

## 2,5-Dihydro-1*H*-1,2,4-triazol-2-yl Radicals: Syntheses and Properties<sup>#</sup>

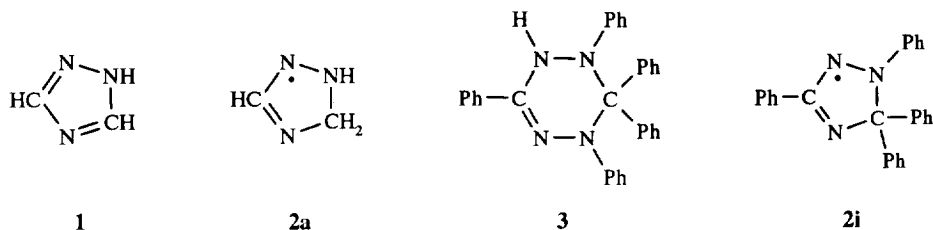
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**Abstract:** A range of 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals **2b–p** has been prepared by dehydrogenation of the corresponding 4,5-dihydro-1*H*-1,2,4-triazoles **5b–p** which have been synthesized using various methods. EPR, ENDOR and NMR studies have led to a complete analysis and full assignment of all hyperfine coupling constants. The  $\pi$ -SOMO, having a node at the C(3) methine carbon, is mainly confined to the nitrogens of the five-membered ring, particularly to those of the hydrazyl moiety.

### INTRODUCTION

Gloux and Lamotte<sup>1-3</sup> discovered that  $\gamma$ -irradiation of single crystals of 1*H*-1,2,4-triazole (**1**) generates 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals (**2a**) being formed by addition of a hydrogen atom to a ring carbon. This  $\pi$ -radical can be considered to be the primary representative of a special type of cyclic hydrazyl radicals. Some time ago, we observed a stable radical of similar structure, when we studied the radical species appearing in acidic solutions of 1,2,5,6-tetrahydro-1,3,5,6,6-pentaphenyl-1,2,4,5-tetrazine (**3**).<sup>4</sup> We isolated the stable monomeric 2,5-dihydro-1,3,5,5-tetraphenyl-1*H*-1,2,4-triazol-2-yl radical (**2i**) by chromatographic separation of the reaction mixtures, *e. g.* of a solution of **3** in formic acid.<sup>5</sup>

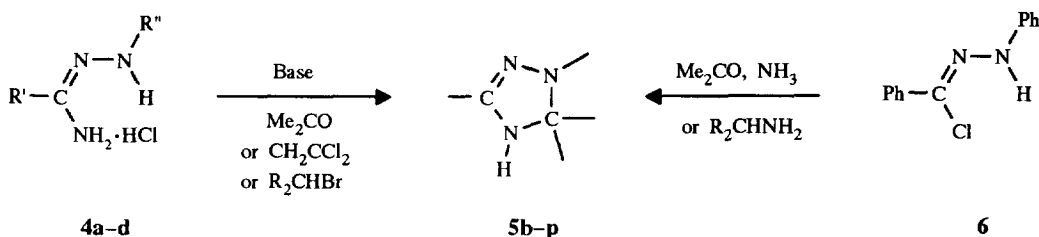


This unexpected result and our continuing interest in the properties of stable radicals prompted us to investigate 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals (**2**) in detail. Hydrazyl radicals can be readily generated by dehydrogenation of corresponding hydrazines. Therefore, 4,5-dihydro-1*H*-1,2,4-triazoles (**5**) seemed to be suitable starting materials for the formation of radicals of type **2**. By dehydrogenation of **5b–p** we generated in solution or isolated in substance, respectively, various 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals (**2b–p**) and studied their properties.

<sup>#</sup> Dedicated to Professor Hans Suschitzky on the occasion of his 80th birthday.

## RESULTS AND DISCUSSION

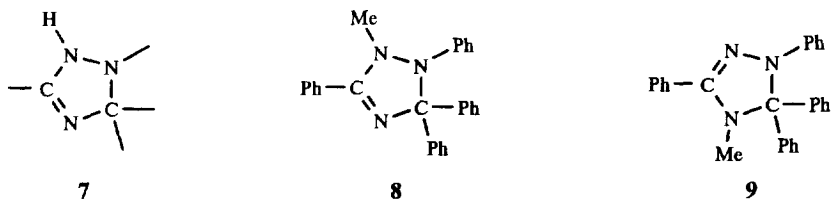
**4,5-Dihydro-1*H*-1,2,4-triazoles.** The required 4,5-dihydro-1*H*-1,2,4-triazoles **5b-p** were synthesized using different approaches. Zelenin *et al.*<sup>6</sup> found that treatment of *N*<sup>2</sup>-methylbenzamidrazone (**4b**) with acetone affords **5c** in 33% yield. Similarly, compounds **5b** and **5g** were prepared from *N*<sup>2</sup>-phenylformamidrazone (**4a**) (produced by hydrogenation of nitroformaldehyde phenylhydrazone) and the <sup>15</sup>N-labelled *N*<sup>2</sup>-phenylbenzamidrazone, respectively. Compounds **5d-f** (ca. 45%) were obtained, when *N*-phenyl-benzohydrazonoyl chloride (**6**) was treated with ammonia in the presence of acetone. These routes are restricted to dialkyl ketones. Owing to the lower carbonyl reactivity, benzophenone and 9-fluorenone gave no cyclization products under these conditions. However, when benzophenone was replaced by  $\alpha,\alpha$ -dichlorodiphenylmethane, the amidrazones **4c** and **4d** cyclized readily to afford the 4,5-dihydro-1*H*-1,2,4-triazoles **5h**, **5i**, and **5l**.



**4a** R' = H, R'' = Ph; **4b** R' = Ph, R'' = Me; **4c** R' = Me, R'' = Ph; **4d** R' = Ph, R'' = Ph.

Compound **5i** is likewise formed by heating a solution of *N*-phenyl-benzohydrazonoyl chloride (**6**) and  $\alpha$ -phenylbenzylamine. Similarly, compound **5m** was prepared using 9-amino-9*H*-fluorene. These results indicated that a ring closure of amidrazones with 9-bromo-9*H*-fluorene should also be feasible. In fact, treatment of *N*<sup>2</sup>-phenylbenzamidrazone (**4d**) with various 9-bromo-9*H*-fluorenes readily gave the corresponding spiro compounds **5m-p**. In this route the formed *N*-(9*H*-fluorene-9-yl)-*N*<sup>2</sup>-phenylbenzamidrazones are probably dehydrogenated to the corresponding 9-fluorenylidene derivatives which cyclize thermally to give the spiro 4,5-dihydro-1*H*-1,2,4-triazoles.

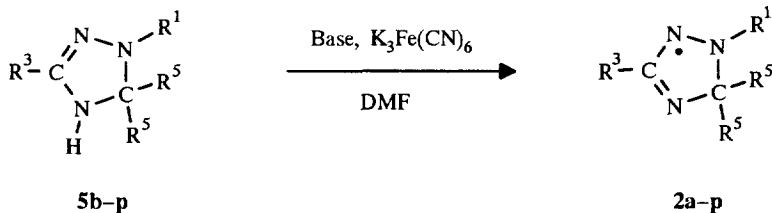
The 4,5-dihydro-1*H*-1,2,4-triazole **5i** can also be obtained in high yield (72%) via a completely different procedure, *i. e.* by thermal ring contraction of the leucoverdazyl **3** in the presence of phenylhydrazine as reducing agent. Using this route the 1,3-di[D<sub>5</sub>]phenyl substituted **5k** was prepared in a one-pot reaction starting from 1,3,5-tri[D<sub>5</sub>]phenylformazan without isolating the intermediate leucoverdazyl.



Dihydro-1*H*-1,2,4-triazoles can exist in two tautomeric forms, namely as 4,5-dihydro- (**5**) or 2,5-dihydro-1*H*-1,2,4-triazoles (**7**). Methylation of **5i** yielded exclusively the 2-methyl derivative **8**. Formation of the 4-methyl compound **9** was achieved by cyclization of *N*-methyl-*N*<sup>2</sup>-phenylbenzamidrazone with  $\alpha,\alpha$ -dichloro-

diphenylmethane. In the electronic spectra (Figure 1) the absorption of **8** [dioxane,  $\lambda_{\max}$  (log  $\epsilon$ ) 315 sh nm (3.23), 241 sh (4.25)] is found at considerably shorter wavelength than that of the parent compound **5i** [dioxane,  $\lambda_{\max}$  (log  $\epsilon$ ) 377 nm (4.02), 320 sh (3.74), 259 (4.04), 224 sh (4.27)], whereas the electronic spectrum of the 4-methyl derivative **9** [dioxane,  $\lambda_{\max}$  (log  $\epsilon$ ) 368 nm (3.90), 318 (3.83), 270 (4.00)] is similar to that of **5i**. The spectra indicate that dihydro-1*H*-1,2,4-triazoles in solution are predominantly present in the 4,5-dihydro tautomeric form **5**. In addition, the  $^1\text{H}$  NMR spectra of the labelled compounds **5f** [ $4\text{-}^{15}\text{N}$ ] and **5g** [ $2,4\text{-}^{15}\text{N}_2$ ] in  $[\text{D}_6]\text{DMSO}$  solution exhibit a typical  $^{15}\text{N}\text{-H}$  doublet (**5f**:  $J = 86.8$  Hz; **5g**:  $J = 86.7$  Hz) arising from the  $4\text{-}^{15}\text{N}\text{-H}$  group. This confirms that the tautomeric equilibrium lies completely on the side of the 4,5-dihydro tautomer **5**.

