Interproton Coupling Constant Variations in 3-Membered Ring Heterocycles. Separation of Lone Pair and Inductive Effects†

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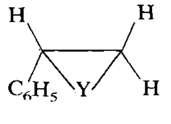
In order to separate inductive and lone pair effects on geminal and vicinal coupling constants in a stereochemically well-defined system, the ^{1}H NMR spectra of phenylcyclopropane (1), *N*-methyl-2-phenylaziridine (2), styrene oxide (3) and 1,1-dimethyl-2-phenylaziridinium fluorosulfonate (4) were compared. In D_2O the heterocyclic ring protons of 4 were split into an ABX pattern which gave *J(cis)* = 8.5, *J(trans)* = 7.4 and *J*(gem) = −4.8 Hz (signs consistent with INDOR results). From the small solvent effects on *J*(vic) determined from 4-d_1, it was concluded that J(gem) is −5.0 ± 1.0 Hz in methylene chloride. The absolute values for the coupling constants for 1 and 4 provide a measure of the inductive effect of the ring hetero group on *J*. Values of *J*(gem) for 2 and 3 deviated from those predicted on the basis of the above inductive effect, suggesting lone pair contributions to *J*(gem) of c. +5.5 Hz per lone pair. With this estimate it was possible to predict accurately the *J*(gem) values for 2-*t*-butyloxaziridine and 1-*t*-butyldiaziridine. The values of *J(cis)* and *J(trans)* for 2 and 3 likewise suggested a contribution of −2.5 Hz to *J(cis)* and −2.7 Hz to *J(trans)* per lone pair. The present results suggest that the major factors causing positive *J*(gem) values in epoxides and aziridines are increased s character to the C—H bonds and lone pair effects, while the so-called electronegativity effect actually operates in the opposite direction to *decrease* *J*(gem). Also, the unusually low *J*(vic) values of epoxides relative to cyclopropanes are now seen to be due more to negative lone pair contributions than to the electron withdrawing ability of oxygen.

Considerable effort has been expended in attempts to correlate ^2J(HCH) and ^3J(HCCH) coupling constants with various structural features.[1–3] While both types of coupling depend on the orientation of substituents,[2a,4] *J*(gem) generally increases with the electronegativity of α substituents[5] and *s* character of the C—H bond[6] and decreases when neighboring π bonds are present.[7] Values of *J*(vic) decrease with electronegativity of α substituents[8] but increase with electronegativity of β substituents.[3] Dihedral angle[9] and hybridization changes involving vicinal carbon atoms[10] also affect *J*(vic) values. These trends are in qualitative agreement with predictions from MO theory for *J*(gem)[11] and VB theory for *J*(vic).[9]

Of particular importance is the effect of heteroatoms, which is complicated by being a composite of electronegativity and lone pair effects. Most 'electronegativity' trends, and even the chemical shift *scale* of electronegativity,[12] result from inductive withdrawal of electrons and lone pair effects averaged for various conformations.[13]

In an effort to separate these factors, Anteunis[14] calculated coupling constants based on the Karplus equation corrected for electronegativity effects. Comparison of calculated with observed values of *J*(*syn*) + *J*(*anti*) suggested a contribution of +2.3 Hz to *J*(vic) and +1.8 Hz to *J*(gem) whenever a lone pair of nitrogen or oxygen is eclipsed with a C—H bond. In another study[15] this contribution to *J*(gem) was estimated as +3.5 Hz and +2.5 Hz for an oxygen and nitrogen, respectively. Both studies, however, involved 5- and 6-membered rings which were conformationally mobile.

As part of our investigations into the properties and reactivity of 3-membered ring compounds,[16] we now report our results on a series of compounds chosen to allow separation of inductive and lone pair effects on coupling constants. Although the unusual bonding in 3-membered rings[17] may restrict specific conclusions to related compounds, the following approach may be more general. Phenylcyclopropane (**1**) and 1,1-dimethyl-2-phenylaziridinium fluorosulfonate (**4**) were used as models to provide an inductive effect baseline, while 1-methyl-2-phenylaziridine (**2**) and styrene oxide (**3**) provide data to estimate lone pair effects on coupling.



