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Conformational analysis of N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-ones using NMR spectra and semiempirical MO calculations

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The stereochemistry of N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-ones **4** and **5** have been studied using NMR spectral techniques and semiempirical MO calculations (AM1 and PM3 methods). The N_1,N_5-diacetyl- and N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin-2-ones (**4** and **5,** respectively) prefer boat conformations **BE** with *endo* orientations of the acyl groups at N1 and *exo* orientations of the acyl groups at N_5 positions. The X-ray crystal structure of N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5- benzodiazepin-2-one **5** also supported the preference for the boat conformation (**BE**) with *endo* and *exo* orientations of benzoyl groups at N1 and N5 positions, respectively.

Keywords: N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-one, NMR spectra, semiempirical MO calculation, boat conformation, N_1,N_5-diacetyl, N_1,N_5-dibenzoyl

1,5-Benzodiazepines are well known for their biological activity[1-6]. Some derivatives such as lofendazam **1**, Clobazam **2a** and Triflubazam **2b** are used for the treatment of anxiety and neuroses including psychosomatic disturbances[1a]. It has been inferred, from a large number of Structure-Activity Relationship (SAR) studies, that the conformations of the diazepines play a key role in deciding their biological activity[3-4]. Hence it is of interest to introduce the conformation-directing moities, such as acyl groups, at the nitrogen site of benzodiazepines and to study the stereochemical consequences on the seven membered rings of benzodiazepines. In continuation of the work on the *N*-acyltetrahydro-1,5-benzodiazepines[5], the present article reports the stereochemistry of N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-ones **4** and **5** using NMR spectra, X-ray crystallography studies and semiempirical MO calculations.

Results and Discussion

The N_1,N_5-diacetyl- and N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin- 2-ones, **4** and **5,** were prepared by the action of acetic anhydride and benzoyl chloride, respectively, on the tetrahydrobenzodiazepin-2-one **3** in dry benzene and triethylamine (**Scheme I**). In the IR spectra of the diacylated compounds **4** and **5**, the stretching bands for both amine NH and amide NH were absent. The compounds **4** and **5** showed IR absorption bands at 1640, 1665 and 1720 and 1655, 1700 and 1715 cm^{-1}, respectively. In the ^1H NMR spectra of compounds **4** and **5**, the amine NH (δ 3.80) and amide NH (δ 8.71) signals were absent. In the mass spectra, the molecular ion peaks were observed at *m*/*z* 260 and 384 and the fragmentation patterns corresponded to the diacetyl and dibenzoyl derivatives, respectively.

The preferred conformations of the N_1,N_5-diacyltetrahydro-1,5-benzodiazepin -2-ones **4** and **5** were derived from the ^1H and ^{13}C NMR spectral data in comparison with those of the parent amine **3** (ref. 6, **Tables I** and **II**). The SEFT (Spin Echo Fourier Transform), SFORD (Single Frequency Off Resonance Decoupled) and NOESY spectra were used for the assignments. The coupling constants $J_{3a,4a}$ and $J_{3e,4a}$ were determined by irradiating the C4-methyl doublet and the corresponding dihedral angles were estimated using DAERM[7].

It has been reported that the parent benzodiazepin-2-one **3** prefers to exist in a boat conformation on the basis of the vicinal coupling constants

