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Stereochemistry of *N*-acetyl-*r*-2,*c*-4-diphenyl-3-azabicyclo[3.3.1]nonanes and *N*-ethoxycarbonyl-*r*-2,*c*-4-diphenyl-3-azabicyclo[3.3.1]nonane

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The conformational preferences of *N*-acetyl-*r*-2,*c*-4- diphenyl-3- azabicyclo[3.3.1] nonane **3** and *N*-ethoxycarbonyl- and *N*-acetyl-*r*- 2,*c*-4,*t*-6,*t*-8-tetraphenyl-3,7-diazabicyclo[3.3.1] nonanes **6** and **7** have been studied using NMR spectral techniques. The azabicyclo[3.3.1]nonane **3** is found to prefer a twin-chair conformation with a slight flattening at the nitrogen end. In the case of diazabicycles **6** and **7** both the ethoxycarbonylation and acetylation reactions are found to take place only at the boat end of the parent amine and the preferred conformation of the products is found to be twin-chair with flattening at C_1-C_2-N_3-C_4-C_5 part of the ring in both cases. The energy barrier for the N-CO rotation in *N*- ethoxycarbonyl derivative **6** has been determined from the dynamic ^{1}H NMR studies and the barrier for N- CO rotation is found to be 50.8 kJ mol^{-1}, much less than that of *N*-nitroso analogues.

The attachment of electron-withdrawing groups like NO, COR, etc., at nitrogen of a 2,6-disubstituted piperidine ring is known to exert a major change in the ring conformation and the orientation of the substituents[1-5]. This conformational change is attributed to the involvement of lone pair of electrons on nitrogen in conjugation with the -X=Y function[1-6]. The conjugation creates a partial double bond character at N-X bond and leads to a restricted rotation around this bond which in turn results in magnetic nonequivalence of the ring carbons and the attached protons[1-6]. The change of hybridisation of the nitrogen from **sp**^{3} to **sp**^{2} is possible only in the coplanar orientation of the -X=Y function with reference to C2-N-C6 plane due to the gain in the resonance energy through delocalisation. The substituents at the equatorial positions alpha to the nitrogen exhibit a severe nonbonded interaction with the coplanar N-X=Y function which is termed as **Allylic strain** or **A**^{1,3}**-strain**[7]. In the case of *N*- substituted 2,6-dimethylpiperidines[1a], the preferred conformation was found to be the one with axial methyl groups, in spite of the 1,3-diaxial interaction between the methyl groups. Since the delocalisation energy in the case of N-COR, (62-95 kJ mol^{-1}) is much larger than that of 1,3-diaxial CH_3/CH_3 interaction energy (14.6 kJ mol^{-1}), the molecule was found to prefer a conformation with diaxial methyl groups[1a].

Most of the *N*-nitroso- and *N*-formyl-cis-2,6-diphenyl-piperidines[2a,i,j] investigated in our laboratory were shown to prefer non-chair conformations ranging from twist-boat to flattened-boat with relatively high energy barriers around 70 to 80 kJ mol^{-1}, determined from dynamic NMR spectral studies. However, in the case of *N*-nitroso-2,4-diaryl-3- azabicyclo[3.3.1]nonanes[2i] the energy barrier for the N-NO rotation was found to be low (60-70 kJ mol^{-1}) compared to those of the monocyclic nitrosamines. Moreover, the delocalisation in these rigid bicyclic amines was partial resulting in a slightly nonplanar geometry around nitrogen[2d-e,i]. Recent report by Polonski *et al.* for similar *N*-nitroso-3-azabicyclic compounds is in fair agreement with our results[8], though our calculations showed that some of the conformations predicted[4] for other *N*- nitrosopiperidines do not correspond to global minima in the calculated heats of formation[2k].

Though several *N*-acetyl-*cis*-2,6-diphenylpiperidin-4-ones have been prepared and the conformations studied, there was difficulty in getting the *N*-acetyl derivatives of *r*-2,*c*-4-diphenyl-3- azabicyclo[3.3.1]nonan-9-one **1** and *r*-2,*c*-4,*t*-6,*t*-8-tetraphenyl- 3,7-diazabicyclo[3.3.1]nonan-9-one **4**. We have now obtained *N*- acetyl-*r*-2,*c*-4-diphenyl-3-azabicyclo[3.3.1]nonane **3** and *N*- ethoxycarbonyl- and *N*-acetyl-*r*-2,*c*-4,*t*-6,*t*-8-tetraphenyl-3,7- diazabicyclo[3.3.1]nonanes (**6** and **7**).

