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Dynamic Processes in *N*-Acylated 1,2-dihydro-2,2,4-trimethylbenzo(*h*)quinoline: A Comparative Study by NMR Spectroscopy and Quantum Chemistry

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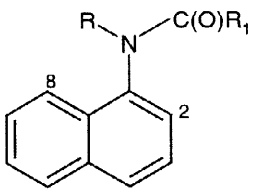
Abstract: The results of conformational studies on several *N*-acyl derivatives of 1,2-dihydro-2,2,4-trimethylbenzo(*h*)quinoline are reported. A comparative study by NMR spectroscopy and semiempirical quantum chemical modelling using the AM1 SCF method revealed that the nitrogen atom is pyramidal with a substantial out-of-plane torsion of the acyl group and that the molecules adopt the *E* conformation in the ground state. Also, the ^{1}H NMR signals revealed the interconversion of a pair of enantiomers for all compounds studied, with $\Delta G^{\neq}$ in the range 56.1-74.1 kJ mol^{-1}. A good correlation exists between the experimental $\Delta G^{\neq}$ values and the energy barriers, E_A, predicted by the semiempirical AM1 SCF model.

INTRODUCTION

Semiempirical quantum chemical calculations have shown the racemisation of *N*-1-naphthylamides[1,2] (Scheme 1) to occur *via* a planar transition state with passage of the acyl group preferred over position (2) of the naphthyl ring rather than over position (8).[2]



Scheme 1

Passage over position (8) causes a considerable out-of-plane deformation of the amide group and therefore it would be energetically less favoured. Consequently, factors reducing the sp^2 character of the amide nitrogen destabilise the ground state of the molecule and both directions of rotation about the *N*-aryl bond should

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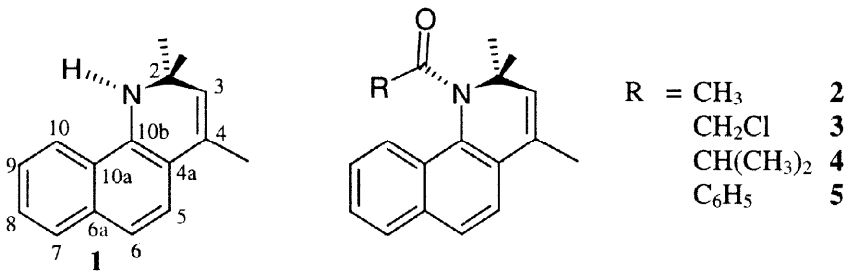
become competitive. The rotation of the acyl group past position (8) of the naphthylamides has been modelled using *N*-tosylbenzo(*h*)quinolone derivatives.[3,4] Due to the steric restrictions, the latter are characterised by high inversion barriers and hence by unusually slow inversion rates.

In this paper, the results of conformational studies on several *N*-acylated 1,2-dihydrobenzoquinolines (*cf.* Scheme 2) are reported. The substituents at the carbonyl carbon were chosen to discern the possible effects of size, electronegativity, and π–π conjugation on the inversion barrier.



Scheme 2

RESULTS AND DISCUSSION

Due to the hindered rotation about the N-C partial double bond, *N,N*-unsymmetrically-substituted amides can prefer to adopt either the *cis* or *trans* conformation.[5] However, at room temperature the proton and carbon-13 NMR spectra of each of the title compounds displayed only a single set of signals, most probably as a result of fast rotation about the N-C(O) bond. This is supported by the semiempirical AM1 SCF calculations, which predict low rotational barriers. The calculated E_A values were 13.8, 19.2, 19.7 and 18.8 kJ mol^{-1} for **2-5**, respectively, which after empirical corrections[6] correspond to $\Delta G^{\neq}$ values of 41.0, 49.8, 50.2, and 49.0 kJ mol^{-1}, respectively. These calculations also predict that the nitrogen atom is highly pyramidalised in the ground state of the molecules with a significantly longer N-C(O) bond (*ca.* 1.41 Å) than the usual C-N partial double bond found in amides (~1.35 Å[1]). The AM1 calculated torsion angles defined by the three C-N bonds are 154.2°, 158.3°, 162.5° and 163.4° in **2-5**, respectively.