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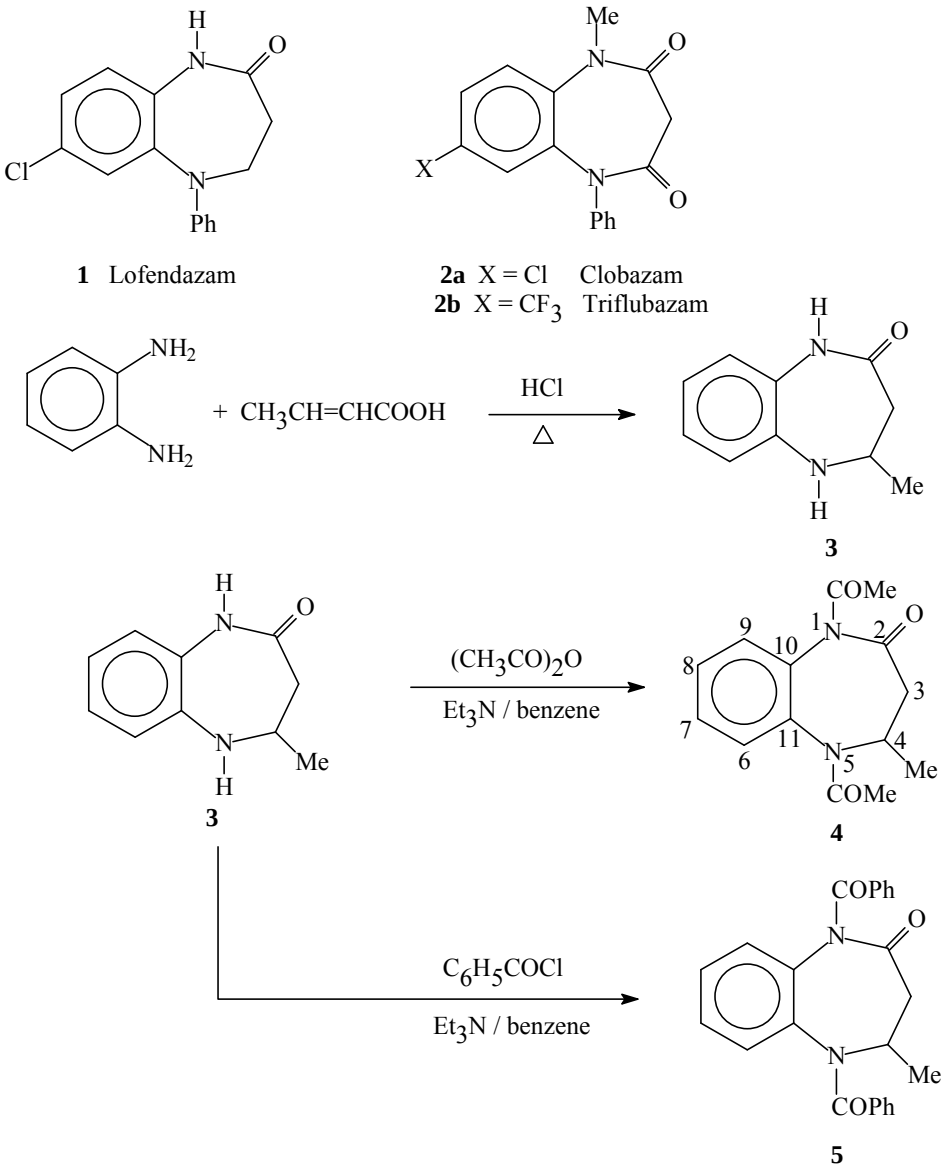

Scheme I

of 7.5 ($J_{3a,4a}$) and 4.2 Hz ($J_{3e,4a}$) between H3a/H3e and H4 protons and also by X-ray crystallography [6b].

The ^{1}H and ^{13}C NMR spectra of the N_1,N_5-diacyltetrahydrobenzodiazepin-2-ones **4** and **5** showed isochronous nature of the proton and carbon signals at room temperature indicating that either a fast rotation about N-CO bond or the N-C=O groups may adopt *exo*/*endo* orientations at N1 and N5 (**Figure 1**).