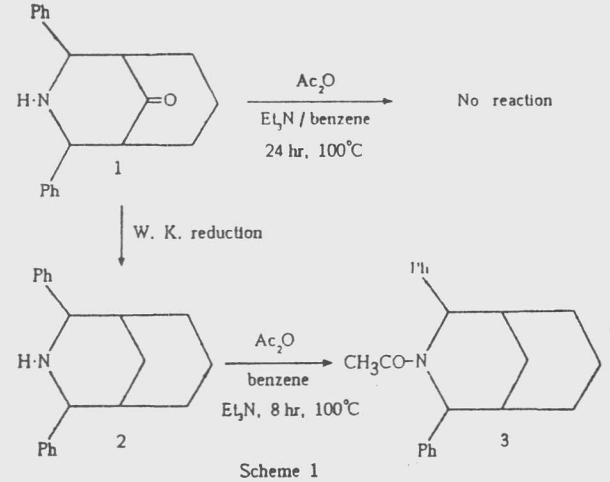
The 3-azabicyclo[3.3.1]nonane **2** has been shown to adopt a twin- chair conformation with the phenyl groups occupying equatorial orientation[9]. The 3,7-

diazabicyclic compound **5** has been shown to prefer a chair-boat conformation with all the phenyl groups at equatorial orientation[10,11].

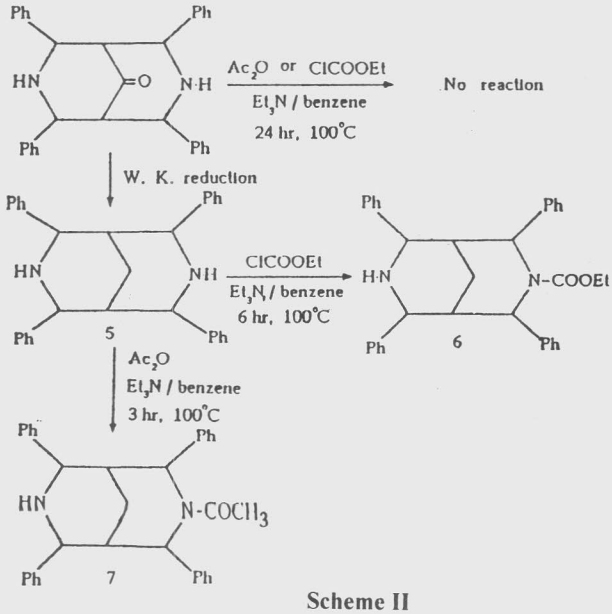
Results and Discussion

The *N*-acetyl-*r*-2, *c* - 4 - diphenyl - 3 - azabicyclo [3.3.1] nonane **3** was prepared by the treatment of the corresponding bicyclic amine **2** with acetic anhydride in the presence of triethylamine and using dry benzene as the medium (Scheme I). The *N*-ethoxycarbonyl and *N*- acetyl derivatives (**6** and **7**) of the diazabicyclic amine **5** were synthesised by the treatment of **5** with ethyl chloroformate and acetic anhydride, respectively, in dry benzene. Triethylamine was used as a catalyst (Scheme II).

In the IR spectrum of the *N*-acetyl derivative **3**. the NH stretching band was absent and a new amide carbonyl stretching band appeared at 1680 cm^{-1} which showed the conversion of NH to *N*-$COCH_3$. In the mass spectrum, the molecular ion peak observed at m/z 319 and the fragmentation pattern corresponded to the molecular structure of the compound **3**.