**2,5-Dihydro-1*H*-1,2,4-triazol-2-yl Radicals.** Dehydrogenation of the 4,5-dihydro-1*H*-1,2,4-triazoles **5d** and **5h-p** in dimethylformamide with potassium hexacyanoferrate (III) in the presence of sodium carbonate yielded the corresponding 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals **2d** and **2h-p** which were readily isolated as darkbrown or black crystals. Using this procedure **2b** and **2c** can also be generated, but attempts to obtain these radicals in a pure state failed. These examples show that aryl substitution in the 1-position (**2d**, **2h-p**) sufficiently stabilizes the 2,5-dihydro-1*H*-1,2,4-triazol-2-yl system to yield stable radicals, owing to the expanded delocalization of the unpaired electron. For studies of **2b**, **2c** and the labelled radicals **2e-g** the corresponding 4,5-dihydro-1*H*-1,2,4-triazoles **5b**, **5c** and **5e-g** in toluene were dehydrogenated with bis(4-methylphenyl)aminyI produced by thermal dissociation of tetrakis(4-methylphenyl)hydrazine.



	R <sup>1</sup>	R <sup>3</sup>	R <sup>5</sup> , R <sup>5</sup>	<sup>15</sup> N
<b>a</b>	H	H	H, H	
<b>b</b>	Ph	H	Me, Me	
<b>c</b>	Me	Ph	Me, Me	
<b>d</b>	Ph	Ph	Me, Me	
<b>e</b>	Ph	Ph	[D <sub>3</sub> ]Me, [D <sub>3</sub> ]Me	
<b>f</b>	Ph	Ph	Me, Me	4- <sup>15</sup> N
<b>g</b>	Ph	Ph	Me, Me	2,4- <sup>15</sup> N <sub>2</sub>
<b>h</b>	Ph	Me	Ph, Ph	
<b>i</b>	Ph	Ph	Ph, Ph	
<b>k</b>	[D <sub>5</sub> ]Ph	[D <sub>5</sub> ]Ph	Ph, Ph	
<b>l</b>	Ph	Ph	[3,5-D <sub>2</sub> ]Ph, [3,5-D <sub>2</sub> ]Ph	
<b>m</b>	Ph	Ph	biphenyl-2,2'-diyl	
<b>n</b>	Ph	Ph	[D <sub>8</sub> ]biphenyl-2,2'-diyl	
<b>o</b>	Ph	Ph	6,6'-dimethylbiphenyl-2,2'-diyl	
<b>p</b>	Ph	Ph	5,5'-dimethylbiphenyl-2,2'-diyl	

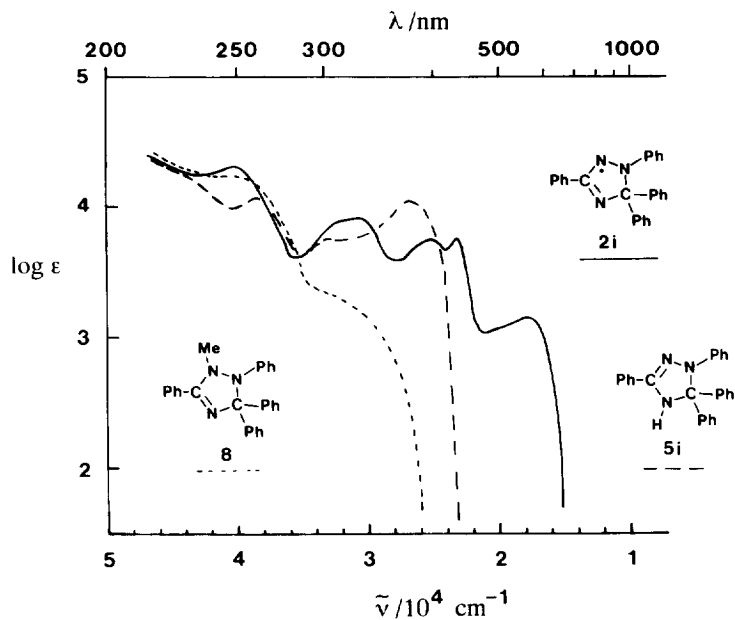


Figure 1. Electron absorption spectra of the compounds **2i**, **5i** and **8** in dioxane.

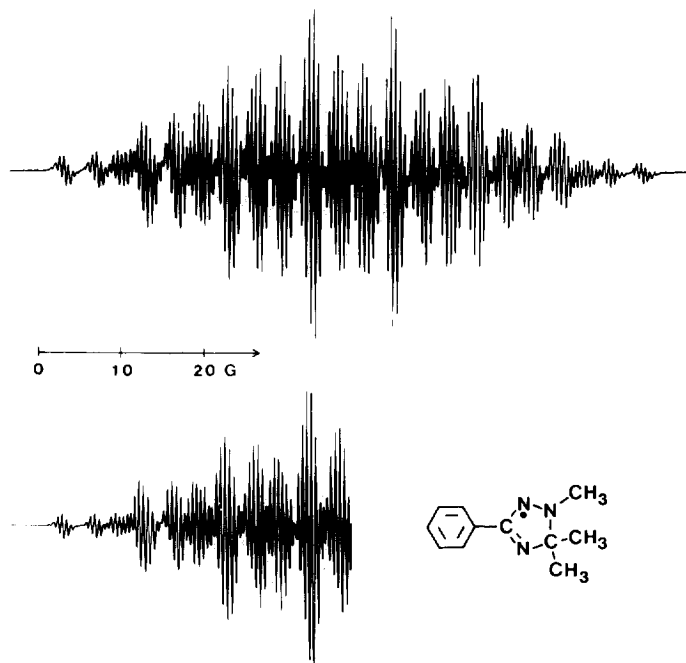
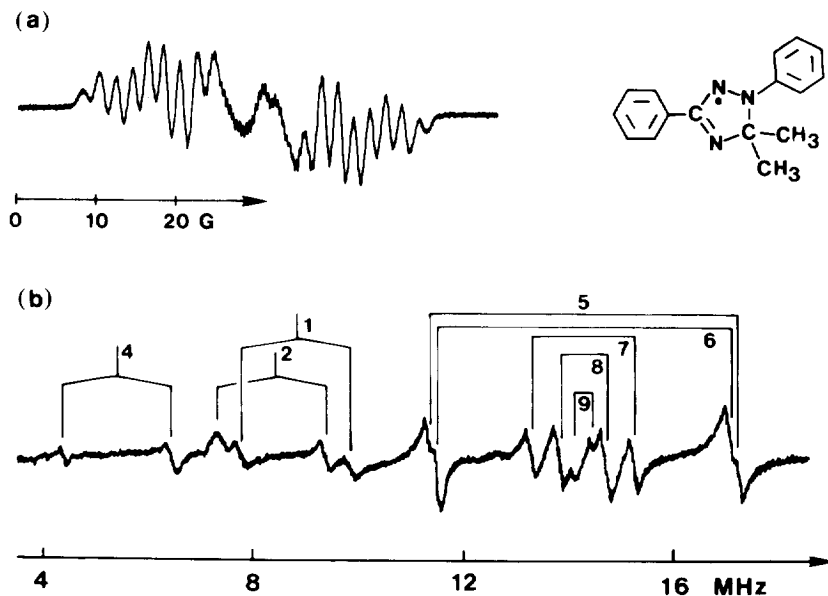


Figure 2. ESR spectrum of 2,5-dihydro-1,5,5-trimethyl-3-phenyl-1H-1,2,4-triazol-2-yl (**2c**) in toluene at 290 K together with a simulation using the data in Table 1.

The electron spectra of the radicals are characterized by a broad band system in the visible region (400–700 nm), where the corresponding leuco compounds, the 4,5-dihydro-1*H*-1,2,4-triazoles, show no absorption (Figure 1). The X-ray structure determination of **2i** revealed an almost planar 2,5-dihydro-1*H*-1,2,4-triazol-2-yl ring with the conjugated phenyl groups at N(1) and C(3) being nearly coplanar.<sup>5</sup> The N(1)–N(2) [1.338(2) Å] and N(2)–C(3) [1.368(2) Å] distances indicate about 50% double bond character and the C(3)–N(4) [1.305(2) Å] bond length is even slightly shorter than a C(2)=N(3) imidazole double bond [1.313 Å]<sup>7</sup>, whereas the N(4)–C(5) [1.469(2) Å] and N(1)–C(5) [1.506(2) Å] distances represent clear single bonds [C–N 1.465 Å].<sup>7</sup> The unusually large N(1)–C(5) bond is probably the result of steric repulsion between the three adjacent phenyl groups at N(1) and C(5).