Orientations of acyl groups at N1 and N5

The semiempirical MO calculations (AM1 and PM3 of MOPAC[8]) and X-ray crystallography[9] suggested that the acetyl and benzoyl groups at N1 end in the N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-ones **4** and **5**, respectively, adopt *endo* orientations. The shielding/deshielding of C4-carbon signal in the ^{13}C NMR spectra of the compounds **4** and **5** compared to that of the parent **3** was used to decide the orientation of the acyl groups at N5 end. It was observed that the C4-carbon signal for the N_1,N_5-diacetyl derivative **4** (δ 51.92 ppm) was shielded significantly compared to that of the parent diazepine **3** (δ 54.0 ppm). The shielding of C4-carbon signal by 2.08 ppm indicates that the acetyl group at N5 position adopts the *exo* orientation (*syn* to C4). The *exo* orientation of the acetyl group at N5 end is supported by semiempirical MO calculations (**Figure 1**, *endo*-*exo*).

The C4-carbon signal for the N_1,N_5-benzoyl derivative **5** was not shielded / deshielded significantly compared to that of the parent diazepine **3.** Hence, the X-ray crystal structure of **5** and semi-empirical MO calculations were utilized to predict the orientation of benzoyl group at N5. The semi-empirical MO calculations (AM1 and PM3) and X-ray crystallography predict the *exo* orientation of the benzoyl group at N5 (**Figure 1**, *endo-exo*).

Ring conformations

The N_1,N_5-diacetyl derivative **4** may prefer to adopt any of the chair conformations **CE, CA** or the boat conformations **BE**, **BA** (**Figure 2**). In the chair **CA** and boat **BA** forms, the coupling constants $J_{3a,4a}$ and $J_{3e,4a}$ are expected to be around 2-5 Hz. But one of the observed coupling constants was larger (12.7 and 4.9 Hz). In addition, analysis using Dreiding models indicated that the chair **CA** and boat conformations **BA** require an approximate *cis* ($\varphi_{3a,4a}$) and *trans* ($\varphi_{3e,4a}$) angle of 60°. But the *cis* and *trans* angles calculated using DAERM from the coupling constant values were 169° and 49°, respectively. Hence, on the basis of the observed coupling constants and calculated dihedral angles the possibility of the chair **CA** and boat **BA** conformations was ruled out.

Since the C2-C3-C4 part of the chair conformation **CE** and boat conformation **BE** are almost similar, protons at C3 and C4 are expected to show similar coupling constants. Hence, the coupling constants can not be used to decide the possibility between the conformations **CE** and **BE**. Thus, the choice between the conformations **CE** and **BE** could be decided by using Drieding models which indicated that the dihedral angle between the planes C10-N1-C2 and N1-C2-C3 would be around 60° for chair conformation **CE** and around 0° for boat conformation **BE**. The dihedral angle C10-N1-C2-C3 calculated from AM1 and PM3 semiempirical MO calculations for the compound **4** were -4.24° and 3.47°, respectively. Hence, the molecule **4** prefers to adopt boat conformation **BE**. The heats of formation values from AM1 and PM3 calculations (**Tables III** and **IV**) also showed a preference for the boat conformation **BE** (**Figure 3**).

The N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin-2-one **5** prefers boat conformation **BE** on the basis of the discussion made in the case of the N_1,N_5-diacetyl derivative **4**. The AM1 and PM3 calculations and X-ray crystallographic studies showed a preference for boat conformation **BE** with *endo* orientation of the benzoyl group at N1 and *exo* orientation of the benzoyl group at N5 (**Figure 3**).

X-Ray crystallography

In order to study the conformation of the ring and orientations of the benzoyl groups in the solid state, the crystal structure of N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin-2-one **5** was solved. The seven membered ring adopts boat conformation[9] **BE** (**Figure 4**). The dihedral angle C2-C3-C4-C13 = -169.59° indicates the equatorial orientation of the methyl group. The dihedral angle C4-N5-C22-O23 =

Table II — The vicinal coupling constant data (in Hz) and the corresponding dihedral angles (in degrees) estimated using DAERM of the N_1,N_5-diacyl tetrahydro-1,5-benzo diazepin-2-ones 4 and **5** and parent amine **3**

