^{15}N NMR spectra, tautomerism and diastereomerism of 4,5-dihydro-1*H*-1,2,3-triazoles

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Despite the great number of 4,5-dihydro-1*H*-1,2,3-triazoles synthesized, ^{15}N NMR data of these heterocycles are extremely rare. The aim of this paper is to present such data and examples of their application. The compounds investigated have been synthesized according to the given references or procedures. Their ^{15}N NMR spectra were measured at natural abundance. For some compounds, the chemical shift assignments were confirmed with the help of ^{15}N labelled material. The influences on ^{15}N chemical shifts of substitution pattern, solvent and concentration were investigated. Additionally, some lanthanide induced shift (LIS) investigations were performed. ^{13}C labelled compounds were employed as tools to provide the assignment of tautomeric structures.

Introduction

^{15}N NMR spectroscopy is a powerful tool for the characterization of nitrogen containing compounds because ^{15}N chemical shifts strongly depend on structural and electronic features which hence result in a broad shift range of approximately 900 ppm, *i.e.* −400 to +500 ppm relative to nitromethane as external reference.[1–3] Despite and sometimes through the influence of solvents as well as concentration, pH value and temperature of the solutions on ^{15}N shifts, many problems, including for example tautomerism[2–4] or positions of protonation of heterocycles,[3,5] could be solved with the help of ^{15}N NMR spectroscopy.

The number (more than 3300) of 4,5-dihydro-1*H*-1,2,3-triazoles that are registered by *Chemical Abstracts* attests to the importance of this class of heterocycles for many areas ranging from organic syntheses to pharmaceutical research.[6] Nevertheless, ^{15}N NMR data of these heterocyclic compounds are surprisingly rare. To the best of our knowledge, only a handful have been published in previous papers from our group.[7–9] The primary goal of the present study is to fill this gap and to utilize such data for the elucidation of the structures of tautomers and diastereomers.

The dihydro-1,2,3-triazoles investigated have been synthesized according to procedures reported in the literature or described in the Experimental section. In most cases, they were prepared by 1,3 dipolar cycloaddition of an azide to an alkene. Their ^{15}N NMR spectra were measured at natural abundance (0.37% ^{15}N) except for some cases (compare Fig. 1) in which the shift assignment had to be confirmed with the help of ^{15}N labelling.

Experimental

The known dihydrotriazoles **1**–**32**, **34**, **36**–**38**, **40**, **41**, **44**, **46**–**53**, **55**–**60** and **62** were prepared according to the procedures given in the references listed in Table 3. The compounds **33**, **35**, **39**, **42**, **43** and **45** were obtained by 1,3 dipolar cycloaddition of the corresponding azides to norbornene (molar ratio azide : norbornene *ca.* 1 : 2) under the reaction conditions specified in Table 1. The physical and spectroscopic data of these new compounds are summarized in Table 2. Chemical shifts are given in ppm and *J* values are given in Hz.

Compound **54**: Butyl azide[10] (600 mg, solution in Et_2O, 64%, 3.88 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (850 mg, 2.21 mmol) were dissolved in benzene (10 ml). The mixture was sealed in a glass tube and heated to 75 °C for 14 days. After filtration, the solvent and remaining BuN_3 were removed *in vacuo* at 45 °C. The residue was treated with ethanol. After separation of the insoluble starting material, the solvent was evaporated to give 610 mg (1.26 mmol, 57%) of pure **54** as yellow crystals, mp 60–61 °C (from EtOH) (Found: C, 82.12; H, 6.21. Calc. for $C_{33}H_{29}N_3O$: C, 81.96; H, 6.04%); ν_{max} (CCl_4)/cm^{-1} 1708 (CO); δ_H(300 MHz; $CDCl_3$) 0.86 (3 H, t, 4′-Me), 1.35 (2 H, sext., 3′-H), 1.81 (2 H, quint., 2′-H), 3.43 (1 H, m, 1′-H), 3.69 (1 H, m, 1′-H), 6.8–7.6 (20 H, m, arom. H); δ_C(75 MHz, $CDCl_3$) 13.7 (C-4′), 20.1 (C-3′), 31.1 (C-2′), 47.1 (C-1′), 77.3 (C-5), 98.7 (C-4), 127.1, 127.5, 127.7, 127.9, 128.4, 129.5, 129.6, 130.6, 131.1, 133.0, 133.1, 135.8 (arom. C), 141.5 (C-7), 167.9 (C-8), 199.5 (C-6).

Compound **61** (with a structure assumed to be analogous to that of allyl azide dimer[16]): A solution of methallyl azide[17] (5.0 g, 51.5 mmol) in toluene (50 ml) was heated under reflux for 3 days. The solvent was removed *in vacuo* to yield the crude product (2.1 g, 42%) which furnished a colorless solid (0.64 g, 13%), mp 220 °C (from CH_2Cl_2–Et_2O); δ_H(300 MHz, $CDCl_3$) 1.40 (3 H, s, Me), 3.37 (1 H, d, *J* 14.4, 6-H), 3.75 (1 H, d, *J* 14.4, 6-H), 3.68 (1 H, d, *J* 16.3, 4-H), 4.40 (1 H, d, *J* 16.3, 4-H); δ_C(75 MHz, $CDCl_3$) 19.6 (Me), 47.0 (C-6), 58.9 (C-5), 74.9 (C-4).

