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Bonding in Functionalized Aziridines: Nitrogen-15 and Carbon-13 Studies*

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Two isomeric pairs of *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines have been synthesized: (1) with a nitrogen-15 labelled nitrogen, and (2) with carbon-13 labelled ring carbons. The carbon-13 to X (where X=nitrogen-15, carbon-13 or hydrogen-1) spin-spin coupling constants were measured and interpreted in terms of stereoelectronic effects. X-ray crystallographic data (earlier determined for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-(*p*-toluyl)aziridines)[1] appear in good agreement with the NMR data. Bonding is discussed for the three-ring itself (NMR studies) and for its substituents (X-ray studies). It is concluded that stereochemical interaction of the Van der Waals type is an important determinant of aziridine bond length. Three-ring to carbonyl hyperconjugation is correlated with stereoelectronic interactions in the *trans* isomer.

INTRODUCTION

The nitrogen-15 and carbon-13 NMR studies have been of considerable assistance in solving structural problems.[2,3] The stereoelectronic properties of *N*-unsubstituted and substituted aziridines have been correlated with C-13 NMR data at the natural abundance levels.[4,5] Theoretical aspects of bonding in three-membered rings are reported by Hoffman et al.[6]

The chemical and physical properties of cyclopropane have been explained by the »bent bonds«. The endocyclic C—C bonds have high p-character[7] and a correspondingly high degree of s-character for the exocyclic C—H bonds. Bent bonds need not necessarily mean weak bonds[8] and in fact overlap may be increased because of bent bonds. The increased acidity of C—H bonds and the fact that ^1J (^{13}C, H) values decrease as the ring size increases, indicate the high s-character in the C—H bonds.[9,10] Even though hybridization does not have much physical significance, the concept is useful in many instances.[11] Very little has been established on the hybridization values of endocyclic bonds in small ring heterocycles.[12] A review of spin-spin coupling between carbon-13 and the first row nuclei is given by Wasylishen.[13]

RESULTS

Observation of C(13)—C(13) coupling constants proved to be very difficult on singly labelled compounds, due to the closeness of the peak due to the

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enriched carbon to the C(13) peak under observation. Some tentative values were taken from 25.2 MHz data (our XL-100 instrument) and from 90 MHz data (determinations made by the Purdue University Biochemical Magnetic Resonance Laboratory). Both types of determinations were hampered because of rapid decomposition of the compounds, however. Because of these difficulties, doubly labelled materials were synthesized, and their spectra determined on a FT-80 (by the Eppley Institute for Cancer Research) and on our XL-100. In this case, it was necessary to collect only 100 transients for C_2 and C_3 of the aziridine ring (the operating characteristics were much the same as previously indicated). These AB spectra are first-order and simulation was not necessary. For other carbons, 10.000 transients were collected, and again decomposition was a problem, as the decomposition products gave intense peaks due to the presence of enriched C-13 carbons (e. g., $Ph^{13}CHO$) in certain spectral regions of interest. Thus, the longrange coupling constants are less secure than the ^1J[C(13)—C(13)] values reported herein.

A preliminary account of carbon-nitrogen and carbon-hydrogen coupling constants has been presented.[14,4] The reported and some further carbon-carbon coupling constants of our functionalized aziridines are given in Table I. The one-bond, carbon-carbon coupling constants in our aziridines appear in good agreement with those found earlier by Weigert and Roberts in cyclopropane derivatives.[14]

TABLE I

Spin-spin Coupling Constants of Cis- *and* Trans-*1-Cyclohexyl-2-phenyl-3-benzoylaziridines,* (1') *and* (2')[a]