Compd	$J_{3e,4a}$	$J_{3a,4a}$	$\phi_{3e,4a}$	$\phi_{3a,4a}$
4	4.89	12.70	49	169
5	5.73	11.47	44	164
3	4.20	7.50	41	161

Table I — Spectral data of compounds prepared **4** and **5**

Compd	IR (cm^{-1})	^{1}H NMR ($CDCl_3$, δ, ppm)	^{13}C NMR ($CDCl_3$, δ, ppm)	Mass (M^+)
4	1720 (C(O)-N1-CO) 1665 1640 (N1-CO, N5-CO)	1.13 (3H, d, Me at C4), 1.84 (3H, s, Me at N5), 2.21 (1H, dd, H3A at C3), 2.49 (1H, dd, H3B at C3), 2.67 (3H, s, Me at N1), 5.23 (1H, m, C4-H), 7.21-7.53 (4H, m, aromatic).	18.6 (Me at C4), 22.8 (Me at N5), 27.8 (Me at N1), 43.0 (C3), 51.9 (C4), 129.0-130.2 (aromatic), 133.5, 136.6 (ipso), 169.5 (C2), 171.3 (COMe at N5), 172.8 (COMe at N1).	260
5	1715 (C(O)-N1-CO) 1700 1655 (N1-CO, N5-CO)	1.29 (3H, d, Me at C4), 2.58 (1H, dd, H3A at C3), 2.62 (1H, dd, H3B at C3), 5.30 (1H, m, C4-H), 7.00-7.85 (14H, m, aromatic)	17.8 (Me at C4), 41.9 (C3), 55.3 (C4), 126.6-131.7 (aromatic), 133.1, 134.7, 135.0, 137.7 (ipso), 170.2 (C2), 171.6 (COPh at N5), 173.8 (COPh at N1).	384
3	1659 (C=O) 3254 & 3296 (N1-H & N5-H)	1.30 (3H, d, Me at C4), 2.41 (1H, dd, H3A at C3), 2.61 (1H, dd, H3B at C3), 3.5 (1H, b,N5-H), 3.99 (1H, m, C4-H), 8.2(1H, b, N1-H) 6.7 – 7.0 (4H, m, aromatic)	23.6 (Me at C4), 41.5 (C3), 54.0 (C4), 120.9-125.5 (aromatic), 128.0, 138.3(ipso) 173.2(C2)	

1.20° indicates the coplanar orientation of the benzoyl group at N5 with reference to C4-N5-C11 plane in N_1,N_5-dibenzoyl derivative **5.** On the other hand the dihedral angle C2-N1-C14-O15 = 136.10° indicates the deviation of benzoyl group at N1 from the coplanarity with reference to C2-N1-C10 plane. This may be due to the partial delocalization of lone-pair on nitrogen (N1) with C_2=O group. In addition, these dihedral angles suggested an *endo* orientation of the benzoyl group at N1 and *exo* orientation of the benzoyl group at N5.

The estimated dihedral angles using DAERM[7] ($\varphi_{3a,4a}$ = 164° and $\varphi_{3e,4a}$= 44°, **Table II**) agree with the angles found in the crystal structure of **5** (H3A-C3-C4-H4 = - 167.1° and H3B-C3-C4-H4 = - 49.2°) and angles found in the AM1 (H3A-C3-C4-H4 = 169.5° and H3B-C3-C4-H4 = 51.1°) and PM3 (H3A-C3-C4-H4 = 162.5° and H3B-C3-C4-H4 = 46.9°) calculations.

