupling constants, where the phosphorus or nitrogen atom possesses a lone pair of electrons. Thus, the considerable difference in $^2J(^{15}NCH)$ for the protons H_A and H_B in imines, hydrazones, and oximes (**1a** and **1b**), and in the aziridine **2** has been ascribed to the orientation of the nitrogen lone pair.[3-5] Axenrod, *et al.*,[6] have shown that the magnitude of $^3J(^{15}NNCH)$ in a series of *N*-nitrosamines is markedly dependent on whether the proton is cis or trans to the nitrogen lone pair; additionally, $^2J(^{14}NCH)$ and $^3J(^{14}NCCH)$ also appear to be stereochemically dependent in aziridines, imines, and oximes.[4b,7,8b] The examples of stereospecific ^{15}NH coupling measured to date are too numerous to describe and have recently been reviewed quite adequately.[9] Gagnaire, *et al.*,[10] have extensively investigated the

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[1] Part of this work has been published in preliminary form: D. M. Jerina, D. R. Boyd, L. Paolillo, and E. D. Becker, *Tetrahedron Lett.*, 1483 (1970).

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stereochemical dependence of two- and three-bond ^{31}PH coupling constants; for example, $^2J(PCH)$ in **3** differs considerably for H_A and H_B. Additionally, Cowley, *et al.*,[11] have suggested that $^3J(PNCH)$ is considerably larger in the rotamer **4a**, where the methyl group is cis to the phosphorus lone pair, than in **4b**.

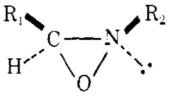
Lone-pair effects from an atom that is not directly involved in the coupling (type II effects) have been well established for geminal proton–proton coupling constants.[12] A similar effect has been suggested to contribute to $^3J(HCCH)$ in some heterocyclic compounds,[12b,13] to $^3J(HCCH)$ and $^4J(HCCCH)$ in **5**,[14] and to $^4J(HCPCH)$ in a cyclic phosphine.[10e]

Recently it has been suggested that directly bonded ^{13}CH coupling constants may be influenced by the presence of neighboring lone pairs of electrons.[8,15] Gil, *et al.*,[15a] have interpreted the rather low value of $^1J(^{13}CH)$ in *N*-benzylidenemethylamine (**1a**, X = CH_3) in terms of the lone-pair orbital on the nitrogen atom, and Yonezawa, *et al.*,[8] have reported that $^1J(^{13}CH)$ in some oximes (**1**, X = OH) and aziridines depends on whether the proton is cis or trans to the nitrogen lone pair. Albrand, *et al.*,[16] have recently shown that there is a difference of ~10 Hz between $^1J(^{13}CH_A)$ and $^1J(^{13}CH_B)$ in some imidazolidines (**6**); the larger coupling constant was assigned to the proton (H_A) cis to the nitrogen lone-pair electrons.

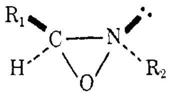
Although there is considerable evidence available to show that proximate lone pairs of electrons can affect the magnitude of coupling constants, in many of the examples cited either the stereochemistry of the molecule has not been rigorously established or else the absolute signs of the coupling constants are uncertain. Boyd, *et al.*,[17] have recently shown that the *Z* and *E* invertomers of oxaziridines can be separated, and the relative stereochemistry of several of these compounds has been rigorously established. Therefore, we have chosen a series of these compounds to investigate the stereochemical dependence of $^2J(^{15}NCH)$ and $^1J(^{13}CH)$ as examples of type I and II lone-pair effects, respectively. We also report the sign and magnitude of $^1J(^{13}C^{15}N)$ in the oxaziridine ring.