1, $Y = CH_2$
2, $Y = NCH_3$
3, $Y = O$
4, $Y = N(CH_3)_2^+$

Advantages of the present series include conformational rigidity,[18] necessarily fully eclipsed lone pair interactions with C—H, and the ability to determine *cis* and *trans* vicinal coupling constants, which was not possible in previous work.[14,19]

RESULTS

The various 3-membered heterocycles were synthesized from styrene oxide as previously reported.[16c]

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Table 1. Coupling constants for phenyl substituted 3-membered ring compounds[a]

Compound	Solvent	*J*(*cis*)	*J*(*trans*)	*J*(gem)	E_Y[b]
1	CCl_4[c]	8.41	5.13	−4.56	2.28
2	CH_2Cl_2	6.5	3.1	1.1	2.40
	CCl_4[d]	6.3	3.1	1.2	
3	CH_2Cl_2	4.2	2.7	5.6	2.68
	neat[e]	4.06	2.52	5.66	
4	CH_2Cl_2	9.5	8.0	−5.0[f]	2.70

[a] Unless otherwise noted, *J* in the present work has an uncertainty of ±0.2 Hz.
[b] Group electronegativities from Ref. 36 of ethyl, dimethylamino, methoxy and trimethylammonium groups for **1**, **2**, **3** and **4**, respectively.
[c] Data from Ref. 20(a).
[d] Data from Ref. 20(d).
[e] Data from Ref 20(c).
[f] Value estimated from $J = -4.8$ Hz in D_2O considering a small solvent effect (see Table 2) and presumed accurate to ±1 Hz.

Since methylene chloride is a suitable nonreactive solvent for aziridinium salts, the spectra of **2** and **3** were taken in this solvent. An ABX analysis of the heterocyclic ring protons, based on the accepted assignments and signs of the coupling constants, gave coupling constants in good agreement with literature values (see Table 1) [For phenylcyclopropane (signs determined by best fit to experimental values) see Ref. 20a; for predicted values for phenylcyclopropane see Ref. 20b; for styrene oxide see Ref. 20c and for 1-methyl-2-phenylaziridine see Ref. 20d.] As shown in Fig. 1(a), these protons resembled an AA′X degenerate system[21] in methylene chloride. However, in trifluoroacetic acid an ABX pattern was observed, and in D_2O [Fig. 1(c)] the AB portion appears as well separated lines suitable for double resonance experiments. Analysis of the three spin system for **4** in the various solvents gave the results in Table 2.

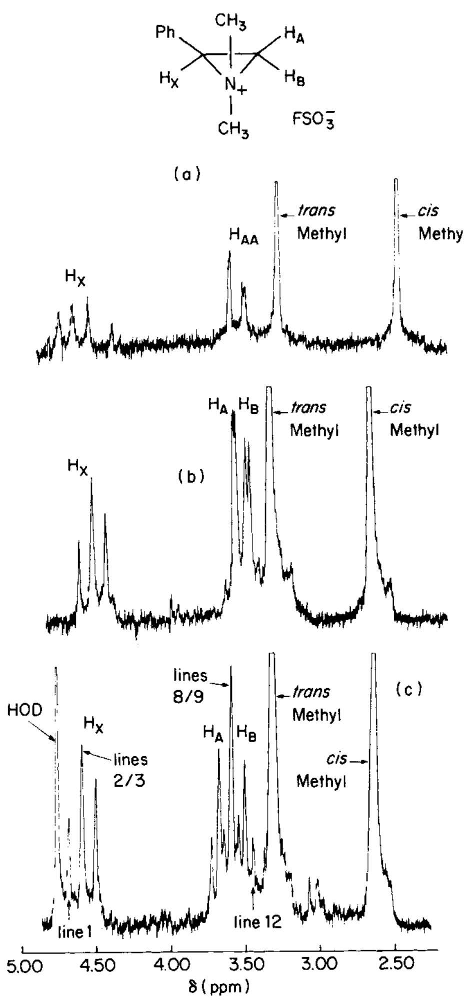
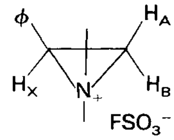
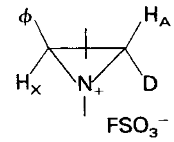
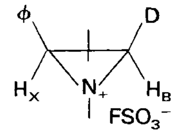


Figure 1. ^{1}H NMR spectra of 1,1-dimethyl-2-phenylaziridinium fluorosulfonate (**4**) in various solvents: (a) methylene chloride; (b) trifluoroacetic acid; (c) D_2O.