Compounds **9a**, **19a**, **27a**, **29a**, **44a**, **50a** and **55a**, ^{15}N labelled in positions 1 and 3 (compare Fig. 1), were synthesized from the corresponding ^{15}N labelled azides. These were obtained by nucleophilic substitution reactions from sodium azide having both terminal positions enriched with ^{15}N (49%). ^{15}N labelled neopentyl azide was synthesized in 97% yield from 1-iodo-2,2-

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Table 1 Synthesis of new 4,5-dihydro-1*H*-1,2,3-triazoles from azides and norbornene at room temperature

Compound	Solvent	Time/d	Yield (%)	Ref. azide
33	Et_2O	10	95	10
35	Et_2O	3	87	11[a], 12
39	$CHCl_3$	3	47	11[a], 13
42	$CHCl_3$	3.5	58	11[a], 14
43	$CHCl_3$	3.5	48	11[a], 15
45	Et_2O	2	100	12

[a] The azide was prepared similarly to the described procedure using the appropriate *p*-substituted aniline.

dimethylpropane and molten $(n\text{-}C_{16}H_{33})Bu_3P^+$ $^{15}N{=}N{=}^{15}N^-$, which was prepared from ^{15}N labelled sodium azide according to the modified method reported in ref. 18. The heterocycles **51a/52a** and **51c/52c** were obtained from appropriately labelled sodium azide according to the procedure described in ref. 19. Compounds **9b** and **44b**, ^{15}N enriched at positions 2 and 3, were obtained by a 1,3 dipolar cycloaddition reaction from *p*-nitrophenyl azide, which was prepared by coupling of *p*-nitrobenzenediazonium chloride with sodium azide, having both terminal positions labelled with ^{15}N (49%). The resulting *p*-nitrophenyl azide was labelled weakly in the β and strongly in the γ position. The ^{13}C labelled compounds **51d/52d**, **53d** were prepared according to ref. 19 and **54d** as described above for **54**, respectively, using 2,3,4,5-tetraphenylcyclopentadienone labelled with 10% ^{13}C in the positions 2 and 5. This starting material was prepared as described[20] from 1,2-diphenylethanedione and 1,3-^{13}C-1,3-diphenylpropan-2-one. The latter was obtained from 2-^{13}C-2-phenylacetic acid (10% ^{13}C by mixing of ^{13}C labelled and unlabelled material in a 1 : 9 ratio).[21] The positions of ^{13}C labelling of all substances were checked by ^{13}C NMR spectroscopy.

NMR spectra were recorded from 0.5 to 1.5 molar solutions in $CDCl_3$ (unless stated otherwise) at a temperature of 309 K (unless stated otherwise) using standard pulse programs. ^{15}N NMR spectra were recorded without proton decoupling on BRUKER WH-400 and AMX-400 spectrometers operating at 40.53 MHz and on a VARIAN Gemini 2000 spectrometer operating at 30.40 MHz. Nitromethane was employed as external reference ($\delta = 0$ ppm) without susceptibility correction using an inner capillary tube of the standard. ^{14}N NMR spectra were recorded on a BRUKER WH-400 spectrometer operating at 28.89 MHz. ^1H NMR spectra were recorded on BRUKER WH-400 and AMX-400 spectrometers operating at 400 MHz and on a VARIAN Gemini 2000 spectrometer operating at 300 MHz and referenced with TMS or solvent signals, which were standardized to TMS. ^{13}C NMR spectra were recorded on BRUKER WH-400 and AMX-400 spectrometers operating at 100.58 MHz and on a VARIAN Gemini 2000 spectrometer operating at 75.43 MHz. Referencing was performed as described for ^1H NMR spectra.

Results and discussion

^{15}N NMR chemical shifts and assignments of signals

The ^{15}N NMR chemical shifts of all dihydrotriazoles studied (**1**–**62**, Schemes 1–5) are summarized in Table 3. Although the ^{15}N NMR spectra were measured without proton decoupling, no long-range J_{NH} couplings could be resolved. The numbering scheme of the molecules does not follow in all cases the nomenclature rules for the sake of the comparability of chemical shifts, *i.e.* N-1 is always the highly substituted, amine-like (saturated) nitrogen atom of the dihydrotriazole ring bonded to N-2 and C-5, see for example **18**–**21**. The sulfur heterocycle **25** [1,2,3,4-thiatriazol-5(4*H*)-one] could be regarded as a formal derivative of a 4,5-dihydro-1*H*-1,2,3-triazole. There were no differences in ^{15}N chemical shifts observed for the ^{15}N labelled (Fig. 1) and the unlabelled compounds.

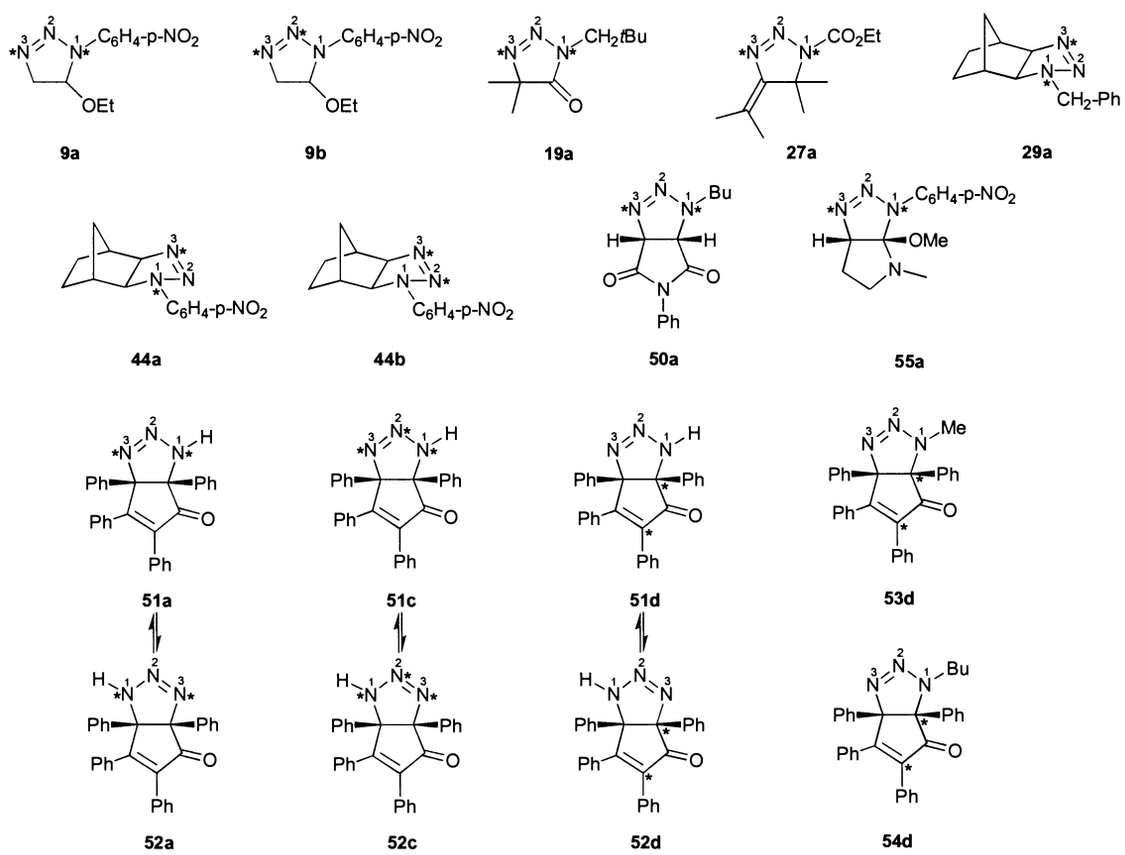
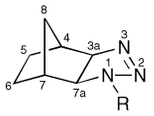


