Stereochemistry and Bonding in *N*-Substituted-2-phenyl-3-cyanoaziridines

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Dedicated to Professor Norman H. Cromwell

A series of ten *N*-alkyl(aralkyl)-2-phenyl-3-cyanoaziridines has been synthesized to continue investigations of the molecular stereochemistry and bonding of functionalized aziridines. Substantial spectroscopic evidence is presented which indicates the presence of stereoselective hyperconjugation between the phenyl and nitrile groups and the aziridine ring. The ^{1}H and ^{13}C nmr chemical shifts are rationalized in terms of the interactions of the substituents on the aziridine ring, and how these interactions vary with the steric bulk of the nitrogen substituents. Various stereoselective coupling constants (^{1}H-^{1}H and ^{13}C-^{1}H) are also reported.

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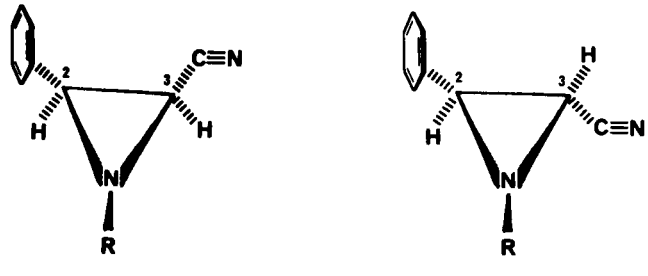
Initial studies of the electronic spectra of 2-phenyl-3-carboaziridines found evidence of a pseudoconjugation phenomena occurring between the aziridine ring and certain p-orbital containing substituents [2]. This three-ring-to-carbonyl hyperconjugation has since been substantiated by ir, nmr, and X-ray crystallography [3,4]. This spectroscopic study was undertaken to determine if similar pseudoconjugation also occurs in substituted cyanoaziridines. The stereochemistry of the aziridine ring and its substituents was also investigated.

The title compounds were synthesized by the reaction of 2,3-dibromo-3-phenylpropionitrile with one of five primary amines. Each primary amine is capable of producing two isomers, called *cis* or *trans*, referring to the stereochemistry between the C-2 and C-3 substituents (the phenyl and the nitrile groups). Each isomer can form two antipodes which can be interconverted by pyramidal inversion of the aziridine ring nitrogen. The antipodes are referred to as *syn* or *anti*, which describes the relationship between the *N*-alkyl substituent and the nitrile group on C-3 (see Chart 1). This follows the nomenclature of previous investigations [5,6].



cis isomer trans isomer

R	cis isomer	trans isomer
Et	1a	1b
i-Pr	2a	2b
c-C_6H_{11}	3a	3b
Bz	4a	4b
t-Bu	5a	5b

Chart 1. Structural Isomers of 1-alkyl(aralkyl)-2-phenyl-3-cyanoaziridines.

No thorough study of the spectral properties of various *N*-substituted 2-phenyl-3-cyanoaziridines has yet been published. Compounds **3a** and **4a** have been isolated a number of times in the past, and their ir and proton nmr characteristics reported [7-12]. Matsumoto and Nakamura [13] describe ^{13}C nmr data for compounds **3a**, **3b**, and **4a** while articles by Merah and Texier [14,15] also report the detection of **2a** and **5a**. To date, only compounds **3a**, **3b**, **4a**, and **5a** have been reported as pure compounds.

Past studies of various functionalized aziridines have indicated that a primary determinant of configurational stereochemistry is the coupling constants of the ring protons. These are near 6 Hz for protons *cis* to one another and 3 Hz for protons in the *trans* configuration [16]. The ^{1}H nmr data presented here are consistent with that assignment. Carbon-13 nmr shift assignments were based on off-resonance decoupled or fully coupled spectra (including long range carbon-hydrogen couplings), as well as chemical shift considerations.