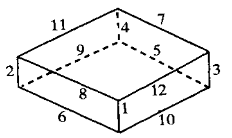
Table 2. Solvent effects on coupling constants for 1,1-dimethyl-2-phenylaziridinium fluorosulfonates[a]

Compound	Solvent	δ_A	δ_B	δ_X	J_{AB}	J_{AX}	J_{BX}
	D_2O[b]	3.66	3.54	4.57	−4.8	+7.4	+8.5
	TFA[b]	3.57	3.52	4.53	−5.0	+7.6	+8.6
	CH_2Cl_2[c]	3.57	3.56	4.58	—[d]	+8.0	+9.5
	D_2O[b]	3.66	—	4.58	—	+7.7	—
	TFA[b]	3.54	—	4.46	—	+7.6	—
	CH_2Cl_2[c]	3.57	—	4.58	—	+8.2	—
	D_2O[b]	—	3.51	4.58	—	—	+8.5
	TFA[b]	—	3.49	4.46	—	—	+8.4
	CH_2Cl_2[c]	—	3.59	4.58	—	—	+9.4

[a] Uncertainty of coupling constants ±0.2 Hz and uncertainty of chemical shifts of ±0.01 ppm.
[b] Measured in ppm from internal Tier's salt.
[c] Measured in ppm from internal TMS.
[d] Not observed.

In order to determine which coupling constant from the ABX pattern of aziridinium salt **4** in D_2O was $J(cis)$ or $J(trans)$, a nuclear Overhauser experiment (NOE) was performed. When the upfield methyl group at $\delta = 2.58$ was irradiated, increases in peak height of 15–25% were noted for the three peaks on the downfield side of the AB part of the spectrum. Since this upfield methyl is most probably in the shielding cone of the benzene ring and hence *cis* to phenyl,[22] the downfield proton at $\delta = 3.66$, *cis* to this methyl by the NOE, must also be *cis* to the phenyl ring. Hence the vicinal coupling constant of 7.4 Hz associated with this downfield proton is the *trans* coupling constant.

The relative signs of coupling constants were determined by INDOR experiments in D_2O. All ten lines of the ABX system were irradiated, but only one line from each nucleus is presented in Fig. 2. All data were consistent with the energy diagram below. Interestingly, since lines 2 and 3 are at opposite corners, all AB transitions should be affected when line 2/3 is irradiated, as was indeed the case.



Only the combinations represented by $\mp J_{AB}$, $\pm J_{AX}$, $\pm J_{BX}$ are consistent with the observed data. As discussed below, the $-J_{AB}$, $+J_{AX}$, $+J_{BX}$ combination is the more reasonable one and therefore is used in Tables 1 and 2. These data for **4** in D_2O (Table 2) gave a simulated spectrum by NMRPLT at 0.7 Hz resolution in excellent agreement with the observed one.

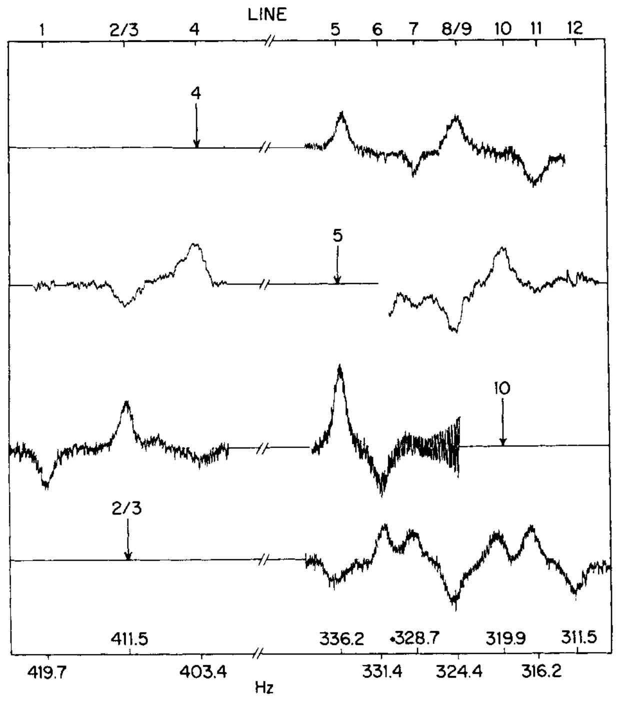


Figure 2. INDOR experiments with 1,1-dimethyl-2-phenylaziridinium fluorosulfonate (**4**) at f_1 frequencies as indicated.