The semiempirical AM1 calculations also predict the *E* conformer of compounds **2-5** (by analogy with the *N*-1-naphthylamides[1] the oxygen is *trans* to the aromatic ring) to be 8-17 kJ mol^{-1} more stable than the *Z* conformer. Thus, even at slow exchange rate, only a single set of signals would be observed in the NMR spectra due to the predominance of the *E* conformer. However, solvent effects may substantially alter the conformer populations as shown for the tertiary *N*-1-naphthylamides.[7]

The quantum-chemically predicted preference for the *E* conformer is supported by the NOE enhancements presented in Table 1 which indicate the protons of the acyl group to be closer to the hydrogen at the *peri* position, H(10), than to the hydrogens of the geminal methyl groups. Several factors may affect the

conformational preference in acylated benzo(*h*)quinolines, including (1) the less effective size of oxygen as compared to the alkyl groups, (2) the weak intramolecular O...H_3C interaction, and (3) the bipolar repulsion between the carbonyl group and the π-electron system of the aromatic ring. None of these effects appears to speak against predominance of the *E* conformer.

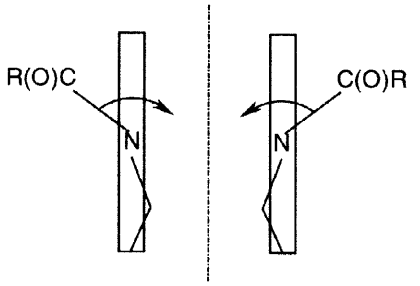
Table 1. NOE enhancements for compounds **2-5**, expressed as a percentage of the original signals upon irradiation of the protons of the geminal methyls and acyl groups. H(3) and H(10) denote the hydrogen atoms at the respective positions of the benzo(*h*)quinoline ring (Scheme 2) and (+) and (-) indicate the up- and downfield signals, respectively.

Compound	Observed protons	Irradiated protons				
		CH_3(-)	CH_3(+)	C(O)CH_3 C(O)CH	ClCH(+) $CHCH_3$(+)	ClCH(-) $CHCH_3$(-)
2[a]	H(10)	1.4	1.5	1.7	-	-
	H(3)	8.5	4.9	0	-	-
	CH_3(+)	-58.2	-100	0	-	-
	CH_3(-)	-100	-55.7	0	-	-
3[b]	H(10)	0.5	2.0	-	0	7.6
	H(3)	7.7	2.0	-	0	0
	CH_3(+)	0	-100	-	0	0
	CH_3(-)	-100	0	-	0	0
4[c]	H(10)	0.8	1.4	4.7	0.9	2.0
	H(3)	7.9	4.0	0	0.3	0
	CH_3(+)	-35.1	-100	0	0	0
	CH_3(-)	-100	-31.2	0	0	0
5[d]	H(10)	0.1	0.8	-	-	-
	H(3)	4.0	1.1	-	-	-
	CH_3(+)	-3.4	-100	-	-	-
	CH_3(-)	-100	-2.1	-	-	-

[a] NOE experiments performed at 5.5°C; [b] at -20°C; [c] at 25°C and [d] at -60°C.

Inversion barriers estimated by dynamic NMR spectroscopy.

At room temperature, a pair of slightly broadened signals for the geminal methyl groups was observed for the acylated benzo(*h*)quinoline derivatives, with the exception of the benzoyl derivative. This implies the existence of a nonplanar molecule (Scheme 3). The flip of the acyl group from one side of the benzoquinoline ring to the other (called inversion below) should lead from one enantiomer to the other, *i.e.* racemisation. The dynamic exchange process is evident from the temperature dependent NMR signals of the geminal methyl groups (see Fig. 1).[8]



Scheme 3

At the coalescence temperature, the barrier to inversion (Table 2) was calculated using equation (1a) for an uncoupled two-site system or equation (1b) when coupling was present[8]

$$\Delta G^{\neq} = 1.914*10^{-2} T_c\,[9.972 + \log (T_c / \Delta\nu)] \quad (1a)$$

$$\Delta G^{\neq} = 1.914*10^{-2} T_c\,[9.972 + \log (T_c / \sqrt{(\Delta\nu^2 + 6J_{AB}^2)})] \quad (1b)$$

where T_c is the coalescence temperature in K, $\Delta\nu$ [Hz] is the difference between resonance frequencies of the A and B sites under the conditions of slow exchange, and J_{AB} is the coupling constant in Hz.