Generally, in ^{13}C nmr, carbons directly bonded to a nitrile group are found 13-17 ppm upfield from carbons directly bonded to carbonyl groups (including ketones, esters, and carboxylic acids) [17]. In comparing compounds **1-5** with their carbonoyl substituted analogs [3], an

average upfield shift of *ca.* -13 ppm is seen for the nitrile substituted carbon (C-3).

The ring protons (H-2 and H-3) for cyanoaziridines are also found upfield from analogous protons in carboaziridines [3,18], but downfield from corresponding aziridines unsubstituted at C-3 [19]. This reflects not only the electronegativity of the nitrile group as compared to carbonyl and hydrogen substituents, but also the cylindrical magnetic anisotropic shielding of the nitrile group which should deshield directly bonded substituents.

Overall, the spectral data indicate conformations where the *N*-substituent prefers to be *anti* to the C-2 substituent. This places the *N*-substituent and the nitrile groups *anti* to one another in the *cis* isomer, and *syn* in the *trans* isomer. This is the same molecular model used for similar systems [3,18,20]. The minimal steric bulk of the nitrile group should emphasize the preference of the *N*-alkyl group for the position *anti* to the C-2 substituent, thus decreasing pyramidal inversion rates [21,22].

The results of theoretical studies on similar aziridines suggest that the C-2 phenyl group should prefer to remain in the plane perpendicular to the aziridine ring and exhibit restricted rotation [23-29]. This allows the p-orbitals of the phenyl and aziridine rings to attain maximum overlap. Experimental evidence to be presented later substantiates this conclusion [30].

Hyperconjugation.

The p-orbitals of a C-3 nitrile group should be able to overlap with the aziridine ring's p-orbitals better than an ester or ketone, especially when C-2 is substituted, for two reasons. First, the smaller, linear, nitrile group would experience fewer steric interactions with either C-2 substituents or *N*-alkyl substituents than a carbonyl substituent. In addition, the nitrile group can freely rotate and have a maximum p-bond overlap with the aziridine ring every 90°, in contrast to a carbonyl group which only has a maximum overlap every 180°. Steric interactions could also selectively hinder certain rotamers of a carbonyl substituent, whereas all rotamers of the nitrile group present equivalent p-orbitals. Overall, this should allow cyanoaziridines to hyperconjugate more easily than carboaziridines.

Previous studies have indicated that substantial hyperconjugation occurs between an aziridine ring and any directly bonded carbonyl groups only for the *trans* isomers of 2-phenyl carboaziridines [2]. It has previously been assumed that steric inhibition prevented such full conjugation in the *cis* isomers. This study indicates that while a nitrile group also hyperconjugates with the aziridine ring when *trans* to a phenyl substituent, hyperconjugation is still less complete in the *cis* isomers, even though steric interactions for *cis*-cyanoaziridines should be substantially minimized in comparison to carbonyl analogues.

Evidence for this hyperconjugation can be seen in the infrared spectral data in Table 1. For nitriles, conjugation decreases the ir stretching frequency, and increases the absorption intensity [31,32]. The results indicate that the nitrile groups in the *trans* isomers are substantially more conjugated than in the *cis* isomers. The nitrile stretching frequencies are on the average 10 cm^{-1} lower, and 2-8 times more intense for the *trans* isomers than for the *cis*. The frequencies for the *trans* isomers (2235 cm^{-1}) imply conjugation much like an aromatic nitrile (typically 2240 to 2221 cm^{-1}; 2231 cm^{-1} for benzonitrile [33]). The frequency of cinnamonitrile, the fully conjugated parent compound, is 2221 cm^{-1} and shows that the aziridine ring (*trans* isomer) offers less conjugation than a double bond. The stretching frequencies of the *cis* isomers (2246 cm^{-1}) are more characteristic of aliphatic nitriles (typically 2260 to 2240 cm^{-1}; 2253 cm^{-1} for butyronitrile [33]), and are virtually independent of the steric bulk of the nitrogen substituents.