Scheme 1



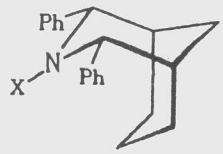
Scheme II

In the IR spectra of **6** and **7**, both NH and amide C=O stretching bands appeared (For **6**: NH 3300, amide C=O 1675 cm^{-1}; For **7**: NH 3300, amide C=O 1665 cm^{-1}). Furthermore, in the ^1H NMR spectrum of **6** and **7**, the signals at δ1.82 and 1.85 ppm, respectively, were assigned to NH protons on the basis of the D_2O exchange studies. Integration of $COCH_3$ protons indicated that acylation had taken place at one of the ring nitrogens in both the diazabicyclic compounds **6** and **7**. In the mass spectra the molecular ion peaks were observed at m/z 502 and 472 and the fragmentation patterns corresponded to the monoethoxycarbonyl and monoacetyl derivatives **6** and **7**, respectively.

The preferred conformations of the *N*-acyl bicyclic amines **3**, **6** and **7** were derived from ^1H and ^{13}C NMR spectral data in comparison to those of the corresponding parent amines[2i,9a,c,10].

Conformational analysis of *N*-acetyl-*r*,2,*c*-4-diphenyl-3- azabicyclo[3.3.1]nonane 3. The ^1H and ^{13}C NMR spectra of *N*-acetyl- *r*-2,*c*-4-diphenyl-3-azabicyclo[3.3.1]nonane **3** showed the isochronous nature of the proton and carbon signals. The isochronous nature of carbons and protons at room temperature may be due to a very low barrier for the N-CO rotation. The decision about the possibility for the perpendicular/coplanar orientation of the acetyl group can be made by examining the NMR spectra at low temperature. The broadening of the signals at low temperature would reveal restricted rotation around the N-CO bond causing a dynamic equilibrium in the system whereas the perpendicular orientation may not show any change in the nature of the signals (absence of restricted rotation). The ^1H NMR spectrum recorded at a temperature as low as -60°C showed the broadening of all the proton signals. The spectrum at the coalescence temperature which is expected well below -60°C, could not be recorded. The above observation indicated the possibility for the restricted N-CO rotation with very low N-CO rotational barrier so that the doubling of the signals could not be observed at room temperature.

The coalescence temperature for the *N*-nitroso[2i] and *N*-formyl[2j] azabicyclic compounds (**8a** and **8b**, respectively) were found to be 68°C ($\Delta G^{\ddagger}$ 67.8 kJ



X

8a CHO

8b NO

mol^{-1}) and -23°C ($\Delta G^{\pm}$ 58.25 kJ mol^{-1}), respectively. But in the case of the *N*- acetylbicyclic amine **3** it is below -60°C and correspondingly the energy barrier is expected to be below 50 kJ mol^{-1}. This decrease in N-C rotational barrier may be due to the increase in bulkiness of the -X=Y function which destabilizes the ground state more than the transition state[1c,12].

Compared to the N-acetyl–*cis*-2,6-diphenylpiperidine which showed doubling of signals at –60°C, the N-acetyl-*r*-2,*c*-4- diphenyl-3-azabicyclo[3.3.1]nonane **3** did not split even at –60°C indicating a lower energy barrier for the N-CO rotation than for *N*-acetylpiperidine. Hence, the degree of delocalisation of the nitrogen lone pair into the C=O group in the azabicyclic compound is lower than that in *N*-acetyl-*cis*-2,6-diphenylpiperidine. Neither twisting around C2- N-C4 nor flipping over to the other chair is prohibited because of the rigidity of the junction with the second ring and the severe interactions that would be introduced between the phenyl groups and second ring (if the ring flips). Thus, the nitrogen is expected to be more pyramidal than planar in compound **3**.

In the ^{1}H NMR spectrum of *N*-acetyl-*r*-2,*c*-4-diphenyl-3- azabicyclo[3.3.1]nonane **3** the benzylic protons at C2 and C4 showed a doublet at δ 5.19 ppm (J = 7.44 Hz). The benzylic protons were deshielded by about 0.87 ppm compared to the parent amine **2** indicating that the α-protons lie in the deshielding region of the amide plane (on the basis of the model proposed by Paulson and Todt for the anisotropic effect of amides)[13]. Also, the coupling constant for the benzylic protons ($^3J_{1,2}$ = $^3J_{4,5}$ = 7.44 Hz) was larger than that for the parent amine (2.44 Hz). This may be explained by considering the partial flattening at the nitrogen end. The partial flattening at nitrogen end resulted in a decrease in the dihedral angles between the benzylic protons and the bridge head protons ($\phi_{2a,1e} = \phi_{4a,5e}$) which in turn increased the coupling constant ($J_{2a,1e} = J_{4a,5e}$).

