1,2,3,4-Tetrahydro-1,4-methanonaphthalenes as model compounds to study the influence of molecular structure on molecular dynamics by ^{13}C NMR relaxation data

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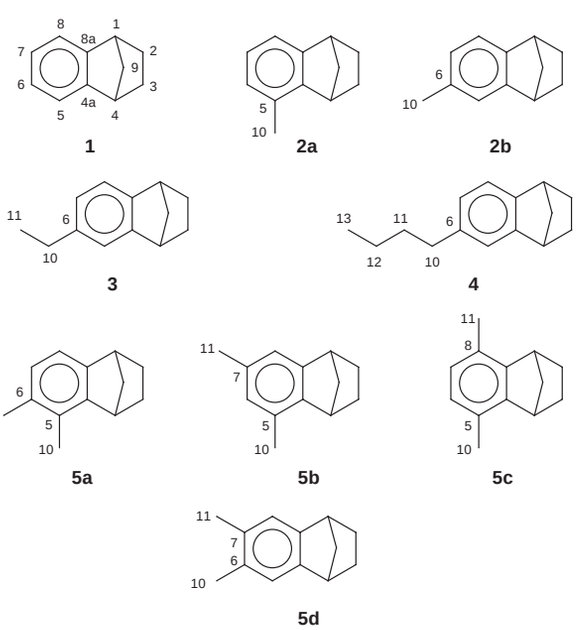
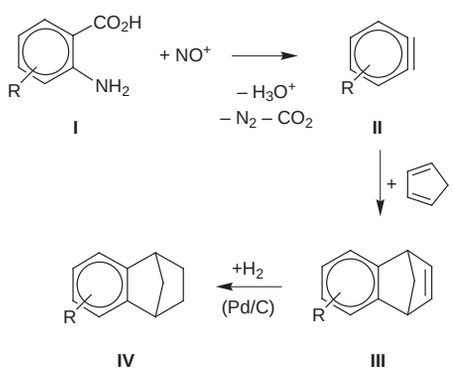
The alkyl 1,2,3,4-tetrahydro-1,4-methanonaphthalenes (THMNs) are proposed as model compounds for studying the influence of molecular shape on reorientational dynamics in liquids. They possess a rigid molecular frame to which different alkyl chains are attached. The synthesis of several alkyl THMNs is described, and the rotational motions of specific ^{13}C–^{1}H vectors have been evaluated by the measurement of ^{13}C relaxation data. The results for the differently-substituted THMNs were compared to each other. The velocity of the reorientational motions could be related to the molecular shape.

Introduction

The liquid state is of great importance in nature and engineering. Almost all chemical and biochemical reactions proceed in solution. Therefore, it is of interest to develop existing models further for describing the structure and dynamics of liquids. The models should mediate a better understanding of the dynamic behaviour of the molecules and thus of the route of chemical reactions in liquids. An often-used model for the description of rotational molecular motions in liquids is that of rotational diffusion. A particularly important method of obtaining data about molecular reorientations is the measurement of spin–lattice relaxation times. From them the reorientational correlation times are obtained which are related to the velocity of the molecular rotational motions.

In recent studies[1–4] 1,2,3,4-tetrahydro-1,4-methanonaphthalenes (THMNs) proved to be ideally suited as model compounds for the investigation of the rotational diffusion process, since they possess a rigid part of the molecular frame which can be easily varied with appropriate substituents. The synthesis of the parent compound THMN[5] **1**, the 6-Me-THMN[1,6] **2b** and the 5,6-Me_2-THMN[2] **5a** has already been described in the literature, and these THMNs were also investigated by ^{1}H[2,6,7,8] and ^{13}C[1,2,9] NMR spectroscopy.





