Motional Dynamics in Liquid 1,2,3,4-Tetrahydro-5,6-dimethyl-1,4-methanonaphthalene. Part 1. A New Model Compound for the Investigation of Anisotropic Rotational Diffusion and Internal Rotations by ^{13}C Spin–Lattice Relaxation Data

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The hydrocarbon 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-methanonaphthalene (**1**) was synthesized and characterized. The molecular structure of (**1**) is rigid and asymmetric. The molecules of (**1**) have at least one hindered rotating methyl group and a sufficient number of non-parallel C–H vectors. The ^{13}C spin–lattice relaxation times and n.O.e. factors of (**1**) were measured and assigned to the corresponding carbon atoms. The dipolar ^{13}C spin–lattice relaxation times n $(T_1^{DD})$of non-methyl carbon atoms bearing directly attached protons (n is the number of these protons) are significantly different from each other, thus indicating the anisotropy of the molecular reorientation.

Although it is relatively easy to describe and investigate molecular motions in the gas phase, this is not the case for the liquid state. Since almost all chemical conversions proceed in solution, it is desirable to obtain such a description of molecular motional behaviour to achieve a deeper understanding of dynamics in fluids and therefore of chemical reactions in them.

A particularly important method for making statements about rotational molecular motions is the measurement of spin–lattice relaxation times, as these depend among other things upon the rotational reorientation of the molecules.[1] Recently it has become possible to calculate the ^{13}C spin–lattice relaxation times for a fully anisotropic motion of molecules with arbitrary positions of internal rotating methyl groups by the formalism developed by Bluhm.[2]

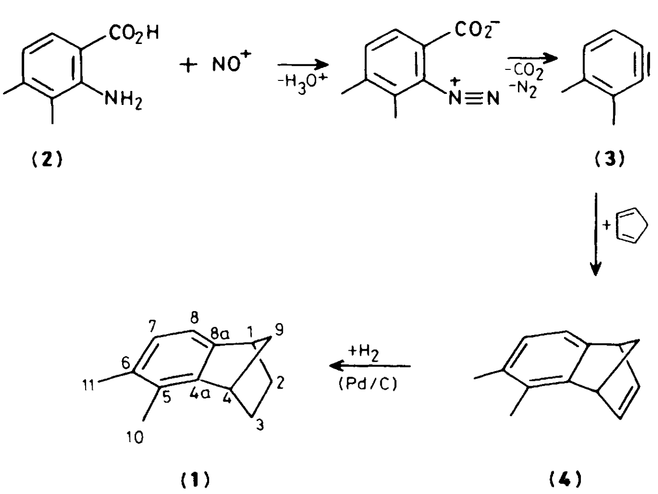
The molecules of an ideal model compound for such investigations should possess the following properties: (*a*) a rigid structure; (*b*) at least one hindered rotating methyl group; and (*c*) as many non-parallel C–H vectors as possible, and should be asymmetric rotators.

We consider all these requirements are met by the new model compound 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-methanonaphthalene (**1**).

Results

Synthesis of 1,2,3,4-*Tetrahydro*-5,6-*dimethyl*-1,4-*methanonaphthalene* (**1**).—The hydrocarbon (**1**) can be prepared by a modification of established procedures.[3] To this end the anthranilic acid (**2**),[4] which is readily available by oxidation of 6,7-dimethylisatin, is converted into the aryne (**3**). This aryne reacts with cyclopentadiene to give the adduct (**4**) in a Diels–Alder reaction. Catalytic hydrogenation[5] affords compound (**1**) in almost quantitative yield.

Assignment of the ^{13}C *Resonances of* (**1**).—The ^{13}C resonances were assigned by comparison with ^{13}C chemical shifts of the unsubstituted compound 1,2,3,4-tetrahydro-1,4-methanonaphthalene[6] and its 6-methyl derivative.[3b] In addition the ^{13}C chemical shifts of (**1**) were calculated from known increments.[7] Further evidence for the assignment resulted from ^{13}C–^{1}H coupling constants. The ^{13}C chemical shifts and their assignments are listed in the Table.



^{13}C *Spin–Lattice Relaxation Times and n.O.e. Factors*.—The experimental ^{13}C spin–lattice relaxation times $(T_1)_{exp}$ and the n.O.e. factors η were determined at 309 K. They are shown in the Table together with the calculated experimental dipolar ^{13}C spin–lattice relaxation times $(T_1^{DD})_{exp}$. The dipolar spin–lattice relaxation times were calculated from equation (1).

$$(T_1^{DD})_{exp} = (T_1)_{exp}\ 1.988/\eta \qquad (1)$$

Since the experimental error in the measurement of the n.O.e. factors is relatively high, all the carbon atoms bearing directly attached protons are assigned the greatest possible n.O.e. factor (η) of 1.988, *i.e.* it is assumed that they are relaxing fully *via* the dipole–dipole mechanism. This assumption seems to be justified, as the observed relaxation times $(T_1)_{exp}$ are relatively short.