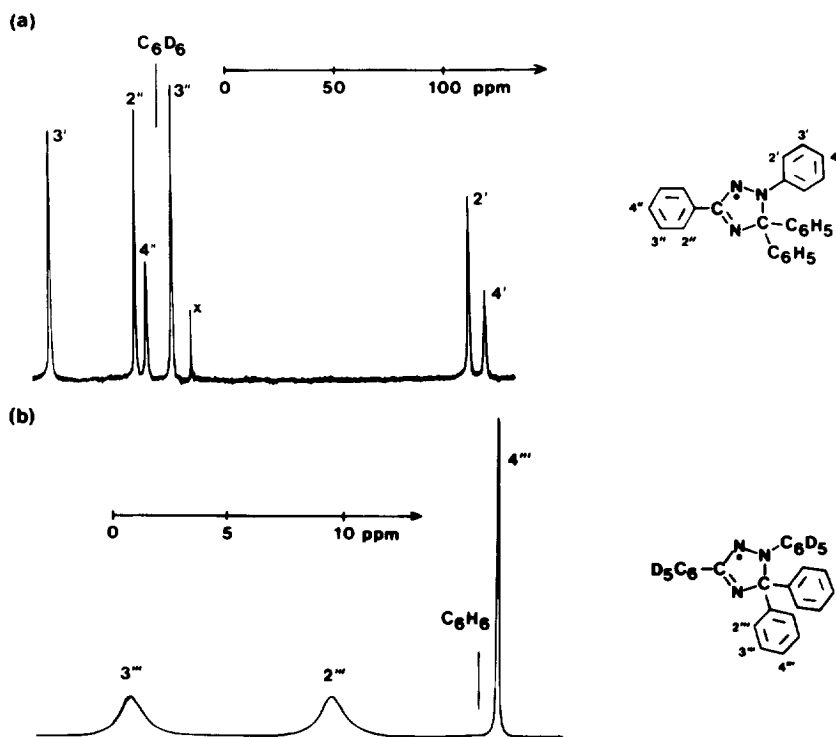
The  $\pi$ -SOMO of the 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals is mainly localized on the N(1), N(2), C(3), N(4) segment, as is clearly shown by the crystal structure of **2i**. This is confirmed by the results of the ESR, ENDOR and <sup>1</sup>H and <sup>2</sup>H NMR studies of the radicals. Tables 1 and 2 summarize the isotropic hyperfine coupling (HFC) constants of **2b–p**. Typical ESR spectra are shown in Figures 2 and 3(a). The ESR spectra of **2b** and **2c** (Figure 2) are well resolved and were well simulated with the values given in Table 1. From the less or poorly resolved ones [Figure 3(a)] only the dominant HFC splittings could be derived. Partial deuteration as in the case of **2n** improves the resolution. The analyses of the ESR spectra of **2b** and **2d–p** clearly gave the magnitude of the nitrogen HFC constants, *ca.* 7.5, 6.3, and 4.0 G, which were unambiguously assigned by <sup>15</sup>N labelling [ $a(^{15}\text{N}) = |1.40| a(^{14}\text{N})$ ] in the 4-position [**2f**:  $a(4\text{-}^{15}\text{N}) = 5.40$  G] and in the 2,4-positions [**2g**:  $a(2\text{-}^{15}\text{N}) = 8.80$ ,  $a(4\text{-}^{15}\text{N}) = 5.45$  G]. ENDOR studies [Figure 3(b)] not only confirmed the nitrogen splittings



**Figure 3.** (a) ESR spectrum of 2,5-dihydro-5,5-dimethyl-1,3-diphenyl-1*H*-1,2,4-triazol-2-yl (**2d**) in toluene at 295 K. (b) <sup>1</sup>H and <sup>14</sup>N ENDOR spectrum of **2d** in toluene at 230 K; 1: 0.5  $a(1\text{-N})$ , 2: 0.5  $a(2\text{-N})$ , 4: 0.5  $a(4\text{-N})$ , 5:  $a(4\text{-H}, 1\text{-Ph})$ , 6:  $a(2,6\text{-H}, 1\text{-Ph})$ , 7:  $a(3,5\text{-H}, 1\text{-Ph})$ , 8:  $a(\text{H}, 5,5\text{-CH}_3)$ , 9:  $a(\text{H}, 3\text{-Ph})$ .

but also clearly revealed all  $^1\text{H}$  HFC constants which are larger than 0.3 G, and, in addition, general triple resonance experiments,<sup>8</sup> provided their relative signs. The results confirm that the  $\pi$ -SOMO is mainly confined to the nitrogens of the 2,5-dihydro-1*H*-1,2,4-triazol-2-yl ring, particularly on those of the hydrazyl moiety, N(1) and N(2). Derived from the splittings [ $a(\text{N}) = 28.6 \rho_{\text{N}}$ ],<sup>9</sup> more than 60% of the spin population resides on these three nitrogens. The very small  $a(3\text{-H}) = 0.1$  G splitting of **2b** shows that the central five- $\pi$ -electron system has a node at the C(3) methine carbon. Therefore, only little delocalization of the unpaired electron into the 3-phenyl group of **2c-g** and **2i-p** can be assumed. The delocalization of the unpaired electron into the 1-phenyl group of **2b** and **2d-p**, on the other hand, is considerable large, as indicated by the hydrogen splittings of the 1-phenyl substituent and the decrease of the  $a(1\text{-N})$  splitting, when the 1-methyl group in **2c** [ $a(1\text{-N}) = 10.45$  G] is replaced by phenyl [**2d**:  $a(1\text{-N}) = 7.57$  G]. The ratio  $a(2,6\text{-H})/a(4\text{-H}) \approx 1.06$  of the 1-phenyl hydrogens in **2d-p** is  $>1$  as in 1,3,5-triphenylverdazyl,<sup>10</sup> indicating little distortion about the N-C(phenyl) bond in agreement with the crystal structure of **2i**.<sup>5</sup>

The stability of **2i-p** makes NMR studies possible, *i. e.* determinations of paramagnetic shifts.<sup>11,12</sup> Measurements of  $^1\text{H}$  and  $^2\text{H}$  paramagnetic shifts were performed in the presence of benzene or [D<sub>6</sub>]benzene as internal standard, and were checked in several cases with the corresponding 4,5-dihydro-1*H*-1,2,4-triazoles as



**Figure 4.** (a)  $^2\text{H}$  NMR spectrum of 2,5-dihydro-5,5-diphenyl-1,3-di[D<sub>5</sub>]phenyl-1*H*-1,2,4-triazol-2-yl (**2k**) in di-*tert*-butyl nitroxide (DBNO) at 300 K (internal standard [D<sub>6</sub>]benzene); X [D]DBNO (natural abundance). (b)  $^1\text{H}$  NMR spectrum of **2k** in [D<sub>2</sub>]dichloromethane at 303 K.

**Table 1.** Hyperfine coupling constants of the 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals **2b–l** in toluene (ESR at 295 K, ENDOR at 230 K) or [D<sub>2</sub>]dichloromethane (NMR at 303 K)

Method	<b>2b</b>		<b>2c</b>		<b>2d</b>		<b>2h</b>		<b>2i</b>		<b>2l</b>	
	ESR	ENDOR	ESR	ENDOR	ESR	ENDOR	ESR	ENDOR	ESR	ENDOR	ESR	NMR <sup>i</sup>
<i>a</i> (1-N)/G	7.50	7.42	10.45	+10.49	7.57	7.44	7.55	7.55	7.58	7.58		
<i>a</i> (2-N)/G	6.20	6.18	6.45	+6.42	6.31 <sup>d</sup>	6.28	6.55	6.54	6.42	6.44		
<i>a</i> (4-N)/G	4.20	<sup>c</sup>	3.95	+3.98	3.92 <sup>d</sup>	3.87	3.80	3.79	3.95	3.95		
R <sup>1</sup> : <i>a</i> (H)/G <sup>a</sup>			9.32	+9.53								
<i>a</i> (2,6-H)/G	1.97	-1.99			2.01	-1.99	2.00	-1.99	1.95	-1.90		
<i>a</i> (3,5-H)/G	0.69	+0.69				+0.70	0.70	+0.69	0.70	+0.69		
<i>a</i> (4-H)/G	1.97	-2.09			2.01	-2.11	2.00	-2.05	1.95	-2.05		
R <sup>3</sup> : <i>a</i> (H)/G		0.10					0.90 <sup>g</sup>	-0.90 <sup>g</sup>				
<i>a</i> (2,6-H)/G						<sup>e</sup>						+0.12
<i>a</i> (3,5-H)/G						<sup>e</sup>						-0.09
<i>a</i> (4-H)/G						<sup>e</sup>						+0.06
R <sup>5</sup> : <i>a</i> (H)/G <sup>b</sup>	0.33	-0.32	0.52	-0.51		-0.31 <sup>f</sup>						
<i>a</i> (2,6-H)/G												+0.08
<i>a</i> (3,5-H)/G												+0.20
<i>a</i> (4-H)/G												+0.20 <sup>k</sup>
<i>g</i>	2.0036		2.0038		2.0036		2.0036		2.0036			

<sup>a</sup> *a*(H, 1-CH<sub>3</sub>), 3H. <sup>b</sup> *a*(H, 5,5-CH<sub>3</sub>), 6H. <sup>c</sup> Not clearly observed. <sup>d</sup> **2f** [4-<sup>15</sup>N], ESR: *a*(4-<sup>15</sup>N) = 5.40 G. **2g** [2,4-<sup>15</sup>N<sub>2</sub>], ESR: *a*(2-<sup>15</sup>N) = 8.80, *a*(4-<sup>15</sup>N) = 5.45 G. <sup>e</sup> One additional broad line pair is observed: *a*(H) = 0.12 G. <sup>f</sup> Not observed in the ENDOR spectrum of **2e**. <sup>g</sup> *a*(H, 3-CH<sub>3</sub>), 3H. <sup>h</sup> One additional broad line pair is observed: *a*(H) = +0.17 G. <sup>i</sup> **2k**, <sup>2</sup>H NMR in di-*tert*-butyl nitroxide at 300 K: R<sup>1</sup>: *a*(2,6-D) = -0.294, *a*(3,5-D) = +0.105, *a*(4-D) = -0.309 G; R<sup>2</sup>: *a*(2,6-D) = +0.021, *a*(3,5-D) = -0.013, *a*(4-D) = +0.011 G. <sup>k</sup> Not observed in the <sup>1</sup>H-NMR spectrum of **2l**.

internal diamagnetic reference compound.

S. F. Nelsen *et al.*<sup>13</sup> pointed out that the dependence of the paramagnetic shift on the radical concentration must be measured and extrapolated to an infinitely dilute solution in order to obtain the correct paramagnetic shift. This certainly applies for external standards. However, when a similar diamagnetic compound or a suitable general standard like benzene is used as internal reference, the standard is in a solution with the same bulk susceptibility as the radical. Hence, the error is expected to be small and should not exceed the typical solvent effect. Recently, Dormann *et al.*<sup>14</sup> studied the effect of concentration on the paramagnetic shifts of various verdazyl radicals, and found that the corrections were small, *ca.* 0.5 ppm corresponding to 0.01 G, or negligible. This agrees with our experience.