In compound **3**, there are two interconverting sets: the C(2) methyls and the protons of the chloromethyl group resulting in the observation of two coalescences (Fig. 1). In the *N*-isobutyryl substituted compound **4**, two coalescences were also observed corresponding to the geminal methyl signals and methyl signals of the isopropyl group (Table 2).

Table 2. The activation energies ($\Delta G^{\neq}$) for nitrogen inversion of the compounds **2-5**, calculated at the coalescence temperature (T_c). The difference of the resonance frequencies ($\Delta\nu$) of the geminal methyl groups at the temperature shown in parentheses; the NMR frequency was 400 MHz. The solvent was tetrachloroethane-d_2 except for compound **5** where it was $CDCl_3$.

Compound	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^{\neq}$ (kJ mol^{-1})
2	379 (303 K)	342.0	64.89
3	368 (298 K)	363.0	69.29
	84[a] (298 K)	342.4	69.16
4	337 (298 K)	383.5	73.60
	65[b] (298 K)	360.8	74.01
5	306 (213 K)	294.0	56.02

[a]Separation of the hydrogens of the chloromethyl group (J_{HH} 13.8 Hz);

[b]Separation of the methyls of the isopropyl group.

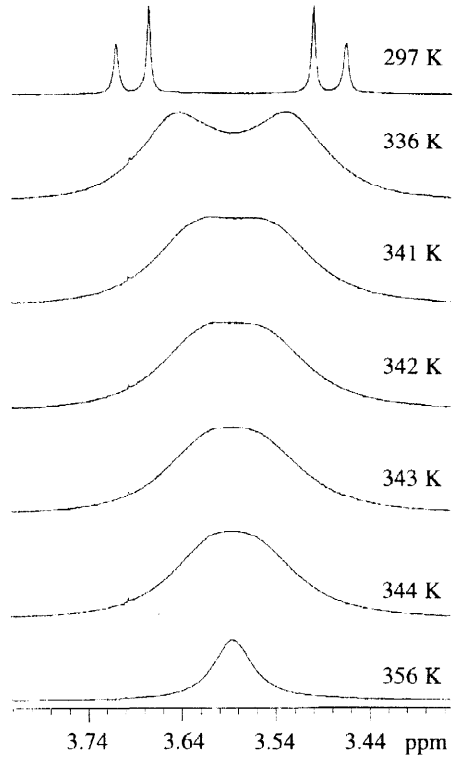


Fig. 1. A selected part of the ^{1}H NMR spectrum of compound **3** at various temperatures showing the coalescence of the methylene protons at 342 K.

Potential energy surface (PES) of inversion.

The semiempirical AM1 SCF method[9] was used to model the potential energy surface of the inversion. The passage of the carbonyl group over the *peri* position, *i.e.* C(10), was modelled by varying the torsion angle C(O)-N-C(10b)-C(10a) in steps of 5 or 10 degrees, and then in smaller steps (0.5 or 1.0 degrees) close to the transition state. The final transition state geometry of inverting molecules was confirmed by the single point calculations at the fixed reaction coordinate. For comparison, the inversion dynamics in *N-para*-tosyl-benzo(*h*)quinolone (**6**) was also investigated. The AM1 SCF calculated heats of formation for ground and transition states of the compounds **1-6** are given in Table 3.

