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Stereochemistry of 4-cyano-4-phenylamino-*r*-2, *c*-6-diphenylpiperidines

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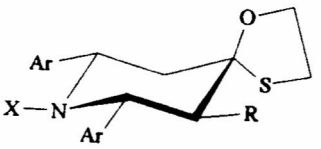
The stereochemistry of four N-phenylaminonitriles 6-9 derived from *r*-2, *c*-6-diphenylpiperdin-4-ones 2-5 has been determined using NMR spectral techniques and DAERM (Dihedral Angle Estimation by the Ratio Method) calculations. They prefer chair conformations with the cyano group in axial position and the phenylamino group being in the equatorial orientation. The presence of alkyl substituents at C-3 position in the aminonitriles 7-9 causes a flattening at C-3 end. The predominant formation of one of the two possible isomers has been rationalized by invoking the Cieplak's concept of π-facial selectivity in which the nucleophilic attack of cyanide ion at the imine carbon takes place from the axial side.

The stereochemical preferences of 2, 6-disubstituted piperidines[1,2], *N*-nitrosopiperidines[3], and *N*-nitroso-3-azabicyclo[3.3.1]nonanes[4,5], etc., have been investigated in detail by us as well as by others[6]. A few spiromonothioketals **1a-j** have been prepared from *r*-2,*c*-6-diphenylpiperidin-4-ones† and the conformational equilibrium as well as the π-facial selectivity have been examined[7]. In order to prepare *N*-substituted spiropiperazines we attempted to prepare isomeric aminonitriles from piperidin-4-ones. However, the reaction yielded only one isomer, the one with axial CN.

In this paper we describe the stereochemistry of four α-(phenylamino)nitriles **6-9** derived from *r*-2, *c*-6-diphenylpiperidin-4-ones **2-5**. α-Aminonitriles have been employed as intermediates in the synthesis of new α-aminoacids[8], spirohydantoins[9], α-aminoamides[10] and alkaloids[11].

The Strecker synthesis is a well-known classical procedure for the preparation of α-aminonitriles from aldehydes or ketones by treatment with alkaline cyanides and salts of amines[12,13]. The α-aminoacids prepared via the Strecker method have been shown to possess axial carboxyl group and equatorial amino function[14]. An α-aminonitrile from the *t*-3-methyl-*r*-2,*c*-6-diphenylpiperidin-4-one (**3**) was found to possess the cyano group in axial position[12].

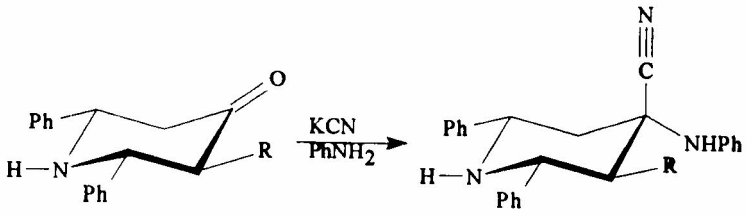


	Ar	R	X
1a	Ph	H	H
1b	Ph	Me	H
1c	Ph	*i*-Pr	H
1d	*p*-nitrophenyl	Me	H
1e	*p*-tolyl	Me	H
1f	Ph	H	Me
1g	Ph	Me	Me
1h	Ph	*i*-Pr	Me
1i	Ph	H	COMe
1j	Ph	Me	COMe

Results and Discussion

The α-phenylaminonitriles **6-9** were prepared by treatment of the piperidin-4-ones **2-5** with aniline, potassium cyanide and gl. acetic acid at 0 to 10°C for 24 h (**Scheme I**) in 15-35% yields. Only one of the possible isomers was obtained in each case. The rest of the reaction mixture did not contain any compound other than the starting material and a small amount of yellowish non-nitrogeneous

†IUPAC nomenclature has been followed. The prefix "r" refers to a substituent that is considered as the reference with which the relative stereochemistry of other substituents are assigned as *c*(*cis*) and *t*(*trans*).
Ref: IUPAC Tentative rules for the Nomenclature of Organic Chemistry. Section E. Fundamental Stereochemistry, *J Org Chem*, 35, 1970, 2849.