In the case of parent 3-azabicyclic amine **2** the signal for the C7-axial proton appeared at δ 2.63 ppm, while the signals of the nearby protons at C6, $C7_{eq}$ and C8 appeared around δ 1.2 - 1.4 ppm[9c]. The downfield shift for the $C7_{ax}$ proton was attributed to the transannular interaction between the $C7_{ax}$ proton and the lone pair on nitrogen in the chair-chair conformation. On the other hand, in the *N*-acetyl-3-azabicyclic compound **3**, the lone pair on nitrogen may not be available due to the extended conjugation with the acetyl group. Hence, the $C7_{ax}$ proton in **3** may be expected to show an upfield shift compared to the parent 3-azabicyclic amine **2**. The ^{1}H NMR spectrum of **3** indicated that the axial proton at C7 did shift upfield (1.44 ppm) by about 1 ppm compared to the parent 3-azabicyclic amine **2** (2.63 ppm) and the $C7_{ax}$ proton was still distinguishable from other methylene protons which appeared between δ 1. 08 and 1.25 ppm. This observation is possible only if the carbocyclic ring adopts a chair conformation. Thus, the *N*-acetyl-3-azabicyclic compound **3** prefers to adopt a twin-chair conformation.

The ^{13}C NMR spectra of **3** showed a signal at δ 64.5 ppm for the benzylic carbons at C2 and C4 (Table I). The α-carbons were shielded only by 0.9 ppm which indicated a weak delocalisation of nitrogen lone pair into the carbonyl π-cloud[5,14]. The carbon atoms C1, C5 and C8 were not affected much which also indicated that the carbocyclic ring retains its chair form.

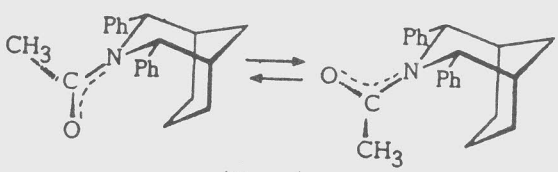


Figure 1

Table I —^{13}C NMR spectral data of N-acetyl-*r*-2,*c*-4- diphenyl-3- azabicyclo[3.3.1]nonan-9-one **3** compared with the 3- azabicyclic amine **2** (chemical shifts in δ ppm)

Compd	$C_{2,4}$	$C_{1,5}$	$C_{6,8}$	C_7	C_9
3	64.5	34.1	27.5	18.6	31.0
2	65.4	35.2	26.1	22.1	37.2

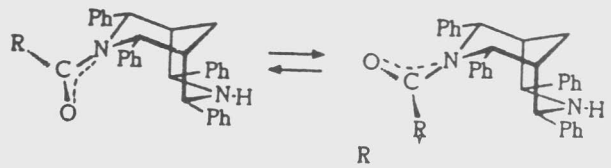
Table II —^{1}H NMR spectral data of the benzylic protons of 3- ethoxycarbonyl- and 3-acetyl-*r*-2,*c*-4,*t*-6,*t*-8- tetraphenyl-3,7- diazabicyclo[3.3.1]nonanes (**6** and **7**) compared with the diazabicyclic amine **5** (chemical shifts in δ ppm)

Compd		H_2 and H_4		H_6 and H_8	
		syn	*anti*	*syn*	*anti*
6		-5.37 (s)		4.38 (s)	
7	(-60°C)	6.00 (s)	4.68 (s)	4.47 (s)	4.39 (s)
5		4.12 (d 3.0 Hz)		4.20 (s)	

Thus, it was concluded that **3** prefers to adopt a chair-chair conformation with coplanar orientation of acetyl group and partial flattening at the nitrogen end as shown in Figure 1. The nitrogen end is more pyramidal than planar. In the planar form a severe $A^{1,3}$ -interaction[7] will exist between the coplanar $COCH_3$ with the allylic α-equatorial phenyl groups which cannot be relieved owing to the rigidity of the junction with second ring.