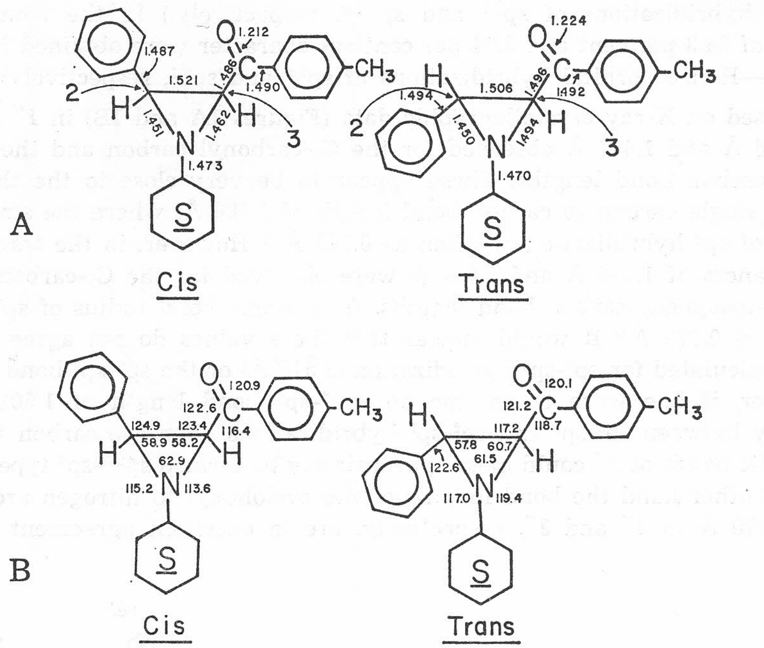
	cis (1') Hz	*trans (2')* Hz
$^1J(C_2—C_3)$	14.6	18.0
$^1J(C_2—N)$	7.8	5.2
$^1J(C_3—N)$	7.3	8.2
$^1J(C_2—H)$	163	166
$^1J(C_3—H)$	162	177

[a] Here, we are talking about coupling of ^{13}C to ^{13}C, ^{13}C to ^{15}N and ^{13}C to ^1H.

The work on the X-ray crystallographic structures of *cis*- and *trans*-1--cyclohexyl-2-phenyl-3-(*p*-toluyl)aziridines (*1″* and *2″*) has also been completed.[1] Depicted in Figures 1A and 1B are selected bond lengths and angels for *1″* and *2″*. Of course, the twelve independent sp^2-sp^2 phenyl carbon-carbon bonds have average lengths of 1.384 Å and 1.382 Å, respectively. The 25 independent C—H bonds each in *1″* and *2″* have averaged values of 0.98 Å and 0.94 Å. The six independent sp^3-sp^3 cyclohexyl carbon-carbon bonds averaged 1.521 Å and 1.518 Å. In all cases these values are in good agreement with values determined for high-precision X-ray studies of compounds containing similar bonds.

DISCUSSION

The $^1J(^{15}N, ^{13}C)$ values for *1* and *2* are in good agreement with Wasylishen's predictions, based on INDO-MO calculations.[15] These calculations correlate $^1J(^{15}N, ^{13}C)$ with P^2 s (n)—s (c), where Ps (n) s (c) is the bond order between the



Figures 1A and 1B. Selected bond lengths in angstroms and angles in degrees for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-(*p*-toluyl)aziridines (*1″* and *2″*) (for details see reference 1).

valence-shell s orbitals of nitrogen and carbon. These density matrix elements may then be related to the hybridization of the ring carbon-nitrogen bond.[16–18] The excellent agreement provides a strong indication that the s character of these ring bonds is very low (~ 20%), indicative of ~ sp^4 hybridization.

In the case of the $^1J(C_2—C_3)$ couplings the percent of »s« character is directly proportional to the coupling constant as depicted in equation (1):[19]

$$^1JC_2C_3 = 0.621\ (\%\ Sc_2)\ (\%\ Sc_3) - 10.2\ \text{Hz} \qquad (1)$$

with a standard deviation of 2.4 Hz. However, as carbons two and three in our aziridines are not equivalent an exact calculation of »s« character is not available in this instance. On the other hand, if one roughly approximates by assuming the C_2 bond has about the same hybridization as the C_3 bond some interesting conclusions may be drawn. Equation (1) gives an s-character of about 21 per cent for the *trans* isomer (i .e., a mean orbital hybridization of $sp^{3.7}$ for the C_2 (or C_3) bond vs. an s-character of 20 per cent for the *cis* isomer (i. e., a mean orbital hybridization of $sp^{4.0}$ for the C_2 (or C_3) bond.