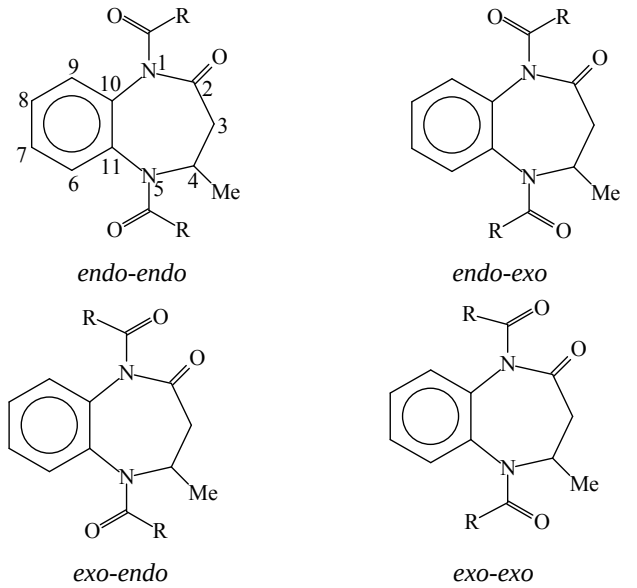

Figure 1

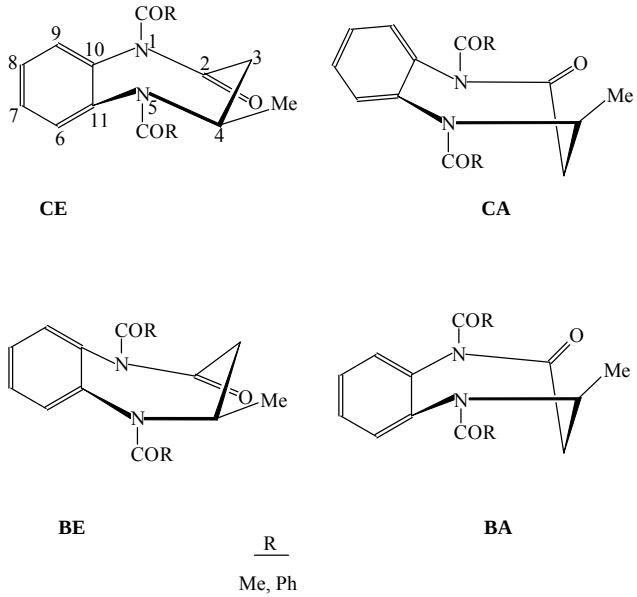

Figure 2 — possible conformatio of *N*-acyltetrahydro-1,5-benzodiazepin-2-ones **4** and **5**

Semiempirical MO calculations

The heats of formation of various ring conformations of the N_1,N_5-diacyltetrahydro- benzodiazepin-2-ones **4** and **5** obtained by semiempirical MO calculations using the AM1 and PM3 methods available in MOPAC-6(ref.8) were used to derive the relative stability of the conformations.

For both N_1,N_5-diacyltetrahydrobenzodiazepin-2-ones **4** and **5** the possible ring conformations with *exo/endo* orientations of acyl groups at N1 and N5 (**Figures 1** and **2**), such as chair (**CE**), a flipped chair in which methyl group occupying axial position (**CA**), a boat form with the methyl group occupying equatorial orientation (**BE**) and a boat conformation with methyl group occupying axial orientation (**BA**), were considered. The optimization of these conformations was carried out by varying the torsion angles C2-N1-C=O and C4-N5-C=O within the possible ranges in 10° increments and the results are summarized in **Table III**.

The relative formation energies obtained for various conformations of the N_1,N_5-diacyltetrahydrobenzodiazepin-2-ones **4** and **5** arrived at by the AM1 and PM3 methods are presented in **Table III**. The calculations indicated that the boat conformation (**BE**) with *endo* orientation of the acyl groups at N1 and *exo* orientation of the acyl groups at N5 is the most favoured conformation for the N_1,N_5-diacyltetrahydrobenzodiazepin-2-ones **4** and **5** in both the AM1 and PM3 methods. The AM1 optimized structures of N_1,N_5-diacetyltetrahydro- benzodiazepin-2-one **4** are given in **Figure 5** as a representative example. An excellent agreement was observed between X-ray crystallographic analysis and semiempirical MO calculations while comparing the bond lengths, bond angles and dihedral angles of **BE** conformation of **5** (**Table IV**).