Discussion

The n.O.e. factors for the carbon atoms with directly attached protons have, within the experimental error of 10%, the greatest possible value of η (1.988), even for the methyl carbon atoms. Thus the spin rotation mechanism makes no contribution to the relaxation of the methyl group ^{13}C nuclei.[1] For the four quaternary carbon atoms an average n.O.e. factor (η) of 1.71 ± 0.03 results, indicating that these carbon atoms are relaxing not only *via* the dipole–dipole mechanism.[1]

Table. ^{13}C Chemical shift data, experimental ^{13}C spin–lattice relaxation times $(T_1)_{exp}$, n.O.e. factors η, and experimental dipolar ^{13}C spin–lattice relaxation times $(T_1^{DD})_{exp}$ of 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-methanonaphthalene (**1**)

	Carbon atom[a]												
	1	2	3	4	4a	5	6	7	8	8a	9	10	11
δ(CDCl$_3$)[b]	−33.3	−49.9	−50.8	−35.7	68.6	50.4	55.6	49.3	40.2	67.6	−28.7	−62.4	−57.8
δ(Me$_4$Si)[c]	43.6	27.0	26.1	41.2	145.5	127.3	132.5	126.2	117.1	144.5	48.2	14.5	19.1
$(T_1)_{exp}$/s	1.65	0.68	0.71	1.72	20.8	23.4	18.6	1.57	1.79	17.4	0.67	5.98	3.82
η	2.01	1.86	1.88	2.09	1.67	1.67	1.70	2.11	1.93	1.78	2.12	1.80	1.99
$(T_1^{DD})_{exp}$/s[d]	1.65	0.68	0.71	1.72	24.8	27.9	21.8	1.57	1.79	19.4	0.67	5.98	3.82

[a] The numbering is defined in the formula of (**1**). [b] ^{13}C Chemical shift with CDCl$_3$ as external standard. [c] ^{13}C Chemical shift, calculated with δ(CDCl$_3$) = 76.9. [d] For the calculation of the $(T_1^{DD})_{exp}$ values of carbon atoms bearing directly attached protons an n.O.e. factor (η) of 1.988 was used.

The $n\ (T_1)_{exp}$ and $n\ (T_1^{DD})_{exp}$ values of the methyl group ^{13}C nuclei (n is the number of directly attached protons) are markedly longer than the values of the methylene and methine ^{13}C nuclei. As the longer relaxation times can be explained only by a faster rotational motion,[1] the internal rotation of the methyl groups must play an important part in the relaxation of their ^{13}C nuclei.

The $n\ (T_1^{DD})_{exp}$ values of non-methyl carbon atoms bearing directly attached protons are significantly different from each other, thus indicating the anisotropy of the molecular rotational reorientation for the hydrocarbon (**1**).

As the results show, the hydrocarbon (**1**) is an ideal model compound for the investigation of anisotropic rotational diffusion and internal rotations.

Experimental

All solvents were dried by standard methods. Solvents for n.m.r. measurements were of the Uvasol type (Merck).

Compounds were identified by ^1H n.m.r. [Varian EM 390; probe temperature 307 K, solvent CCl$_4$, internal standard and lock Me$_4$Si, B_0 2.114 T, $\nu_0(^1H)$ 90 MHz], mass spectrometry (Varian MAT 311 A; electron impact), and elemental analysis (Perkin-Elmer 240).

1,4-*Dihydro*-5,6-*dimethyl*-1,4-*methanonaphthalene* (**4**).—The preparation was performed under nitrogen. To a refluxing solution of 3-methylbutyl nitrite (5.2 g, 44 mmol) in dichloromethane (56 ml), a suspension of 3,4-dimethylanthranilic acid (6.6 g, 40 mmol) and cyclopentadiene (2.6 g, 40 mmol) in acetone (75 ml) was added within 10 min, with stirring. The mixture was then refluxed for 30 min. After cooling, the solvent was evaporated off, the residue extracted with light petroleum, and the precipitate filtered off. After evaporation of the solvent distillation yielded 1,4-*dihydro*-5,6-*dimethyl*-1,4-*methanonaphthalene* (**4**) (3.1 g, 45%), b.p. 116—118 °C (9 mbar), 62—65 °C (0.4 mbar) (Found: C, 91.4; H, 8.6. $C_{13}H_{14}$ requires C, 91.7; H, 8.3%); δ_H 2.00—2.30 (2 H, m, C–CH$_2$–C), 2.22 (3 H, s, CH$_3$–Ar), 2.25 (3 H, s, CH$_3$–Ar), 3.65—3.75 (1 H, m), 3.85—3.95 (1 H, m), 6.54 (1 H, d, J 5.5 Hz, ArH), 6.60—6.70 (2 H, m, HC=CH), and 6.80 (1 H, d, J 5.5 Hz, ArH); m/z 170 (M^+, 70%), 156 (11), 155 (100), 153 (14), 129 (13), and 128 (14).