The NMR method is particularly useful for determinations of small splittings. In the ENDOR spectra of **2c-p** the small <sup>1</sup>H splittings are not resolved or not detectable. The <sup>1</sup>H and <sup>2</sup>H NMR spectra, *e. g.* of **2k** in Figure 4, on the other hand, show clearly separated paramagnetic shifts, and the corresponding HFC constants can be readily determined. The measurements of **2i-p** in [D<sub>2</sub>]dichloromethane or di-*tert*-butyl nitroxide<sup>15</sup> (Tables 1 and 2) confirmed the <sup>1</sup>H ENDOR results, and provided absolute signs of the splittings. As expected, the sign pattern of the 1- and 3-phenyl hydrogen HFC constants in **2i-p** matches exactly with that of triphenyl-verdazyl.<sup>10</sup>

**Table 2.** Hyperfine coupling constants of the 2',5'-dihydro-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazol]-2'-yl radicals **2m-p** in toluene (ESR at 295 K, ENDOR at 230 K) or [D<sub>2</sub>]dichloromethane (NMR at 303 K)

Method	<b>2m</b>	<b>2m</b>	<b>2m</b> <sup>b</sup>	<b>2o</b>	<b>2o</b>	<b>2o</b>	<b>2p</b>
	ESR	ENDOR	NMR	ESR	ENDOR	NMR	NMR
<i>a</i> (1-N)/G	7.35	7.28		7.34	7.25		
<i>a</i> (2-N)/G	6.45	6.43		6.45	6.50		
<i>a</i> (4-N)/G	3.80	3.80		3.80	3.83		
R <sup>1</sup> : <i>a</i> (2,6-H)/G	2.00	-1.97		1.97	-1.98		
<i>a</i> (3,5-H)/G		+0.68		0.68	+0.67		
<i>a</i> (4-H)/G	2.00	-2.08		1.97	-2.09		
R <sup>3</sup> : <i>a</i> (2,6-H)/G			+0.11		+0.16 <sup>d</sup>	+0.11	+0.12
<i>a</i> (3,5-H)/G			-0.07			-0.07	-0.08
<i>a</i> (4-H)/G			+0.05			+0.05	+0.06
R <sup>5</sup> : <i>a</i> (4,5-H)/G		+0.43 <sup>a</sup>	+0.43 <sup>c</sup>			+0.03 <sup>e,f</sup>	+0.43 <sup>g</sup>
<i>g</i>	2.0036			2.0036			

<sup>a</sup> An additional broad line pair is observed consisting of superposed lines, *a*(H) = +0.19 G. <sup>b</sup> **2n**, <sup>2</sup>H NMR, R<sup>5</sup>: *a*(4,5-D) = +0.066, *a*(D) = +0.036 (2D), *a*(D) = +0.027 (2D), *a*(3,6-D) = +0.005 G. <sup>c</sup> Further coupling constants of R<sup>5</sup>: *a*(H) = +0.23 (2H), *a*(H) = +0.18 (2H), *a*(3,6-H) = +0.04 G. <sup>d</sup> Broad line pair, superposed are further line pairs of R<sup>5</sup>. <sup>e</sup> *a*(H, 4,5-CH<sub>3</sub>). <sup>f</sup> Further coupling constants of R<sup>5</sup>: *a*(H) = +0.18 (4H), *a*(H) = +0.04 G (2H). <sup>g</sup> Further coupling constants of R<sup>5</sup>: *a*(H) = +0.24 (2H), *a*(H) = +0.17 (2H), *a*(H, 3,6-CH<sub>3</sub>) = -0.05 G.



A point of special interest is the long-range interaction within the C(5)-bridge segment. The  $\beta$ -coupling of the C(5)-methylene hydrogens in the parent compound **2a** is one of the largest known proton splittings,  $a(5,5\text{-H}) \approx 50.6 \text{ G}$ ,<sup>1-3</sup> representing a spin population of about 11% on each methylene hydrogen. This unusual large splitting is the result of exceptional hyperconjugation based on the binding of the methylene group to the two terminal atoms of a five- $\pi$ -electron system (Whiffen rule<sup>16,17</sup>). Replacement of the methylene hydrogens by methyl groups leads to drastic changes. The observed  $\gamma$ -proton splittings are small and lie in the expected range; **2b**, **2d**:  $a(\text{H}, 5,5\text{-CH}_3) \approx -0.32 \text{ G}$ , **2c**:  $-0.51 \text{ G}$ . Specific long-range interactions are observed for the hydrogens in the 5-phenyl substituents of **2i** and in the 9*H*-fluorene segment of the spiro compounds **2m-p**. Deuteriation of the *meta*-hydrogens in the 5-phenyl groups (**2l**) proves that the largest interaction takes place with the 3,5-hydrogens. In the spiro compounds **2m-p** the arrangement of the 9*H*-fluorene segment is exactly orthogonal with respect to the 2,5-dihydro-1*H*-1,2,4-triazol-2-yl ring plane. Within the 9*H*-fluorene segment the largest splitting refers to the 4,5-hydrogens, as is confirmed by the NMR results of the 4,5-dimethyl substituted compound **2o** (Table 2). These are the only hydrogens which are related to the five- $\pi$ -electron framework by a clear *zigzag(W)*-arrangement. Apparently, the long-range 3,5-hydrogen splitting of the freely rotating 5-phenyl substituents in **2i** predominantly arises from the contribution of the inner *meta*-hydrogens.

In summary, by means of a simple synthetic approach, we prepared stable 2,5-dihydro-1*H*-1,2,4-triazol-2-yl radicals which are characterized by a cyclic five- $\pi$ -electron system with a node at the C(3) methine carbon. The stability of these radicals, comparable to that of verdazyl radicals, has its roots in the optimal delocalization of the unpaired electron in the *s-cis*-arranged amidrazonyl system.

## EXPERIMENTAL

**General.** UV/Vis: Cary 17, Cary 2300 (Varian). – MS: DuPont CEC 21-492; Finnigan MAT 212 (ionization potential 70 eV; only the most prominent peaks are listed, usually with  $I_{\text{rel}} > 10\%$ ). – <sup>1</sup>H and <sup>13</sup>C NMR: Bruker Physik AM 500, HX 360 (internal reference tetramethylsilane, temperature 303 K unless otherwise indicated). <sup>2</sup>H NMR paramagnetic shift measurements<sup>18</sup> were carried out on a Bruker MSL 400 spectrometer. – Microanalysis: Elemental Analyzer 1106 Carlo Erba. – Analytical TLC: DC Micro Cards Polygram SIL G/UV<sub>254</sub> and ALOX N/UV<sub>254</sub>, Macherey-Nagel. Compounds were detected by UV light or by development with iodine. – Column chromatography was performed on Merck silica gel 60 or on Merck aluminium oxide 90 (Brockmann) with the solvents specified. – EPR and ENDOR: Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; *g*-values were determined by using a NMR gaussmeter and the Hewlett-Packard 5342A microwave frequency counter; this was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = (0.7145/g) G.

**4,5-Dimethyl-9*H*-fluoren-9-ol.** To a solution of 4,5-dimethyl-9*H*-fluoren-9-one<sup>19</sup> (5.21 g, 25 mmol) in ethanol (200 ml) and water (50 ml) sodium borohydride (1.5 g, 40 mmol) was added in small portions with stirring. After addition of water, the precipitate was collected and recrystallized from methanol-water to give the product (4.84 g, 92%), m.p. 139–140°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO)  $\delta$  2.66 (s, 6H, 4,5-CH<sub>3</sub>), 5.30 (s, 1H, 9-H), 5.69 (br. s, 1H, OH), 7.18 (d, *J* = 7.5 Hz, 2H, 3,6-H), 7.22 (dd, 2H, 2,7-H), 7.42 (d, *J* = 7.1 Hz, 2H, 1,8-H); irradiation of 4,5-CH<sub>3</sub> at  $\delta$  = 2.66 yielded a positive NOE response for 3,6-H at  $\delta$  = 7.18. MS (EI) *m/z* (%) 210 (38) [M]<sup>+</sup>, 196 (19), 195 (100), 166 (13), 165 (30), 152 (13). Anal. calcd. for C<sub>15</sub>H<sub>14</sub>O (210.3): 85.68% C, 6.71% H; found: 85.61% C, 6.52% H.

**3,6-Dimethyl-9H-fluoren-9-ol.** Prepared as described above using 3,6-dimethyl-9H-fluoren-9-one<sup>20</sup> (5.21 g, 25 mmol): 3,6-dimethyl-9H-fluoren-9-ol (4.76 g, 91%), colourless needles from methanol, had m.p. 172–173°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 2.37 (s, 6H, 3,6-CH<sub>3</sub>), 5.38 (d, J = 6.7 Hz, 1H, 9-H), 5.68 (d, 1H, OH), 7.10 (d, J = 7.6 Hz, 2H, 2,7-H), 7.44 (d, 2H, 1,8-H), 7.55 (s, 2H, 4,5-H); irradiation of 3,6-CH<sub>3</sub> at δ = 2.37 yielded a positive NOE response for 2,7-H at δ = 7.10 and for 4,5-H at δ = 7.55. MS (EI) m/z (%) 210 (26) [M]<sup>+</sup>, 196 (10), 195 (100), 165 (10). Anal. calcd. for C<sub>15</sub>H<sub>14</sub>O (210.3): 85.68% C, 6.71% H; found: 85.66% C, 6.88% H.