Fig. 1 ^{15}N and ^{13}C labelled compounds.

Table 2 Data of new 4,5-dihydro-1*H*-1,2,3-triazoles (3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-benzotriazoles)



33 R=Bu
35 R=*p*-C_6H_4-NMe_2
39 R=*p*-C_6H_4-F
42 R=*p*-C_6H_4-COMe
43 R=*p*-C_6H_4-CN
45 R=*p*-C_6H_4-OH

Compound	**33**	**35**	**39**	**42**	**43**	**45**
δ ^{1}H (ppm)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in DMSO-d_6)
3a-H	4.34 (d, *J* 10)	4.52 (d, *J* 9.4)	4.57 (d, *J* 9.7)	4.64 (d, *J* 9)	4.67 (d, *J* 8.8)	4.51 (d, *J* 9.4)
4-H	2.61 [a] (broad s)	2.62 (broad s)	2.61 (broad s)	2.65 (broad s)	2.63 (broad s)	
5-H/6-H	1.15–1.70 (m)	1.20–1.85 (m)	1.20–1.80 (m)	1.20–1.80 (m)	0.9–1.9 (m)	
7-H	2.30 [a] (broad s)	2.74 (broad s)	2.78 (broad s)	2.80 (broad s)	2.85 (broad s)	
7a-H	3.19 (d, *J* 10)	3.72 (d, *J* 9.4)	3.69 (d, *J* 9.7)	3.73 (d, *J* 9)	3.70 (d, *J* 8.8)	3.78 (d, *J* 9.4)
8-H	1.12 (s)	1.16 (s)	1.15 (s)	1.15 (s)	[in 0.9–1.9 (m)]	
Other hydrogens	0.93 (t, 4′-H) 3.53 (t, 1′-H) 1.15–1.70 (m, 2′-H/3′-H)	6.79 (m, arom.) 7.23 (m, arom.)	6.80–7.40 (m, arom.)	7.30 (m, arom.) 7.95 (m, arom.)	7.32 (m, arom.) 7.62 (m, arom.)	6.75 (m, arom.) 7.10 (m, arom.)
δ ^{13}C (ppm)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in $CDCl_3$)	(in DMSO-d_6)
C-3a	85.3	84.7	85.9	86.4	86.9	84.8
C-4/C-7	40.8, 41.3	39.6, 40.6, 40.8 (C-1′)	39.5, 40.9	39.2, 40.4	39.5, 40.5	
C-5/C-6	24.8, 25.7	24.3, 24.9	24.4, 25.0	24.2, 24.8	24.2, 24.9	24.1, 24.8
C-7a	62.8	60.6	60.1	59.0	58.9	60.1
C-8	30.7, 32.3 (C-2′)	31.5	31.7	31.4	31.5	
Other carbons	13.7 (C-4′) 20.0 (C-3′) 48.0 (C-1′)	113.4, 115.1, 130.9, 146.2 (arom.)	114.7, 115.6, 136.4, 157.8 (arom.)	25.6 (CO*Me*) 112.5, 129.6, 130.1, 143.3 (arom.), 195.5 (CO)	103.5 (CN) 113.4, 118.7, 133.1, 143.0 (arom.)	115.4, 115.8, 132.5, 152.5 (arom.)
Melting point /°C	(colorless oil)	123 (ether–petroleum ether)	100.5–101 (ether–petroleum ether)	144–145	140–140.5 (petroleum ether–ether–methanol)	156–160 (THF)
Analysis						
Formula	$C_{11}H_{19}N_3$	$C_{15}H_{20}N_4$	$C_{13}H_{14}FN_3$	$C_{15}H_{17}N_3O$	$C_{14}H_{14}N_4$	$C_{13}H_{15}N_3O$
Found (calc.) (%)						
C	68.19 (68.35)	70.15 (70.28)	67.56 (67.51)	70.39 (70.57)	70.64 (70.57)	67.84 (68.10)
H	9.86 (9.91)	7.88 (7.80)	6.10 (6.10)	6.70 (6.71)	5.93 (5.92)	6.65 (6.59)
N	22.00 (21.74)	21.90 (21.86)	18.20 (18.17)	16.30 (16.46)	23.60 (23.51)	18.20 (18.33)
IR/cm^{-1}	(in CCl_4) 1450, 1460, 1470, 2880, 2960	(in CCl_4) 1095, 1260, 1330, 1475, 1510, 2960	(in CCl_4) 1225, 1490, 1505, 2960	(in CCl_4) 1265, 1365, 1495, 1595, 1675 (CO), 2960	(in CCl_4) 1370, 1495, 1510, 1600, 2220 (CN), 2960	(KBr) 1125, 1140, 1230, 1360, 1440, 1460, 1510, 2960

[a] May be exchanged.

For the assignment of the ^{15}N NMR signals of the 4,5-dihydro-1*H*-1,2,3-triazoles to N-1, N-2 and N-3, the electronic difference between pseudo-sp^3 and sp^2 hybridized nitrogen atoms was used to assign the signal at highest field to N-1. For the unequivocal distinction of N-2 and N-3 (both sp^2 hybridized nitrogen atoms), **29a** was investigated, which is labelled at the N-1 and N-3 positions.