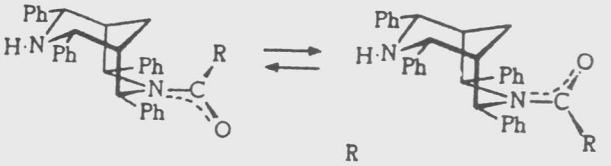
Conformational analysis of N-acyl derivatives of *r*-2,*c*- 4,*t*-6,*t*-8-tetraphenyl-3,7-diazabicyclo[3.3.1] nonanes 6 and 7. At room temperature the ^{1}H NMR spectrum of 3-ethoxycarbonyl-*r*-2,*c*- 4,*t*-6- 8-tetraphenyl-3, 7-diazabicyclo[3.3.1]nonane **6** showed only a time averaged (isochronous) signal. The two pairs of benzylic protons appeared as singlets at δ5.37 and 4.38 ppm (Table II). But the ^{1}H NMR spectrum recorded at -80°C showed anisochronous signals for all the protons and confirmed the presence of dynamic equilibrium between *syn* and *anti* rotamers with coplanar orientation of the amide moiety. In the case of *N*- acetyl compound **7**, the room temperature ^{1}H NMR spectrum showed only broad (anisochronous) signals. Upon lowering the temperature to -60°C well resolved signals for both *syn* and *anti* forms were observed. The presence of anisochronous nature of signals at room temperature showed that the energy barrier for the rotation of N-CO in the case of 3-acetyl-diazabicycle **7** is higher than that of the 3-ethoxycarbonyl analogue **6** and also the orientation of amide function is coplanar.

There are two possible conformations for the compounds **6** and **7**, i.e. **6A** and **7A** with acyl groups located at the piperidine ring having chair conformation (Figure 2) and **6B** and **7B** with the acyl group attached to the piperidine ring having boat conformation (Figure 3). In ^{1}H NMR spectra the benzylic protons of both **6** and **7** showed only singlets indicating that the acyl groups may be attached to the same end in both the compounds.



	R
6A	OEt
7A	Me

Figure 2



	R
6B	OEt
7B	Me

Figure 3

If the ethoxycarbonyl and acetyl groups are located in the piperidine ring having the chair conformations **6A** and **7A**, a flattening may be induced at the C1-C2-N3-C4-C5 part of the ring causing a decrease in torsional angle between C2 and C1 protons (also C4 and C5 protons) of the conformations **6A** and **7A** compared to that of the parent diazabicyclic amine **5** similar to that observed for the *N*-acetyl 3-azabicycle **3**. Consequently the coupling constants would increase and the benzylic protons of the piperidine ring containing acyl groups would appear as doublets. On the other hand, if the conformations were **6B** and **7B**, where the acyl group is located in the boat end, the flattening would cause a decrease in the coupling constant between H2 and H1 (as well as H4 and H5). In addition, to avoid the $A^{1,3}$- strain between the coplanar acyl group and the α-equatorial phenyl groups the boat and (C_2-N_3-C_4) may flip over to a flattened chair.

In the ^{1}H NMR spectra of the compound **6** and **7**, only singlets were observed for the benzylic protons of the ring containing acyl groups. This indicates that the monoacylated derivatives **6** and **7** might have the acyl group at boat ring of the parent as in **6B** and **7B** and may prefer to adopt a twin-chair conformation with flattening at c_1-c_2-N_3-c_4-c_5 part of the ring (Figure 3).

In the ^{1}H NMR spectrum of the *N*-ethoxycarbonylated derivative **6** at -60°C, among the two sets of signals for benzylic protons, the one at at δ 5.37 ppm was separated well and appeared at 5.2 and 5.6 ppm (Δδ = 0.4 ppm) while the pother around 4.4 ppm was not separated well (Δδ = 0.03 ppm). Thus, the signal at δ 5.37 ppm in the room temperature spectrum which has larger chemical shift difference has been assigned to the benzylic protons alpha to the nitrogen containing the ethoxycarbonyl function. The anisotropic influence of the carbamate moiety would be higher only for the α- protons. The peaks at δ 5.6 and 5.2 ppm have been assigned[13] to *syn* and *anti* benzylic protons (C2 and C4), respectively. The other signal at δ 4.38 ppm has been assigned to the other set of benzylic protons at C6 and C8 in which the amine site is free. From the variable temperature ^{1}H NMR spectral studies (Figure 4) the coalescence temperature was found to be -14°C and the energy barrier[15] for the N- CO rotation was calculated as 50.8 kJ mol^{-1}.