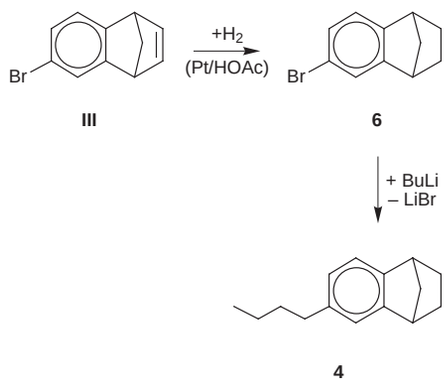
Scheme 1

Since it is generally not well known and since rather few experimental studies exist on how the molecular shape influences the molecular reorientational dynamics in liquids, it is the aim of the present work to study these effects. For this kind of investigation the class of alkyl THMNs is ideally suited: they do not possess polar groups so that the rotational molecular dynamics are only influenced by the differing molecular shape for the differently-substituted alkyl THMNs. The synthesis of a number of alkyl THMNs is described. The major advantages of the alkyl THMNs as model compounds for the study of the rotational motions in liquids are that they are liquid at ambient temperature, are easily synthesised and modified and are asymmetric rotators. The rigid part of the molecular frame remains unchanged while the type and position of the flexible alkyl chains at the aromatic ring are varied. The reorientational motions of the THMNs in neat liquid were determined by measurement of ^{13}C relaxation data and then compared for the differently-substituted alkyl THMNs.

Results

Synthesis of the 1,2,3,4-tetrahydro-1,4-methanonaphthalenes (THMNs)

Synthesis of THMN 1, the methyl-THMNs 2, ethyl-THMN 3 and the dimethyl-THMNs 5. The THMNs **1**–**3** and **5** were prepared by a modification of established procedures.[2,10,11] To this end the anthranilic acids **I** were converted into the arynes **II**, which reacted with cyclopentadiene to give the Diels–Alder



Scheme 2

adducts **III**. Catalytic hydrogenation afforded the THMNs **IV** in almost quantitative yields (Scheme 1). Besides the already-described compounds THMN[5,7,9] **1**, 6-Me-THMN[1,6,8] **2b** and 5,6-Me_2-THMN[2] **5a**, the hydrocarbons 5-Me-THMN **2a**, 6-Et-THMN **3**, 5,7-Me_2-THMN **5b**, 5,8-Me_2-THMN **5c** and 6,7-Me_2-THMN **5d** were also obtained by this procedure. When the corresponding 2-aminobenzoic acid was not commercially available, it was synthesised in three steps from the corresponding aniline *via* the isonitrosoacetanilide and isatin.[12]

Synthesis of the 6-butyl-THMN (4). The 6-butyl-THMN was obtained *via* Diels–Alder addition of the aryne **II** from the commercially-available 2-amino-4-bromobenzoic acid to cyclopentadiene (*cf.* Scheme 1). The obtained adduct[13] **III** was hydrogenated by established procedures[14] to the corresponding 6-bromo-THMN **6**,[13] which reacted with butyllithium[15] to give the desired 6-butyl-THMN **4** (Scheme 2).

^{13}C NMR chemical shifts and their assignment

The ^{13}C resonances were assigned to the corresponding carbon atoms of the alkyl-THMNs by comparison of the ^{13}C chemical shift data with reference data from the literature for the parent compound THMN **1**[9], the 6-Me-THMN **2b**[1] and 5,6-Me_2-THMN.[2] Furthermore, the ^{13}C chemical shifts were calculated for the different compounds from increments[16] and also compared to those from the corresponding substituted alkylbenzenes.[17] In some cases the assignments obtained by these methods were ambiguous; especially difficult was the assignment of the quaternary carbon atoms. For this reason 2D ^{13}C–^{13}C INADEQUATE[18] spectra were recorded, by which an unambiguous assignment was possible. For 6-Me-THMN **2b** in neat liquid the assignment of carbons 1 and 4 has to be exchanged compared to the results by Levy *et al.*[1] The ^{13}C chemical shifts and their assignments are given in Table 1 for all THMNs.

^{13}C Relaxation data

The ^{13}C relaxation times T_1 and nuclear Overhauser enhancement (NOE) factors η were measured for THMNs **1**, **2a** and **3** at a ^{13}C resonance frequency of 75.47 MHz and for the others at 62.89 MHz. The values observed for the bridging carbon 9 and the carbon atoms in the aliphatic side chains are given in Table 2. The dipolar spin–lattice relaxation times T_1^{DD} in Table 2 were obtained from eqn. (1).[19]

$$T_1^{DD} = \frac{1.988}{\eta} T_1 \qquad (1)$$

The dipolar spin–lattice relaxation times of aliphatic ^{13}C nuclei should not be frequency-dependent in the extreme narrowing region. Since the experimental error in the NOE factors is known to be relatively large, all aliphatic carbon atoms except the methyl carbons were taken to have the maximum NOE factor η of 1.988 when calculating the dipolar relaxation times T_1^{DD}, *i.e.* it was assumed that these ^{13}C nuclei are relaxing fully *via* the dipolar relaxation pathway.