To compensate for this elevated »p« character in the endocyclic aziridine bonds, it is suspected that the external three-ring orbitals have elevated »s« character. In fact, using equation (2) one may approximate the per cent »s« character in C_2—H and C_3—H:[19]

$$^1JCH = 5.70\ (\%\ S) - 18.4\ \text{Hz} \qquad (2)$$

which has a standard deviation of 5.7 Hz. Here, for the *cis* isomer »s« characters of 31.8 per cent and 31.3 per cent were calculated for C_2—H and C_3—H (i. e., orbital hybridizations of $sp^{2.1}$ and $sp^{2.2}$, respectively.) In the *trans* isomer values of 34.3 per cent and 32.4 per cent »s« character were obtained for C_2—H and C_3—H (i. e., orbital hybridizations of $sp^{1.9}$ and $sp^{2.1}$, respectively).

Based on X-ray crystallographic data (Figures 1A and 1B) in *1″* distances of 1.486 Å and 1.487 Å observed for the C_3-carbonyl carbon and the C_2-ipsophenylcarbon bond lengths. These appear to be very close to the theoretical sp^2-sp^2 single carbon to carbon bond length of 1.486 Å, where the single bond radius of sp^2 hybridization is taken as 0.743 Å.[20] However, in the *trans* isomer *2″* distances of 1.496 Å and 1.494 Å were observed for the C_3-carbonylcarbon and C_2-ipsophenylcarbon bond lengths. As a single bond radius of sp^3 hybridization is 0.772 Å[21] it would appear that these values do not agree with the value calculated for sp^3-sp^2 hybridization (1.515 Å) or the sp^2-sp^2 bond distance. However, if one were to assume an $sp^{2.5}$-sp^2 bond length of 1.501 Å, i. e., midway between sp^3-sp^2 and sp^2-sp^2 hybridizations, then the carbon to carbon exocyclic bonds of *2″* could most appropriately be termed $sp^{2.5}$-sp^2 type orbitals. On the other hand the bond lengths of the cyclohexyl to nitrogen are 1.473 Å and 1.470 Å in *1″* and *2″*, respectively, are in excellent agreement with the