**9-Bromo-4,5-dimethyl-9H-fluorene.** With vigorous stirring a mixture of 4,5-dimethyl-9H-fluoren-9-ol (4.20 g, 20 mmol), aqueous 40% hydrobromic acid (35 ml) and toluene (15 ml) was heated to reflux for 10 min. After cooling, the crystalline solid was collected and recrystallized to give the product (4.48 g, 82%), m.p. 98–99°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 2.70 (s, 6H, 4,5-CH<sub>3</sub>), 6.40 (s, 1H, 9-H), 7.24 (d, J = 7.1 Hz, 2H, 3,6-H), 7.28 (dd, 2H, 2,7-H), 7.48 (d, J = 7.1 Hz, 2H, 1,8-H); irradiation of 4,5-CH<sub>3</sub> at δ = 2.70 yielded a positive NOE response for 3,6-H at δ = 7.24. MS (EI) m/z (%) 274 (3), 272 (3) [M]<sup>+</sup>, 194 (25), 193 (100), 192 (10), 189 (11), 179 (13), 178 (19). Anal. calcd. for C<sub>15</sub>H<sub>13</sub>Br (273.2): 65.95% C, 4.80% H; found: 65.99% C, 4.57% H.

**9-Bromo-3,6-dimethyl-9H-fluorene.** Prepared as described above using 3,6-dimethyl-9H-fluoren-9-ol (4.20 g, 20 mmol): 9-bromo-3,6-dimethyl-9H-fluorene (4.00 g, 73%), colourless needles from methanol, had m.p. 143–144°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 2.39 (s, 6H, 3,6-CH<sub>3</sub>), 6.33 (s, 1H, 9-H), 7.17 (d, J = 7.6 Hz, 2H, 2,7-H), 7.49 (d, 2H, 1,8-H), 7.63 (s, 2H, 4,5-H); irradiation of 3,6-CH<sub>3</sub> at δ = 2.39 yielded a positive NOE response for 2,7-H at δ = 7.17 and for 4,5-H at δ = 7.63. MS (EI) m/z (%) 274 (4), 272 (4) [M]<sup>+</sup>, 194 (23), 193 (100), 192 (13), 191 (13), 179 (9), 178 (16). Anal. calcd. for C<sub>15</sub>H<sub>13</sub>Br (273.2): 65.95% C, 4.80% H; found: 66.21% C, 4.79% H.

**N<sup>2</sup>-Phenylformamidrazone Hydrochloride (4a).** Nitroformaldehyde phenylhydrazone<sup>21</sup> (16.5 g, 0.1 mol) in methanol (300 ml) was hydrogenated (0.3 mol H<sub>2</sub>) in the presence of Raney nickel (10 g). After filtration, hydrogen chloride was passed into the filtrate, and the acidic mixture was concentrated to about 10 ml in *vacuo*. Addition of diethyl ether precipitated a solid which was collected and recrystallized from ethanol-diethyl ether to give as first fraction ammonium chloride and as second fraction N<sup>2</sup>-phenylformamidrazone hydrochloride (4a) (8.9 g, 52%) as colourless prisms, m. p. 172–173°C (decomp.). <sup>1</sup>H NMR (360 MHz, [D<sub>6</sub>]DMSO) δ 6.84 (d, J = 7.7 Hz, 2H, 2,6-H<sub>pb</sub>), 6.88 (t, J = 7.2 Hz, 1H, 4-H<sub>pb</sub>), 7.24 (dd, 2H, 3,5-H<sub>pb</sub>), 8.30 (t, J = 10.6 Hz, 1H, CH), 8.71 (s, 1H, exchangeable), 9.53 (br. s, 2H, exchangeable), 11.73 (s, 1H, exchangeable). MS (EI) m/z (%) 135 (55) [M]<sup>+</sup>, 93 (22), 91 (100). Anal. calcd. for C<sub>7</sub>H<sub>10</sub>ClN<sub>3</sub> (171.6): 48.99% C, 5.87% H, 24.48% N; found: 49.06% C, 5.84% H, 24.70% N.

**4,5-Dihydro-5,5-dimethyl-1-phenyl-1H-1,2,4-triazole (5b).** A mixture of N<sup>2</sup>-phenylformamidrazone hydrochloride (4a) (1.37 g, 8 mmol) and triethylamine (700 mg, 7 mmol) in acetone (50 ml) was heated to reflux with stirring for 4 h. After cooling, the acetone was evaporated off, and the residue was partitioned between diethyl ether and 1 M acetic acid. The separated organic layer was repeatedly washed with water, dried (MgSO<sub>4</sub>) and evaporated. The remaining crude product was purified by column chromatography (silica gel; CH<sub>2</sub>Cl<sub>2</sub>-EtOAc 9:1, eluent) to give compound 5b (850 mg, 61%) as crystals from cyclohexane, m.p. 70–71°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 1.44 (s, 6H, 5,5-CH<sub>3</sub>), 6.74 (t, J = 7.2 Hz, 1H, 4-H<sub>pb</sub>), 6.83 (br. s, 1H, 4-H), 6.98 (s, 1H, 3-H), 7.11 (d, J = 8.4 Hz, 2H, 2,6-H<sub>pb</sub>), 7.16 (dd, 2H, 3,5-H<sub>pb</sub>); irradiation of 5,5-CH<sub>3</sub> at δ = 1.44 yielded a positive NOE response for NH at δ = 6.83 and for 2,6-H<sub>pb</sub> at δ = 7.11 and irradiation of NH at δ = 6.83 yielded a positive response for 5,5-CH<sub>3</sub> at δ = 1.44 and for 3-H at δ = 6.98. MS (EI) m/z (%)

175 (30) [M]<sup>•+</sup>, 160 (100) [M-Me]<sup>+</sup>, 91 (8). Anal. calcd. for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub> (175.2): 68.54% C, 7.48% H, 23.98% N; found: 68.57% C, 7.32% H, 23.96% N.

**4,5-Dihydro-1,5,5-trimethyl-3-phenyl-1*H*-1,2,4-triazole (5c).**<sup>22</sup> This had m.p. 141–142°C (lit.<sup>22</sup> m.p. 124–126°C). UV (dioxane) λ<sub>max</sub> (log ε) 333 nm (3.83), 226 (4.05). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 1.27 (s, 6H, 5,5-CH<sub>3</sub>), 2.62 (s, 3H, 1-CH<sub>3</sub>), 6.60 (s, 1H, 4-H), 7.29–7.39 (m, 3H), 7.61 (dd, J = 7.8, J = 1.7 Hz, 2H, 2,6-H<sub>3-ph</sub>). MS (EI) m/z (%) 189 (10) [M]<sup>•+</sup>, 174 (100) [M-Me]<sup>+</sup>, 104 (20), 77 (9).

**4,5-Dihydro-5,5-dimethyl-1,3-diphenyl-1*H*-1,2,4-triazole (5d).** Ammonia (1.1 l, 50 mmol) was passed into a solution of *N*-phenyl-benzohydrazonoyl chloride (6)<sup>23</sup> (3.70 g, 16 mmol) in acetone (25 ml) with stirring. Then the mixture was heated under reflux for 1 h. After evaporation of the solvent the residue was chromatographed on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to give compound 5d (1.90 g, 47%) as pale yellow needles from cyclohexane–pentane, m.p. 115–116°C (lit.<sup>24</sup> m.p. 113–115°C). UV (dioxane) λ<sub>max</sub> (log ε) 363 nm (4.06), 262 (3.91), 226 (4.14). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 1.57 (s, 6H, 5,5-CH<sub>3</sub>), 6.78 (tt, J = 6.8, J = 1.8 Hz, 1H, 4-H<sub>1-ph</sub>), 7.18–7.24 (m, 4H), 7.26 (s, 1H, NH), 7.39–7.46 (m, 3H), 7.75 (dd, J = 8.0, J = 1.7 Hz, 2H, 2,6-H<sub>3-ph</sub>). MS (EI) m/z (%) 251 (12) [M]<sup>•+</sup>, 237 (11), 236 (100) [M-CH<sub>3</sub>]<sup>+</sup>, 91 (23). Anal. calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>3</sub> (251.3): 76.46% C, 6.82% H, 16.72% N; found: 76.55% C, 6.72% H, 16.73% N.

**4,5-Dihydro-5,5-di[D<sub>3</sub>]methyl-1,3-diphenyl-1*H*-1,2,4-triazole (5e).** Prepared as described above using [D<sub>6</sub>]acetone (20 ml): 1.80 g 5e (44%), m.p. 115–116°C. MS (EI) m/z (%) 257 (16) [M]<sup>•+</sup>, 256 (9), 240 (27), 239 (100) [M-CD<sub>3</sub>]<sup>+</sup>, 238 (27), 105 (10), 92 (11), 91 (69), 77 (10).

**4,5-Dihydro-5,5-dimethyl-1,3-diphenyl-1*H*-[4-<sup>15</sup>N]-1,2,4-triazole (5f).** Prepared as described above, using *N*-phenyl-benzohydrazonoyl chloride (6)<sup>23</sup> (115 mg, 0.5 mmol) in acetone (5 ml) and [<sup>15</sup>N]ammonia (40 ml): 45 mg 5f (36%), m.p. 115–116°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 7.27 (d, <sup>2</sup>J = 86.8 Hz, 1H, <sup>15</sup>NH), further data see 5d. MS (EI) m/z 252 (10) [M]<sup>•+</sup>, 238 (10), 237 (100) [M-CH<sub>3</sub>]<sup>+</sup>, 91 (23).

**4,5-Dihydro-5,5-dimethyl-1,3-phenyl-1*H*-[2,4-<sup>15</sup>N<sub>2</sub>]-1,2,4-triazole (5g).** 1,3,5-Triphenyl[2,4-<sup>15</sup>N<sub>2</sub>]-formazan<sup>25</sup> (302 mg, 1 mmol) in ethanol (20 ml) was hydrogenated (2 mmol H<sub>2</sub>) in the presence of 5%Pd on charcoal (150 mg). After filtration, the solvent was evaporated, and the residue dissolved in acetone (10 ml) was heated under reflux for 1 h. Work-up as described above afforded compound 5g (25 mg, 10% referred to 1,3,5-triphenyl[2,4-<sup>15</sup>N<sub>2</sub>]formazan), m.p. 114–115°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 7.26 (d, <sup>2</sup>J = 86.7 Hz, 1H, <sup>15</sup>NH), further data see 5d. MS (EI) m/z (%) 253 (9) [M]<sup>•+</sup>, 239 (11), 238 (100) [M-CH<sub>3</sub>]<sup>+</sup>, 91 (18).