In the ^{1}H NMR spectrum of **7** recorded at -60°C two sets of benzylic protons were observed at δ 6.0 and 4.68 ppm as singlets (Δδ = 1.32 ppm) with a significant shift difference, while the other singlets at 4.47 and 4.39 ppm were close (Δδ = 0.08 ppm) (Table II). The set with larger chemical shift difference, i.e. at δ 6.00 and 4.68 ppm, has been assigned to the C2 and C4 benzylic protons alpha to the nitrogen containing the acetyl group. The singlet at δ 6.0 ppm has been assigned to the *syn* C2 and C4 benzylic protons[13] and the other at δ4.68 to the *anti*-protons. The other set with a very low chemical shift differ-

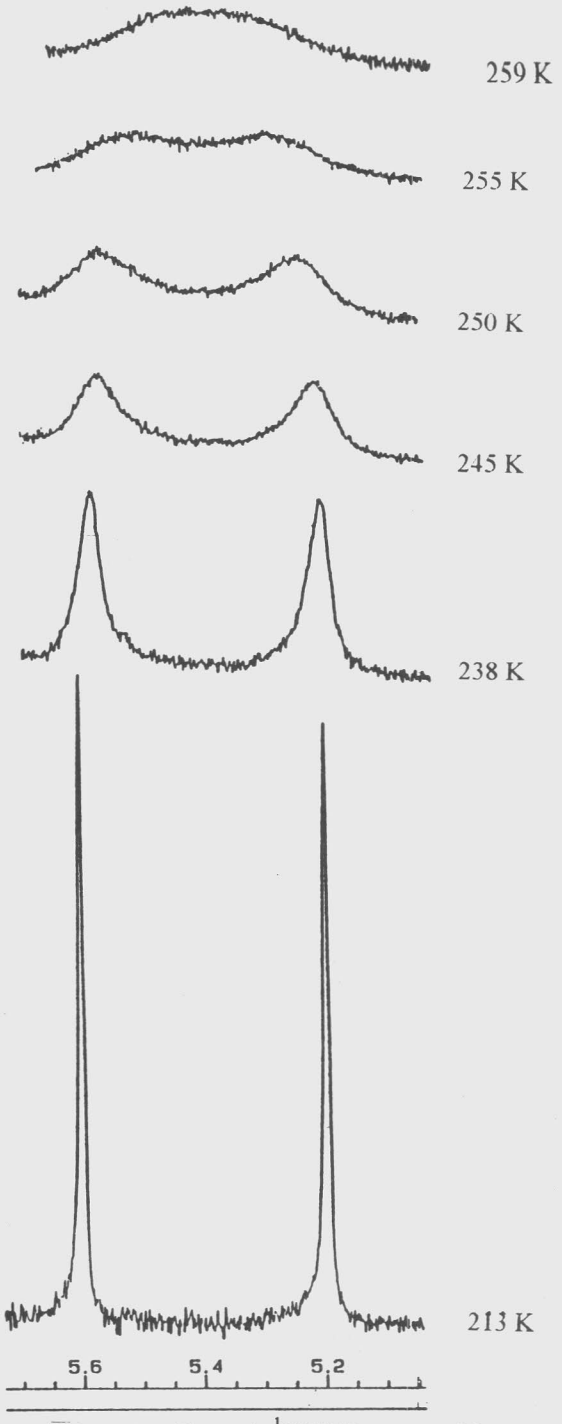


Figure 4 -- Dynamic ^{1}H NMR spectra of **6**

Table III - ^{13}C NMR spectral data of 3-ethoxycarbonyl- and 3-acetyl-*r*-2,*c*-4,*t*-6,*t*-8-tetraphenyl-3,7- diazabicyclo[3.3.1] nonanes (**6** and **7**) compared with the diazabicyclic amine **5** (chemical shifts in δ ppm)

Compd	$C_{2,4}$	$C_{1,5}$	$C_{6,8}$	C_9
6	53.3	38.4	65.7	25.8
7 (–55°C)	57.3 and 49.2	41.2 and 36.0	65.4 and 63.5	25.3
5	63.7	42.8	54.9	27.8

ence at δ 4.47 and 4.39 ppm has been assigned to the C6 and C8 benzylic protons, respectively.