Thus, it was concluded that the N_1,N_5-diacetyl and N_1,N_5-dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin-2-ones (**4** and **5,** respectively) prefer a boat

Table III — Calculated relative heats of formation (kcal mol^{-1}) of various ring conformations of the N_1,N_5-diacyltetrahydro-1,5-benzodiazepin-2-ones **4** and **5** by AM1 and PM3 methods

		Relative heats of formation (kcal mol^{-1})							
		Conformations AM1				Conformations PM3			
Compd	Rotamers	CE	CA	BE	BA	CE	CA	BE	BA
4	*endo-endo*	11.12	9.62	2.56	7.13	4.40	2.19	0.96	3.73
	endo-exo	5.80	5.50	0.00	3.28	2.82	2.09	0.00	2.14
	exo-endo	10.84	9.44	5.17	8.99	2.14	2.09	0.61	4.41
	exo-exo	8.09	7.50	4.38	7.17	1.98	0.98	0.09	3.30
5	*endo-endo*	8.85	6.37	1.71	5.43	4.39	3.16	0.97	4.80
	endo-exo	3.88	3.34	0.00	2.40	2.86	3.11	0.00	2.50
	exo-endo	7.14	4.91	0.91	5.17	3.85	2.92	0.25	5.40
	exo-exo	5.52	5.19	1.78	4.04	2.71	1.95	1.55	3.17

Table IV — Comparison of selected bond lengths (Å), bond angles (degrees) and dihedral angles (degrees) of N_1,N_5-dibenzoyltetrahydro-1,5-benzodiazepin-2-one **5** from X-ray crystallography and semiempirical MO calculations (AM1 and PM3)

	X-ray	AM1	PM3
	Bond length (Å)		
N1-C2	1.40	1.41	1.44
N1-C10	1.44	1.43	1.45
N1-C14	1.43	1.43	1.49
C14-O15	1.21	1.24	1.21
C4-N5	1.48	1.46	1.50
N5-C11	1.43	1.42	1.46
N5-C22	1.38	1.40	1.44
C22-O23	1.23	1.25	1.22
	Bond angle (degrees)		
C2-N1-C10	120.10	119.39	119.63
C2-N1-C14	121.68	122.51	119.52
C10-N1-C14	116.64	117.17	116.15
N1-C14-O15	119.10	119.10	118.77
C4-N5-C11	15.70	117.45	115.12
C4-N5-C22	118.62	119.08	119.48
C11-N5-C22	122.70	122.55	119.42
N5-C22-O23	120.50	119.04	118.38
	Dihedral angle (degrees)		
N1-C2-C3-C4	81.40	-77.09	-81.46
C2-C3-C4-N5	-45.60	49.82	41.29
C3-C4-N5-C11	-44.50	36.80	47.34
C4-N5-C11-C10	71.50	-68.77	-75.20
N5-C11-C10-N1	3.40	-0.73	2.94
C11-C10-N1-C2	-45.80	46.29	36.63
C10-N1-C2-C3	-10.90	5.63	17.50
C2-C3-C4-C13	-169.59	176.44	166.50
C2-N1-C14-O15	136.10	-141.16	-99.33
C10-N1-C14-O15	-29.60	27.71	56.30
C4-N5-C22-O23	1.20	-3.37	6.19
C11-N5-C22-O23	-158.30	165.38	157.68