Results and Discussion

^{13}CH Coupling Constants. The ^{13}CH coupling constants for the ring proton in a series of (*Z*)- and (*E*)-oxaziridines (**7**–**17**) determined from their ^1H nmr spectra are given in Table I. The stereochemistry of **10Z** and **17E** has previously been rigorously established by X-ray crystallography[18,19] and for **7**, **11**, **14**, and **15** by nuclear Overhauser effects.[20] The stereochemistry of the other oxaziridines was assigned from their ^1H nmr spectra using the characteristic signal position of the ring proton in the *Z* and *E* isomers, and by benzene-induced solvent shifts.[17]



Z



E

Compd	R_1	R_2
7	4-nitrophenyl	methyl
8	4-nitrophenyl	ethyl
9	4-nitrophenyl	benzyl
10	4-nitrophenyl	isopropyl
11	4-nitrophenyl	*tert*-butyl
12	phenyl	methyl
13	1-naphthyl	methyl
14	2-naphthyl	methyl
15	*tert*-butyl	methyl
16	H	*tert*-butyl
17	4-bromo-2,6-dimethylphenyl	methyl

Table I. Stereochemical Dependence of ^{13}CH Coupling Constants in Oxaziridines

	$^1J(^{13}CH)$, Hz[a]		
Compd	*Z* (cis)	*E* (trans)	ΔJ, Hz
7	185	179.5	5.5
8	185	180	5
9	185	180	5
10	185.6	179	6.6
11	*b*	179	
12	183	178.5	4.5
13	184	177	7
14	184.5	179	5.5
15	*b*	173	
16	181.5[c]	175.5[c]	6
17	182.5	176.6	5.9

[a] The coupling constants for **12**, **15**, and **16** were determined as neat liquids; otherwise saturated solutions in $CDCl_3$ were employed. [b] The *Z* isomer was not formed due to adverse steric interactions. [c] The coupling constants refer to the protons cis and trans to the nitrogen lone pair.

It can be seen from the data in Table I that there is a small but consistent difference in the ^{13}CH coupling constants for the *Z* and *E* isomers. The values are ~6 Hz larger for the *Z* isomer where the nitrogen lone pair is cis to the CH bond. Therefore, as $^1J(^{13}CH)$ is known to be positive, and both the magnetogyric ratios are positive, $^1K(^{13}CH)$ is more positive when cis to the lone pair. A similar effect has been observed in the oxime **1** (R = CH_3; X = OH), where $^1J(^{13}CH)$ = 177 and 163 Hz for the cis (**1b**) and trans (**1a**) isomers, respectively,[8] in *N*-alkylaziridines where $^1J(^{13}CH)$ = 171 and 161 Hz for the ring protons cis and trans to the nitrogen lone-pair electrons,[8] and in imidazolidines (**6**) where $^1J(^{13}CH)$ = 142 and 132 Hz for the protons H_A and H_B, cis and trans to the nitrogen lone pair, respectively.[16] However, in the former example the effect of the oxygen atom is uncertain and in the latter two cases the stereochemistry was not rigorously established.

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^{15}N Coupling Constants. The ^{15}NCH coupling constants for the ring proton in several isotopically enriched oxaziridine diastereomers determined from their ^{1}H nmr spectra are presented in Table II. The absolute values for the Z isomers are *ca.* 5 Hz, whereas those for the corresponding E isomers are too small to be resolved (<0.5 Hz) (Figure 1). The ^{1}H, ^{13}C, and ^{15}N nuclei in the oxaziridine ring constitute a classic AMX system in which double resonance methods can provide conclusive determination of the relative signs of the coupling constants.[21] Since $\gamma(^{15}\mathrm{N})$ is negative, the signs of all coupling constants involving ^{15}N are opposite to those for the ^{14}N analog. However, with the reduced coupling constants, $K_{ij} = 4\pi^2 J_{ij}/h\gamma_i\gamma_j$, the usual generalizations applicable to the perturbation of high- or low-frequency multiplets apply.[22]

Table II. Stereochemical Dependence of ^{15}NH Coupling Constants in (Z)- (Cis) Oxaziridines[a]

Compd	$^2J(^{15}\mathrm{NCH})$, Hz	$^2K(^{15}\mathrm{NCH})$,[b] 10^{20} cm^{-3}
7	-5.4	$+4.4$
9	-5.3	$+4.4$
10	-5.0[c]	$+3.9$
11	*d*	
17	-4.8	$+3.9$

[a] No coupling between ^{15}N and the oxaziridine ring proton was observed in the E (trans) isomers. [b] $K(\mathrm{NH}) = 4\pi^2 J/h\gamma_\mathrm{N}\gamma_\mathrm{H}$. [c] Sign determined for this compound (see text), all other signs by analogy. [d] The Z isomer was not obtained.