The ^{13}C NMR signal positions for the compounds **6** and **7** have been assigned on the basis of SFORD (Single Frequency Off Resonance Decoupled) spectra and in comparison with the parent amine **5**[10] (Table III). In the case of *N*-acetyl compound **7**, the room temperature ^{13}C NMR spectrum showed the anisochronous signals but the signals were broad. The ^{13}C NMR spectrum recorded at low temperature (–55°C) for the compound **7** showed two well resolved sharp signals corresponding to *syn* and *anti* conformations. Here also the benzylic carbons of the flattened chair was shielded by 6.4 and 14.5 ppm. Since the γ- eclipsing interaction is known to be more in the *syn* side[14], the signal at δ 49.2 ppm was assigned to the *syn* carbon and the signal at 57.3 ppm was assigned to the *anti* carbon.

The carbons of flattened chair (C2 and C4), bridgehead C1 and C5 and C9 were shielded while the benzylic carbons of the chair ring (C6 and C8) were deshielded as a result of the introduction of acyl groups at the boat ring (N3). In the case of 3-ethoxycarbonyl compounds the shielding of bridgehead carbon was 4.4 ppm while the benzylic carbons were shielded to a greater extent (10.4 ppm) which may be due to the γ-eclipsing interaction between the N3-C2/N3-C4 and C-O bonds.

The C9 carbons of compounds **6** and **7** were shielded by about 2.0 ppm and 2.5 ppm, respectively, which may be due to the expansion of valence angle of C2-N3-C4 site which in turn results in a contraction at C1-C9-C5 end (reflex effect)[16].

On the basis of the above observations, it was concluded that the *N*-ethoxycarbonyl (**6**) and *N*-acetyl (**7**) diazabicycles prefer to adopt a twin-chair conformation with flattening at C_1-C_2-N_3-C_4-C_5 part of the ring in which two of the pheynl groups at *c*-2 and C-4 occupying axial protons due to the coplanar orientation of acyl group (Figure 3). The large deshielding of benzylic protons and shielding of benzylic carbons at boat ring suggested a nearly planar arrangement at the nitrogen end of the boat ring.

Experimental Section

General. 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 Bruker AMX-400 and Jeol GSX-400 MHz spectrometers in $CDCl_3$ solution using TMS as internal reference. Dynamic ^1H NMR spectra were recorded in acetone-d_6 solution and the other low temperature studies were carried out in $CDCl_3$ solution using Jeol GSX-400 MHz NMR spectrometer. The azabicyclic amines **2** and **5** were prepared by following the literature methods[17,10]. The Wolf-Kishner reduction of 3-azabicyclic ketone **1**[17] and 3,7-diazabicyclic ketone **4**[18] yielded the reduced 3-azabicyclic amine **2**[17] and 3,7-diazabicyclic amine **5**[10], respectively.

***N*-Acetyl-*r*-2,*c*-4-diphenyl-3-azabicyclo [3.3.1] nonane 3**. A mixture of azabicyclic amine **2** (0.69 g, 2.5 mmoles), acetic anhydride (0.7 mL, 7.5 mmoles) and triethylamine (1.0 mL, 7.5 mmoles) in anhydrous benzene (50 mL) was kept under reflux on a water-bath and the progress of the reaction monitored by TLC (silica, $CHCl_3$ as eluent). After 8 hr the reaction mixture was washed with 10% sodium bicarbonate solution (2 X 25 mL) and then with water (4 X 25 mL). The organic layer was dried (Na_2SO_4), passed through a short column of silica (eluent: $CHCl_3$) and evaporated. Recrystallisation from pet. ether (60-80°C) yielded colourless crystals of **3**, yield 0.63 g (79.0%), m.p. 160-61° (Found: C, 82.41; H, 7.80; N, 4.53. $C_{22}H_{25}NO$ requires C, 82.72; H, 7.89; N, 4.39%); IR (KBr): 1680 cm^{-1} (C=O); ^1H NMR: δ1.17 (5H, m, C7- equatorial, C6- and C8-axial and equatorial), 1.44 (1H, m, C7-axial), 1.81 (3H, s, CH_3), 1.93 (2H, m, Cl- and C5-equatorial), 2.46 (2H, br, CH_2- 9), 5.19 (2H, d, C2- and C4-H), 7.10-7.69 (10H, m, aromatic); ^{13}C NMR: δ18.6 (C7), 25.3 (*C*H_3), 27.5 (C6 and C8), 31.0 (C9), 34.1 (Cl and C5), 64.5 (C2 and C4), 128.4, 126.1, 125.3 (aromatic), 144.1 (ipso), 176.2 (CO); MS: m/z 319 (M^+).