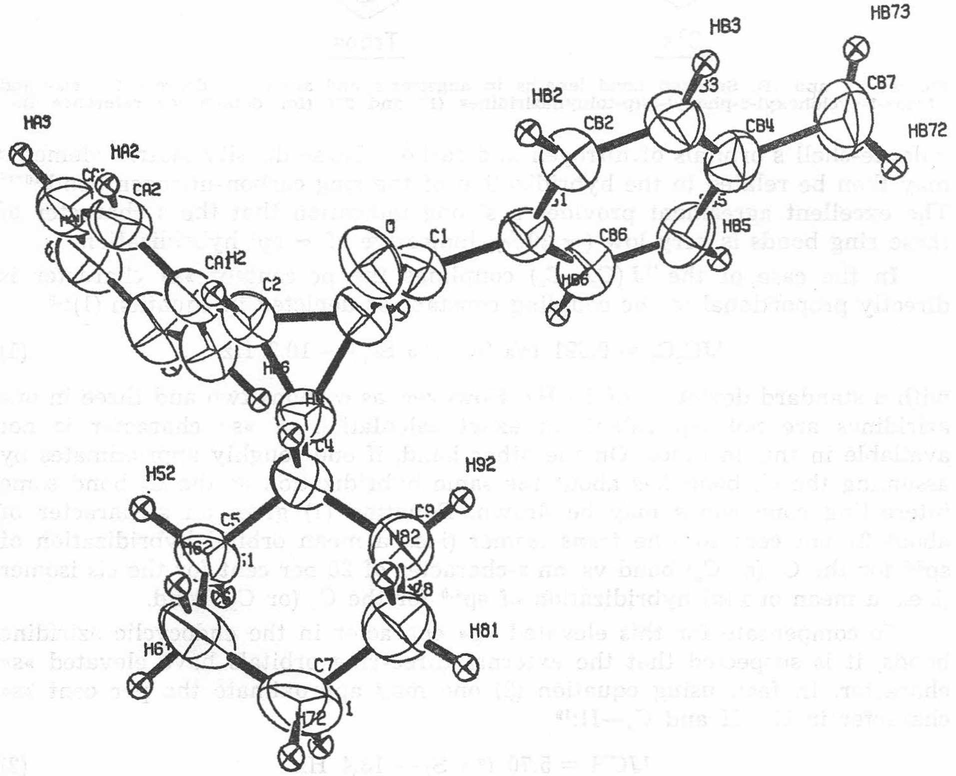


Figure 2. ORTEP plot of *trans*-1-cyclohexyl-2-phenyl-3-(*p*-toluyl)aziridine (2″) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius (cf., reference 1.)

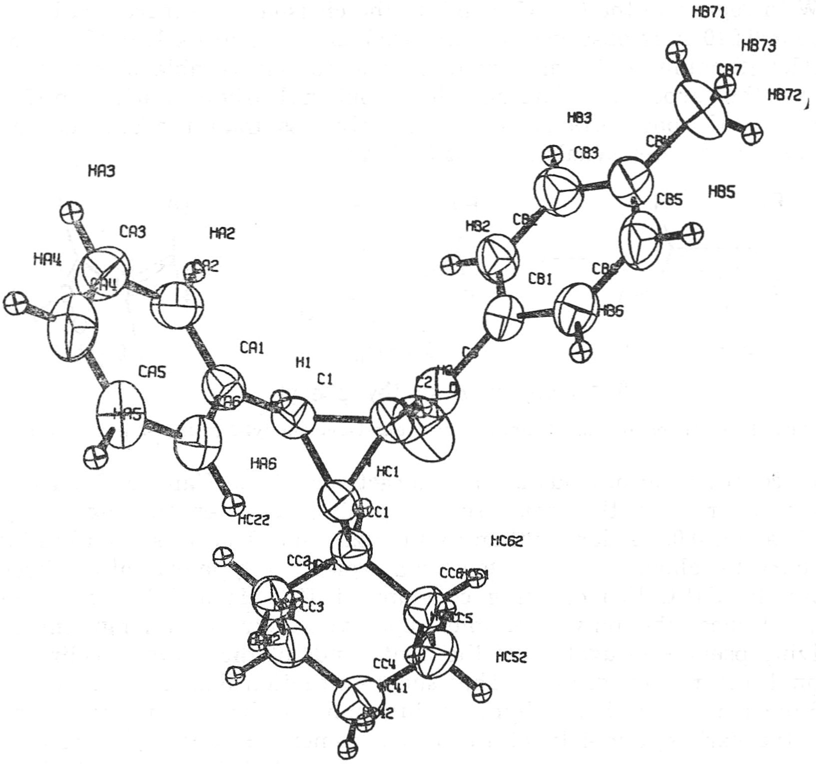


Figure 3. ORTEP plot of *cis*-1-cyclohexyl-2-phenyl-3-(*p*-toluyl)-aziridine (*1″*) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius (cf., reference 1).

value of 1.47 Å predicted for an sp^3-N type. It is possible, however, that the lone pair at nitrogen maintains high s character, thus permitting greater p character in the endocyclic bonding orbitals of nitrogen. For example, Aue, Webb and Bowers[12] consider the lone pair on aziridine nitrogen to occupy an $sp^{2.3}$ orbital. Also, Lippert and Prigge[22] have shown that aziridine and other three-ring heterocycles are not hydrogen bond acceptors and this is presumably due to the high s character of the lone pair.