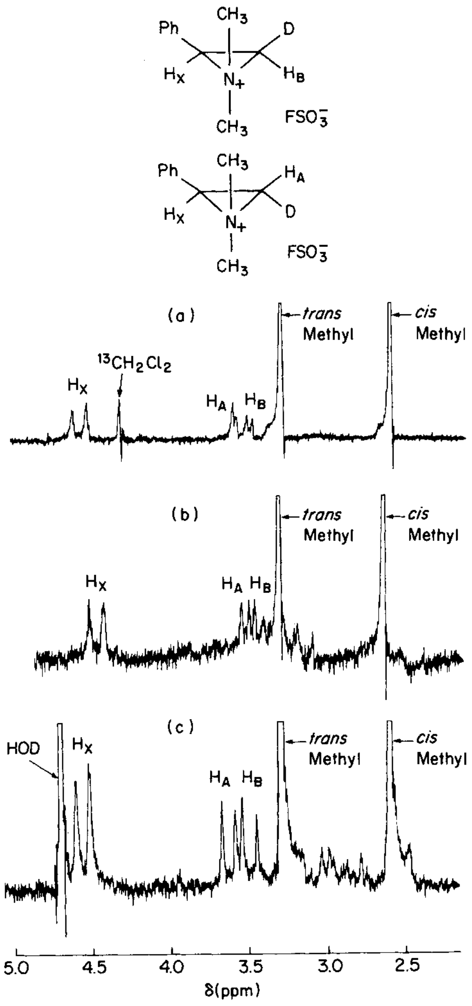


Figure 3. ^1H NMR spectra of 1,1-dimethyl-3-deuterio-2-phenylaziridinium fluorosulfonate (**4**-d_1) in various solvents: (a) methylene chloride; (b) trifluoroacetic acid; (c) D_2O.

Since coupling constants for the other heterocycles were obtained in methylene chloride, an unsuccessful attempt was made to determine J(gem) for **4** in this solvent by the indirect method[23] of measuring ^2J(HCD) for 1,1-dimethyl-3-deuterio-2-phenylaziridinium fluorosulfonate (**4**-d_1). Unfortunately, the geminal coupling in **4**-d_1 was not resolvable in methylene chloride [Fig. 3(a)] even after ^{14}N decoupling. However, its value can be estimated from the solvent effect data in Table 2. For neutral compounds including 2,2-dichlorocyclopropylbenzene, styrene oxide and styrene sulfide, Smith and Cox found that J(gem) becomes more negative in more polar solvents,[24] an observation which can be used to predict the sign of J(gem). However, they predicted[24b] that protonated solute molecules should give the reverse behavior, as indeed we observed for **4** in TFA (−5.0 Hz) vs D_2O(−4.8) Hz). Since the polarity of methylene chloride is probably comparable to TFA, J(gem) can be taken as -5.0 ± 0.7 Hz, where the uncertainty represents the spread of J(gem) in various solvents.[24]

DISCUSSION

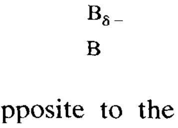
The INDOR results indicate that the absolute signs of the coupling constants in **4** are $-J_{AB}$, $+J_{AX}$, $+J_{BX}$ or, alternatively, $+J_{AB}$, $-J_{AX}$, $-J_{BX}$. On the basis of an apparent electronegativity trend of J(gem) increasing through the series **1, 2** and **3,** it was suggested[2b] that J(gem) values in aziridinium salts are positive. However, a positive J_{AB} taken with the present INDOR results would require negative vicinal coupling constants which are improbable for the following reasons: (1) vicinal coupling constants are almost always positive and, in the few cases where they are negative, their magnitude is small, e.g. -0.23 in mycarose,[14] and (2) positive values for J_{AX} and J_{BX} in **4** result in $J(cis) > J(trans)$, in agreement with the Karplus relationship which is valid for 3-membered ring compounds including heterocycles.[25] In addition, a $+J$(gem), $-J(cis)$, $-J(trans)$ combination for **4**, taken with data for phenylcyclopropane[20a] [$J(\text{gem}) = -4.56$, $J(cis) = 8.41$, $J(trans) = 5.13$] would require unreasonably large differences in corresponding coupling constants, e.g. *c.* 10 Hz for J(gem) and -18 Hz for $J(cis)$ in substituting $N(CH_3)_2^+$ for CH_2. The opposite combination involves much smaller differences, in agreement with comparisons between vicinal coupling constants in cyclopentane and pyrrolidinium derivatives.[19] For these reasons the absolute signs of coupling constants of the aziridinium salt **4** will be taken as $-J_{AB}$, $+J_{AX}$, $+J_{BX}$.