	R	
2	H	6
3	Me	7
4	Et	8
5	*i*-Pr	9

Scheme I

resinous material. Our attempts to isolate the other isomer by changing the conditions of reaction, methods of separations, isomerization/equilibration, etc., failed.

The assignment of ^{1}H NMR signals to the protons was straightforward (**Table I**). The orientation of the phenylamino and cyano groups at C-4 was confirmed by NOE (Nuclear Overhauser Enhancement Differential) experiments. The results of the NOE difference spectra were obtained from selective presaturation of the H2, $H3_{ax}$ and C-3 methyl resonances of one of the α-aminonitriles **7**. The selective presaturation of the $H3_{ax}$ resonance resulted in an enhancement of the aryl resonance and that of C-3 methyl resonance resulted in an enhancement of the C4-NH proton signal. On the other hand the selective presaturation of H_{2ax} resonance did not show significant enhancement in the C4-NH intensity showing that the configuration is the one shown in **Scheme I** with the axial CN group. The configurations of the compounds **6**, **8** and **9** have also been assigned in a similar manner and found to be similar to that of **7**.

For the compound **6**, the observed coupling constants (**Table II**) of 11.4 and 1.6 Hz for $^3J_{2a,3a}$ [$=^3J_{6a,5a}$] and $^3J_{2a,3e}$ [$=^3J_{6a,5e}$], respectively, indicate a chair conformation. In the case of **7**, the coupling constants $^3J_{2,3}$ of 9.9 Hz suggested that the phenyl group at C-2 and the methyl group at C-3 were in equatorial positions. The ^{1}H NMR chemical shifts and coupling constants of the protons H(2) and H(6) in **8** and **9** were similar to those of **7**, indicating that these compounds **8** and **9** also preferred chair conformations.

Analysis of the coupling constant data (**Table II**) showed that in comparison with compound **2**[6], the *trans* coupling constant $^3J_{2a,3a}$ [$=^3J_{6a,5a}$] in **6** was increased by 1.4 Hz while the *cis* coupling constant $^3J_{2a,3e}$ [$=^3J_{6a,5e}$] was decreased by 2.9 Hz. This can be explained with the help of Karplus equation[15-17] which relates the vicinal coupling constant (J) to the dihedral angle (ϕ). The flattening would increase the distance between the axial hydrogens making the $\phi_{2a,3a}$ and $\phi_{2a,3e}$ dihedral angles decrease from 180° and 60°, respectively. The conversion of sp^2 center to sp^3 center would revert back the dihedral angles close to 180° and 60°, respectively.

Table I—^{1}H NMR Chemical shift data (δ, ppm) of aminonitriles **6-9** and piperidin-4-ones **2-5**

Compd	H2	H3 ax	H3 eq	H5 ax	H5 eq	H6
6	4.25	1.79	2.55	1.79	2.55	4.25
2	4.07	←———	2.60	——→		4.07
7	3.92	2.03	—	1.75	2.77	4.20
3	3.62	2.68	—	←2.68→		4.09
8	3.97	1.88	—	1.75	2.74	4.19
4	3.73	2.68	—	←2.68→		4.07
9	4.25	2.08	—	1.74	2.72	4.20
5	3.99	2.67	—	2.67	2.56	4.09

Table II—Various vicinal and geminal coupling constants (Hz) of aminonitriles **6-9** and their parent ketones **2-5**.

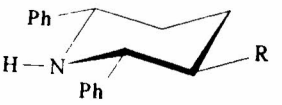
Compd	$^3J_{2a3a}$	$^3J_{2a3e}$	$^2J_{3a3e}$	$^3J_{5a6a}$	$^3J_{5e6a}$	$^2J_{5a5e}$
6	11.4	1.6	12.7	11.4	1.6	12.7
2	10.0	4.5	12.1	10.0	4.5	12.1
7	9.9	—	—	11.7	2.0	13.0
3	10.3	—	—	11.4	3.2	—
8	10.3	—	—	11.7	2.4	13.2
4	10.4	—	—	—	—	—
9	10.4	—	—	11.6	2.2	13.0
5	10.5	—	—	11.3	3.4	13.5

The observed coupling constants are in accordance with these expectations. The dihedral angles calculated by DAERM[15] (Dihedral Angle Estimation by the Ratio Method) also revealed that the dihedral angle $\phi_{2a,3a(=5a,6a)}$ for the aminonitrile **6** increases from 166° (for the parent **2**) to 185° and the corresponding dihedral $\phi_{2a,3e(=5e,6a)}$ increases from 46° (for the parent **2**) to 65° supporting the results derived from the NMR data.