As revealed in Figure 2. the *N*-cyclohexyl group exists in a *syn* relationship to the C_3-benzoyl group in the *trans* aziridine. Here the C_3—N bond is about 0.019 Å longer than the carbon-nitrogen bond length of aziridine.[23] The ^1J (^{15}N, ^{13}C) couplings in Table I show the same trend wherein a value of 8.2 Hz was found for *2* as compared with the value of 7.6 Hz attributed to aziridine.[15] (Note: According to reference[15], Figure 2, as ^{15}N to ^{13}C coupling increases, the ^1J (^{15}N, ^{13}C) value becomes increasingly negative, i. e., the value becomes more positive as coupling decreases). The bond lengthening of the C_3—N bond, not observed for the C_2—N bond, might be due to an unfavorable steric interaction between oxygen and H^4 where the separation of about 2.31 Å is significantly smaller than the summation of the oxygen and hydrogen Van der Waals radii of 2.6 Å.[21] As shown in Figures 1A and 3. in the *cis* isomer no bond lengthening is observed for the carbon to nitrogen bonds.

With regard to the C_2—C_3 bond, in the *cis* isomer an increased bond length of about 0.040 Å is observed as compared to aziridine itself.[23] This substantial bond lengthening in *1″* may well be due to unfavorable steric interactions between the carbonyl carbon and the ipsophenylcarbon attached to C-2. Their separation of about 3.19 Å is significantly less than the summation of the two carbon Van der Waals radii of 3.40 Å.[21]

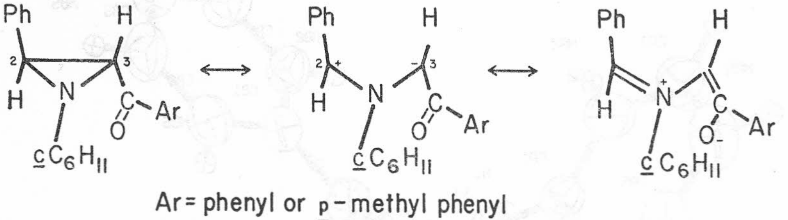


Figure 4. Some canonical structures of *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines.

In contrast, no obvious steric interactions of the Van der Waals type are readily apparent in the *trans* isomer causing bond lengthening and yet this bond is about 0.025 Å longer than that of aziridine. That this bond has increased »p« character above that expected for a typical sp^3 type orbital has been borne out by its ^1J (^{13}C, ^{13}C) coupling constant of 18.0 Hz and has been discussed earlier. Hence, the only available explanation for bond lengthening is one involving pseudoconjugation of the bent bonds of the *trans* aziridine with the carbonyl and phenyl groups.[4] That such a situation does indeed exist (we call it »three ring to carbonyl hyperconjugation«) is borne out by several facts. First, the carbonyl moiety of the *trans* isomer has undergone relative bond lengthening as compared to its *cis* analog, i. e. 1.224 Å vs. 1.212 Å. Further, *in* the case of acetophenone, where no pseudoconjugation with a three-ring exists, an X-ray crystallographic determination revealed a carbonyl bond length of 1.216 Å, which is marginally shorter than the *trans* carbonyl bond length.[24] Further, canonical structures of the type depicted in Figure 4. reveal that a lengthening of the carbonyl bond is required with a concomitant lengthening of the C_3—N bond while the C_2—N bond is somewhat shortened. In fact, this is observed (see Figure 1A).

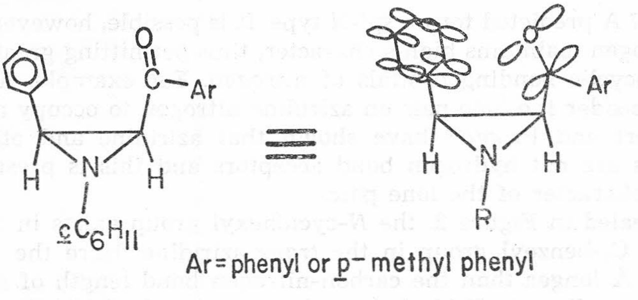


Figure 5. *Gauche* conformer of *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridines.

In contrast to this the *cis*-1-cyclohexyl-2-phenyl-3-arylaziridine does not exhibit this type of pseudo conjugation owing to the fact that it assumes a *gauche* conformation as depicted in Figure 5. That is to say, in the *gauche* conformer repulsion between the C_2 aryl group and C_3 carbonyl group will not allow for the orbital overlap needed for three-ring to carbonyl hyperconjugation.