The amine-like nitrogen N-1 shows in all cases the signal at the highest field in the range δ = −201 to −138 ppm. The resonance of nitrogen N-2 is observed usually at lowest field, *i.e.* in the range δ = 12 to 62 ppm. The chemical shift of nitrogen N-3 is found in the range −54 to 6 ppm, except in the case of compounds with a ring carbonyl group (**18**–**21**) which causes strong downfield shifts to δ values of *ca.* 30 ppm.

Generally, the ^{15}N NMR data of 4,5-dihydro-1*H*-1,2,3-triazoles are clearly distinguished from those of cyclic azimines (4,5-dihydro-1*H*-1,2,3-triazol-2-ium-1-ides) as structurally isomeric compounds[54] and those of open chain triazenes[55] as well.

The four ^{15}N NMR resonances of **9** could be assigned by means of labelling N-1 and N-3 (**9a**) and N-2 and N-3 (**9b**), respectively (Fig. 1). Thus, the ^{15}N NMR signals of N-3 (−17.6 ppm) and NO_2 (−12.7 ppm) became assignable. For the compounds **44** (labelled **44a** and **44b**) and **55** (labelled **55a**), a similar assignment was done.

For the ^{15}N chemical shift assignment of dihydrotriazolone **19**, especially to N-2 and N-3, the corresponding N-1 and N-3 ^{15}N labelled isotopomer **19a** was prepared. The signal at δ = 32.8 ppm stems from N-3 without doubt; nitrogen N-2 gives rise to the remaining ^{15}N resonance at δ = 44.0 ppm.

The assignments of the ^{15}N NMR signals of the thiatriazolone **25**[8] are easily performed by comparison with the data of **18**–**21**.

The four nitrogen NMR signals of compound **50**, especially the differentiation of N-1 and the imide-N, could be achieved by ^{15}N labelling of N-1 and N-3 (compound **50a**, Fig. 1).

Tautomeric and diastereomeric compounds

Several years ago, two of us employed ^{15}N NMR spectroscopy for the elucidation of the prevailing tautomer of 5,5-diphenyldihydro-1,2,3-triazol-4(4*H*)-one, which exhibits the structure **20**.[7]

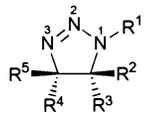
The bicyclic [3 + 2] cycloadduct obtained from tetraphenylcyclopentadienone and sodium azide under acidic conditions has been reported to have a single tautomeric structure, namely **51**, without experimental evidence.[19] However, our ^{15}N spectrum of this substance in DMSO-d_6 shows two signal sets with different intensity (ratio *ca.* 4 : 1) in accord with the possible tautomers **51** and **52** (Fig. 1, Scheme 4, Table 3). The

Table 3 ^{15}N chemical shifts and synthesis references for compounds of Schemes 1–5

Compound	^{15}N Chemical shifts N-1	N-2	N-3	Other nitrogen	Reference for preparation
1	−195.5	54.6	−31.4		22, 23
2	−194.6	53.3	−28.4		22, 24
3	−182.8	35.0	−29.3		25
4	−182.7	33.3	−42.0		26
5	−174.4	35.7	−34.4		27
6	−178.8	34.7	−29.9		28
7	−195.5	52.8	−56.2	−127.1 (CN)	29
8	−175.4	34.6	−30.4		28
9	−168.3	32.7	−17.6	−12.7 (NO_2)	30, 31
10	−182.5	37.6	−50.7	−286.4 (NEt_2)	32
11	−182.6	34.1	−46.8		26
12	−177.1	36.3	−48.4		33
13	−176.9	35.8	−46.8		33
14	−177.6	44.4	−5.3		34
15	−179.5	43.5	−8.2		34
16	−172.5	52.4	−12.1		35
17	−172.4	52.0	−10.4		35
18	−148.4	43.7	32.2		36
19	−163.1	44.0	32.8		36
20[a,b]	−169.1	39.6	30.4		37
21[b]	−173.1	42.8	27.4		37
22	−179.7	32.4	−6.9		35
23	−172.9	36.4	3.5	−160.4 (NMe)	38
24	−183.1	34.6	5.4	−161.2 (NMe)	38
25[c]	−140.2	36.5	−18.8		8
26	−167.7	18.3	−36.3		39
27	−159.3	12.4	−11.4		39
28	−184.0	48.0	−25.8		40
29	−188.3	47.6	−36.1		41
30	−166.9	47.0	−36.5		42
31	−201.2	38.2	−17.4		43
32	−162.9	33.3	2.5		44
33	−190.1	47.9	−39.0		see Exp.
34	−168.7	38.5	−25.4		45
35	−176.9	33.5	−35.4	−339.5 (NMe_2)	see Exp.
36	−176.5	33.5	−31.2		46
37	−175.0	33.5	−29.3		46
38	−173.9	33.5	−27.5		41, 46, 47
39	−176.0	33.1	−26.7		see Exp.
40	−174.9	32.6	−24.0		41
41	−175.0	32.2	−23.8		44, 46
42	−170.9	32.2	−17.0		see Exp.
43	−170.8	31.6	−14.5	−127.5 (CN)	see Exp.
44	−169.7	31.7	−12.1	−12.5 (NO_2)	41, 46
45[d]	−175.7	33.9	−28.7		see Exp.
46	−172.6	33.8	−26.8	−324.7 (pyrrolidino)	48
47	−137.9	38.1	5.6	−318.1 (pyrrolidino)	31
48	−175.9	33.9	−23.7	−329.3 (morpholino)	48, 49
49[d]	−178.5	34.2	−37.1	−197.6 (imide-N)	44, 50
50	−193.7	46.2	−53.6	−198.3 (imide-N)	44
51[e]	−189.4[f]	34.6	−40.9		19
52[e]	−193.4[f]	37.0	−37.6		(19)
53	−200.1	36.0	−46.2		19
54	−183.2	40.0	−41.9		see Exp.
55	−170.0	41.4	−11.9	−12.4 (NO_2) −321.0 (NMe)	51
56	−172.1	34.3	−15.9		28
57	−168.9	35.0	−12.0		52
58	−159.4	62.3	−12.1		53
59	−161.3	58.4	−5.4		53
60	−152.7	59.4	−11.2		53
61	−194.1	51.0	−32.9		see Exp.
62[g]	−170.5	36.5	−26.8		9
	−170.5	36.5	−27.3		

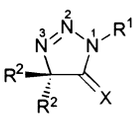
[a] In CD_3OD. [b] The chemical shifts have been reported in ref. 7. [c] The chemical shifts have been reported in ref. 8. [d] In DMSO-d_6. [e] In DMSO-d_6 at 363 K. [f] Doublet with $^1J_{NH}$ = 100.5 Hz. [g] No assignment of *meso* and *rac* compounds, the chemical shifts have been reported in ref. 9.