Reorientational correlation times

The dipolar spin–lattice relaxation rate $(1/T_1^{DD})_i$ of nucleus i resulting from interaction with n_H protons j is connected in the extreme narrowing regime to molecular reorientations by eqn. (2),[19] where μ_0 is the relative permittivity of a vacuum, γ_C

$$\left(\frac{1}{T_1^{DD}}\right)_i = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^2_C \gamma^2_H \hbar^2 n_H}{r^6_{ij}} (\tau_c)_i \qquad (2)$$

and γ_H are the gyromagnetic ratios of ^{13}C and ^{1}H, respectively, and r_{ij} is the length of the internuclear vector between i and j. The effective reorientational correlation time $(\tau_c)_i$ is a measure of the velocity of rotational motion of the corresponding internuclear ^{13}C–^{1}H vectors between the ^{13}C nuclei i and the directly-bonded protons. The effective correlation times at 308 K are listed together with the C–H distances used in Table 2. The distances were obtained from semi–empirical geometry optimisations. The correlation times are also shown in a semi–logarithmic plot in Fig. 1.

Table 1 ^{13}C Chemical shift data δ_C/ppm for THMN **1**, 5-Me-THMN **2a**, 6-Me-THMN **2b**,[a] 6-Et-THMN **3**, 6-Bu-THMN **4**, 5,6-Me_2-THMN **5a**, 5,7-Me_2-THMN **5b**, 5,8-Me_2-THMN **5c** and 6,7-Me_2-THMN **5d** at 308 K

	Compound								
Carbon atom[b]	**1**	**2a**	**2b**	**3**	**4**	**5a**	**5b**	**5c**	**5d**
1	43.8	43.6	42.9	43.1	43.2	43.6	43.6	41.0	43.1
2	27.1	26.7	26.9	27.0	27.1	27.0	26.8	25.8	27.0
3		25.9	26.8	26.9	27.1	26.1	26.1		
4		40.8	43.3	43.5	43.6	41.2	40.6		
4a	148.1	146.8	147.5	147.5	147.5	145.5	142.5	144.9	144.9
5	120.4	128.6	121.0	119.7	120.2	127.3	128.3	125.9	121.4
6	125.5	126.3	134.0	140.7	139.3	132.5	126.9	126.2	132.1
7		124.9	125.6	124.4	125.1	126.2	133.8		
8		117.4	119.7	119.6	119.7	117.1	118.4		
8a		145.3	144.5	144.6	144.7	144.5	147.1		
9	49.3	48.2	48.7	48.8	48.9	48.2	48.2	47.8	48.7
10		17.6	20.8	28.7	35.7	14.5	17.5	17.3	19.1
11				15.5	33.9	19.1	20.8		
12					22.2				
13					13.7				

[a] The ^{13}C chemical shifts were referenced to external $CDCl_3$ with $\delta_C = 76.9$ ppm. [b] For Et-THMN **3** carbon atom C-10 is the methylene, C-11 the methyl carbon; for Bu-THMN **4** carbon C-10 is the first methylene carbon in the alkyl chain starting from the aromatic ring, C-11 the second, C-12 the third carbon atom and C-13 the methyl carbon; for the Me_2-THMNs **5** the carbon C-10 is the one attached to the aromatic carbon with the smaller number.

Discussion

^{13}C Relaxation data

The $n_H T_1^{DD}$ values of the methylene and methyl carbons in the alkyl chains are significantly longer than the values for the bridging methylene carbon C-9. Since the longer relaxation times can only be explained by a faster rotational motion, the internal motion of the C–H vectors in the alkyl chains must play an important role in the relaxation of the ^{13}C nuclei. The NOE factors of the ^{13}C nuclei in the methyl groups which do not reach the maximum value of 1.988 indicate the importance of the spin–rotation mechanism (SR) for the relaxation of these ^{13}C nuclei.