EXPERIMENTAL

A. Synthesis of C-13, and N-15 labelled aziridines

1. *Cyclohexylamine N-15*

Labelled cyclohexylamine was prepared by the reductive amination of cyclohexanone with sodium cyanoborhydride in the presence of N-15 labelled ammonium chloride (obtained from Stohler). Labelled compounds being quite expensive, some modifications and improvements were made over the procedure of making the unlabelled cyclohexylamine.[25]

To a magnetically stirred solution of 10.4 g (193 mmole) of ammonium chloride (50 : 50 labelled and unlabelled) in 120 ml of anhydrous methanol 3.1 g of potassium hydroxide was added in one portion. When the pellets were completely dissolved 15.1 g (154 mmol) of distilled cyclohexanone was added in one portion. The resulting solution was stirred at room temperature for 15 minutes and then a solution of 3.65 g (58.7 mmol) of sodium cyanoborohydride was added dropwise over 30 minutes. It was then stirred for 30 minutes, 11.6 g of potassium hydroxide was added and the flask was kept air tight to prevent any loss of labelled ammonia generated in solution. The suspension was kept and stirred in ice for four days. The reaction mixture was filtered with suction and the volume of the filtrate reduced to 40 ml with a rotavap at $\geqslant$ 45 °C. 25 ml of saturated sodium chloride solution was added and the aqueous layer extracted with two 40 ml portions of ether. Organic layer was acidified to pH 1 with 6 M HCl (ice cooling) saturated with NaCl and extructed with ether (4 × 25 ml.) The cyclohexylamine was brought out of the aqueous layer by carefully adding potassium hydroxide pellets until the solution was very basic. The amine was separated, the aqueous layer was washed twice with 30 ml portions of ether and the organic portion dried over molecular sieves. Further purification was done by converting the amine to amine hydrochloride by bubbling hydrogen chloride gas through the solution. The salt was washed with ether to remove any trace of cyclohexanol, neutralized with potassium hydroxide pellets, extracted with ether, dried over molecular sieves. Evaporation of ether gave 8.35 g (54.4% yield) of cyclohexylamine N-15.

2. cis *and* trans *N-15 1-Cyclohexyl-2-phenyl-3-benzoylaziridines* (1, 2)

Following the procedure of Tarburton, Chung, Badger and Cromwell[26], 5.41 g (54.4 mmol) of enriched N-15 cyclohexylamine in 15 ml dry benzene was added dropwise to a suspension of 7.81 g (27.2 mmol) of α-bromochalcone in 30 ml of dry benzene over a 15 minute period. The mixture was stirred at 10 °C for an hour and then at room temperature for five days in the dark. Later 0.8 g (16.34%) of what we suspected was a 50 : 50 mixture of N-15/N-14 cyclohexylamine hydrobromide was recovered. The mother liquor was vaccum stripped down to 20 ml volume and 20 ml of petrol ether (b.p. 38—47 °C) was added and the mixture stored in the freezer overnight. Filtration and recrystallization from 50 : 50 benzene-pet. ether (b.p. 38—47 °C) mixture gave 1.05 g (12.24% yield) of *cis* isomer m.p. 99—100 °C. Mass spectral investigation showed that the sample is only 33% N-15 enriched.

The mother liquor was vacuum stripped down to an oil and mixed with 15 ml methanol and stored in the freezer for one week. Square white crystals of the *trans* isomer weighing 0.95 g (11.45% yield) was recovered m.p. 94—95 °C.

3. *Chalcone-β-C-13*

A 1.0 g sample of 90% benzaldehyde-α-C-13 was obtained from Merck, Sharp and Dohme. Low resolution mass spectrometry revealed the sample to be of at least this purity. Following the procedure of *Org. Syn.*[27] a 0.5 g (12 mmol) solution of sodium hydroxide in 4.3 ml water and 2.8 ml of pure ethanol are placed together and stirred at t = 0 °C. Then 1.4 g (12 mmol) of pure acetophenone was added. Next 0.875 g (8.18 mmol) of 90% benzaldehyde-α-C-13 was added and the mixture was allowed to warm to room temperature. Routine work-up afforded a total of 1.669 g

(7.94 mmol) of crude chalcone-β-C-13 (97.1% yield): m.p. = 52 °C. High resolution mass spectrometry (HRMS) showed a molecular ion (M.$^+$) indicative of chalcone-β--C-13 at 209.0919.