^{13}C NMR and ^{1}H NMR spectra also indicate the presence of both tautomeric forms. To assign the tautomers, the ^{13}C enriched compounds **51d/52d** were investigated. ^{13}C NMR spectroscopy proved that **51** is the major and **52** the minor tautomeric structure. By ^{13}C labelling (**53d**), it could be evidenced that the methylation product of **51**/**52**, proposed to be **53**,[19] really possesses this structure, which is homologous to that of **51**. The other conceivable methylation product with

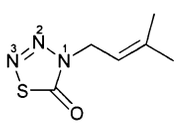


Compound	R^1	R^2	R^3	R^4	R^5
1	Bu	H	H	H	H
2	CH_2Ph	H	H	H	H
3	Ph	H	H	H	H
4	Ph	H	H	CO_2Me	H
5	Ph	Ph	H	H	H
6	*p*-C_6H_4-Br	C(Me)=CH_2	H	H	H
7	Bu	H	H	CN	H
8	*p*-C_6H_4-Br	Bu	H	H	H
9	*p*-C_6H_4-NO_2	OEt	H	H	H
10	Ph	H	H	SO_2NEt_2	H
11	*p*-C_6H_4-OMe	CO_2Me	H	CO_2Me	H
12	Ph	Ph	H	CO_2Me	CO_2Me
13	Ph	Ph	H	CO_2Et	CO_2Et
14	CH_2Ph	OH	$CHMe_2$	Me	Me
15	CH_2Ph	OH	Ph	Me	Me
16	CH_2tBu	OH	CH_2SiMe_3	Me	Me
17	CH_2tBu	OH	Me	Me	Me

Scheme 1



18–24



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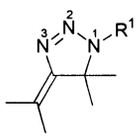
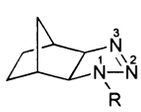


26, 27

Compound	X	R^1	R^2
18	O	*t*Bu	Me
19	O	CH_2tBu	Me
20	O	H	Ph
21	O	Me	Ph
22	CH_2	CH_2tBu	Me
23	NMe	CH_2tBu	Me
24	NMe	Me	Me
26	–	Ph	–
27	–	CO_2Et	–

Scheme 2

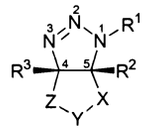


Compound	R	Compound	R
28	$SiMe_3$	**37**	*p*-C_6H_4-Me
29	CH_2Ph	**38**	Ph
30	1-adamantyl	**39**	*p*-C_6H_4-F
31	C_6F_5	**40**	*p*-C_6H_4-Cl
32	CO_2Et	**41**	*p*-C_6H_4-Br
33	Bu	**42**	*p*-C_6H_4-COMe
34	C(Ph)=CH_2	**43**	*p*-C_6H_4-CN
35	*p*-C_6H_4-NMe_2	**44**	*p*-C_6H_4-NO_2
36	*p*-C_6H_4-OMe	**45**	*p*-C_6H_4-OH

Scheme 3

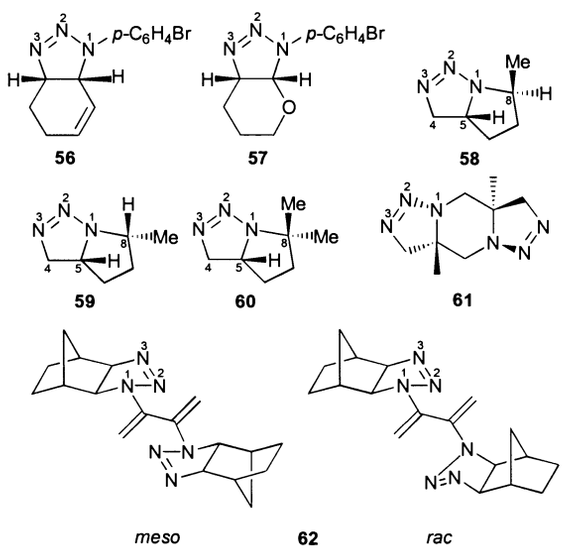
a structure similar to that of **52** was not observed. The ^{13}C chemical shifts of the bridgehead carbons (C-4, C-5) and the carbonyl groups of **51**–**53** and of the related compound **54** are summarized in Table 4.

The intramolecular 1,3 dipolar cycloaddition reaction of 5-azidohex-1-ene did not afford a single diastereomer as reported in ref. 53; instead, a 4 : 1 mixture of the *exo* (**58**)



Compound	X	Y	Z	R^1	R^2	R^3
46	-CH_2-	-CH_2-	-CH_2-	Ph	*N*-pyrrolidino	H
47	-CH_2-	-CH_2-	-CH_2-	COPh	*N*-pyrrolidino	H
48	-CH_2-	-CH_2-	-CH_2-	Ph	*N*-morpholino	H
49	-C(O)-	-N(Ph)-	-C(O)-	Ph	H	H
50	-C(O)-	-N(Ph)-	-C(O)-	Bu	H	H
51	-C(O)-	-C(Ph)=	C(Ph)-	H	Ph	Ph
52	-C(Ph)=	C(Ph)-	-C(O)-	H	Ph	Ph
53	-C(O)-	-C(Ph)=	C(Ph)-	Me	Ph	Ph
54	-C(O)-	-C(Ph)=	C(Ph)-	Bu	Ph	Ph
55	-N(Me)-	-CH_2-	-CH_2-	*p*-C_6H_4-NO_2	OMe	H

Scheme 4



56 **57** **58**

59 **60** **61**

meso **62** *rac*

Scheme 5

Table 4 Selected ^{13}C NMR chemical shifts of **51**–**54** (ppm, in $CDCl_3$)

Carbon	**51**	**52**	**53**	**54**
C=O	200.8	198.8	199.0	199.5
C-4	97.7	97.2	99.0	98.7
C-5	75.1	77.2	76.6	77.3

In the case of the labelled compounds, signal enhancements were observed for C-4 of **52d** and for C-5 of **51d**, **53d** and **54d**.

and the *endo* diastereomer (**59**) was formed (Scheme 5). The structure assignment was performed both by lanthanide induced shift experiments (Fig. 2) and by 2D NOESY NMR spectroscopy.