The dipolar relaxation times of the methylene carbon C-9 reflect the velocity of reorientation of the molecular frame. They decrease from the unsubstituted parent compound THMN **1** *via* the monosubstituted Me-THMNs **2** and 6-Et-THMN **3** to the disubstituted Me_2-THMNs **5**. For the 6-Bu-THMN **4** the relaxation time of C-9 is the smallest. These experimental facts can be explained by the increasing efficiency of the relaxation being determined by a decreasing velocity of the rotational motion of the larger molecules. The 6-Et-THMN **3** has the same molecular mass as the Me_2-THMNs **5**. Since the dipolar relaxation time of C-9 for compound **3** is, however, smaller than those of THMNs **5**, the differences in the rotational motions of the molecules cannot be explained by the differing molecular masses or moments of inertia. Instead, the rotational motion has also to be correlated to the structure of the molecules.

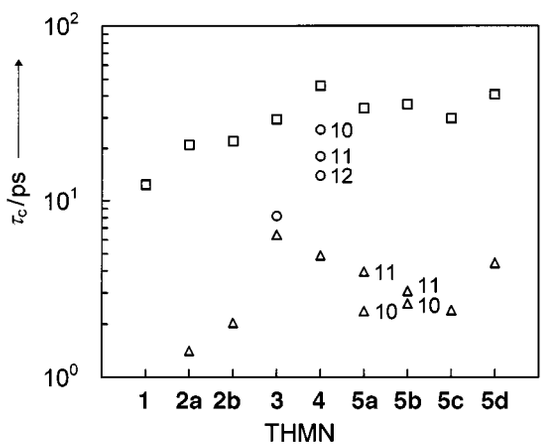


Fig. 1 Effective correlation times τ_c for the methylene carbon C-9 (□) of the rigid molecular frame and for the methylene (○) and methyl carbon atoms (△) of the alkyl side chains of THMN **1**, 5-Me-THMN **2a**, 6-Me-THMN **2b**, 6-Et-THMN **3**, 6-Bu-THMN **4**, 5,6-Me_2-THMN **5a**, 5,7-Me_2-THMN **5b**, 5,8-Me_2-THMN **5c**, and 6,7-Me_2-THMN **5d** at 308 K

Reorientational correlation times

For all correlation times determined, the extreme narrowing condition ($\omega\tau_c \ll 1$) is fulfilled and eqn. (2) holds. The ^{13}C–^{1}H vectors of the methylene bridge (C-9) in the THMNs are part of the rigid molecular frame. The effective correlation times of C-9 can thus be taken as a measure of the velocity of the rotational motion of the whole molecule. The correlation times in Fig. 1 increase with molecular size from the parent compound THMN **1**, the Me-THMNs **2**, the 6-Et-THMN **3** and the Me_2-THMNs **5** to the 6-Bu-THMN **4**. The correlation times of the Me-THMNs and those of the Me_2-THMNs divide into two groups with almost the same value for the monomethylated THMNs on the one hand and the dimethylated THMNs on the other hand. Of special interest is the position of the 6-Et-THMN which lies in between both. Although the 6-Et-THMN possesses the same average moment of inertia as the Me_2-THMNs, its reorientational velocity lies between that of both types of compounds. If the reorientations of the THMNs had been determined by inertial effects, the molecular rotational motion of 6-Et-THMN and the Me_2-THMNs would have been of the same velocity. Apparently, the existence of an ethyl group hinders the rotational motion of the THMNs more strongly than a methyl group. The reason for this behaviour might be that a methyl group internally rotates in its own volume while the ethyl group also rotates about the bond between the aromatic carbon and the methylene carbon. This results in a larger volume which is needed for the internal motion of the ethyl group and in the fact that the methyl group in the ethyl group also moves above the aromatic ring.