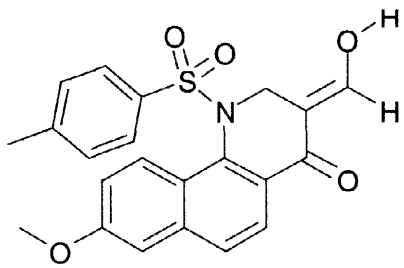


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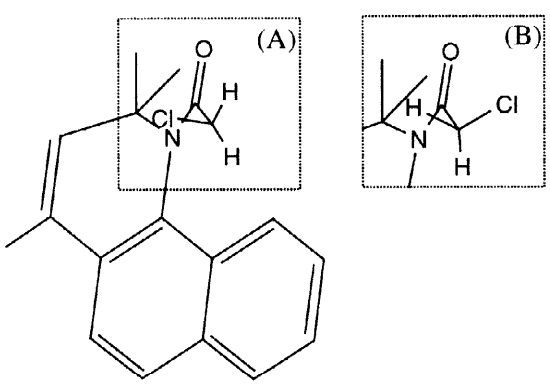
Table 3. The AM1 SCF calculated heats of formation for the *E* (E_{GS1}) and *Z* conformers (E_{GS2}), the transition state of inversion (E_{TS}) and the energy barriers for inversion ($E_{A(INV)}$).

Compound	E_{GS1}[a] (kJ mol^{-1})	E_{GS2}[b] (kJ mol^{-1})	E_{TS}[c] (kJ mol^{-1})	$E_{A(INV)}$ (kJ mol^{-1})
1	205.64		206.48	0.8
2	107.95	121.17	146.02	38.1
3	85.90	104.39	128.87	43.0
4	68.83	86.94	119.66	50.8
5	262.76	268.32	292.46	29.7
6	-349.57	-335.93	-296.65	52.9

[a] Corresponds to the *E* conformation in the amides **2-6**; [b] Corresponds to the *Z* conformation in the amides **2-6**; [c] Corresponds to the maximum point on the potential curve for inversion.

Evidently, the nitrogen atom in **1** undergoes a rapid inversion with a very small energy barrier ($E_{A(AM1)}$ = 0.8 kJ mol^{-1}). Also, the benzo(*h*)quinoline ring in **1** has almost planar geometry in the transition state, with a symmetric potential curve as expected for classical nitrogen inversion. However, acylation of the nitrogen substantially increases the inversion barrier, as shown in Table 3.

For the *E* conformer of compound **3**, rotation around the chloromethyl-C(O) bond produced two different energy minima on PES. The rotamers are depicted in Scheme 4.



Scheme 4

Therefore, the grid search for the transition state of inversion was carried out for both the (A) and (B) rotamers. It was found that the calculated activation energy was higher for the more stable rotamer. Since the AM1 SCF calculated barrier for the **3***E*-(A)→**3***E*-(B) interconversion was rather low, *i.e.* 8.8 kJ mol^{-1}, it was presumed that the inversion is accompanied by the simultaneous rotation of the chloromethyl group. The full PES of *N*-

isobutyryl derivative (**4**) is even more complicated due to the conformationally flexible acyl group. To establish the most probable geometry of **4** in the ground state we utilised the experimentally determined NOE ratios (for the method, see ref.[10,11]). The NOE enhancements (η) of the NMR proton signals of the isopropyl group upon irradiation of the H(10) proton of the benzo(*h*)quinoline ring are presented in Fig. 2.

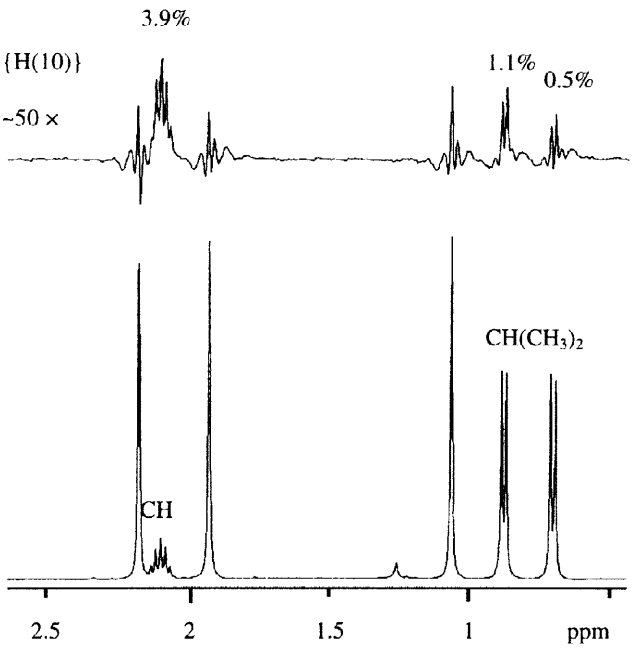
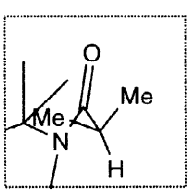