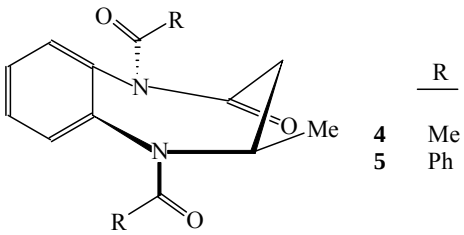

Figure 3 — Preferred conformation of N_1,N_5-diacyltetrahydro-1,5-benzodiazepines **4** and **5**

conformations **BE** with *endo* orientation of the acyl groups at N1 position and *exo* orientation (*syn* to C4) of acyl groups at N5 position on the basis of observations made from NMR spectral techniques and semiempirical MO calculations. The X-ray crystallography of N_1,N_5-dibenzoyl-tetrahydro-4-methyl-1,5-benzodiazepin-2-one **5** also supported the preference for the boat conformation (**BE**) with *endo* and *exo* orientations of benzoyl groups at N1 and N5 positions, respectively.

Experimental Section

All the melting points were determined using an electrically heated block with a calibrated thermometer and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-435 spectrohotometer as KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded[5c] on a Bruker AMX-400 MHz and Bruker DRX-500 MHz spectrometers in $CDCl_3$ solution using TMS as internal reference. Mass spectra were recorded on a Jeol JMS-D 300 spectrometer operating at 70 eV.