**4,5-Dihydro-3-methyl-1,5,5-triphenyl-1*H*-1,2,4-triazole (5h).** To a solution of *N*<sup>2</sup>-phenylacetamidrazone hydrochloride (4c)<sup>26,27</sup> (4.65 g, 25 mmol) and α,α-dichlorodiphenylmethane (6.18 g, 26 mmol) in dimethylformamide (50 ml) cooled to 5°C were added under stirring powdered barium oxide (10 g) and barium hydroxide octahydrate (0.1 g). The mixture was stirred for 2 h at 5°C and then 3 h at ambient temperature. After addition of diethyl ether (300 ml) the mixture was filtered. The filtrate was repeatedly washed with water, dried (MgSO<sub>4</sub>), and evaporated to provide the crude product, which was chromatographed on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to give compound 5h (3.52 g, 45%) as crystals from benzene–pentane, mp. 179–180°C. UV (dioxane) λ<sub>max</sub> (log ε) 279 nm (4.06). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 1.95 (s, 3H, 3-CH<sub>3</sub>), 6.45 (t, J = 7.2 Hz, 1H, 4-H<sub>1-ph</sub>), 6.71 (d, J = 8.1 Hz, 2H, 2,6-H<sub>1-ph</sub>), 6.87 (dd, 2H, 3,5-H<sub>1-ph</sub>), 7.25–7.40 (m, 10H), 8.13 (s, 1H, NH). MS (EI) m/z (%) 313 (13) [M]<sup>•+</sup>, 236 (100), 165 (10), 91 (36), 78 (23). Anal. calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub> (313.4): 80.48% C, 6.11% H, 13.41% N; found: 80.59% C, 6.32% H, 13.17% N.

**4,5-Dihydro-1,3,5,5-tetraphenyl-1*H*-1,2,4-triazole (5i).**

**Method A.** To a solution of *N*<sup>2</sup>-phenylbenzamidrazone hydrochloride (1.5)hydrate (4d)<sup>26</sup> (6.86 g, 25 mmol), α,α-dichlorodiphenylmethane (6.18 g, 26 mmol) in dimethylformamide (120 ml) were added powdered barium

oxide (10 g) and barium hydroxide octahydrate (0.1 g), and the mixture was stirred for 24 h at ambient temperature. Work-up as described above for **5h** afforded compound **5i** (4.26 g, 45%) from cyclohexane as pale yellow needles, m.p. 193–194°C. UV (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 377 nm (4.02), 320 sh (3.74), 259 (4.04), 224 sh (4.27).  $^1\text{H NMR}$  (500 MHz,  $[\text{D}_6]\text{DMSO}$ )  $\delta$  6.55 (t,  $J = 7.2$  Hz, 1H, 4- $\text{H}_{1\text{-ph}}$ ), 6.87 (d,  $J = 8.1$  Hz, 2H, 2,6- $\text{H}_{1\text{-ph}}$ ), 6.95 (dd, 2H, 3,5- $\text{H}_{1\text{-ph}}$ ), 7.32 (t,  $J = 7.2$  Hz, 2H, 4- $\text{H}_{5\text{-ph}}$ ), 7.39 (dd, 4H, 3,5- $\text{H}_{5\text{-ph}}$ ), 7.42–7.48 (m, 7H), 7.87 (dd,  $J = 7.8$  Hz,  $J = 1.7$  Hz, 2H, 2,6- $\text{H}_{3\text{-ph}}$ ), 8.56 (s, 1H, NH); irradiation of NH at  $\delta = 8.56$  yielded a positive NOE response for 2,6- $\text{H}_{3\text{-ph}}$  at  $\delta = 7.87$  and for 2,6- $\text{H}_{5\text{-ph}}$  at  $\delta = 7.45$  (d). MS (EI)  $m/z$  (%) 375 (14)  $[\text{M}]^{*+}$ , 298 (86), 194 (9), 165 (10), 91 (32), 78 (23), 73 (100). Anal. calcd. for  $\text{C}_{26}\text{H}_{21}\text{N}_3$  (375.5): 83.17% C, 5.64% H, 11.19% N; found: 83.28% C, 5.66% H, 11.15% N.

**Method B.** A solution of 1,2,5,6-tetrahydro-1,3,5,6,6-pentaphenyl-1,2,4,5-tetrazine<sup>4</sup> (1.17 g, 2.5 mmol) and phenylhydrazine (0.54 g, 5 mmol) in toluene (10 ml) was heated at reflux for 1 min. After cooling the mixture was passed through a pad of silica gel (eluent toluene), and the filtrate was evaporated. Recrystallization of the residue from cyclohexane afforded compound **5i** (0.68 g, 72%), m.p. 192–193°C.

**Method C.** A mixture of N-phenyl-benzohydrazonoyl chloride (**6**)<sup>23</sup> (2.30 g, 10 mmol) and  $\alpha$ -phenylbenzylamine (4.00 g, 22 mmol) in dimethylformamide (30 ml) was heated at reflux for 1 min. After cooling the mixture was partitioned between diethyl ether and water, and the organic phase was repeatedly washed with water, dried ( $\text{MgSO}_4$ ), and evaporated. The residue was chromatographed over silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent to give compound **5i** (0.88 g, 23%), m.p. 193–194°C.

**4,5-Dihydro-5,5-diphenyl-1,3-di $[\text{D}_5]$ phenyl-1H-1,2,4-triazole (**5k**).** To a stirred mixture of 1,3,5-tri $[\text{D}_5]$ phenylformazan<sup>28</sup> (3.15 g, 10 mmol), powdered barium oxide (5.0 g) and barium hydroxide octahydrate (0.3 g) in dimethylformamide (50 ml) under argon a solution of  $\alpha$ -phenylbenzyl bromide (2.72 g, 11 mmol) in dimethylformamide (25 ml) was added dropwise over a period of 5 h. After addition, the mixture was stirred under argon at ambient temperature for 20 h. Phenylhydrazine (2 ml, 20 mmol) was added to the deep violet mixture which was then heated at reflux for 1 min, cooled and partitioned between diethyl ether and water. The organic layer was repeatedly washed with water, dried ( $\text{MgSO}_4$ ) and evaporated. Chromatography of the residue over silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent afforded **5k** (2.20 g, 57% referred to 1,3,5-tri $[\text{D}_5]$ phenylformazan) as yellow needles from cyclohexane, m.p. 192–193°C.  $^1\text{H NMR}$  (500 MHz,  $[\text{D}_6]\text{DMSO}$ )  $\delta$  7.32 (t,  $J = 7.2$  Hz, 2H, 4- $\text{H}_{5\text{-ph}}$ ), 7.39 (dd, 4H, 3,5- $\text{H}_{5\text{-ph}}$ ), 7.45 (d,  $J = 7.9$  Hz, 4H, 2,6- $\text{H}_{5\text{-ph}}$ ), 8.55 (s, 1H, NH). MS (EI)  $m/z$  (%) 385 (14)  $[\text{M}]^{*+}$ , 309 (15), 308 (100), 307 (25), 165 (9), 96 (77). Anal. calcd. for  $\text{C}_{26}\text{H}_{11}\text{D}_{10}\text{N}_3$  (385.5): 81.00% C, 8.10% H+D, 10.90% N; found: 81.45% C, 8.49% H+D, 10.91% N.

**4,5-Dihydro-1,3-diphenyl-5,5-di $[\text{3,5-D}_2]$ phenyl-1H-1,2,4-triazole (**5l**).** Prepared from N<sup>2</sup>-phenylbenzamidrazone hydrochloride (1.5)hydrate (**4d**)<sup>26</sup> (1.10 g, 4 mmol),  $\alpha,\alpha$ -dichlorodi $[\text{3,5-D}_2]$ phenylmethane<sup>29</sup> (1.01 g, 4.2 mmol), powdered barium oxide (2.0 g) and barium hydroxide octahydrate (0.1 g) in dimethylformamide (25 ml) as described above (method A): from cyclohexane yellow needles (460 mg, 30%), m.p. 193–194°C.  $^1\text{H NMR}$  (500 MHz,  $[\text{D}_6]\text{DMSO}$ )  $\delta$  6.55 (t,  $J = 7.1$  Hz, 1H, 4- $\text{H}_{1\text{-ph}}$ ), 6.87 (d,  $J = 8.0$  Hz, 2H, 2,6- $\text{H}_{1\text{-ph}}$ ), 6.95 (dd, 2H, 3,5- $\text{H}_{1\text{-ph}}$ ), 7.32 (s, 2H, 4- $\text{H}_{5\text{-ph}}$ ), 7.42–7.48 (m, 7H), 7.87 (dd,  $J = 7.9$  Hz,  $J = 1.7$  Hz, 2H, 2,6- $\text{H}_{3\text{-ph}}$ ), 8.56 (s, 1H, NH). MS (EI)  $m/z$  (%) 379 (14)  $[\text{M}]^{*+}$ , 301 (17), 300 (100), 194 (8), 91 (46). Anal. calcd. for  $\text{C}_{26}\text{H}_{17}\text{D}_4\text{N}_3$  (379.5): 82.29% C, 6.64% H+D, 11.07% N; found: 82.33% C, 6.41% H+D, 10.94% N.