Fig. 2. Aliphatic region of the 400 MHz NOE difference spectrum (above), vertically amplified *ca.* 50 times with respect to the reference spectrum (below) of compound **4** obtained upon irradiation of H(10).

The results of the NOE analysis were in accordance with the conformation predicted by the AM1 SCF calculations:



It is well known that the AM1 method significantly underestimates the intramolecular conformational transition barriers in the amides.[2,6,9] However, for certain dynamic processes, a satisfactory correlation between the calculated and experimental transition barriers have been obtained. In particular, a good linear relationship has been found for the amide bond rotation barriers in amides and their thioderivatives.[6]

In this work, a good correlation between the computed inversion barriers, E_A, and the experimentally determined activation free energies, $\Delta G^{\neq}_{exp}$, was obtained (Fig. 3):

$$\Delta G^{\neq}_{exp} = (0.9\pm0.1)E_{A(AM1)} + (30.9\pm2.7) \quad (kJ\ mol^{-1}) \qquad (2)$$

$$R^2 = 0.986;\ s = 1.15$$

From equation (2), compound **1** should have a free energy of activation 31.6 kJ mol^{-1}, which is close to the experimental barriers for nitrogen inversion in ammonia and simple alkyl-substituted amines[12] (~25 kJ mol^{-1}). Our results also display the increase of the inversion barriers with the increasing effective size of the acyl substituent (Ph < Me < CH_2Cl < ^iPr). A substantially smaller barrier for **5** (R = Ph) is unexpected from the simple consideration of steric interactions. However, it can be related to the destabilising repulsion of aromatic π-electron systems of aromatic rings in the ground state conformation. Alternatively, the effective size of the carbonyl group in **5**, interacting with the other parts of molecule, could be reduced in the transition state due to the possible electron delocalisation between the phenyl and carbonyl groups.

Inv. barriers (kJ mol^{-1})	**2**	**3**	**4**	**5**	**6**[a]
E_A (AM1)	38.1	43.0	50.8	29.7	52.9
$\Delta G^{\neq}_{exp}$	64.9	69.2	73.8	56.0	77.4

[a] the experimental $\Delta G^{\neq}$ is calculated from the kinetic data reported in ref.[4].

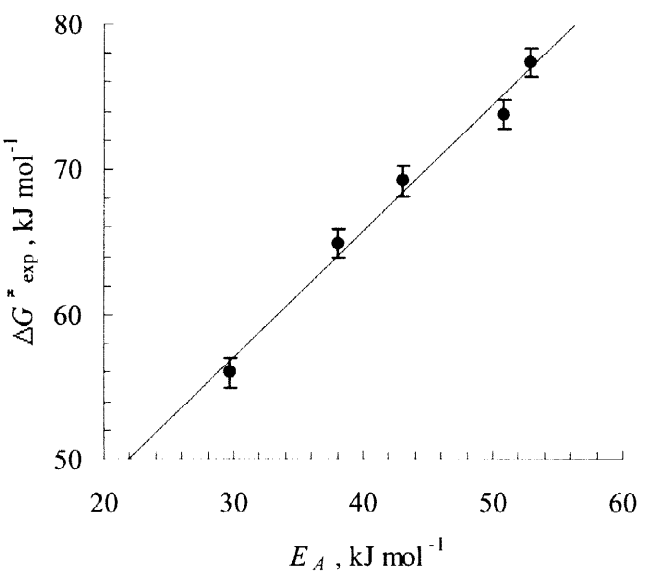


Fig. 3. Graphical plot of the experimentally determined $\Delta G^{\neq}_{exp}$ *vs.* the AM1 SCF calculated E_A for the inversion barrier in the compounds **2-6**.