As proved by ^{15}N NMR LIS experiments (see below) and by strong downfield shifts of the adjacent protons 4-H, the complexing site of 4,5-dihydro-1*H*-1,2,3-triazoles is N-3. Thus, the lanthanide induced shift of the signal of the methyl group is less effective in the case of **58** since the *exo*-methyl group is more distant from N-3 as compared to the case of **59**. Additionally, the *endo*-proton geminal to the *exo*-methyl group of **58** (8-H) shows nearly the same LIS as the bridgehead proton (5-H). So a second piece of evidence for the *exo* position of the methyl group of the major isomer **58** is given. By adding the shift reagent to **60**, the same influence on proton chemical shifts was observed although the effect was not as strong as for

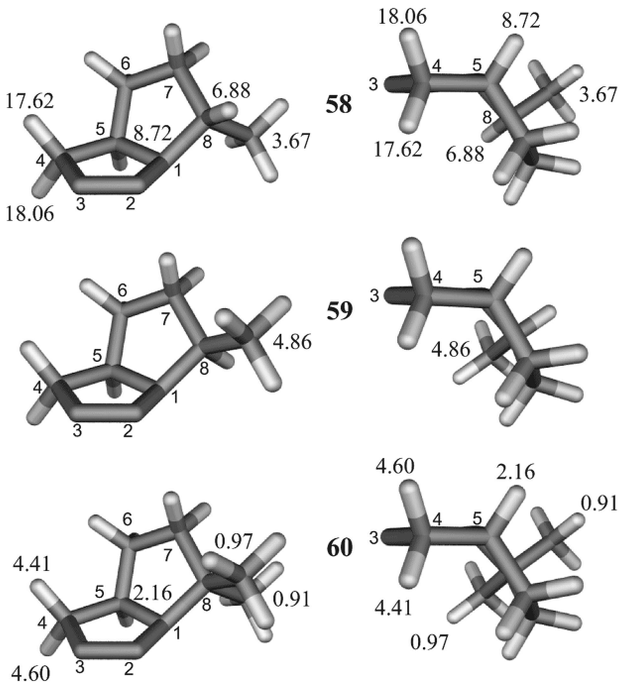


Fig. 2 Effects of Yb(thd)$_3$ shift reagent on ^{1}H chemical shifts in $\Delta\delta$ (in ppm, downfield) at 1 : 1 molar ratio (calculated by linear regression with a correlation coefficient better than 0.97) of selected protons of **58**–**60** (concentrations during LIS measurement: **58**/**59** *ca.* 45 mmol l^{-1}, **60** *ca.* 3 mmol l^{-1}).

58 and **59** (compare Fig. 2), probably caused by a smaller concentration of **60** during the measurement. The 2D NOESY spectrum shows cross signals between the methyl group and 5-H for **58** which indicates also the *exo* position of the methyl group. If the methyl group were in the *endo* position, a NOE should be observed between 5-H and 8-H which was not detected, however. The ^{1}H and ^{13}C NMR data of the 1,2,3-triazabicyclo[3.3.0]oct-2-enes **58**–**60** are summarized in Table 5.

Influence of concentration, solvents and shift reagents

The effect $\Delta\delta$ on the ^{15}N chemical shifts caused by different concentrations of 4,5-dihydro-1*H*-triazoles was less than 2 ppm. For example, on comparison of a 0.64 molar and a 1.1 molar solution of **15** in $CDCl_3$, the absolute $\Delta\delta$ values were as follows: 0.05 ppm for N-1, 0.39 ppm for N-2 and 1.64 ppm for N-3. The use of solvents other than $CDCl_3$ (see Table 6) affects the signals of N-1 and N-2 ($\Delta\delta$ < 2 ppm) less than that of N-3 whose shift values vary up to 15 ppm (for **1** in CD_3OD *vs.* cyclohexane-d_{12}).

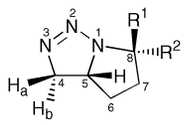
The application of lanthanide induced shift reagents to 4,5-dihydro-1*H*-triazoles can cause strong changes of ^{15}N shifts ($\Delta\delta$ > 150 ppm). Interaction of Yb(thd)$_3$ [tris(2,2,6,6-tetramethylheptane-3,5-dionato)ytterbium(III)] and **38** leads to the strongest downfield shift for N-3 while the effect on N-1 was the smallest. This behavior was found with all investigated compounds. Its accordance with the calculated preference for protonation[56] at N-3 allows the conclusion that this is the nitrogen which interacts with the shift reagent. The results are summarized in Fig. 3.

For **50a**, not so strong downfield shifts were observed. This is probably caused by the additional two complexing sites (C=O groups) in the molecule.

^{14}N NMR measurements

Despite considerable line broadening, the ^{14}N NMR spectrum of **1** (Fig. 4) consists of singlets which are sharp enough for the measurement of accurate chemical shifts. But this example is, unfortunately, not representative. In most other cases, no ^{14}N NMR chemical shifts could be measured because of excessive broad lines.