Ultraviolet spectra indicate that this hyperconjugation also affects the phenyl ring on C-2 (Table 1). The absorption maxima of the *trans* isomers are at longer wavelengths by 4.5-6.5 nm, and the molar absorption coefficients are more intense, indicating that the *trans* compounds are of lower energy in the excited state than the *cis* isomers.

In Table 1, the ^{13}C chemical shifts of C-2 of the *trans* isomers are downfield from the *cis* isomers for every compound. The shift differences between isomers (*trans* - *cis*) averages 1.88 ppm for compounds **1-5**. The proposed hyperconjugation would induce a slight positive charge on carbon C-2. In contrast, the ^{13}C chemical shifts for C-3 of the *trans* isomers are upfield from the corresponding shifts for the *cis* isomers. The shift difference for this carbon averages 1.09 ppm. This would be consistent with the idea that a net negative charge resides on the C-3 carbon in the *trans* isomers due to hyperconjugation.

Steric Influences of the Nitrogen Substituent.

The steric bulk of the various nitrogen substituents influences the chemical shifts of virtually all carbons in or directly bonded to the aziridine ring. Steric perturbations are known to shift carbon resonances to higher fields [34]. Similar interactions in the proton spectrum (van der Waal's or dispersion effects) cause a proton to resonate at a lower field [35]. The aziridine ring's carbon atoms of the title compounds resonate at higher fields as the steric bulk of the *N*-alkyl substituents increase, with the exception of compounds **4a** and **4b** which are perturbed by the anisotropy of the *N*-benzyl group.

Previous proton nmr studies of aziridines have unanimously found that the H-2 ring protons in the *trans*

Table 1

Spectral Parameters of Selected *cis*- and *trans*-1-Alkyl(aralkyl)-2-phenyl-3-cyanoaziridines

Configuration			Carbon NMR, ppm from $Me_4$5i [a]								Proton NMR, ppm from $Me_4$5i [a]						Ultraviolet Absorptions [j]				Infrared [k]
			Ring Carbons		Substituent Carbons		*N*-Alkyl Carbons		Coupling Constants		Ring Protons [b]				*N*-Alkyl Protons						
R		*cis*/*trans*	C_2	C_3	Nitrile Carbon	*ipso*-Phenyl Carbon	C	C	$^1J_{C2\text{-}H2}$	$^1J_{C3\text{-}H3}$	H_2	H_3	$^3J_{H2\text{-}H3}$	Phenyl Protons	H	H	max		max		(cm^{-1})
Et	**1a**		45.84	31.61	116.56	134.08	53.60	13.17	169.8	180.2	2.86	2.30	6.0	7.36	2.56 [f]	1.23	260	310	217.5	8990	2246.5
	1b		47.35	30.38	115.69	135.63	50.24	13.42	165.5	192.5	2.90	2.51	2.8	7.29	2.82	1.29	264.5	350	220.5	11500	2235.5
i-Pr	**2a**		45.79	31.31	116.75	134.31	60.56	20.92/21.22	169.0	180.1	2.89	2.31	5.9	7.36	1.79 [g]	1.16/1.26 [h]	260	310	218	8970	2246
	2b		47.16	30.33	116.19	135.89	56.81	21.16/21.63	166.6	192.5	2.94	2.51	2.7	7.29	2.40	1.24/1.30 [h]	265	490	221	12500	2235
c-C_6H_{11}	**3a**		45.36	30.87	116.81	134.43	67.66	31.20/31.62	166.0	179.3	2.89	2.31	5.9	7.35	[i]	[i]	260	260	218	10300	2246
	3b [c]										2.93	2.49	2.7	[e]	[i]	[i]					2235
Bz	**4a**		46.23	31.99	116.52	133.66	62.45	136.41	166.3	180.3	3.02	2.42	5.9	7.34	3.73	–	258	420	216	16300	2246.5
	4b		48.00	31.04	115.94	135.40	59.33	136.86	170.3	193.0	3.02	2.51	2.6	7.21	3.88/3.92 [h]	–	264.5	610	216	14800	2235
t-Bu	**5a**		39.53	26.04	117.23	134.78	53.76	25.45	166.5	178.7	3.12	2.52	5.6	7.37	–	1.08	260	260	218	8920	2245
	5b		41.39	25.86	117.88	136.75	54.52	27.00	165.1	191.8	3.39	2.37	2.4	7.35	–	1.29					2231.3