A summary of coupling constants with absolute signs for 3-membered ring compounds appears in Table 1. The values of J(gem) for **1** and **4**, which fall in the usual range for cyclopropanes (-3 to -9 Hz),[26] are more positive than those for cyclohexane (-12.6 Hz),[27] probably because of sp^2-like hybridization (cf. values of -2 to $+2$ Hz for J(gem) in $R_2C{=}CH_2$ compounds).[26] The value of J(gem) for **4** is the same as that reported[28] for an aziridinium salt with no aromatic groups present (sign undetermined).

Inductive effect

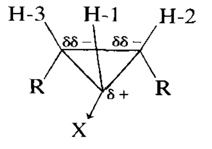
The inductive effect of a ring group on the coupling constants can be seen by comparing results for **1** and **4**. When the ring group becomes more electronegative, $Y = N(CH_3)_2^+$ vs $Y = CH_2$ in A, J(gem) decreases and $J(vic)$ increases, a result opposite to the usual trend. [One cannot simply dismiss the increased J(vic) for **4** compared with **1** on the basis of 'sp^2-like hybridization' of 3-membered rings since, in agreement with theoretical expectations, J(vic) in $RCH{=}CHX$ derivatives decreases to an even greater degree than sp^3-hybridized systems as X becomes more electron withdrawing.[29] It has been reported[29c] that the electronegativity dependence of coupling constants in substituted cyclopropanes is intermediate to that for sp^3 and sp^2 systems. However, the possibility that hybridization *changes* are partly responsible for a decreased J(vic) in **4** compared with **1** cannot be completely ruled out.] That J(vic) should be larger for the aziridinium salt is reasonable, based on extended Hückel calculations[30a] on aziridine which show that protonation of nitrogen causes an increase in the overlap population of the opposite C—C bond. Similarly, MINDO/2 calculations on **1** and the 1,1-dimethyl-2-phenylaziridinium ion[30b] show an increased Mulliken overlap for the C—C bond of the aziridinium ion, which should lead to more positive vicinal coupling constants as observed.

A

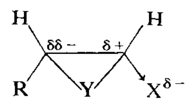


B

Unlike the present case, it might be noted that earlier observations of J(vic) values for various substituted 3-membered ring compounds can be readily interpreted by an alternating induced charge model. This model, favored as early as 1935 by Arndt and Eistert,[31] [and tentatively proposed by W. O. Kermack and R. Robinson, *J. Chem. Soc.* **121,** 427 (1922)] was rediscovered in calculations by Pople and Gordon[32] and has been subsequently used to explain various NMR results.[33] Based on the charge development indicated in B, aziridines[25b] ($A = N$ and $B = Cl$ vs H) and cyclopropanes[34] ($A = C$ and $B = Cl_2$ vs H_2) should have larger J(vic) values for the more electronegative substituent as observed. Electron withdrawing groups X on cyclopropanes[34] decrease $^3J(12)$ but increase $^3J(23)$, in agreement with the charge development indicated in C. Electronegative substituents X on a ring *carbon* of aziridines (D) decreased J(vic),[25b] an opposite trend to that found for substitution on nitrogen, but in agreement with the charge alternation model assuming that the $\delta+$ charge on the substituted carbon in D is the predominating charge perturbation.



C



D

Decreasing J(vic) values with more electronegative groups in substituted epoxides[35a] and 1,1-dichlorocyclopropanes[35b] can be explained similarly with structure D ($Y = O$ and $Y = CCl_2$, respectively). However, for the present case it is not clear how to apply the charge alternation model.

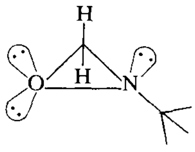
Lone pair effects

Within the structurally similar series **1–4**, lone pair effects can be estimated by plotting coupling constants against electron withdrawing ability of the ring hetero group. A suitable scale which includes the $N(CH_3)_2^+$ group and does not depend on entropy or solvation factors is that developed by Huheey.[36] Group electronegativity values for ethyl, dimethylamino, methoxy and trimethylammonium groups were used as a measure of the electron withdrawing ability of the CH_2, N—CH_3, O and $N(CH_3)_2^+$ groups in **1**, **2**, **3** and **4**, respectively, and are listed in Table 1. Following Radeglia,[37] we have normalized the electronegativity effect of ring members with respect to CH_2 and generalized to 3-membered rings with up to two heteroatoms X and Y by using the function $E_Y+E_X-2E_C$, where E represents Huheey's group electronegativity values (Pauling scale) as defined above and $X=C$ for rings containing only one heteroatom.