Computational details

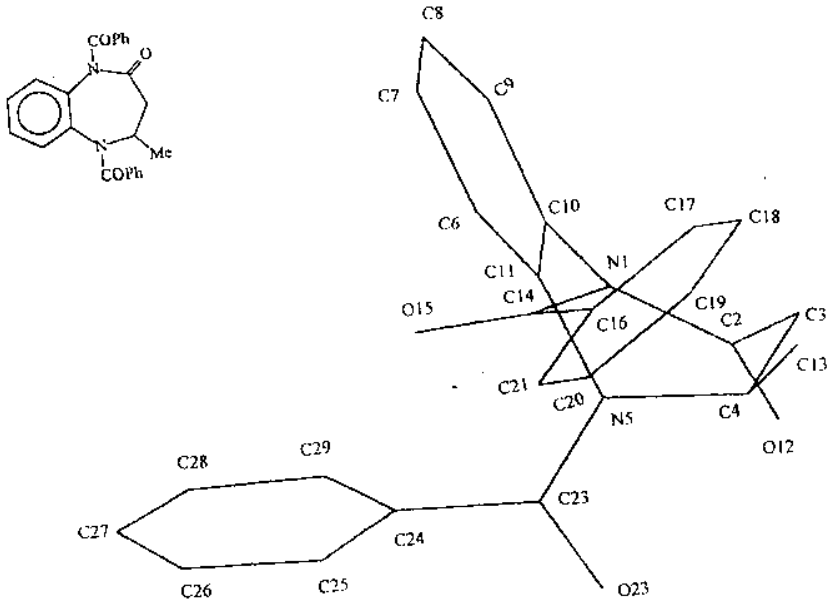

Figure 4 — X-ray crystal structure of **5**

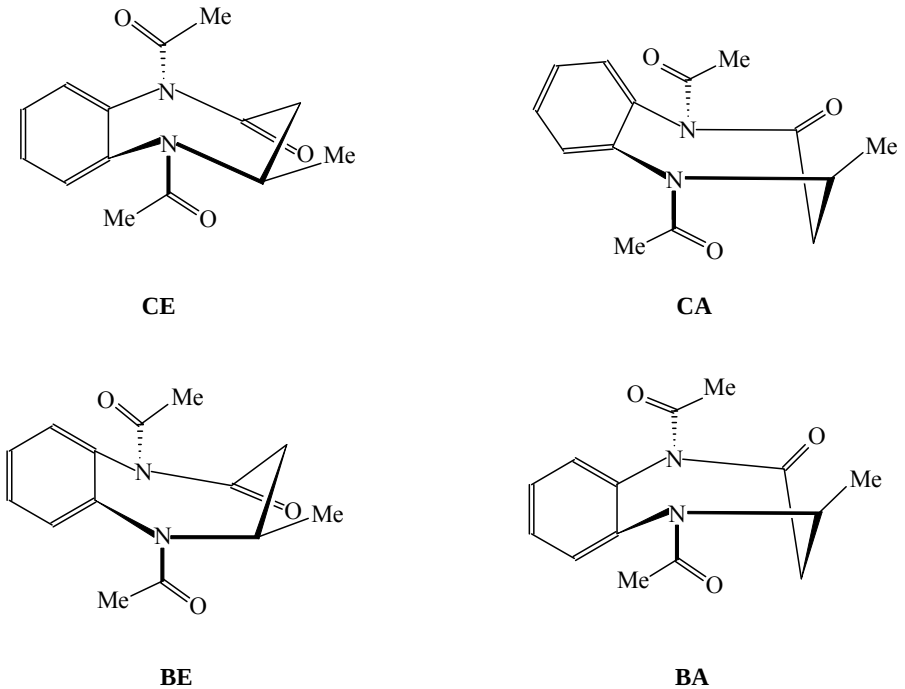

Figure 5 — AM1 optimized structures of **4**

The AM1 and PM3 methods available in MOPAC 6.1 version were used to perform the calculations on Pentium personal computers. The optimization of the conformations was performed by using an analytic gradient minimization method (BFGS, Precise option). Moreover, eigenvector (EF option) procedure was used to lower the mean gradient up to values below 0.01 kcal mol^{-1}.

Tetrahydro-4-methyl-1,5-benzodiazepin-2-one 3. A mixture of 1,2-diaminobenzene (10.80 g, 100 mmole), 5.5 *N* hydrochloric acid (15 mL), crotonic acid (13 g, 100 mmole) were heated at 100 °C for 6 hr. The reaction-mixture was then poured into crushed ice and basified with ammonia solution. The precipitated solid

was separated, washed thoroughly with water and dried. The solid was dissolved in ethanol, allowed to reflux with charcoal, filtered through fluted filter paper, evaporated partially over water-bath and kept aside at 10-15°C. Colourless crystals of **3** obtained were separated. m.p. 182-83°C (lit. m.p. 184-85°C, ref.10).

***N*$_1$,*N*$_5$-Diacetyltetrahydro-4-methyl-1,5-benzodiazepin-2-one 4**: To a solution of tetrahydrobenzodiazepin-2-one **3** (0.88 g, 5 mmole) in anhydrous benzene (50 mL) was added triethylamine (2.8 mL, 20 mmole) and acetic anhydride (2 mL, 20 mmole). The contents were allowed to reflux on a water-bath for 6 hr. The reaction-mixture was washed with sodium bicarbonate solution (10%), water and dried with sodium sulphate. Evaporation of the solvent and purification by recrystallization from ethanol gave colourless crystals of **4**, yield 0.95 g (73.0 %), m.p. 98-99°C. Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.62; H, 6.15; N, 10.77. Found: C, 64.36; H, 6.37; 10.52%.

***N*$_1$,*N*$_5$-Dibenzoyltetrahydro-4-methyl-1,5-benzodiazepin-2-one 5**. To a solution of tetrahydrobenzodiazepin-2-one **3** (0.88 g, 5 mmole) in anhydrous benzene (50 mL) was added triethylamine (2.8 mL, 20 mmole) and benzoyl chloride (2.4 mL, 20 mmole). The reaction mixture was allowed to reflux on a water-bath for 5 hr. The reaction mixture was poured into water (200 mL) and the organic layer was separated. The aqueous layer was extracted with benzene (4×10 mL). The organic layers were combined and washed with 2*N* solution of HCl (5×25 mL) followed by water (5×100 mL) and dried with anhydrous sodium sulphate. The solvent was evaporated and purification by crystallization of the solid from ethanol gave colourless crystals of **5**, yield 1.42 g (74.0%), m.p. 155-56°C. Anal. Calcd for $C_{24}H_{20}N_2O_3$: C, 75.00; H, 5.20; N, 7.29. Found: C, 75.32; H, 5.43; N, 7.05%.

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