[a] Coupling constants reported in Hz; Carbon nmr resolution = 0.025 ppm. Proton nmr resolution = 0.002 ppm. [b] All resonances appear as doublets. [c] Observed only as a mixture of **3a** and **3b**. [d] Long-range coupling observed (d, J = 0.4 Hz). [e] Resonance not discernible in spectrum of mixture. [f] Long-range coupling observed (d, J = 3.0 Hz). [g] Long-range coupling observed (d, J = 0.6 Hz). [h] Non-equivalent protons. [i] Broad multiplet, 1-2 ppm. [j] Measured in methanol. [k] Measured in chloroform, 0.1 mm cells.

isomers, which are *syn* to the *N*-alkyl group, are downfield from H-2 in the *cis* isomers (Table 1). This could be due to steric perturbations caused by the proximity of both the nitrile and *N*-alkyl groups. Nitrile anisotropy could also shift the H-2 resonance downfield. (It should be noted that when the nitrile is on the other side of the ring, *syn* to the C-2 phenyl group, the protons of the phenyl group are downfield.) Overall, any selective deshielding by the C-2 substituent is not responsible, since similar effects are seen in aziridines with only methyl and hydrogen substituents at C-2 [30].

This isomeric difference in the H-2 chemical shift is of the same value for compounds **1-3**, but differs for compounds **4** and **5** for two different reasons. The benzyl group of compound **4** can adopt one of three spatial conformations in relation to the aziridine ring. The sterically demanding *cisoid* conformation, in which the benzyl group bends in under the aziridine ring and should deshield the H-2 proton by aromatic anisotropy, is sterically inhibited by the *syn* nitrile group in the *trans* isomer, and this results in a loss of the aromatic deshielding of the H-2 proton present in the *cis* isomer. This causes the isomeric shift difference for the H-2 protons to be less for compound **4** than for compounds **1-3**.

The isomeric shift difference for H-2 is much larger in compound **5** (0.27 ppm). In this case, the *t*-butyl group, which is extremely sterically demanding, regardless of the conformation, is already affecting the H-2 proton in the *cis* isomer as evidenced by the lower proton chemical shift of **5a** as compared to compounds **1a-4a**. When the nitrile group is shifted to the same side of the ring as the *t*-butyl group, the dispersion effect is substantially increased. The *t*-butyl group cannot avoid exerting stronger steric effects on H-2, and this increases the isomeric difference in chemical shifts.

With the exception of **5b**, no steric effects are seen in the H-3 protons of the *trans* isomers. The similarity of the chemical shifts in compounds **1b** to **4b** indicates that the H-3 protons enjoy the same relative amount of room, and are little affected by the size or anisotropy of the *N*-alkyl groups on the opposite side of the ring. In **5b**, the exception, H-3 actually resonates upfield from the corresponding *cis* isomer. This effect has been noted before in other *N*-substituted aziridines [19,36], and has been ascribed by Brois to be due to a "dispersion induced deshielding and shielding" (DIDIS) effect in which the electron cloud is actually distorted away from the *N*-alkyl side of the ring towards the other side. The excess electrons induce a shielding effect on the *anti* proton (H-3). The fact that the effect is due to a distortion of either the lone pair electrons or of the ring's bonding electrons, and not a distortion of the ring's substituent geometries, is substantiated by the fact that the magnitude of the effect is almost independent of the substituents located on C-2 and C-3. The ability of lone pair electrons to shield ring protons has been demonstrated before in other aziridine systems [6].