**4',5'-Dihydro-1',3'-diphenyl-spiro[9H-fluorene-9,5'-[1H-1,2,4]triazole] (**5m**).**

**Method A.** A mixture of N<sup>2</sup>-phenylbenzamidrazone hydrochloride (1.5)hydrate (**4d**)<sup>26</sup> (2.75 g, 10 mmol), powdered barium oxide (4.0 g) and barium hydroxide octahydrate (0.20 g) in dimethylformamide (40 ml) was stirred at ambient temperature for 1 h. Then a solution of 9-bromo-9H-fluorene (2.70 g, 11 mmol) in

dimethylformamide (15 ml) was added dropwise over a period of 4 h and stirring was continued for a further 3 h. After addition of diethyl ether (200 ml), the mixture was filtered, and the filtrate was repeatedly washed with water, dried (MgSO<sub>4</sub>) and evaporated. Chromatography of the residue over silica gel using cyclohexane as eluent afforded compound **5m** (780 mg, 21%) as yellow crystals from toluene-pentane, mp. 231–232°C. UV (dioxane) λ<sub>max</sub> (log ε) 368 nm (4.03), 260 (4.31), 237 (4.63). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 6.50 (t, J = 7.2 Hz, 1H, 4-H<sub>1'-pb</sub>), 6.59 (d, J = 8.2 Hz, 2H, 2,6-H<sub>1'-pb</sub>), 6.87 (dd, 2H, 3,5-H<sub>1'-pb</sub>), 7.29 (dd, 2H), 7.42–7.50 (m, 7H), 7.83–7.90 (m, 4H), 8.23 (s, 1H, NH). MS (EI) m/z (%) 373 (100) [M]<sup>+</sup>, 372 (28), 296 (9), 194 (28), 91 (28). Anal. calcd. for C<sub>26</sub>H<sub>19</sub>N<sub>3</sub> (373.5): 83.62% C, 5.13% H, 11.25% N; found: 83.93% C, 5.24% H, 11.08% N.

**Method C.** A mixture of N-phenyl-benzohydrazonoyl chloride (**6**)<sup>23</sup> (2.30 g, 10 mmol) and 9-amino-9*H*-fluorene (4.00 g, 22 mmol) in diethyl acetate (100 ml) was heated at reflux for 3 h. The hot mixture was filtered and the filtrate evaporated. Recrystallization of the residue afforded compound **5m** (1.15 g, 31%), m.p. 231–232°C.

The following compounds were similarly prepared.

**4',5'-Dihydro-1',3'-diphenyl-spiro[9*H*-[D<sub>8</sub>]fluorene-9,5'-[1*H*-1,2,4]triazole] (5n).** Using 9-bromo-9*H*-[D<sub>9</sub>]fluorene<sup>35</sup> (2.80 g, 11 mmol): compound **5n** (720 mg, 19%), yellow needles from toluene-pentane, had m.p. 232–233°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 6.50 (t, J = 7.2 Hz, 1H, 4-H<sub>1'-pb</sub>), 6.58 (d, J = 8.2 Hz, 2H, 2,6-H<sub>1'-pb</sub>), 6.86 (dd, 2H, 3,5-H<sub>1'-pb</sub>), 7.42–7.50 (m, 3H, 3,4,5-H<sub>3'-pb</sub>), 7.87 (d, J = 8.0 Hz, 2H, 2,6-H<sub>3'-pb</sub>), 8.22 (s, 1H, NH). MS (EI) m/z (%) 382 (10), 381 (29) [M]<sup>+</sup>, 380 (13), 194 (16), 92 (12), 91 (100). Anal. calcd. for C<sub>26</sub>H<sub>11</sub>D<sub>8</sub>N<sub>3</sub> (381.5): 81.86% C, 7.13% H+D, 11.02% N; found: 81.99% C, 7.78% H+D, 10.82% N.

**4',5'-Dihydro-4,5-dimethyl-1',3'-diphenyl-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazole] (5o).** Using 9-bromo-4,5-dimethyl-9*H*-fluorene (3.01 g, 11 mmol): compound **5o** (240 mg, 6%), yellow crystals from ethyl acetate-methanol, had m.p. 217–218°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 2.73 (s, 6H, 4,5-CH<sub>3</sub>), 6.48 (t, J = 7.2 Hz, 1H, 4-H<sub>1'-pb</sub>), 6.55 (d, J = 7.9 Hz, 2H, 2,6-H<sub>1'-pb</sub>), 6.86 (dd, 2H, 3,5-H<sub>1'-pb</sub>), 7.19 (dd, 2H, 2,7-H), 7.26 (d, J = 7.2 Hz, 2H, 3,6-H), 7.30 (d, J = 7.2 Hz, 2H, 1,8-H), 7.42–7.48 (m, 3H, 3,4,5-H<sub>3'-pb</sub>), 7.84 (dd, J = 7.6, J = 1.7 Hz, 2H, 2,6-H<sub>3'-pb</sub>), 8.13 (s, 1H, NH); irradiation of 4,5-CH<sub>3</sub> at δ = 2.73 yielded a positive NOE response for 3,6-H at δ = 7.26. MS (EI) m/z (%) 402 (11), 401 (41) [M]<sup>+</sup>, 400 (37), 310 (15), 91 (100). Anal. calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>3</sub> (401.5): 83.76% C, 5.77% H, 10.47% N; found: 83.96% C, 5.99% H, 10.13% N.

**4',5'-Dihydro-3,6-dimethyl-1',3'-diphenyl-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazole] (5p).** Using 9-bromo-3,6-dimethyl-9*H*-fluorene (3.01 g, 11 mmol): compound **5p** (350 mg, 9%), yellow crystals from ethyl acetate-methanol, had m.p. 240–241°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ 2.38 (s, 6H, 3,6-CH<sub>3</sub>), 6.49 (t, J = 7.3 Hz, 1H, 4-H<sub>1'-pb</sub>), 6.58 (d, J = 8.0 Hz, 2H, 2,6-H<sub>1'-pb</sub>), 6.87 (dd, 2H, 3,5-H<sub>1'-pb</sub>), 7.08 (d, 2H, J = 7.6 Hz, 2H, 2,7-H), 7.32 (d, 2H, 1,8-H), 7.42–7.49 (m, 3H, 3,4,5-H<sub>3'-pb</sub>), 7.65 (s, 2H, 4,5-H), 7.85 (dd, J = 7.5, J = 1.6 Hz, 2H, 2,6-H<sub>3'-pb</sub>), 8.10 (s, 1H, NH); irradiation of 3,6-CH<sub>3</sub> at δ = 2.38 yielded a positive NOE response for 2,7-H at δ = 7.08 and for 4,5-H at δ = 7.65. MS (EI) m/z (%) 402 (10), 401 (32) [M]<sup>+</sup>, 400 (17), 194 (20), 91 (100). Anal. calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>3</sub> (401.5): 83.76% C, 5.77% H, 10.47% N; found: 83.68% C, 6.06% H, 10.28% N.

**2,5-Dihydro-2-methyl-1,3,5,5-tetraphenyl-1*H*-1,2,4-triazole (8).** To a solution of 4,5-dihydro-1,3,5,5-tetraphenyl-1*H*-1,2,4-triazole (**5i**) (1.13 g, 3 mmol) in dimethylformamide (50 ml) under argon was added powdered barium oxide (5.0 g), barium hydroxide octahydrate (0.1 g) and methyl iodide (5 ml), and the mixture was stirred for 16 h at ambient temperature. After addition of diethyl ether (200 ml) the mixture was

filtered. The filtrate was repeatedly washed with water, dried ( $\text{MgSO}_4$ ) and evaporated. Recrystallization of the residue from methanol afforded compound **8** (0.68 g, 58%) as colourless crystals, m. p. 146–147°C. UV (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 315 sh nm (3.23), 241 sh (4.25).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]$ DMSO)  $\delta$  2.92 (s, 3H, 2- $\text{CH}_3$ ), 6.69 (t,  $J = 7.2$  Hz, 1H, 4- $\text{H}_{1\text{-ph}}$ ), 6.89 (d,  $J = 7.9$  Hz, 2H, 2,6- $\text{H}_{1\text{-ph}}$ ), 6.99 (dd, 2H, 3,5- $\text{H}_{1\text{-ph}}$ ), 7.15–7.40 (m, 10H), 7.55 (dd, 2H, 3,5- $\text{H}_{3\text{-ph}}$ ), 7.60 (t,  $J = 7.3$  Hz, 1H, 4- $\text{H}_{3\text{-ph}}$ ), 7.88 (d,  $J = 8.3$  Hz, 2H, 2,6- $\text{H}_{3\text{-ph}}$ ); irradiation of 2- $\text{CH}_3$  at  $\delta = 2.92$  yielded a positive NOE response for 2,6- $\text{H}_{1\text{-ph}}$  at  $\delta = 6.89$  and for 2,6- $\text{H}_{3\text{-ph}}$  at  $\delta = 7.88$ . MS (EI)  $m/z$  (%) 389 (15)  $[\text{M}]^+$ , 312 (100)  $[\text{M}-\text{C}_6\text{H}_5]^+$ , 269 (55), 166 (44), 165 (56), 77 (8). Anal. calcd. for  $\text{C}_{27}\text{H}_{23}\text{N}_3$  (389.5): 83.26% C, 5.95% H, 10.79% N; found: 83.49% C, 5.99% H, 10.64% N.