Induction effects raise the rotational barrier about the amide N-C(O) bond.[14] Consequently, the inversion barrier in **3** should be increased due to the concerted rotation about the N-C(O) bond. However, this effect, while important in the gas phase, is usually rather small in liquids.[14] Therefore, the higher inversion barrier in *N*-chloroacetyl derivative (**3**) as compared to the *N*-acetyl derivative (**2**) is a result of steric effects.

EXPERIMENTAL

The proton and carbon-13 NMR spectra were recorded on JEOL LAMBDA 400 (400 MHz) and JEOL ALPHA 500 (500 MHz) spectrometers in $CDCl_3$ at 298 K. The chemical shifts are given in ppm relative to TMS used as an internal standard. The temperature in dynamic NMR measurements, performed in either $C_2D_2Cl_4$ or $CDCl_3$, was calibrated using the ethylene glycol thermometer for high temperature and the methanol thermometer for low temperature. The infrared (IR) spectra were recorded on a GALAXY Series FT-IR 6030 (Mattson Instruments). The electron ionization mass-spectra were recorded on a VG 7070E (VG Analytical) spectrometer with direct inlet and the electron impact energy 70 eV. The accurate mass measurements were performed on a ZABSpec spectrometer using the peak matching technique at a resolution of 8000-9000.
The semiempirical AM1 SCF[9] calculations were performed using the MOPAC 6.0 program package.[15]

The title compounds were prepared by acylation of 1,2-dihydro-2,2,4-trimethyl-benzo(*h*)quinoline (**1**) with the respective commercially available acyl chlorides. The synthesis of **1** is described elsewhere.[16] The synthesis of *N*-acetyl-1,2-dihydro-2,2,4-trimethylbenzo(*h*)quinoline (**2**) is described as a general method for the preparation of the *N*-acylated compounds (**2-5**). The syntheses were carried out at room temperature and the yields ranged between 38 and 58%. An exception was the synthesis of **4**, which was accelerated by heating of the reaction mixture for 48 hours at 60°C to give the product in 9.3% yield.

N-Acetyl-1,2-dihydro-2,2,4-trimethylbenzo(h)*quinoline* (**2**). A magnetically stirred mixture of 0.5 g (2.2 mmol) of 1,2-dihydro-2,2,4-trimethylbenzo(*h*)quinoline (**1**) and 0.1 ml (1.4 mmol) of acetyl chloride in 10 ml of dioxane was left to react for 48 hours at room temperature, at which time the reaction mixture was quenched with 10 ml of water and extracted with ether. The ether extracts were collected, dried over sodium sulphate and concentrated at reduced pressure to yield 0.63 g of yellow oil. The crude product was passed through a silica gel column eluting with the mixture of dichloromethane-hexane (4:1) to yield 0.14 g (37.7 %) of *N*-acetyl-1,2-dihydro-2,2,4-trimethylbenzo(*h*)quinoline (**2**) as a slightly yellow oil and 0.27 g of starting material (**1**).
IR (cm^{-1}): 3060, 2966, 2919, 2849, 1731, 1673 (C=O), 1558, 1508, 1463, 1363, 1310, 1265, 1243, 1175, 826, 752; MS (EI, 70 eV): 265 (M^+, $[C_{18}H_{19}NO]^+$, 9%), 250 ($[M-CH_3]^+$, 9%), 222 ($[M-C_2H_3O]^+$, 8%), 208 ($[M-C_3H_5O]^+$, 100%), 43 ($[CH_3CO]^+$, 15%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): 7.91 (d, ^{3}J 8.4, 1H, H(10)), 7.83 (d, ^{3}J 8.1, 1H, H(7)), 7.74(d, ^{3}J 8.5, 1H, H(6)), 7.52 (m, ^{3}J 8.4, 6.8, 1H, H(9)), 7.50 (d, ^{3}J 8.5, 1H, H(5)), 7.45 (m, ^{3}J