The proton resonances of H-2 and H-3 also illustrate the increasing steric demands of the *N*-alkyl group. Both ring protons of the *cis* isomers resonate at consistently lower fields as the *N*-alkyl group gets larger. This order was also noted by Brois for similar systems [19], and he demonstrated that increasing dispersion shift nullified the upfield shift caused by carbon-carbon bond anisotropy of the *N*-alkyl substituents. (This bond anisotropy is reflected in the upfield shift seen upon alkylation of the aziridine ring nitrogen.) Compound **4a** is inconsistent due to anisotropy of the benzyl group; as it folds in under the aziridine ring in the *cisoid* conformation, the benzyl group can deshield any protons in the plane of the phenyl ring. This effect is seen in other aziridine series [3,18].

The α-carbon and proton atoms located in the *N*-alkyl substituent for compounds **1-4** are also influenced sterically (Table 1). The carbons are upfield in the *trans* isomers compared to the corresponding *cis* isomers, probably due to steric effects since the C-3 nitrile group is *syn* to the *N*-alkyl substituent in the *trans* isomers. Anisotropy might play a role, but the shift changes for protons vs. carbons are in opposite directions which indicates that dispersion effects are dominant.

This explanation is strengthened by comparing these results with data for carboaziridines, where the C-3 substituted carbonyl group should be more sterically demanding than a nitrile group when *syn* to the *N*-alkyl substituent. Tarburton [3] presents data for carboaziridines where the *N*-alkyl α-carbon's average shift difference between *cis* and *trans* isomers is 10.51 ppm (range 8.9-11.6 ppm). As expected, the cyanoaziridines show a substantially smaller difference of 2.8 ppm (range 0.8-3.8 ppm) between the *cis* and *trans* isomers. In general, the cyanoaziridine's *N*-alkyl α-carbons show less extremes: the downfield *cis* carbons are less deshielded, and the upfield *trans* carbons are less shielded, than the respective compounds in the carboaziridines.

There is some evidence showing that the nitrile group itself is more susceptible to external interactions from the *N*-alkyl group than ketones. Carbon-13 nmr data show that, as the *N*-alkyl group changes, the resonance of the nitrile carbon varies up to 1.5 ppm for the *cis* isomers and up to 0.5 ppm for the *trans* isomers. For the corresponding ketones, the carbonyl resonance varies up to 0..9 ppm for the *cis* and 0.3 ppm for the *trans* isomers, for similar changes in *N*-substitution.

Conformation Effects.

As noted before, the *N*-benzyl substituent exerts anisoptopic effects on the aziridine ring carbons and their respective protons. In comparing compounds **1a** and **1b**

with **4a** and **4b** (Table 1), one can see that the ^{13}C nmr shifts of the two aziridine ring carbons in **4a** are 0.38 ppm downfield from **1a**. In the proton spectra, H-2 of **4a** is 0.16 ppm downfield from **1a**, while H-3 is downfield 0.12 ppm. For the *trans* isomers, the ring carbons of **4b** resonate 0.65 ppm downfield from **1b** while in the proton spectra, H-2 (*syn* to the benzyl group) is deshielded 0.12 ppm, while H-3 (*anti* to the benzyl group) has the same chemical shift in both **4b** and **1b**; therefore, only H-2 is selectively deshielded. This is undoubtedly due to the anisotropy of the *N*-benzyl substituent.

The *N*-benzyl group of compound **4** also appears to experience selective restricted rotation. In the proton spectrum of **4a** (Table 1), the two methylene protons of the α-carbon are equivalent, and form a broad singlet at room temperature. The corresponding protons for the *trans* isomer, **4b**, resonate as two sharp singlets. This has also been observed in carboaziridines [18].