The effective correlation times of the internally-rotating methylene and methyl groups are smaller than the corresponding correlation times for C-9 by up to one order of magnitude. The smallest correlation times and thus the fastest rotation were

Table 2 ^{13}C Spin–lattice relaxation times T_1, ^{1}H–^{13}C nuclear Overhauser factors η, dipolar ^{13}C spin–lattice relaxation times T_1^{DD}, ^{13}C–^{1}H bond lengths r_{C-H} and effective correlation times of the corresponding ^{13}C–^{1}H vectors τ_c for THMN **1**, 5-Me-THMN **2a**, 6-Me-THMN **2b**, 6-Et-THMN **3**, 6-Bu-THMN **4**, 5,6-Me_2-THMN **5a**, 5,7-Me_2-THMN **5b**, 5,8-Me_2-THMN **5c** and 6,7-Me_2-THMN **5d** at 308 K

Compound	Carbon atom	T_1/s	η	T_1^{DD}/s	r_{C-H}/pm	τ_c/ps
1	9	2.10	1.91	2.10	111.0	12.4
2a	9	1.24	2.00	1.24	111.0	20.9
	10	8.31	1.29	12.8	111.8	1.41
2b	9	1.18	1.95	1.18	111.0	22.0
	10	6.18	1.41	8.89	111.8	2.03
3	9	0.886	2.06	0.886	111.0	29.3
	10	3.41	1.92	3.41	112.3	8.16
	11	2.82	2.17	2.82	111.7	6.37
4	9	0.569	1.91	0.569	111.0	45.6
	10	1.09	2.05	1.09	112.3	25.5
	11	1.54	2.07	1.54	112.2	18.0
	12	1.99	2.00	1.99	112.2	13.9
	13	3.21	1.73	3.69	111.7	4.87
5a	9	0.765	1.96	0.765	111.0	33.9
	10	6.64	1.72	7.69	111.9	2.36
	11	3.81	1.85	4.61	111.9	3.94
5b	9	0.726	1.97	0.726	111.0	35.8
	10	5.41	1.61	6.94	111.8	2.60
	11	4.56	1.56	5.90	111.8	3.06
5c	9	0.872	2.05	0.872	111.0	29.8
	10/11	5.84	1.59	7.54	111.8	2.40
5d	9	0.639	2.02	0.639	111.0	40.6
	10/11	4.12	2.00	4.12	111.9	4.41

Table 3 Analytical data for the DHMNs **III**

Compound	Yield (%)	Bp/K (*p*/mbar)	δ_H/ppm	*m*/*z* (IE), (I_{rel}(%))
6-Br	17	349 (0.5)		
5-Me	64	311–315 (0.3)	2.08–2.18 (2H, m, CH_2), 2.20 (3H, s, CH_3), 3.60–3.75 (1H, m, CH), 3.80–3.95 (1H, m, CH), 6.50–6.90 (5H, m, HC=CH, 3 × Ph)	
6-Et	43	393 (0.3)	1.19 (3H, t, CH_3), 2.15–2.23 (2H, m, CH_2), 2.35–2.53 (2H, q, CH_2–CH_3), 3.58–3.76 (2H, m, 2 × CH), 6.49–6.61 (3H, m, HC=CH, Ph), 6.67–6.93 (2H, m, 2 × Ph)	170 (M^+, 38), 155 (60), 141 (100), 129 (40), 128 (45), 115 (55)
5,7-Me_2	64	333 (0.2)	2.01–2.21 (2H, m, CH_2), 2.19 (3H, s, CH_3), 2.21 (3H, s, CH_3), 3.73 (1H, m, CH), 3.87 (1H, m, CH), 6.41 (1H, d, Ph), 6.66 (2H, m, HC=CH), 6.74 (1H, d, Ph)	170 (M^+, 54), 155 (100), 153 (36), 129 (50), 128 (60), 115 (43)
5,8-Me_2	62	318 (0.4)	2.00–2.30 (2H, m, CH_2), 2.22 (6H, s, 2 × CH_3), 3.80–4.05 (2H, m, 2 × CH), 6.55 (2H, m, HC=CH), 6.70 (2H, s, 2 × Ph)	170 (M^+, 56), 155 (100), 153 (40), 129 (52), 128 (61)
6,7-Me_2	38	324 (0.2)	2.10–2.30 (2H, m, CH_2), 2.32 (6H, s, 2 × CH_3), 3.71–3.90 (2H, m, 2 × CH), 6.52 (2H, m, HC=CH), 6.90 (2H, s, 2 × Ph)	170 (M^+, 60), 155 (100), 153 (37), 129 (40), 128 (50)