Compared to the aminonitrile **6**, the $^3J_{2a,3a}$ values of the 3-methyl, 3-ethyl and 3-isopropyl analogues (**7**, **8** and **9**, respectively) were smaller while the $^3J_{6a,5a}$ values were found to be nearly the same (**Table II**). In the parent 3-alkylpiperidin-4-ones **3-5** also such a flattening about C-3 end has been observed compared to the piperidin-4-one **2**[16]. The explanation offered for **3-5** is also applicable to **7-9**. The C3-equatorial alkyl group may experience a *gauche* interaction with the C2-equatorial phenyl group (**Figure 1**) in the compounds **7-9** and it would result in flattening of the ring about the C-3 end. This flattening would reduce the Ph-alkyl *gauche* interaction (**Figure 2**) leading to a decrease of $\phi_{2a,3a}$ which in turn would decrease the $^3J_{2a,3a}$ values in compounds **7-9** compared to **6**. The flattening of the ring at C-3 end in the aminonitriles **7-9** will also reduce the *gauche* interaction between the C-3 alkyl group and the C-4 equatorial NHPh group.

^{13}C NMR Spectra

The ^{13}C NMR signals for the compounds **6-9** were assigned on the basis of additivity values and by comparison with those of piperidines[16] **10-13**, respectively. An upfield shift of -3.6 to -5.1 ppm has been observed for the C-2 and C-6 benzylic carbons of **6-9** compared to those of the corresponding piperidines[16] **10-13** (**Table III**). The γ-*gauche* effects of axial CN and NH_2 were reported[18] as −5.1 and −7.0 ppm, respectively. In our case, we observed the γ-*gauche* effect between −3.6 to −5.1 ppm and it is close to the γ-*gauche* effect of axial CN (−5.1 ppm). Thus, the shielding of C-2 and C-6 benzylic carbons may be explained due to the γ-*gauche* effect of axial cyano group. The C-3 and C-5 carbons of **6-9** absorb downfield by about 10 ppm compared to the corresponding carbons of the piperidines **10-13**.



	R
10	H
11	Me
12	Et
13	*i*-Pr

The lone pair of electrons present in the equatorial phenylamino group exerted a shielding effect on the 3-alkyl substituent of **7, 8, 9**. The degree of shielding effect was decreased with the increase in the bulkiness of 3-substituents. The resulted deviation of 3-alkyl group from perfect equatorial orientation was well observed in the ^{1}H NMR spectra. Similar observations have been made earlier in other cases[19].

The orientation of the cyano group was predicted to be axial on the basis of the intensity of peaks in the mass spectrum. It is interesting to note that the intensity of molecular ion peak was very low. Instead, a peak corresponding to the elimination of HCN (M-HCN) was observed. Such a facile elimination of HCN could be possible only if the cyano group is in the axial position.