Table III gives the results of the double resonance experiments on a representative oxaziridine, **10Z**. The data in Table III have been corrected for field variation; therefore it is more convenient to refer to the various peaks as though the observing frequency were varied. The *high*-frequency ^{13}C satellite of the ring proton collapsed from a doublet to a singlet on irradiating with an ^{15}N frequency that was *lower* than that required to decouple the low-frequency satellite. Thus, $^1K(^{13}\mathrm{C}^{15}\mathrm{N})$ and $^1K(^{13}\mathrm{CH})$ have opposite signs; since the latter is known to be positive, $^1K(^{13}\mathrm{C}^{15}\mathrm{N})$ is negative. From the difference in decoupling frequencies, $^1J(^{13}\mathrm{C}^{15}\mathrm{N}) \approx +5$ Hz.

Table III. Effect of Double Resonance on ^{13}C Satellites of Oxaziridine **10Z**

^{1}H line frequency[a]	Optimum ^{13}C or ^{15}N frequency[b]	Effect
	^{15}N Decoupling	
1086.8 1091.6	22 296 283	Decoupled to singlet
1272.4 1277.2	22 296 278	Decoupled to singlet
	^{13}C Tickling	
1086.8	55 323 503	Split to doublet[c]
1091.6	55 323 499	Split to doublet[c]
1272.4	55 323 320	Split to doublet[c]
1277.2	55 323 315	Split to doublet[c]
1086.8	55 323 318	Broadened[d]
1091.6	55 323 313	Broadened[d]

[a] In Hz from TMS at 220.01 MHz (average of six measurements). [b] In Hz, in magnetic field where ^{1}H in TMS resonates at exactly 220 MHz; corrected for magnetic field sweep and for use of 9999.8-Hz upper side band. [c] A rather "broad" doublet is observed, as expected from the tickling of one of a pair of progressive transitions.[21] [d] Since the observed and irradiated transitions constitute a regressive pair, a sharp doublet would be expected if the observing frequency, rather than the magnetic field, were swept.[21] However, with the actual field sweep it is difficult to establish optimum conditions for tickling; this limitation is probably responsible for our observation only of a line broadening, rather than a sharp splitting.

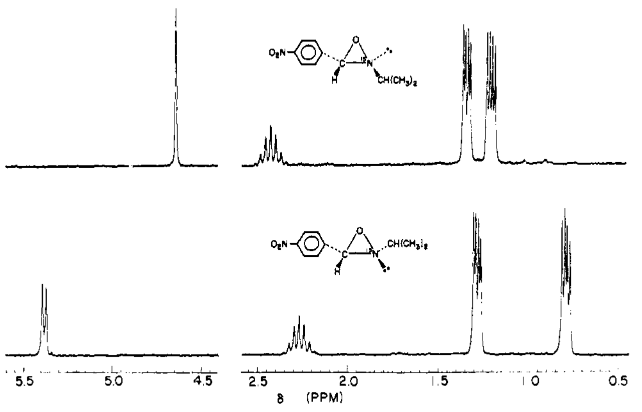

Figure 1. Proton nmr spectrum (220 MHz) of **10E** (top) and **10Z** (bottom) in CDCl$_3$.