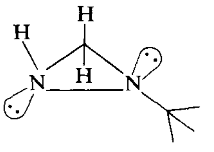
In sharp contrast to the pure inductive effect determined by **1** and **4** and approximated by the dashed lines in Figs 4 and 5, 3-membered rings containing lone pairs of electrons *appear* to exhibit the normal electronegativity behavior for J(gem) and J(vic), as previously noted[19,20b] for **1**, **2** and **3** and for methylcyclopropane, aziridine and ethylene oxide. However, on the basis of the present data for 1,1-dimethyl-2-phenylaziridinium fluorosulfonate, we believe that these trends are better explained as *lone pair effects which predominate over opposing electron withdrawing inductive effects.*

As indicated in Fig. 4, the differences for J(gem) in **2** and **3** from the inductive baseline are +5.8 and +10.6 Hz, respectively, suggesting an average contribution of +5.5 Hz per eclipsed lone pair.

With this estimate it is possible to predict J(gem) in 2-*t*-butyloxaziridine (**5**) and 1-*t*-butyldiaziridine (**6**).



5



6

For **5** the *N*-*t*-butyl group (assumed to have the same group electronegativity as dimethylamino in Table 1) and oxygen (taken to have the same group electronegativity as methoxy in Table 1) give an overall ring electronegativity effect on the remaining CH_2 of 0.52 relative to cyclopropane [2.40+2.68−2(2.28)].

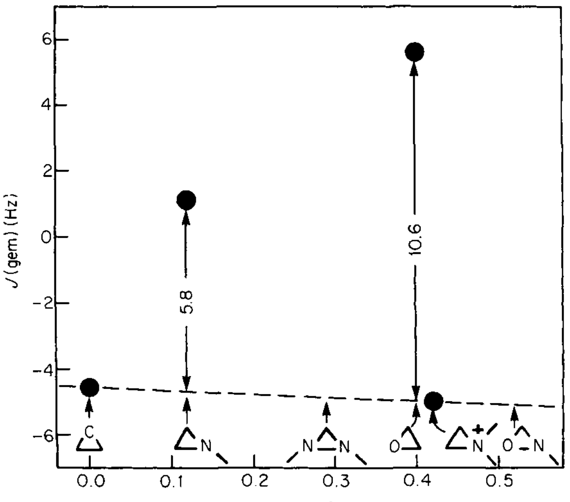


Figure 4. Effect of ring member electronegativity on J(gem).

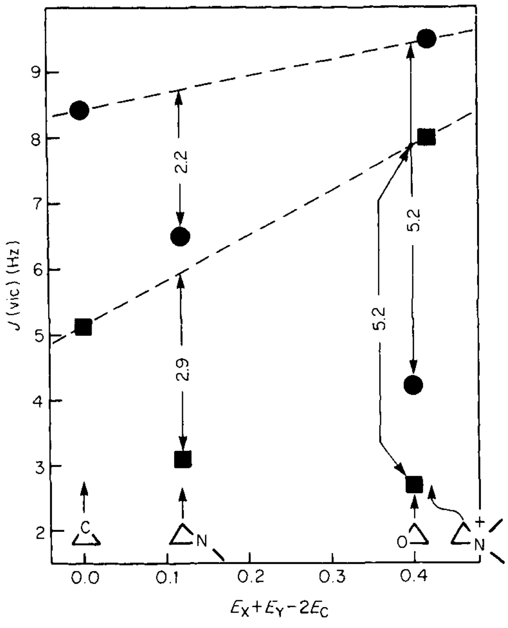


Figure 5. Effect of ring member electronegativity on J(vic); (●) J(*cis*); (■) J(*trans*).

The predicted value of 11.4 Hz for J(gem), based on −5.1 Hz from the inductive effect baseline of Fig. 4 plus contributions from three lone pairs at +5.5 Hz each, is reasonably close to the observed value of 9.9 Hz.[37] For **6** the E values for dimethylamino and methylamino give a ring electronegativity of 0.29 in a similar way. The predicted value of J(gem) of 6.1 Hz, based on −4.9 Hz plus contributions from two lone pairs at +5.5 Hz each, is in excellent agreement with the observed value of 5.9 Hz.[37]

Our estimate for lone pair contributions to J(gem) (+5.5 Hz) is larger than those previously reported of +1.8[14] to +3.5[15] Hz, which were determined by comparing 5-membered ring heterocycles assumed to have eclipsed lone pair interactions to 6-membered ring heterocycles assumed to have *gauche* interactions with negligible back donation of the lone pair.[11] The larger estimate found in the present study is probably due to more complete eclipsing in the 3-membered ring series and thus more efficient back donation of lone pair electrons into antisymmetric C—H orbitals[11] compared to the puckered 5-membered ring heterocycles.