3-Ethoxycarbonyl-*r*-2,*c*-4,*t*-6,*t*-8-tetraphenyl-3,7-diazabicyclo[3.3.1]nonane 6. To an ice-cold solution of diazabicyclic amine **5** (1.08 g, 2.5 mmoles) in anhydrous benzene (75 mL) was added triethylamine (2.8 mL, 20 mmoles) and ethyl chloroformate (2.9 mL, 30 mmoles). The reaction mixture was allowed to reflux on a water-bath for 6 hr and monitored by TLC (silica gel G, $CHCl_3$ as eluent). The precipitated ammonium salt was filtered and the filtrate washed with water (4 X 25mL). The organic layer was dried (anhydrous Na_2SO_4), passed through a short coloumn of silica gel (eluent: $CHCl_3$) and concentrated. Crystallisation from benzene:petroleum ether (60-80°C) mixture (1:2) at 0°C afforded colourless crystals of **6**, yield 0.83 g (66.1%), m.p. 181- 83° (Found:

C, 81.02; H, 6.61; N, 5.82. $C_{34}H_{34}N_2O_2$ requires C, 81.24; H, 6.82; N, 5.57%); IR(KBr): 1675 (C=O), 3300 cm^{-1} (NH); ^1H NMR: δ 1.22 (3H,t,OCH_3), 1.82 (1H, br s, NH exchangeable with D_2O), 2.1 (1H, br, C_9-H), 2.46 (2H,br s, C1- and C5-H), 2.62 (1H, br,C9-H), 4.20 (2H, q, OCH_2), 4.38 (2H, s, C6- and C8-H), 5.37 (2H, s, C2- and C4-H), 6.95-7.89 (20H, m, aromatic); ^{13}C NMR: δ 14.7 (CH_3), 25.8 (C9), 38.4 (C1 and C5), 53.3 (C2 and C4), 61.3 (OCH_2), 65.7 (C6 and C8), 126.2 - 128.4 (aromatic), 143.2, 143.3 (ipso), 157.3 (CO); MS: m/z 502 (M^+).

3-Acetyl-*r*-2,*c*-4,*t*-6,*t*-8-tetraphenyl-3, 7-diazabicyclo [3.3.1] nonane 7. The procedure described for the preparation of **3** was followed for the acetylation of diazabicyclic amine **5** (1.075 g, 2.5 mmoles) and the reaction mixture allowed to reflux for 3 hr. Crystallisation from benzene-pet. ether (60-80°C) (1:2) at 0°C afforded colourless crystals of **7**, yield 0.86 g (72.9 %); m.p. 223-24° (Found: C, 83.51; H, 6.92; N, 5.62. $C_{33}H_{32}N_2O$ requires C, 83.86; H, 6.83; N, 5.93%); IR(KBr): 1665 (C=O), 3300 cm^{-1} (NH); ^1H NMR: δ 1.85 (1H, br s, NH exchangeable with D_2O), 1.93 (3H, s, CH_3), 2.21 (1H, m, C_9-H), 2.56 (3H, m, C1- and C5-H and C9-H), 4.47 and 4.39 (2H, s, C6- and C8-H), 4.68 (1H, s, *anti* C2- and C4-H), 6.00 (1H, s, *syn* C2- and C4-H), 7.60-7.80 (20H, m, aromatic); ^{13}C NMR: δ 23.4 (CH_3), 25.3 (C9), 41.2 and 36.0 (C1 & C5), 49.2 (*syn* C2 and C4), 57.3 (*anti* C2 and C4), 63.5 & 65.4 (C6 and C8), 126.1-128.7 (aromatic), 141.1, 142.7, 142.9, 143.3 (ipso), 172.7 (CO); MS: m/z **472** (M^+).

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