Because of the large value of $J(^{13}\mathrm{CH})$ it is not feasible to carry out a ^{13}C decoupling experiment, but ^{13}C spin tickling can readily be used to provide unambiguous information on relative signs.[23] Table III shows that the *higher* the frequency of the ^{1}H line, the *lower* the ^{13}C frequency required for optimum spin tickling. Thus, $^2K(^{15}\mathrm{NCH})$ and $^1K(^{13}\mathrm{C}^{15}\mathrm{N})$ have opposite signs; since the latter was shown to be negative, $^2K(^{15}\mathrm{NCH})$ is positive and therefore $^2J(^{15}\mathrm{NCH}) = -5.0$ Hz. The differences in ^{13}C frequencies are in accord with the values found for $^1J(^{13}\mathrm{CH})$ and $^1J(^{13}\mathrm{C}^{15}\mathrm{N})$.

Thus, as in the case of the ^{13}CH coupling considered above, $^2K(^{15}\mathrm{NCH})$ is more positive in the Z isomer where the lone pair is cis to the ring proton. It is interesting to note that in the aziridine **2**, $^2K(^{15}\mathrm{NCH_A})$ also appears to be more positive than $^2K(^{15}\mathrm{NCH_B})$, though the stereochemistry of the molecule and the absolute signs of the coupling constants have not been conclusively established.[4] A similar effect is present in the aldoximes **1**, where the proton cis to the nitrogen lone pair is coupled to ^{15}N with a large reduced coupling constant, the sign of which is very probably positive.[3c]

Wasylishen and Schaefer[24] very recently applied the INDO–MO method to the calculation of ^{15}N–H coupling constants over two and three bonds in a large number of compounds. For **10Z** and **10E** they calculated $^2J(^{15}\mathrm{NH})$ as -5.78 and $+0.95$ Hz, respectively.

The value of $^1J(^{13}\mathrm{C}^{15}\mathrm{N})$ in **10Z**, as determined from the ^{13}C or ^{15}N tickling or decoupling frequencies, is $\sim$5 Hz. A more accurate value, observed directly in the proton-decoupled ^{13}C spectrum, is 4.9 Hz. The isomer **10E** gave a value $^1J(^{13}\mathrm{C}^{15}\mathrm{N}) = 3.1$ Hz, also from direct observation of the ^{13}C spectrum. In **10Z** the sign of $^1K(^{13}\mathrm{C}^{15}\mathrm{N})$ is negative, the first demonstrated negative one-bond reduced coupling constant between

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(21) See, for example, R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

(22) R. B. Johannesen, *ibid.*, **48**, 1414 (1968).

(23) E. F. Friedman and H. S. Gutowsky, *ibid.*, **45**, 3158 (1966).

(24) R. Wasylishen and T. Schaefer, private communication.

carbon and nitrogen. The few previously determined signs of ${}^1K({}^{13}C{}^{15}N)$ are all positive—$CH_3C{\equiv}N$,[25] $CH_3N{\equiv}C$,[26] CH_3NH_2,[27] and CH_3NO_2.[28] Lichter and Roberts[5] have suggested that a change in sign of ${}^1J({}^{13}C{}^{15}N)$ in pyridine occurs when the nitrogen is protonated, but their argument, while cogent, is based on expected systematic behavior of the coupling, rather than on direct sign determinations. Theoretical treatment of CN coupling by the INDO method predicts a variation in sign depending upon the exact molecular structure, but the agreement between calculated and experimental values is rather poor.[29]

The difference between ${}^1J({}^{13}C{}^{15}N)$ in **10Z** and **10E** is small (1.8 Hz provided there is no change in sign between the two isomers)[30] but may well represent subtle differences in electronic distribution that depend on the proximity of the nitrogen lone pair to the oxaziridine ring proton or to the aromatic substituent.