For vicinal coupling constants, inspection of Fig. 5 shows that differences in J(*cis*) from the inductive effect baseline is −2.2 Hz for the aziridine and −5.2 Hz for the epoxide, suggesting a contribution of *c.* −2.5 Hz per lone pair of electrons. Differences in J(*trans*) due to lone pairs is seen to be −2.9 and −5.2 Hz for the aziridine and epoxide, respectively, indicating a contribution of *c.* −2.7 Hz per lone pair.

Interestingly, lone pair contributions to J(vic) are in the opposite direction for 3-membered rings (−2.5 to −2.7 Hz) compared to estimates based on 5- and 6-membered rings [+2.3 Hz as an average for J(*syn*)+J(*anti*)].[14] It seems likely that this opposite direction cannot be attributed entirely to the fact that Anteunis's electronegativity correction included averaged lone pair effects or to the possibility that the parameters chosen for the Karplus equation were inappropriate. It is tempting to seek an explanation for this different direction in terms of the unusual bonding characteristics of 3-membered rings. With regard to J(vic) variations, MINDO/2 calculations[30b] show that the overlap populations of the C—C bond in **1**, **3** and **4** are 0.648, 0.496 and 0.664, respectively. The decreased bond order for the epoxide seems consistent with its lower J(vic) values, and this type of explanation is in agreement with the experimental finding that a lone pair of electrons makes contributions to J(vic) regardless of whether or not it eclipses one of the C—H bonds (e.g. J(*cis*) for the aziridine). [A lone pair orientation effect has been reported for aziridines,[38] however, in which J(*cis*) can differ by 1.7 Hz depending on the orientation of the hydrogen with respect to the lone pair. A problem with the present interpretation is that the overlap population for **2** was 0.652 instead of intermediate to **1** and **3**, perhaps reflecting approximation errors in the calculation.]

An observation which suggests a more general phenomenon, however, is that analogous results have been reported for pyrrolidine.[19] Compared to cyclopentane, this 5-membered ring heterocycle had a lower $[J(cis)+J(trans)]/2$ value for adjacent vicinal coupling (-0.3 Hz negative lone pair contribution) and the pyrrolidinium ion had a larger value ($+0.2$ Hz for the change CH_2 to NH_2^+). The effects are much smaller than in the present case, however, and Δ^2-pyrroline and indoline did not show parallel behavior to pyrrolidine. Nonetheless, it might be productive to suggest as a working hypothesis the idea that vicinal coupling constants may follow a Karplus-like relationship with respect to adjacent lone pairs of electrons. Fully (3-membered rings) or partially (5-membered rings) eclipsed lone pairs may make negative contributions, while *gauche* (6-membered rings) orientations may make a positive one. Further work to explain the pyrrolidine results and extend the present method of separating lone pair and inductive effects to other systems is in progress.

CONCLUSIONS

The present results emphasize in a new way the dangers in applying structural correlations based on freely rotating systems to conformationally rigid molecules. In particular, it has been shown that a commonly accepted 'electronegativity' trend in 3-membered rings is apparently determined by lone pair effects which oppose the inductive effect of the heteroatom. The major factors causing positive geminal coupling in epoxides and aziridines are now seen to be increased *s* character of the C—H bonds and a strong lone pair effect. Also, the unusually low J(vic) values of epoxides relative to cyclopropanes, first noted by Mortimer,[39] is now seen to be due more to negative lone pair contributions than the electron withdrawing ability of oxygen.

Conclusions regarding J(gem) appear to be of predictive value for other 3-membered ring compounds and thus may be useful in structural work. The J(vic) trends in 3-membered ring systems can be interpreted in terms of their unique bonding arrangement, though other explanations such as a Karplus-like relationship for lone pairs of electrons may be possible.

Generalization of the estimates of lone pair contributions determined for 3-membered rings to unstrained systems may not be possible. However, the approach developed herein seems appropriate for separating inductive and lone pair effects in other systems.