Table 5 ^{1}H and ^{13}C NMR data (δ in ppm, J in Hz, solvent $CDCl_3$) of **58**–**60** (obtained by ^{13}C APT, ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and simulation of 4-H$_a$, 4-H$_b$ and 5-H couplings)



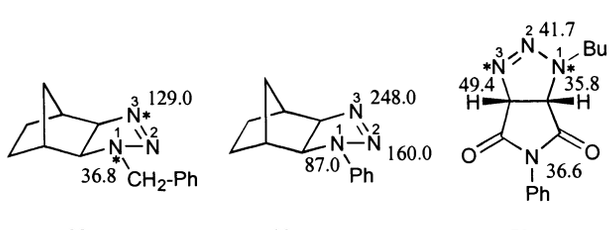
58 R^1=Me R^2=H
59 R^1=H R^2=Me
60 R^1=Me R^2=Me

	^{1}H		^{13}C	
58	6-H (m)	1.17	Me	21.7
	Me (d, *J* 6.9)	1.33	C-6	30.0
	7-H (m)	1.41	C-7	31.7
	6-H (m)	1.81	C-5	56.8
	7-H (m)	1.84	C-8	57.5
	5-H (m)	3.66	C-4	71.8
	4-H$_a$ (dd, *J* 16.5, 9.6)	4.07		
	4-H$_b$ (dd, *J* 16.5, 2.6)	4.29		
	8-H (m)	4.34		
59[a]	Me (d, *J* 6.7)	1.66	Me	16.8
	5-H (m)	3.60	C-6/C-7	30.3
	4-H$_a$ (dd, *J* 16.5, 9.7)	4.13		31.8
			C-5/C-8	57.0
				59.9
			C-4	73.7
60	*exo*-Me (s)	1.28	*exo*-Me	25.9
	6-H (m)	1.30	*endo*-Me	25.6
	7-H (m)	1.55	C-6	30.0
	endo-Me (s)	1.65	C-7	37.4
	6-H (m)	1.86	C-5	56.2
	7-H (m)	1.86	C-8	64.9
	5-H (m)	3.76	C-4	73.0
	4-H$_a$ (dd, *J* 16.5, 9.9)	4.10		
	4-H$_b$ (dd, *J* 16.5, 2.7)	4.32		

[a] Signals of **59** partially covered by those of **58**.

Table 6 Solvent influence on ^{15}N chemical shifts

Compound	Solvent	^{15}N Chemical shifts		
		N-1	N-2	N-3
1	$CDCl_3$	−195.5	54.6	−31.4
	Cyclohexane-d_{12}	−195.9	56.4	−24.4
	CD_3OD	−195.1	54.6	−39.1
28	$CDCl_3$	−184.0	48.0	−25.4
	Acetone-d_6	−184.1	48.0	−21.2
	Benzene-d_6	−184.8	47.7	−20.9
	DMSO-d_6	−183.7	48.0	−22.4
50	$CDCl_3$	−193.7	46.2	−53.6
	DMSO-d_6	−193.1	47.1	−48.7



29a **38** **50a**

Fig. 3 Effects of Yb(thd)$_3$ shift reagent on ^{15}N chemical shifts ($\Delta\delta$ in ppm, downfield) at 1 : 1 molar ratio calculated by linear regression with a correlation coefficient better than 0.989.

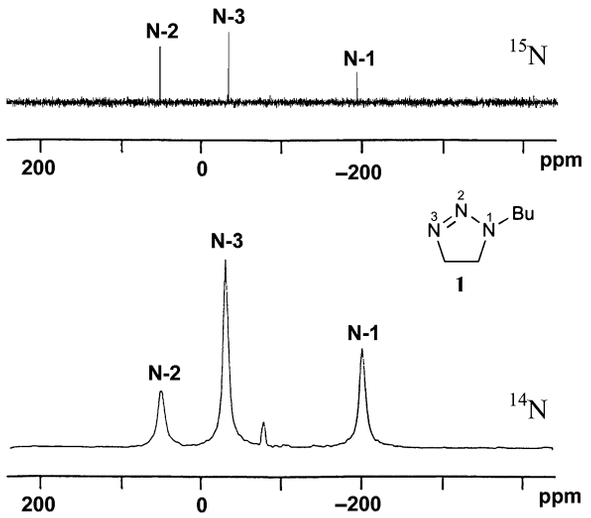


Fig. 4 ^{15}N and ^{14}N NMR spectra of compound **1**.

The effect of substituents on the ^{15}N chemical shifts

Effects of substituents at N-1. If the number of β carbons of the N-1 substituent increases, a substantial downfield shifting of the N-1 resonance is found, compare **19** (CH_2tBu) *vs.* **18** (tBu) and **24** (Me) *vs.* **23** (CH_2tBu, Scheme 2, Table 3) as well as **33** (Bu) *vs.* **30** (1-adamantyl, Scheme 3). This β effect resembles that observed with aliphatic amines.[57]

Formal change of the N-1 substituent from aliphatic to aromatic causes strong and variable downfield shifts of the N-1 and N-3 signals, respectively, and a strong upfield shift of the N-2 resonance, see compounds **1** (Bu) and **2** (CH_2Ph) *vs.* **3** (Ph, Scheme 1) and **33** (Bu) and **29** (CH_2Ph) *vs.* **38** (Ph, Scheme 3) as well as **50** (Bu) *vs.* **49** (Ph, Scheme 4). The effect on the N-1 shielding is similar in the case of amines, compare, for example, butylamine ($\delta = -359.4$ ppm) with aniline ($\delta = -320.3$ ppm).[58] Furthermore, electronic (resonance) effects cause changes of the N-2 and N-3 chemical shifts.

If the N-1 substituent is changed from a phenyl to a carbonyl group, strong or even very strong downfield shifts of N-1 and N-3 signals are observed, compare **26** (Ph) *vs.* **27** (CO_2Et, Scheme 2) and **38** (Ph) *vs.* **32** (CO_2Et, Scheme 3) as well as **46** (Ph) *vs.* **47** (COPh, Scheme 4).

A change from alkyl to silyl substituent at N-1 causes downfield shifts both of N-1 and N-3 signals, see **33** (Bu) *vs.* **28** ($SiMe_3$, Scheme 3). The fact that this shift is towards *lower* field is remarkable because in the case of amines the same structural change results in a shift into the opposite direction, see, for example, Bu–NMe_2 ($\delta = -352.8$ ppm)[57] and Me_3Si–NMe_2 ($\delta = -378.5$ ppm).[58]

As may be anticipated on consideration of the substituent effects discussed above, the downfield shifts of the signals of N-1 and N-3, and the opposite shifts of N-2, which originate from increasingly electron-withdrawing substituents at the *para* position of the phenyl rings of **35**–**44**, result in satisfactory linear relationships with Hammett's σ_p constants[59] (Fig. 5). While the signs of the slopes are as expected, their absolute values surprise, however. The signal of N-3 rather than that of N-1, to which the *p*-substituted phenyl ring is actually attached, is affected most strongly by variation of the *p*-substituent. On the other hand, the signal of N-2 is almost invariant toward these changes.