Table 4 Analytical data for the THMNs **IV**

Compound	Yield (%)	Bp/K (*p*/mbar)	δ_H/ppm	*m*/*z* (IE), (I_{rel}(%))
5-Me **2a**	95	309–311 (0.3)	1.08–1.93 (6H, m, 3 × CH_2), 2.30 (3H, s, CH_3), 3.39 (2H, m, 2 × CH), 6.85–7.00 (3H, m, 3 × Ph)	158 (M^+, 79), 143 (37), 130 (88), 128 (79), 115 (100)
6-Et **3**	98	322 (0.4)	1.22–1.85 (6H, m, 3 × CH_2), 1.25 (3H, t, CH_3), 2.58 (2H, q, CH_2–CH_3), 3.30 (2H, m, 2 × CH), 6.65–7.05 (3H, m, 3 × Ph)	172 (M^+, 43), 157 (17), 144 (62), 129 (100), 128 (64), 115 (66)
6-Bu **4**	94	353 (0.3)	0.93 (3H, t, CH_3), 1.14–1.86 (10H, m, 3 × CH_2, CH_2–C$H_2$$CH_3$), 2.42–2.50 (2H, m, Ph–CH_2–C), 3.16–3.24 (2H, m, 2 × CH), 6.70–6.92 (3H, m, 3 × Ph)	200 (M^+, 53), 172 (75), 157 (40), 129 (100), 128 (66), 127 (26), 115 (48)
5,7-Me_2 **5b**	98	336 (0.3)	1.08–1.90 (6H, m, 3 × CH_2), 2.27 (3H, s, CH_3), 2.29 (3H, s, CH_3), 3.34 (2H, m, 2 × CH), 6.71 (1H, s, Ph), 6.82 (1H, s, Ph)	172 (M^+, 53), 157 (28), 144 (100), 129 (83), 128 (46)
5,8-Me_2 **5c**	96	348–353 (0.6)	1.40–1.87 (6H, m, 3 × CH_2), 2.26 (6H, s, 2 × CH_3), 3.43 (2H, m, 2 × CH), 6.78 (2H, s, 2 × Ph)	172 (M^+, 37), 157 (21), 144 (100), 129 (70), 128 (34)
6,7-Me_2 **5d**	97	338 (0.2)	1.19–1.86 (6H, m, 3 × CH_2), 2.21 (6H, s, 2 × CH_3), 3.28 (2H, m, 2 × CH), 6.94 (2H, s, 2 × Ph)	172 (M^+, 48), 157 (36), 144 (100), 129 (77), 128 (50)

observed for the Me-THMNs. The rotational motion of the methyl groups at the end of a chain appears to be more hindered than for the methyl groups directly attached to the aromatic ring, because they project more into the surrounding fluid and have a stronger contact to it which results in greater friction. The methyl groups directly attached to the rigid molecular frame, however, easily rotate in the cage of the surrounding molecules. The fastest motion in the classification by Bluhm[20] was exhibited by the isolated methyl groups of type 1a (C-10 in the Me-THMNs **2** and C-10 and C-11 in the Me_2-THMNs **5b** and **5c**), and the slowest rotation by the isolated *ortho* methyl groups of type 2 (C-11 in **5a** and C-10 and C-11 in **5d**). The methyl group C-10 in **5a** possesses a kind of special position because of the additional interaction with the hydrogen at C-4.[3] The decreasing correlation times in the side chain of 6-Bu-THMN **4** with increasing distance to the rigid molecular frame is a known phenomenon[19] which results from the increasing flexibility with increasing distance from the anchoring point of the chain.

Conclusions

The results demonstrate that the class of alkyl THMNs is ideally suited for investigating the influence of molecular structure on the molecular reorientational dynamics. The alkyl THMNs are relatively easily obtained by standard procedures and show optimum properties as model compounds for the study of rotational diffusion.

Experimental

Synthesis

Solvents were dried by standard methods.

General procedure for synthesis of the 1,4-dihydro-1,4-methanonaphthalenes (DHMNs) III. A solution of the corresponding anthranilic acid (0.13 mol) and cyclopentadiene (0.26 mol) in tetrahydrofuran (100 ml) was added, with stirring and under nitrogen, to a refluxing solution of 3-methylbutyl nitrite (0.13 mol) in dichloromethane (180 ml). The reaction mixture was then refluxed for a further 90 min. After 12 h the solvent was evaporated and the residue extracted with *n*-hexane. The solution was dried, the solvent evaporated and distillation yielded the desired product. The physical data for compounds **III** are given in Table 3.