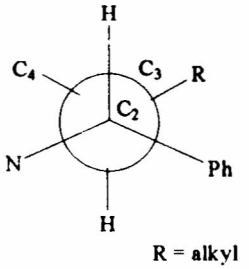


Figure I

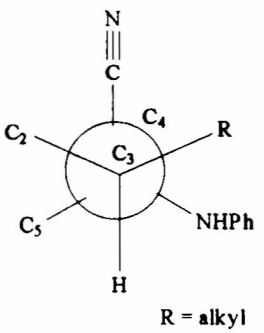
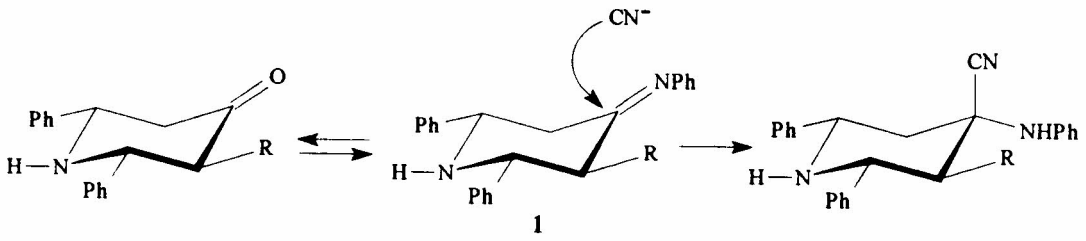


Figure II

Table III—^{13}C Chemical shifts (δ ppm) for C2 and C6 carbons of the aminonitriles **6-9** and parent piperidines **10-13**

Compd	C(2)	C(6)	C(3)	C(5)	C(4)
6	58.3	58.3	44.7	—	55.3
10	62.5	62.5	34.8	—	25.8
7	65.1	58.8	46.1	44.3	59.9
11	70.2	62.7	37.5	35.6	35.0
8	65.0	57.9	53.1	44.6	60.4
12	68.6	62.5	43.7	35.6	30.9
9	61.7	58.9	55.2	45.8	57.9
13	66.3	62.8	47.5	35.5	24.4



Scheme II

The axial orientation of the cyano group draws further support from the difference in conformational energies[20] of the two groups viz., CN and NHPh. The linear CN group with very low conformational energy (C.E.=0.17 kcal mol^{-1}) will strongly prefer the axial position compared with substituted amino functions (C.E.=1.0 to 2.1 kcal mol^{-1}).

On the basis of the foregoing discussions, it can be predicted that compound **6** prefers a chair conformation while compounds **7-9** prefer a chair conformation with slight flattening about the C-3 end wherein the nitrile and amino groups occupy the axial and equatorial orientations (β-series), respectively.

The selective formation of one isomer of the aminonitrile can be explained by invoking the concept of π-facial selectivity[21]. The probable mechanism is depicted in **Scheme II**. The literature information reveals that the intermediate formed in the Strecker aminonitrile synthesis is an imine[22]. The first step involves the formation of an intermediate imine **I** which exists in equilibrium with the ketone. The selective attack of the cyanide ion along the axial side to produce the isomer containing the axial cyano group and equatorial NHPh group can be rationalised by employing the model proposed by Cieplak[21].

Cieplak's model focuses on the differences in the relative stabilities of the transition states resulting from the interactions of incipient bond (developed between the nucleophile and the imine, for example) with the environment of the two nonequivalent faces of the trigonal center. The principal electronic factor differentiating two faces of sp^2 centre placed in an asymmetric environment is assumed to be the nature of the bonds interacting with the incipient bond.

In the present case the electronegative ring nitrogen in **I** withdraws electron density along the C(2)-C(3) and C(5)-C(6) bonds and the electron density around these bonds gets depleted. Thus, relatively, the C(3)-H and C(5)-H axial bonds become more σ-electron donors than the C(2)-C(3) and C(5)-C(6) bonds. As a consequence, the filled orbitals of the C-H bonds interact with the vacant orbital σ^* that developed along with the formation of the incipient bond between the cyanide group and the imino carbon. The effect of hyperconjugative σ assistance favours the axial attack, because C-H bonds are better donors than the C- C bonds and σ_{CH}, σ^* stabilisation energy is greater than the σ_{CC}, σ^* stabilisation energy. Such a donor type interaction stabilises the transition state complex between the cyanide ion and the imine, thus facilitating the attack of the cyanide from the axial side and this is not favoured in the case of equatorial attack.

Thus, the IR, Mass, ^1H and ^{13}C NMR spectral analysis and DAERM establish the conformation of the four α-phenylaminonitriles **6-9** of *r*-2, *c*-6-diphenylpiperidin-4-ones **2-5** as chair and the cyano group was found to occupy the axial position while the amino group occupies the equatorial position. The predominant formation of one of the two possible isomers agrees with the Cieplak's concept of π-facial selectivity.