4. *α, β-Dibromochalcone-β-C-13*

Following the procedure of *Org. Syn.*[28] 1.55 g (7.55 mmol) of chalcone-β-C-13 was brominated to afford 2.232 g (6.05 mmol) of α,β-dibromochalcone-C-13 (80.1% yield): m.p. = 162 °C. Mass spectrum shows a fragmentation pattern indicative of α,β-dibromochalcone-β-C-13.

5. cis- *and* trans-*1-Cyclohexyl-2-(1-C-13-phenyl)-3-benzoylaziridines* (3, 4)

Following the procedure of Tarburton, Chung, Badger and Cromwell[26] 1.720 g (17.34 mmol) of cyclohexylamine was added dropwise to a suspension of 2.132 g (5.78 mmol) of α,β-dibromochalcone-β-C-13 at 15 °C in 20 ml of benzene over a 10 minute period and the mixture was kept in the dark at room temperature for one day. 1.979 g (95.1% yield) of cyclohexylamine hydrobromide was removed by filtration. After reducing the volume of the residual oil to a minimum, 20 ml. of petrol ether (b.p. 38—47 °C) was added and the mixture stored in the freezer for 3 hours. Filtration and recrystallization from a 50 : 50 benzene pet. ether (b.p. 38—47 °C) mixture gave 0.492 g (28.0% yield) of *3:* m.p. 103—104 °C with HRMS revealing M.$^+$ at 106.1800 indicative of $C_{20}H_{23}NO^{13}C$. The ^1H NMR ($CDCl_3$, TMS) gave a one bond C_β-13 to H_β-1 coupling of +163 Hz and a two bond C_β-13 to H_β-1 coupling of $\simeq$3 Hz.

The benzene-petrol ether (b.p. 38—47 °C) filtrate from the *cis* isomer was evaporated to an oil, the residue mixed with 10 ml of methanol and stored in the freezer. Square white crystals of the trans isomer (4) weighing 0.850 g (48.0% yield) was recovered (m.p. 97—98 °C) with HRMS revealing M.$^+$ at 306.1817 indicative of $C_{20}H_{23}NO^{13}C$. The ^1H NMR ($CDCl_3$, TMS) gave a one bond C_β-13 to H_α-1 coupling of +166 Hz and a two bond C_β-13 to H_α-1 coupling of $\simeq$2.5 Hz.

6. *Chalcone-α-C-13, β-C-13*

To make the double-labelled ring via chalcone-α-C-13, β-C-13 1.0 g sample of acetophenone-methyl-C-13 (19.3 atom %) and 1.0 g sample of benzaldehyde α-C-13 (90.5 atom %) were obtained from B.O.C. Limited, Deer Park Road, London.

The procedure employed[27] utilized a 0.332 g (5.3 mmol) solution of sodium hydroxide in 4.3 ml water and 2.8 ml pure ethanol which are placed together and stirred at t = 0 °C. Then 1.0 g (8.3 mmol) of acetophenone-α-C-13 is added. Next 0.610 g (5.7 mmol) of benzaldehyde-α-C-13 is added, stirred for 15 min cold and allowed to warm to room temperature with stirring. The solution is allowed to stir for 4 hours and kept in the freezer overnight. A pale yellow solid was filtered, washed with water until neutral, and recrystallized from ubs ethanol. Pale yellow crystals were collected and vacuum dried m.p. 52.5 °C; yield 0.75 g (65% yield).