8.1, 6.8, 1H, H(8)), 5.82 (q, ^{4}J 1.5, 1H, H(3)), 2.17 (d, ^{4}J 1.5, 3H, =CCH$_3$), 2.01 (br s, 3H, CH$_3$), 1.59 (s, 3H, C(O)CH$_3$), 1.05 (br s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): 173.7 (C(O)), 138.5 (C(3)), 133.6 (C(10b)), 133.2 (C(6a)), 130.7 (C(10a)), 128.9 (C(4)), 128.3 (C(7)), 128.1 (C(4a)), 126.8 (C(9)), 125.9 (C(6)), 125.7 (C(8)), 123.7 (C(10)), 121.1 (C(5)), 58.5 (C(2)), 28.0 (CH$_3$), 26.4 (CH$_3$CO), 25.3 (CH$_3$), 18.0 (=CCH$_3$). (Found for [C$_{18}$H$_{19}$NO]$^+$: 265.1467. Calcd.: 265.1469.).

N-Chloroacetyl-1,2-dihydro-2,2,4-trimethylbenzo(h)quinoline (**3**):

Yield: 58%; a yellow viscous oil; IR (cm^{-1}): 3059, 2974, 1690 (C=O), 1349, 1219, 828, 752, 677; MS (EI, 70 eV): 299 (M$^+$, [C$_{18}$H$_{18}$NOCl]$^+$, 10.5%), 284 ([M-CH$_3$]$^+$, 24.8%), 222 ([M-C$_2$H$_2$ClO]$^+$, 8.4%), 208 ([M-C$_3$H$_5$ClO]$^+$, 100%), 28 ([CO]$^+$); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): 7.87 (d, ^{3}J 8.4, 1H, H(10)), 7.86 (d, ^{3}J 8.1, 1H, H(7)), 7.78(d, ^{3}J 8.5, 1H, H(6)), 7.55 (m, ^{3}J 8.4, 6.8, 1H, H(9)), 7.51 (d, ^{3}J 8.5, 1H, H(5)), 7.48 (m, ^{3}J 8.1, 6.8, 1H, H(8)), 5.83 (q, ^{4}J 1.5, 1H, H(3)), 3.67 (d, ^{2}J 13.5, 1H, CH$_2$), 3.47 (d, ^{2}J 13.5, 1H, CH$_2$), 2.18 (d, ^{4}J 1.5, 3H, =CCH$_3$), 2.00 (br s, 3H, CH$_3$), 1.08 (br s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): 169.0 (C(O)), 138.1 (C(3)), 133.3 (C(6a)), 131.2 (C(10b)), 130.3 (C(10a)), 129.1 (C(4)), 128.9 (C(4a)), 128.6 (C(7)), 127.7 (C(9)), 126.7 (C(6)), 126.0 (C(8)), 122.5 (C(10)), 121.2 (C(5)), 59.3 (C(2)), 45.3 (CH$_2$), 27.6 (CH$_3$), 24.9 (CH$_3$), 18.0 (=CCH$_3$). (Found for [C$_{18}$H$_{18}$NOCl]$^+$: 299.1077. Calcd.: 299.1080.)

N-Isobutyryl-1,2-dihydro-2,2,4-trimethylbenzo(h)quinoline (**4**):