Experimental Section

The melting points are uncorrected. IR spectra were recorded on a Shimadzu IR-435 infrared spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz and Jeol GSX-400 MHz spectrometer in $CDCl_3$ solution at ambient temperature using TMS as internal reference. Ketones **2-5** were prepared according to the reported procedures[23]. α-Phenylaminonitriles **6-9** were synthesised by reacting the appropriate ketones with potassium cyanide and aniline.

The IR spectra of **6-9** showed the N-H stretching band at 3300-3350 cm^{-1} and the weak cyanide absorption at 2225 cm^{-1}. The ring N-H stretching was observed around 3300 cm^{-1}. In the mass spectrum, the molecular ion peaks at m/z 353, 367, 381 and 395 and the fragmentation pattern corresponded to the structure of the compounds **6-9**, respectively.

***t*-4-Cyano-*r*-2, *c*-6-diphenyl-*c*-4-*N*-phenylaminopiperidine 6**. To a solution of *r*-2, *c*-6-diphenylpiperidin-4-one **2** (3.14 g, 12.5 mmoles) in glacial acetic acid (30 mL), aniline (1.2 mL, 12.5 mmoles) and potassium cyanide (40.0 mmoles) were added. The mixture was stirred in an ice-bath for 24 hr with excess addition of cyanide for three times. It was then poured onto crushed ice containing excess ammonia solution. The light yellow coloured precipitate formed was filtered and washed thoroughly with water. The fractional recrystallization of the precipitate from benzene: pet. ether 60-80°C (1:4) mixture gave **6** as colourless solid, yield 1.5 g (34%), m.p. 175-77°. (evaporation of the mother liquor gave the unreacted starting material) (Found: C, 81.66; H, 6.75; N, 12.02. $C_{24}H_{23}N_3$ requires C, 81.55; H, 6.56; N, 11.89%); IR(KBr): 2225 (CN), 3280, 3350 cm^{-1} (NH); ^1H NMR: δ 1.79 (2H, unsymmetrical t, C-3 and C-5 axial CH), 2.06 (1H, s, NH), 2.55 (2H, d, *J*=13.67 Hz, C-3 and C-5 equatorial CH), 3.65 (1H, s, NHPh), 4.25 (2H, dd, *J*=1.58 and 11.41 Hz, C-2 and C-6 CH), 6.87-7.50 (15H, m, aromatic); ^{13}C NMR: δ 44.7 (C-3 and C-5), 55.3 (C-4), 58.3 (C-2 and C-6), 120.9 (CN), 117.2, 120.2, 121.2, 129.0 (aromatic) 143.2 and 142.7 (ipso); MS: m/z 353 (M^+).

***t*-4-Cyano-*t*-3-methyl-*r*-2, *c*-6-diphenyl-*c*-4-*N*-phenylaminopiperidine 7**. Strecker reaction of **3** (3.31 g, 12.5 mmoles) was carried out by following the procedure as described for the compound **6**. The product was separated from the reaction mixture by fractional recrystallisation using benzene:pet. ether 60-80°C (4:1) mixture, yield 1.39 g (30.3 %); m.p. 174-76° (Found: C, 81.74; H, 7.14; N, 11.66. $C_{25}H_{25}N_3$ requires C, 81.71; H, 6.86; N, 11.43 %); IR(KBr): 2225 (CN), 3300, 3340 cm^{-1} (NH); ^1H NMR: δ 1.04 (3H, d, *J*=6.69 Hz, C-3 CH_3), 1.75 (1H, dd, *J*=11.75 and 13.05 Hz, C-5 axial), 1.97 (1H, s, NH), 2.03 (1H, m, C-3 axial), 2.77 (1H, dd, *J*=2.00 and 12.66 Hz, C-5 equatorial), 3.60 (1H, s, NHPh), 3.92 (1H, d, *J*=9.86 Hz, C-2 axial), 4.20 (1H, dd, *J*=1.99 and 11.57 Hz, C-6 axial), 6.85-7.49 (15H, m, aromatic); ^{13}C NMR: δ 12.4 (C-3 CH_3), 44.3 (C-5), 46.1 (C-3), 58.8 (C-6), 59.9 (C-4), 65.1 (C-2), 126.7 (CN), 118.5, 119.6, 121.1, 126.8, 127.7, 128.1, 128.5, 129.3 (aromatic), 143.4, 142.8 and 141.7 (ipso); MS: m/z 367 (M^+).