Since ^{19}F chemical shifts of *p*-substituted fluorobenzenes[60] are linearly correlated with the σ_p constants of the substituents, it comes as no surprise that the ^{15}N shifts of the 1-aryldihydrotriazoles **35**–**44** yield linear relationships with those ^{19}F shifts as well (Fig. 6). Their slopes, *viz.* 0.302 for N-1, −0.078 for N-2 and 0.877 for N-3, show that the electronic effects

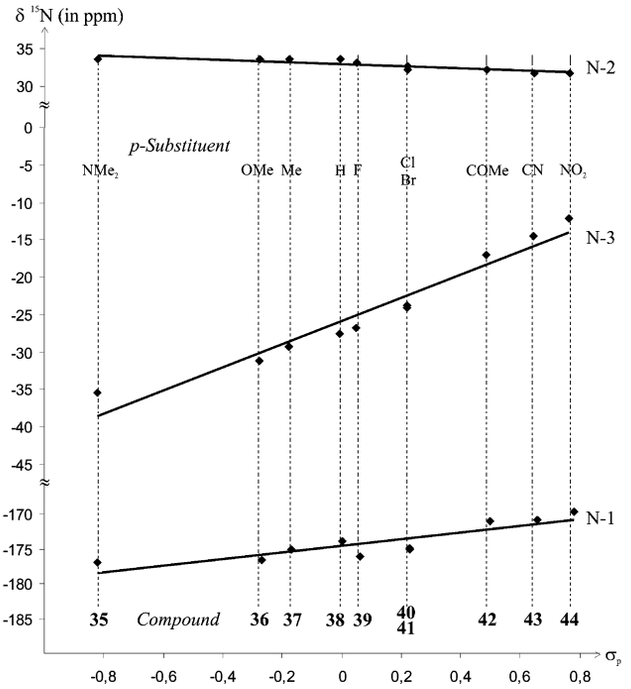


Fig. 5 Correlation of Hammett σ_p constants *vs.* ^{15}N chemical shifts of compounds **35**–**44**.

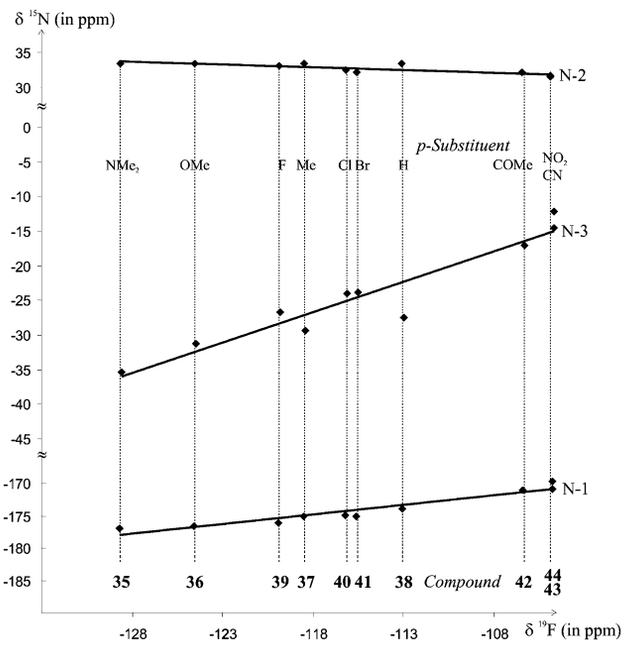


Fig. 6 Correlation of ^{19}F chemical shifts of *p*-substituted fluorobenzenes *vs.* ^{15}N chemical shifts of compounds **35**–**44**.

of *p*-substituents on the ^{15}N nuclei of **35**–**44** indeed closely resemble those on the ^{19}F nuclei in the corresponding fluorobenzenes.

Effects of substituents at C-4. If electron acceptors, like –COR, –SO_2NR_2, or –CN are bound to C-4, the N-3 signal is strongly shifted upfield, compare **1** (H) *vs.* **7** (CN) and **3** (H) *vs.* **4** (CO_2Me) and **10** (SO_2NEt_2) as well as **5** (H) *vs.* **12** (CO_2Me) and **13** (CO_2Et, Scheme 1). The explanation of this effect may, perhaps, be based on the polarization of the π bond between the nitrogens N-2 and N-3 affording an increased electron density at N-3. Surprisingly, however, no significant effects on the shifts of N-2 and N-1 are found.

Effects of substituents at C-5. A formal exchange of hydrogen at C-5 for phenyl [compare **3** *vs.* **5** (Scheme 1)] shifts the N-1 signal downfield and the N-3 signal upfield because of the β effect of the phenyl group on N-1 and the γ effect on N-3, respectively.

The butyl group at C-5 of **8** has a γ effect on N-1 while the C-5 isopropenyl group of **6** causes two γ effects on the same nitrogen. Thus, a small overall upfield shift is observed in the latter case.

Upfield shifts of the N-1 and N-2 resonances and very strong upfield shifts for the N-3 resonance are observed when the oxo group in position 5 is formally exchanged for an *N*-methylimino or a methylene group [compare **19** *vs.* **23** *vs.* **22** (Scheme 2)]. These upfield shifts are readily interpreted in terms of the electronegativity of the elements that are doubly bonded at C-5. However, the differences between the oxo compound (**19**) and the imino compound (**23**) are surprisingly greater than that between the latter (**23**) and the methylene compound (**22**).

Conclusions

^{15}N NMR spectroscopy is still not widely used, and the presented chemical shift data of 4,5-dihydro-1*H*-triazoles and their dependence on the nature of substituents detailed here may be useful for further structure determinations of such heterocycles by this method or for the assignment of ^{15}N signals of similar heterocyclic compounds.

Acknowledgements

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