The methylene and methine protons of the *N*-alkyl groups in compounds **1a** and **2a** (the *cis* isomers) show additional ^1H-^1H couplings of 0.5-3.0 Hz which are not seen in the *trans* isomers. This is best explained by assuming that the *cis* isomers have additional long-range coupling to the aziridine ring protons that the *trans* isomers don't enjoy. This stereoselective coupling is not detectable in compounds **3a** and **4a**; the methine proton of the cyclohexyl group in **3a** is buried in the methylene multiplets, and the methylene protons of the benzyl group in **4a** form an unresolved broad singlet. It is thought that the observed coupling is to ring proton H-3, since the H-3 resonance in compound **5a** (the only *cis* isomer with a nonprotonated *N*-α-carbon) is always noticeably sharper than the corresponding H-3 resonances in compounds **1a-4a**. This resonance sharpness is probably not due to increased rates of molecular inversion of the aziridine nitrogen (caused by the *t*-butyl group) since the H-2 linewidth is fairly constant for compounds **1a-5a**, however, H-2 is normally broader than H-3, probably due to unresolved couplings to the protons of the phenyl ring on C-2.

An analysis of the ^{13}C-^1H coupling constants of the aziridine ring atoms indicates that the couplings depend upon molecular stereochemistry, with the primary factor being the position of the C-H bond in relation to the lone pair of the ring nitrogen. Similar effects have been noted before for aziridines and other carbon-nitrogen bonds with hindered rotation [3,37-40]. In accord with previous reports, the ring hydrogens *syn* to the lone pair exhibit larger one-bond couplings to ring carbons than hydrogens *anti* to the lone pair. This effect has been studied theorectically [41-43] and experimentally [44,45].

One initial aim of this study was to determine if cyanoaziridine isomers could be distinguished by mass spectrometry. Other functionalized aziridines have been shown to possess either relative differences in intensities of fragment for different isomers, or slightly different sets of fragments altogether for each of the two isomers [46]. The results of this study indicate that the title compounds show no observable differences in fragmentation between isomers in electron impact mass spectrometry.

A study by Texier, *et al.*, of compounds **3a**, **4a**, and **5a** [15] not only verified that the $[M-1]^+$ peak is the most likely fragment, but demonstrated that this peak is due specifically to the loss of the H-2 proton. The low intensity of the $[M]^+$ peak for compound **5a** was also noted and attributed to molecular instability due to the *t*-butyl group.

EXPERIMENTAL

Amines were freshly dried by distillation from barium monoxide prior to use. Boiling points were determined at reduced pressures using a standard McLeod gauge and melting points were determined with a Thomas-Hoover Unimelt Capillary Melting Point apparatus. Both are uncorrected. Ultraviolet spectra were recorded on a Cary 14 UV-Vis Spectrometer. Infrared spectra were recorded on a Beckman IR-9. Gas chromatography was achieved with both a Varian 3700 and a Beckman GC-45 using SE-30, SP-2100, and OV-17 stationary phases. Mass spectra (EI) were determined by GC-MS on a MS-9 spectrometer (Associated Electrical Ind.) at Eppley Institute except for compounds **3a**, **4a**, **4b**, **17**, and **18** which were analyzed by the direct probe technique with a AEI-MS-5076 spectrometer at the University of Nebraska-Lincoln. Elemental analyses were performed by Micro-Tech Laboratories Inc., Skokie, Illinois. Proton and ^{13}C nmr data were determined on a Varian CFT-20 spectrometer operating at 79.55 MHz and 20 MHz, respectively, at a normal probe temperature of 31.1-32.7°. Chemical shifts are reported in ppm downfield from tetramethylsilane (δ). All solutions were in deuteriochloroform (99.8%) and were 2 *M* for carbon spectra (both decoupled and coupled) and 0.1 *M* for proton spectra.

2,3-Dibromo-3-phenylpropionitrile (**17**).

Cinnamonitrile in carbon tetrachloride was treated with bromine to produce **17** as white needles, mp 87.5-89°, lit mp 92-93° [47-49] and 88-89° [8]; ms: Calcd. for $C_9H_7Br_2N$: 286.89463. Found: 286.89402 (direct probe technique).

2-Bromo-3-phenyl-2-propenenitrile (**18**).