General Conclusions

In the examples investigated to date, it is evident that a proximate lone-pair orbital makes a positive contribution to the reduced coupling constant (K) in ${}^{13}CH$ and HCH[12] couplings (type II) and in ${}^{15}NCH$ coupling (type I). Additionally the type I couplings, ${}^2K(PCH)$,[10e] ${}^3K(PCCH)$,[10e] ${}^3K(POCH)$,[10c] and ${}^3K(PNCH)$,[11] and the type II coupling ${}^4K(HCPCH)$[10e] appear to be more positive when the phosphorus lone-pair electrons are cis to the proton, though in the latter cases the stereochemistry of the molecule or the signs of the coupling constants have not been conclusively established. Therefore, from the limited data available it would appear that a proximate lone-pair lobe makes a positive contribution to the reduced coupling constant irrespective of the number of bonds linking the coupled nuclei or whether the effect is type I or type II in nature.[31] On this basis it seems reasonable to postulate that the lone-pair effect arises from direct (*i.e.*, through space) overlap of the filled lone-pair orbital with the proximate antibonding C–H orbital. Pople and Bothner-By[12] and Gil and Teixeira-Dias[15b] have discussed an effect of this type in HCH and ${}^{13}CH$ type II couplings, respectively. Generalization of this effect to include type I coupling does not *necessarily* imply that the coupling occurs through space,[32] since there could be a through-space effect on the through-bond coupling as in the ${}^{13}C$–H case. However, the observation that a similar effect appears to be present in both two- and three-bond PH couplings and in two-bond ${}^{15}NH$ coupling would be in accord with a positive through-space contribution to the cis coupling.

If this effect can be verified for a wider range of compounds, it may provide a useful method for assigning stereochemistry in compounds possessing a lone pair of electrons.

Acknowledgment. We thank J. B. Robert for helpful correspondence, T. Axenrod for a preprint of ref 9, H. M. McIntyre and D. Torchia for obtaining the ${}^{13}C$ spectra of **10Z** and **10E**, and H. J. C. Yeh for measuring some of the ${}^{13}CH$ coupling constants.

Experimental Section

The preparation and characterization of the oxaziridines have been described previously;[17] the ${}^{15}N$-enriched compounds were prepared from ammonia-${}^{15}N$ (>97% ${}^{15}N$) *via* the corresponding amines.

${}^1H$ nmr spectra were determined at 100 MHz on a Varian HA-100 or at 220 MHz on a Varian HR-220 spectrometer. The double resonance experiments were carried out on the latter spectrometer modified to accept irradiating frequencies of 22.3 MHz (${}^{15}N$) and 55.3 MHz (${}^{13}C$). Both the observing and the irradiating frequencies were derived from a single General Radio 1164-A frequency synthesizer, with 220 MHz obtained by appropriate multiplication of the 5-MHz output from the synthesizer. Since our HR-220 spectrometer can be used only in field sweep mode, the observed optimum irradiating frequencies depend on the precise magnetic field at resonance for each line. Corrections for the effect of field variation on the observed decoupling and tickling frequencies were made by converting the observed frequencies to the values that would have been observed if the ${}^1H$ resonance of TMS were at exactly 220.000 MHz. Thus the values given in the second column of Table III (ν_{corr}) were obtained from the observed irradiating frequencies (ν_{obsd}) as follows: $\nu_{corr} = 220/220.01\,[\nu_{obsd} + (\nu_H/220.01)\nu_x]$, where ν_H is the ${}^1H$ resonance frequency of the observed line, as given in the first column of Table III, and ν_x is 22.3 MHz for the ${}^{15}N$ decoupling experiments and 55.3 MHz for the ${}^{13}C$ tickling experiments. The factor 220/220.01 arises from the use of the 10-kHz upper side band as the observing frequency.

${}^{13}C$ spectra were obtained by Fourier transform methods with a 15-MHz pulse spectrometer at the National Bureau of Standards.

All samples were $CDCl_3$ solutions except for those used for direct ${}^{13}C$ observation, where the solvent was CH_2Cl_2.

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(31) In the case of vicinal HCCH coupling, it has been suggested[12b,13] that in several heterocyclic compounds a proximate lone pair of electrons increases the coupling constant (*i.e.*, makes K more positive); however, in some aziridines[8a] and imidazolines,[16] it appears that ${}^3K(HCCH)$ is *smaller* for the protons cis to the lone-pair electrons. Possibly other factors contribute to the stereochemical dependence of vicinal coupling in these compounds.

(32) For a general discussion of through-space coupling, see M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).