EXPERIMENTAL

Instrumentation

All NMR spectra were run on a Bruker HFX-90 spectrometer at 90 MHz. Nuclear Overhauser (NOE) and internuclear double resonance experiments were performed in 99.97% D_2O (Thompson–Packard) using coaxial TMS as an external standard and lock. Samples for NOE were degassed by bubbling dry nitrogen through the sample for 10 min.

Materials

1-Methyl-2-phenylaziridine (2). Reaction of N-methyl-2-bromo-2-phenethylamine hydrobromide[40] with methyllithium[16c] gave the product in 45% yield as a colorless liquid, b.p. 35–36 °C (1.0 Torr) [lit.[41] 39–40 °C (0.5 Torr)]; IR (neat): ν_{max} 3040 (m), 2970 (s), 2940 (s) 2890 (m), 2840 (m), 2780 (m), 1605 (m), 1490 (s), 1450 (s), 1385 (s), 1210 (s), 800 (s), 735 (s), 695 (s) cm^{-1}; NMR (CH_2Cl_2, 90 MHz): δ 1.46 (H_A of ABX pattern, $\phi\text{—}\overline{\text{CH—}CH_2\text{—N}}$ *cis* to phenyl, 1H, $J_{AB}=1.1$), 1.72(H_B, $\phi\text{—}\overline{\text{CH—}CH_2\text{—N}}$ *trans* to phenyl, 1H), 2.13(H_X, $\phi\text{—}\overline{CH\text{—CH}_2\text{—N}}$, 1H, $J_{AX}=6.5$, $J_{BX}=3.1$), 2.37(s, N—CH_3, 3H), 7.11(s, Ar—H, 5H).

1,1-Dimethyl-2-phenylaziridinium fluorosulfonate (4). This salt was prepared from the aziridine **2** by reaction with methyl fluorosulfonate (Aldrich 'Magic Methyl') in 90% yield as a white solid, m.p. 70–71 °C (lit.[16c] 69–70 °C) IR (KBr): ν_{max} 3120 (m), 3040 (m), 2980 (m), 1585 (w), 1460 (s), 1300 (vs), 1060 (s), 970 (s), 795(m), 780(s), 710(vs), 575(s) cm^{-1}; NMR (CH_2Cl_2, 90 MHz): δ 2.58(s, N—CH_3 *cis* to phenyl, 3H), 3.33(s, N—CH_3 *trans* to phenyl, 3H), 3.57(d, $\phi\text{—}\overline{\text{CH—}CH_2\text{—N}^+}$, 2H, $J=8.0$), 4.58 (t, $\phi\text{—}\overline{CH\text{—CH}_2\text{—N}^+}$, 1H, $J=8.0$), 7.50(s, Ar—H, 5H).

1,1-Dimethyl-3-deuterio-2-phenylaziridinium fluorosulfonate (4-d_1). *cis*-2-Deuteriostyrene, prepared from 97–98% isotopically pure phenylacetylene-d_1[42] by the method of Baldwin and Kapecki,[42] was oxidized with 85% m-chloroperoxybenzoic acid to give *cis*-2-deuterio-3-phenyloxirane (**3**-d_1) in 92–93% isotopic purity. Treatment of **3**-d_1 with methylamine[43] and phosphorous tribromide[40] gave N-methyl-1-deuterio-2-bromo-2-phenethylamine hydrobromide as a mixture of two monodeuterated stereoisomers. Cyclization with methyllithium[16c] gave a 1:1 mixture of *cis* and *trans* **2**-d_1 of 91–92% isotopic purity. Alkylation of this mixture with methyl fluorosulfonate[16c] gave the product in 85% yield as a white solid with m.p. 64–65 °C; IR(KBr): $\nu_{\max}$ 3080(m), 3040(m), 2940(w), 2300(w), 1585(w), 1460(s), 1300(vs), 970(m), 720(vs), 575(s) cm^{-1}; NMR (CD_2Cl_2, 90 MHz): δ2.61 (*s*, N—CH_3 *cis* to phenyl, 3H), 3.20 (*s*, N—CH_3 *trans* to phenyl, 3H), 3.36 (pair of doublets, $\phi\text{—}\overline{\mathrm{CH}\text{—}CHD\text{—}\mathrm{N}}^{+}$, *c.* 1H, $J=9.4$, 8.2), 4.59 (pair of doublets, $\phi\text{—}\overline{CH\text{—}\mathrm{CHD}\text{—}\mathrm{N}}^{+}$, *c.* 1H, $J=9.4$, 8.2), 7.52 (s, Ar—*H*, 5H).

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