General procedure for the synthesis of the 1,2,3,4-tetrahydro-1,4-methanonaphthalenes (THMNs) IV. The 1,4-dihydro-1,4-methanonaphthalenes **III** (15 mmol) were hydrogenated in dried ethyl acetate (40 ml) at 5 bar and room temperature over 10% Pd on charcoal. After 1 h the catalyst was filtered off and the solvent evaporated. Distillation gave the 1,2,3,4-tetrahydro-1,4-methanonaphthalenes. The THMNs were further purified by chromatography over a column with Silicagel 60 and *n*-hexane. The data for the THMNs **IV** are given in Tables 1 and 4.

6-Bromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene 6. 6-Bromo-1,4-dihydro-1,4-methanonaphthalene (0.50 g, 2.25 mmol) was hydrogenated in acetic acid (10 ml) with PtO_2 (5 mg) as catalyst at 4 bar and room temperature. After 40 min the catalyst was filtered off and the solvent evaporated. Distillation in an argon atmosphere yielded 6-bromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene **6** (0.48 g, 95%); bp 70 °C (0.6 mbar); δ_H(250 MHz, $CDCl_3$) 1.15–1.89 (6H, m, 3 × CH_2), 3.30 (2H, m, 2 × CH), 7.00–7.23 (3H, m, Ph); *m*/*z* (EI) 224.22 (M^+, 45%), 196.19 (56), 143 (33), 128 (53), 115 (100).

6-Butyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene 4. To a solution of 6-bromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene (0.5 g, 2.3 mmol) in dry THF (15 ml) was slowly added, under an argon atmosphere, a solution of butyllithium in hexane (2.56 M; 1.3 ml, 3.3 mmol), and the whole was stirred for 1 h. After addition of 1-bromobutane (0.45 g, 3.3 mmol)

the reaction mixture was washed with water and aqueous sodium chloride and extracted with dichloromethane. The combined organic phases were dried and the solvent evaporated. Distillation yielded 6-butyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene **4** contaminated with 5% THMN **1** (GC-MS) which could not be further purified. The physical data for 6-Bu-THMN are given in Tables 1 and 4.

NMR measurements

^{1}H and ^{13}C NMR chemical shift measurements were performed on Bruker AM 250 and CXP 300 spectrometers [B_0 = 5.875 T, $\nu_0(^{13}C)$ = 62.89 MHz, $\nu_0(^1H)$ = 250.13 MHz and B_0 = 7.047 T, $\nu_0(^{13}C)$ = 75.47 MHz, $\nu_0(^1H)$ = 300.13 MHz, respectively] in neat liquid with $CDCl_3$ as external standard. The temperature of 308 K was controlled by using the temperature dependence of the ^{1}H chemical shift for the hydroxy group in methanol.[22] The accuracy of the temperature was about ±1 K.

The pulse sequence for the ^{13}C–^{13}C INADEQUATE 2D NMR spectra[18] was used with a modification by Turner.[21] The data were collected with 64 scans subsequent to 4 dummy scans in F_2 into 1024 or 2048 time domain points with a relaxation delay of 15 s. The long relaxation delay was necessary to obtain enough signal intensity from the quaternary ^{13}C nuclei. In F_1 64 or 128 experiments were performed with subsequent zero filling to 512 or 1024 data points. The spectral width was 10.5 kHz in F_2 and half of that in F_1 at a resonance frequency of 75.47 MHz for ^{13}C. Thus, a digital resolution of 20.3 or 10.2 Hz per data point was obtained, depending on the resolution which was required to resolve the resonances properly. After application of a sine bell window function in both dimensions the spectra were obtained by a magnitude calculation.

Measurements of the spin–lattice relaxation times were carried out with ^{1}H broadband decoupling and repeated five times, those for the NOE factors five to ten times. The reproducibility of the spin–lattice relaxation times was better than 2% and that for the NOE factors better than 6%. For further details refer to references 2 and 3.

Molecular geometries

The distances between the ^{13}C and the ^{1}H nuclei were obtained by optimising the molecular structures with the semi–empirical method AM1[23] in the program package MOPAC.[24]

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