Compound **17** was treated with triethylamine by the method of Petit and Touratier [7] to yield **18** as a yellow oil [7,14,50]; ms: Calcd. for C_9H_6BrN: 206.96842. Found: 206.96872 (direct probe technique).

General Procedure for the Preparation of *N*-Substituted 2-phenyl-3-cyanoaziridines **1-4**.

A stirring solution of **17** in benzene was slowly treated with a three molar equivalent of the appropriate amine. After stirring overnight, the suspension was filtered, concentrated *in vacuo*, and diluted with methylene chloride. The mixture was refiltered, and washed with minimal amounts of 0.01 *N* hydrochloric acid and water. The solution was dried over magnesium sulfate, flash evaporated, and the resulting oil usually purified by gravity flow liquid chromatography on Baker silica gel (60/200). The separations were followed by glc. All ir, uv and nmr data are reported in tables in the text. Mass spectrometry fragmentation data, reported only for the *cis* isomers, are virtually identical to data obtained for the *trans* isomers.

cis and *trans* *N*-Ethyl-2-phenyl-3-cyanoaziridine (**1a** and **1b**).

A 17.0 g (59.3 mmole) sample of **17** in 150 ml of benzene at 10° was treated with 11.5 ml (175.7 mmoles) anhydrous ethylamine in 20 ml of benzene (at 10°), and worked up as described above to give a pinkish brown liquid with an aziridinal *cis*:*trans* (**1a**:**1b**) ratio of 56:44 (by gc).

The liquid was separated on 350 g silica gel using hexane-ether (95:5). The *trans* isomer eluted first to give 2.5 g (25%) of **1b** as a clear oil; ms: Calcd. for $C_{11}H_{12}N_2$: 172.10005. Found: 172.0985.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.45; H, 7.00; N, 16.16.

Further elution of the silica column produced 3.2 g (32%) of **1a** which was crystallized from methylene chloride-ether-hexane mixtures to produce white needles, mp 31-32°; ms: Calcd. for $C_{11}H_{12}N_2$: 172.10005. Found: 172.0985; m/e (%) 172 (M^+, 29), 171 (100), 144 (4), 143 (37), 117 (11), 116 (71), 90 (4), 89 (11).

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.61; H, 7.00; N, 16.22.

Reaction of the monobromide **18** with ethylamine in a similar manner produced aziridines **1a** and **1b** identical in all respects to samples produced from the dibromide **17**.

cis and *trans* *N*-Isopropyl-2-phenyl-3-cyanoaziridine (**2a** and **2b**).

A 5.5 g (19.2 mmole) sample of **17** in 75 ml benzene was treated with 4.9 ml (57.5 mmole) isopropylamine and worked up as described above to give a colorless oil with an aziridinal *cis:trans* (**2a:2b**) ratio of 93:7 (by integration of the ring protons in the nmr). The oil was separated on 100 g silica gel with hexane-ether (98:2). The *trans* isomer eluted first, to 0.17 g (4.6%) **2b** as a clear oil; ms: Calcd. for $C_{12}H_{14}N_2$: 186.1157. Found: 186.1177.

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.17: H, 7.59: N, 14.66.

Further elution of the silica column produced 2.0 g (56%) of **2a** which was crystallized from methylene chloride-ether-hexane mixtures to produce white needles, mp 45-47°; lit ^{1}H nmr: δ 2.83 (d, H-3, J = 6.1), 2.23 (d, H-2) [14]; ms: Calcd. for $C_{12}H_{14}N_2$: 186.1157. Found: 186.1157; m/e (%) 186 (M^+, 13), 185 (35), 144 (22), 143 (51), 117 (100), 116 (55), 90 (18), 89 (16), 43 (13).

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.30; H, 7.55; N, 15.08.

cis and *trans* *N*-Cyclohexyl-2-phenyl-3-cyanoaziridine (**3a** and **3b**).