1,2,3,4-*Tetrahydro*-5,6-*dimethyl*-1,4-*methanonaphthalene* (**1**).—The hydrocarbon (**4**) (2.5 g, 15 mmol) was hydrogenated in ethyl acetate (15 ml) at 4 bar over 10% Pd on charcoal (0.1 g). After 45 min the catalyst was filtered off and the solution evaporated. Distillation gave 1,2,3,4-*tetrahydro*-5,6-*dimethyl*-1,4-*methanonaphthalene* (**1**) (2.5 g, 95%), b.p. 76—78 °C (0.4 mbar) (Found: C, 90.3; H, 9.7. $C_{13}H_{16}$ requires C, 90.6; H, 9.4%); δ_H 1.00—1.25 (2 H, m, C–CH$_2$–C), 1.30—2.00 (4 H, m, C–CH$_2$–C), 2.14 (6 H, s, CH$_3$–Ar), 3.15—3.25 (1 H, m), 3.33—3.43 (1 H, m), and 6.68 (2 H, s, ArH); m/z 172 (M^+, 34%), 157 (15), 145 (11), 144 (100), 141 (10), 129 (36), and 128 (20).

^{13}C *N.m.r. Measurements on* (**1**).—All measurements were carried out with a Bruker SXP 4-100/15″ spectrometer [probe temperature 309 K, neat liquid, external standard and lock CDCl$_3$, B_0 2.114 T, $\nu_0(^{13}C)$ 22.63 MHz], and at 309 K. The temperature of the probe was controlled by the Bruker B-ST 100/700 automatic temperature control unit with a dried and heated air stream. The temperature at the sample position was controlled before and after the measurements with a calibrated copper–constantan thermocouple; the temperature accuracy and constancy was *ca.* ±1 K.

Sample preparation. The n.m.r. tubes (Wilmad, USA) had an external diameter of 7.5 mm. The sample volume was limited to the height of the coil in the n.m.r. probe by narrowing the internal diameter of the tube to *ca.* 1 mm just above the position of the coil. This was expected to reduce errors due to inhomogenities of the H_1 field, by diffusion, and by an exchange of molecules between the liquid and the gas phase. The liquid hydrocarbon (**1**) was added to the tube until the surface of the liquid was *ca.* 1 cm above the narrowing of the tube. Since the vapour pressure of (**1**) is very low, the sample could be degassed and melted off at a pressure of 0.02 mbar at room temperature. The sample tube was then centred with the help of Teflon rings in a second n.m.r. tube, which had an external diameter of 10 mm. [^{2}H]Chloroform was used as lock and external reference in the outer tube.

Measurement of relaxation times. The inversion–recover pulse sequence was employed to determine the ^{13}C spin–lattice relaxation times $(T_1)_{exp}$ under broad-band ^1H decoupling. The waiting time between the 180°–τ–90° pulse sequences was *ca.* five times the longest $(T_1)_{exp}$ value.

For the calculation of the $(T_1)_{exp}$ values the signal areas of the spectra were calculated. These values $S(\tau)$ were then fitted to the relaxation function $S(\tau) = A\,[1-2\exp(-\tau/T_1)]$. For this purpose the parameters A and T_1 were iteratively optimized. Each $(T_1)_{exp}$ measurement was repeated five times. The reproducibility of the resultant $(T_1)_{exp}$ values was better than five per cent.

Determination of n.O.e. factors. The n.O.e. factors η were determined from five measurements of the signal areas of the ^1H broad-band decoupled and of the ^1H gated-decoupled spectra, using *ca.* five times the longest $(T_1)_{exp}$ value in the former and *ca.* 10 times the value in the latter case as waiting times. The reproducibility of the values of the n.O.e. factors and therefore of the dipolar ^{13}C spin–lattice relaxation times $(T_1^{DD})_{exp}$ was better than 5%.

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