**4,5-Dihydro-4-methyl-1,3,5,5-tetraphenyl-1H-1,2,4-triazole (9)**. It was prepared from N-methyl-N<sup>2</sup>-phenylbenzamidrazone<sup>37</sup> (4.51 g, 20 mmol),  $\alpha,\alpha$ -dichlorodiphenylmethane (4.97 g, 21 mmol), powdered barium oxide (8.0 g) and barium hydroxide octahydrate (0.5 g) in dimethylformamide (70 ml) as described above (method A). Recrystallization of the crude product from benzene-cyclohexane afforded compound **9** (5.60 g, 72%) as yellow crystals, m.p. 161–162°C. UV (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 368 nm (3.90), 318 (3.83), 270 (4.00).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]$ DMSO)  $\delta$  2.57 (s, 3H, 4- $\text{CH}_3$ ), 6.55 (t,  $J = 7.2$  Hz, 1H, 4- $\text{H}_{1\text{-ph}}$ ), 6.81 (d,  $J = 7.9$  Hz, 2H, 2,6- $\text{H}_{1\text{-ph}}$ ), 6.93 (dd, 2H, 3,5- $\text{H}_{1\text{-ph}}$ ), 7.38 (t,  $J = 8.3$  Hz, 2H, 4- $\text{H}_{5\text{-ph}}$ ), 7.46 (dd, 4H, 3,5- $\text{H}_{5\text{-ph}}$ ), 7.48–7.58 (m, 7H), 7.67 (dd,  $J = 8.1$ ,  $J = 1.7$  Hz, 2H, 2,6- $\text{H}_{3\text{-ph}}$ ); irradiation of 4- $\text{CH}_3$  at  $\delta = 2.57$  yielded a positive NOE response for 2,6- $\text{H}_{3\text{-ph}}$  at  $\delta = 7.67$  and for 2,6- $\text{H}_{5\text{-ph}}$  at  $\delta = 7.54$ . MS (EI)  $m/z$  (%) 389 (11)  $[\text{M}]^+$ , 312 (100)  $[\text{M}-\text{C}_6\text{H}_5]^+$ , 118 (8), 91 (19), 77 (7). Anal. calcd. for  $\text{C}_{27}\text{H}_{23}\text{N}_3$  (389.5): 83.26% C, 5.95% H, 10.79% N; found: 83.03% C, 5.96% H, 10.80% N.

**2,5-Dihydro-5,5-dimethyl-1,3-diphenyl-1H-1,2,4-triazol-2-yl (2d)**. To a solution of **5d** (502 mg, 2 mmol) in dimethylformamide (40 ml) in a separating funnel a solution of potassium hexacyanoferrate (III) (1.0 g, 3 mmol) in water (20 ml) and aqueous 2 N sodium carbonate (1.5 ml) were added. The mixture was briefly shaken, then diluted with water and the product extracted with diethyl ether. The organic layer was repeatedly washed with water, dried ( $\text{MgSO}_4$ ) and evaporated. Chromatography of the residue on aluminium oxide (Brockmann) using  $\text{CH}_2\text{Cl}_2$  as eluent afforded compound **2d** (170 mg, 34%) as brown crystals from pentane, m. p. 58–59°C. UV/VIS (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 570 nm sh (3.03), 536 (3.14), 500 (3.17), 419 (3.84), 387 (3.88), 331 (4.08), 244 (4.23). MS (EI)  $m/z$  (%) 251 (14), 250 (100)  $[\text{M}]^+$ , 236 (20), 235 (19), 194 (15), 145 (16), 104 (31), 91 (79). Anal. calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_3$  (250.3): 76.77% C, 6.44% H, 16.79% N; found: 77.02% C, 6.32% H, 16.92% N.

The following compounds were similarly prepared.

**2,5-Dihydro-3-methyl-1,5,5-triphenyl-1H-1,2,4-triazol-2-yl (2h)**. From compound **5h** (626 mg, 2 mmol): Chromatography on aluminium oxide (Brockmann) using cyclohexane as eluent provided compound **2h** (340 mg, 54%) as darkbrown crystals from pentane, m. p. 82–83°C. UV/VIS (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 520 nm (3.35), 382 sh (3.39), 341 (3.88), 320 sh (3.83), 255 (3.45). MS (EI)  $m/z$  (%) 312 (18)  $[\text{M}]^+$ , 236 (15), 235 (17), 207 (13), 166 (32), 165 (38), 132 (18), 91 (100), 77 (28). Anal. calcd. for  $\text{C}_{21}\text{H}_{18}\text{N}_3$  (312.4): 80.74% C, 5.81% H, 13.45% N; found: 80.80% C, 5.87% H, 13.35% N.

**2,5-Dihydro-1,3,5,5-tetraphenyl-1H-1,2,4-triazol-2-yl (2i)**. From compound **5i** (751 mg, 2 mmol): Addition of water to the reaction mixture precipitated the product **2i**, which was recrystallized from ethyl acetate-methanol to give 675 mg (90%) black prisms, m. p. 142–143°C. Microhydrogenation of **2i** (11 mg) in dimethylformamide (2 ml), 5% Pd/BaSO<sub>4</sub> (20 mg): 0.49 mol H<sub>2</sub>. UV/VIS (dioxane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 603 sh nm (2.97), 560 (3.16), 496 sh (3.06), 429 (3.79), 398 (3.80), 330 (3.91), 319 (3.91), 249 (4.31). MS (EI)  $m/z$

(%) 375 (30), 374 (40) [M]<sup>+</sup>, 298 (100), 297 (38), 269 (30), 194 (35), 166 (21), 165 (31), 90 (50). Anal. calcd. for C<sub>26</sub>H<sub>20</sub>N<sub>3</sub> (374.5): 83.39% C, 5.38% H, 11.22% N; found: 83.39% C, 5.64% H, 11.06% N.

**2,5-Dihydro-5,5-diphenyl-1,3-di[D<sub>2</sub>]phenyl-1*H*-1,2,4-triazol-2-yl (2k).** From compound **5k** (771 mg, 2 mmol): compound **2k** (650 mg, 85%) had m. p. 142–143°C. MS (EI) m/z (%) 384 (17) [M]<sup>+</sup>, 308 (12), 307 (21), 274 (11), 204 (19), 166 (11), 165 (18), 96 (100). Anal. calcd. for C<sub>26</sub>H<sub>10</sub>D<sub>10</sub>N<sub>3</sub> (384.5): 81.21% C, 7.86% H+D, 10.93% N; found: 80.96% C, 8.23 H+D, 10.93% N.

**2,5-Dihydro-1,3-diphenyl-5,5-di[3,5-D<sub>2</sub>]phenyl-1*H*-1,2,4-triazol-2-yl (2l).** From compound **5l** (759 mg, 2 mmol): compound **2l** (660 mg, 87%) had m. p. 141–142°C. MS (EI) m/z (%) 379 (27), 378 (58) [M]<sup>+</sup>, 377 (20), 300 (20), 299 (17), 273 (33), 194 (21), 170 (33), 169 (100), 168 (34), 167 (10), 91 (76), 79 (22), 77 (13). Anal. calcd. for C<sub>26</sub>H<sub>16</sub>D<sub>4</sub>N<sub>3</sub> (378.5): 82.51% C, 6.39% H+D, 11.10% N; found: 82.21% C, 6.66% H+D, 11.06% N.

**2',5'-Dihydro-1',3'-diphenyl-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazol]-2'-yl (2m).** From compound **5m** (747 mg, 2 mmol): compound **2m** (570 mg, 77%), black crystals from cyclohexane, had m. p. 170–171°C. UV/VIS (dioxane) λ<sub>max</sub> (log ε) 605 sh nm (2.98), 563 (3.17), 532 sh (3.12), 496 sh (3.07), 426 (3.78), 398 (3.79), 386 sh (3.74), 328 (3.96), 253 (4.46), 234 (4.56), 226 (4.55). MS (EI) m/z (%) 374 (30), 373 (45), 372 (82) [M]<sup>+</sup>, 269 (14), 268 (23), 267 (95), 194 (14), 165 (17), 164 (100), 163 (47), 91 (49). Anal. calcd. for C<sub>26</sub>H<sub>18</sub>N<sub>3</sub> (372.5): 83.85% C, 4.87% H, 11.28% N; found: 83.96% C, 4.99% H, 11.08% N.

**2',5'-Dihydro-1',3'-diphenyl-spiro[9*H*-[D<sub>8</sub>]fluorene-9,5'-[1*H*-1,2,4]triazol]-2'-yl (2n).** From compound **5n** (382 mg, 1 mmol): compound **2n** (275 mg, 72%) had m. p. 170–171°C. MS (EI) m/z (%) 381 (64), 380 (100) [M]<sup>+</sup>, 379 (24), 277 (12), 276 (24), 275 (98), 274 (18), 194 (25), 172 (73), 170 (30), 91 (54). Anal. calcd. for C<sub>26</sub>H<sub>10</sub>D<sub>8</sub>N<sub>3</sub> (380.5): 82.07% C, 6.88% H+D, 11.04% N; found: 82.05% C, 7.20% H+D, 11.02% N.

**2',5'-Dihydro-4,5-dimethyl-1',3'-diphenyl-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazol]-2'-yl (2o).** From compound **5o** (402 mg, 1 mmol): compound **2o** (290 mg, 72%), black crystals from cyclohexane, had m. p. 159–160°C. MS (EI) m/z (%) 402 (19), 401 (48), 400 (38) [M]<sup>+</sup>, 399 (10), 386 (20), 384 (19), 310 (25), 194 (12), 91 (100). Anal. calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>3</sub> (400.5): 83.97% C, 5.54% H, 10.49% N; found: 84.16% C, 5.49% H, 10.54% N.

**2',5'-Dihydro-3,6-dimethyl-1',3'-diphenyl-spiro[9*H*-fluorene-9,5'-[1*H*-1,2,4]triazol]-2'-yl (2p).** From compound **5p** (402 mg, 1 mmol): compound **2p** (280 mg, 72%), black crystals from cyclohexane-pentane, had m. p. 167–168°C. MS (EI) m/z (%) 402 (25), 401 (65), 400 (70) [M]<sup>+</sup>, 399 (23), 324 (12), 295 (33), 194 (31), 192 (34), 191 (15), 91 (100), 77 (11). Anal. calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>3</sub> (400.5): 83.97% C, 5.54% H, 10.49% N; found: 83.86% C, 5.73% H, 10.25% N.

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