***t*-4-Cyano-*t*-3-ethyl-*r*-2, *c*-6-diphenyl-*c*-4-*N*-phenylaminopiperidine 8**. Strecker reaction of **4** (3.49 g, 12.5 mmoles) was carried out by following the procedure as described for the compound **6**. The product was separated from the reaction mixture by fractional recrystallisation using benzene:pet. ether 60-80° C (4:1) mixture, yield 1.4 g (29.4%); m. p. 180-81°C. (Found: C, 81.70; H, 7.56; N, 10.80. $C_{26}H_{27}N_3$ requires C, 81.85; H, 7.13; N, 11.01%); IR(KBr): 2225 (CN), 2290, 3350 cm^{-1} (NH); ^1H NMR: δ 0.53 (3H, t, *J*=7.5 Hz, C-3 CH_3), 1.50 (2H, m, C-3 CH_2), 1.75 (1H, t, *J*=11.72 Hz, C-5 axial), 1.80 (1H, s, NH), 1.88 (1H, m, C-3 axial), 2.74 (1H, dd, *J*=2.44 and 13.88 Hz, C-5 equatorial), 3.61 (1H, s, NHPh), 3.97 (1H, d, *J*=10.25 Hz, C-2 axial), 4.19(1H, d, *J*=9.27 Hz, C-6 axial), (15H, m, aromatic); ^{13}C NMR: δ 14.5 (C-3 CH_3), 21.3 (C-3 CH_2), 44.6 (C-5), 53.1 (C-3), 57.9 (C-6), 60.4 (C-4), 65.0 (C-2), 127.7 (CN), 118.4, 118.5, 120.1, 121.2, 126.8, 127.7, 128.2, 128.5, 129.3 (aromatic), 141.4, 142.7 and 143.4 (ipso); MS: m/z 381 (M^+).

***t*-4-Cyano-*t*-3-isopropyl-*r*-2, *c*-6-diphenyl-*c*-4-*N*-phenylaminopiperidine 9**. Strecker reaction of **5** (3.66 g, 12.5 mmoles) was carried out by following the procedure described for the compound **6**. The product was separated from the reaction mixture .by fractional recrystallisation using benzene:pet. ether 60-80°C (4:1) mixture, yield 0.75 g (15.2 %); m.p. 150-51°C (Found: C, 82.19; H, 7.21; N, 10.60 . $C_{27}H_{29}N_3$ requires C, 81.99; H, 7.39; N, 10.62%). IR(KBr): 2225 (CN), 3290, 3330 cm^{-1} (NH); ^1H NMR: δ 0.77 (3H, d, *J*=0.655 Hz, C-3 CH_3), 1.13 (3H, d, *J*=0.593 Hz, C-3 CH_3), 1.74 (1H, dd, *J*=0.66 and 0.14 Hz, C-5 axial), 1.79 (1H, s, NH), 2.04 (1H, dd, *J*=0.89 and 0.14 Hz, C-3 axial), 2.3 (1H, m, C-3 CH), 2.72 (1H, dd, *J*=0.12 and 0.32 Hz, C-5 equatorial), (1H, s, NHPh), 4.20 (1H, dd, *J*=1.00 and 1.20 Hz, C-6 axial), 4.25 (1H, d, *J*=2.89 Hz, C-2 axial), (15H, m, aromatic); ^{13}C NMR: δ 19.8 (CH_3), 23.7 (CH_3),

26.8 (CH), 45.8 (C-5), 55.2 (C-3), 57.9 (C-4), 58.9 (C-6), 61.7 (C-2), 126.7 (CN), 118.6, 120.8, 121.2, 126.8, 127.7, 128.1, 128.4, 128.5, 129.0, 129.3 (aromatic), 142.2, 142.6 and 143.5 (ipso); MS: m/z 395 (M^+).

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