7. *α, β-Dibromo chalcone -α-C-13, -C-13*

A 0.75 g (3.6 mmol) sample of chalcone -α-C-13, β-C-13 was dissolved in (~15 ml) carbon tetrachloride. The solution was cooled to 10 °C in an ice bath and 0.576 g (3.6 mmol) of bromine was added dropwise over a 20 min period with stirring at room temperatures for 4 hours. The precipitate was collected and recrystallized form chloroform. A white solid was collected and vacuum dried.
m.p. 160.5—161.5 °C; yield 1.10 g (82.7% yield)

8. Cis *and* trans-*1-Cyclohexyl-2-[1-C-13-phenyl]-3-[1-C-13-phenyl]-benzoylaziridine* (5, 6)

A 0.90 g (9.0 mmol) sample of cyclohexylamine was added dropwise to a suspension of 1.10 g (3.0 mmol) α,β-dibromochalcone-α-C-13, β-C-13 in 20 ml benzene over a period of 10 min. The mixture, which was at 15 °C, was stirred for one hour. Next the mixture was stirred in the dark, at room temperature, for one day.

A 1.0 g (92.6% yield) sample of cyclohexylamine hydrobromide was removed by filtration. The volume was reduced to a minimum, leaving a yellow residual oil. 12 ml of petrol ether was added and the mixture was stored in the freezer for 3 hours. The white precipitate was filtered and recrystallized from benzene-petrol ether [1 : 1] ratio. The white solid was vacuum dried. m. p. 102—103 °C; yield 0.30 g (32.8% yield) of *cis* isommer.

The benzene-pet. ether filtrate from the *cis* isomer was evaporated to an oil, the residue mixed with 7 ml methanol and stored in the freezer for 6.5 hours. Square white crystals were collected, and vacuum dried.
m.p. 97—98 °C; yield 0.4 g (43.7% yield) of *trans* isomer.

For both the *cis* and *trans* isomers NMR studies corroborated the presence of 5 and 6.

B. Determination of the Coupling Constants[29]

For the N(15)-C(13) coupling constants, NMR runs were made on a Varian XL-100 instrument. The C(13) nuclei were observed at 25.2 MHz, i. e. C$_2$ and C$_3$ of the aziridine ring, as well as carbonyl and other relevant carbons for longrange coupling constants. For the N(15)-H(1) coupling constants, determinations were made at 100. 1 MHz. In both cases the intense signal due to the unlabelled material was troublesome; the split peaks due to the labelled material appeared on either side of the singlet due to the unlabelled material, but the split peaks were each only ca. 20% of the intensity of the singlet due to the unlabelled material. This made it impossible to determine small coupling constants, due to the width of the large singlet near its base. Knowing the intensity of the doublet, however, it was possible to establish an upper limit of the magnitude of coupling constants for certain carbons such as C (alpha). The C(13) runs were made using the maximum labelled material available (ca. 200—300 mg) dissolved in 3 ml of CDCl$_3$ at normal probe temperature, ca. 35 °C. Approximately 4000—10,000 transients were collected using ca. 50 °C tip angle, with a 4.2 s pulse repetition rate, as appropriate for a 1000 Hz spectral width. Several runs were usually made for each spectral region at varying spin rate. The error in line position indicated by the computer was ±0.25 Hz, but in actual practice, the error may be somewhat larger.

The H(1) determinations were made using the continuous wave mode of operation. Coupling constants were determined from 100 Hz expansions of the region in question. The spectra were simulated using the LAOCON3 program.

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SAŽETAK

Vezivanje u aziridinima: ^{15}N i ^{13}C studije

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Sintetizirani su izomerni parovi *cis-* i *trans*-1-cikloheksil-2-fenil-3-benzoilaziridini: (1) markirani sa ^{15}N, i (2) markirani sa ^{13}C u prstenu. Mjerene su spin-spin konstante sprezanja ^{13}C sa X, gdje je X = ^{15}N, ^{13}C, ili ^{1}H, i interpretirane su s pomoću stereoelektronskih efekata. Kristalografski podaci se dobro slažu sa NMR-podacima. Vezivanje je diskutirano za tri prstena sama (NMR-studije) i za njihove supstituente (studije X-zrakama). Zaključeno je da je stereokemijska interakcija van der Waalsova tipa važan činilac duljine aziridinske veze. Hiperkonjugacija tri prstena s karbonilom korelirana je sa stereoelektronskim interakcijama u trans-izomeru.

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