A 12.6 g (43.9 mmoles) sample of **17** in 150 ml benzene was treated with 15.2 ml (132.9 mmoles) cyclohexylamine and worked up as described above to give a tan solid. Recrystallization from hexane gave 6.38 g (64%) of **3a** as a white powder, mp 109-111°, (mp 111-112° from methanol); ms: Calcd. for $C_{15}H_{18}N_2$: 226.146998. Found: 226.14595 (direct probe technique); m/e (%) 226 (M^+, 61), 225 (100), 183 (33), 144 (41), 135 (67), 117 (29), 92 (41), 91 (40), 83 (100), 55 (95).

Anal. Calcd. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.45; H, 7.99; N, 12.43. Compound **3a** has been reported before, including mp (101° to 114°); ir: (2236 cm^{-1} to 2253 cm^{-1}), nmr, ms, and analysis [7-9,11,13,14].

The gc and nmr of the mother liquor from the hexane recrystallizations indicated the presence of a minor component, subsequently identified as **3b**; nmr (deuteriochloroform): δ 2.49 (d, H-3, J = 2.0); ms: Calcd. for $C_{15}H_{18}N_2$: 226.146998. Found: 226.1464. This compound has been reported before in a wide range of levels of purity [13,14].

cis and *trans* *N*-benzyl-2-phenyl-3-cyanoaziridine (**4a** and **4b**).

An 8.0 g (27.9 mmoles) sample of **17** in 100 ml benzene was treated with 9.11 ml (83.4 mmole) of benzylamine and worked up as described above, washing the methylene chloride solution well with dilute hydrochloric acid and water. The proton nmr of the resulting yellow oil gave an aziridinal *cis:trans* (**4a:4b**) ratio of 83:17 (integration of the ring protons). This oil was separated on silica gel with hexane-ether (93:7). The *trans* isomer eluted first to give 0.9 g (14%) of **4b** as a yellow oil; ms: Calcd. for $C_{16}H_{14}N_2$: 234:11569. Found: 234.11548 (direct probe technique).

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.14; H, 6.36; N, 12.16.

Further elution of the silica column produced **4a**, which was recrystallized from hexane or ether to produce 3.4 g (52%) **4a** as a white powder, mp 84.5-85.5°, lit mp 85° to 86° [9,14,51]; proton nmr previously described [9,13,49]; ms: Calcd. for $C_{16}H_{14}N_2$: 234.11569. Found: 234.11554 (direct probe technique).

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.91; H, 6.15; N, 12.05.

cis and *trans* *N*-(*t*-Butyl)-2-phenyl-3-cyanoaziridine (**5a** and **5b**).

To a 45° solution of 18.0 g (62.7 mmoles) of **17** in 250 ml carbon tetrachloride was added a solution of 65 ml (618.5 mmole) of *t*-butylamine in 65 ml of carbon tetrachloride. The solution was maintained at a gentle reflux for two weeks, then cooled and washed with water (5 x 50 ml). After drying over magnesium sulfate, the solution was concentrated *in vacuo* to a yellow oil with an aziridinal *cis:trans* (**5a:5b**) ratio of 98:2 (by gc). The oil was separated on 500 g of silica gel with hexane-ether (98:2). The *trans* isomer eluted first to give 0.15 g (1.3%) **5b** as a yellow oil; ms: (no $[M]^+$) Calcd. for $[M-C_2H_4N]^+$ $C_{11}H_{12}N$: 158.09697. Found: 158.0983.

Further elution of the silica column produced a yellow oil which was crystallized from ethanol-water (1:1) to produced 9.6 g (77%) of **5a** as an off-white solid. Recrystallization produced white crystals, mp 51-51.5°; ms: (no $[M]^+$) Calcd. for $[M-C_2H_4N]^+$ $C_{11}H_{12}N$: 158.09697. Found: 158.0983; m/e (%) 185 (M^+-15,1), 158 (1), 144 (54), 143 (29) 117 (86), 90 (11), 57 (100), 41 (26). Previously published ir, proton nmr and ms data [14,15] agree with these data.

Anal. Calcd. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.98; H, 7.82; N, 13.81.

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