Yield: 9.3%; a pale yellow powder, m.p. 135-137°C (hexane-dichloromethane); IR (cm^{-1}): 3062, 2968, 2931, 2869, 1680 (C=O), 1557, 1508, 1466, 1379, 1299, 1208, 1175, 1080, 836, 787; MS (EI, 70 eV): 293 (M$^+$, [C$_{20}$H$_{23}$NO]$^+$, 19.6%), 278 ([M-CH$_3$]$^+$, 10,9%), 222 ([M-C$_4$H$_7$O]$^+$, 45.1%), 208 ([M-C$_5$H$_9$O]$^+$, 100%), 71 ([C$_4$H$_7$O]$^+$), 43 ([C$_3$H$_7$]$^+$); ^{1}H NMR (500 MHz, CDCl$_3$, 25°C): 7.88 (d, ^{3}J 8.5, 1H, H(10)), 7.82 (d, ^{3}J 8.1, 1H, H(7)), 7.70 (d, ^{3}J 8.5, 1H, H(6)), 7.49 (m, ^{3}J 8.5, 6.8, 1H, H(9)), 7.49 (d, ^{3}J 8.5, 1H, H(5)), 7.44 (m, ^{3}J 8.1, 6.8, 1H, H(8)), 5.76 (q, ^{4}J 1.5, 1H, H(3)), 2.17 (d, ^{4}J 1.5, 3H, =CCH$_3$), 2.10 (sept., ^{3}J 6.7, 1H, CH), 1,93 (s, 3H, CH$_3$), 1.06 (s, 3H, CH$_3$), 0.87 (d, ^{3}J 6.5, 3H, CH$_3$), 0.70 (d, ^{3}J 7.0, 3H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25°C): 181.8 (C(O)), 137.7 (C(3)), 133.2 (C(6a)), 133.1 (C(10b)), 131.1 (C(10a)), 128.9 (C(4)), 128.2 (C(7)), 127.9 (C(4a)), 126.8 (C(9)), 125.7 (C(8)), 125.4 (C(6)), 123.3 (C(10)), 121.1 (C(5)), 58.3 (C(2)), 35.4 (CH), 28.1 & 25.0 (2xCH$_3$), 20.1 & 17.4 (2x CH$_3$) 18.0 (=CCH$_3$). (Found for [C$_{20}$H$_{23}$NO]$^+$: 293.1780. Calcd.: 293.1783.)

N-Benzoyl-1,2-dihydro-2,2,4-trimethylbenzo(h)quinoline (**5**):

Yield: 42%; the yellow crystals, m.p. 92-93.5°C (hexane-dichloromethane); IR (cm^{-1}): 3063, 2972, 2928, 2861, 1656 (C=O), 1557, 1510, 1467, 1383, 1314, 1276, 1177, 844, 788, 713; MS (EI, 70 eV): 327 (M$^+$, [C$_{23}$H$_{21}$NO]$^+$, 21.4%), 312 ([M-CH$_3$]$^+$, 34.5%), 222 ([M-C$_7$H$_5$O]$^+$, 20.3%), 207 ([M-C$_8$H$_8$O]$^+$, 10.6%), 105

($[C_7H_5O]^+$, 100%), 77 ($[C_6H_5]^+$, 36.4%); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): 7.90 (d, ^{3}J 8.5, 1H, H(10)), 7.54 (d, ^{3}J 8.1, 1H, H(7)), 7.53 (d, ^{3}J 8.4, 1H, H(6)), 7.45 (d, ^{3}J 8.4, 1H, H(5)), 7.27 (m, ^{3}J 8.5, 6.8, 1H, H(9)), 7.20 (m, 2H, H(2') & H(6')) 7.19 (m, ^{3}J 8.1, 6.8, 1H, H(8)), 6.99 (tt, ^{3}J 7.4, ^{4}J 1.3, 1H, H(4')), 6.89 (m, 2H, H(3') & H(5')), 5.83 (q, ^{4}J 1.5, 1H, H(3)), 2.26 (d, ^{4}J 1.5, 3H, =CCH$_3$), 2.03# (s, 3H, CH$_3$), 1.27# (s, 3H, CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): 172.6 (C(O)), 138.6 (C(1'))136.7 (C(3)), 133.8 (C(10b)), 133.3 (C(6a)), 130.2 (C(4')), 130.0 (C(10a)), 128.8 (C(4)), 128.7 (C(2') & C(6')), 127.7 (C(7)), 127.2 (C(3') & C(5')), 126.8 (C(4a)), 125.8 (C(9)), 125.3 (C(6)), 125.3 (C(8)), 123.9 (C(10)), 120.8 (C(5)), 58.5 (C(2)), 27.8# (CH$_3$), 24.4# (CH$_3$), 18.3 (=C<u>C</u>H$_3$). (Found for $[C_{23}H_{21}NO]^+$: 327.1623. Calcd.: 327.1623.)

observed at 213 K

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