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NMR STUDIES OF VERDAZYLS WITH ALIPHATIC SUBSTITUENTS[1]

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Abstract—Using PMR the isotropic hyperfine H coupling constants of three series of substituted verdazyls have been measured and assigned. The experimental data are compared with series of other radical groups and with theoretical concepts published recently.[2,3]

ESR and NMR investigations of many organic radicals have yielded clear experimental information about the spin transfer to hydrogen and first row elements in the α- and β-positions† to the radical site, and the mechanisms of interaction have been thoroughly discussed in the literature. Less data, however, is available for spin transfer to atoms in the γ-position, and this data does not directly offer a comprehensive concept of the modes or mechanisms of the spin transfer involved. Recently, detailed theoretical studies of the long range interactions between γ-hydrogens and the radical centre through the sigma framework have been published,[2,3] and the results of the calculations in these papers agree quite well with most of the experimental data known from the literature.

In connection with our verdazyl studies[4] we collected NMR data‡ of verdazyls with aliphatic substituents, in which spin transfer to γ-protons is observed. We report the observed NMR data in this paper and compare the experimental findings with the theoretical results.[2,3]

NMR paramagnetic shifts of neutral organic radicals[5] and radical ions[6] have been shown to render directly both the sign and the magnitude of electron-nuclei coupling constants. In addition small coupling constants below the resolution of ESR can frequently be measured. This second advantage makes NMR particularly useful for the study of radicals like the verdazyls,[7-10] where several slightly different small coupling constants have to be determined. A single shifted NMR line from each set of equivalent nuclei is observed, if the spin lattice relaxation time τ_1 and/or the exchange time τ_e of the electronic spins is short compared to the reciprocal coupling constant measured in Hz: $\tau_1 \ll 1/a_i$ and/or $\tau_e \ll 1/a_i$. In concentrated radical solutions spin exchange is usually very rapid. When measuring NMR of nuclei with larger coupling constants (>1 G) the NMR linewidth may be broadened beyond detection, but it can be reduced by using the liquid free radical di-t-butylnitroxide (DBNO) as a solvent.[11] The magnitude of the paramagnetic shift δ_p is related to the hyperfine coupling constant a_i by

$$\delta_p(T) = \frac{\nu_p - \nu_d}{\nu_d} = \frac{a_i h \gamma_i}{4kT\gamma_i} \qquad (1)$$

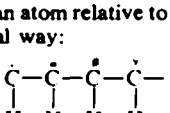
which can be written $a_i = C_i(T)\delta_p$. The constant $C_i(T)$ for protons at room temperature is $C_H(295°K) = 1{\cdot}33 \times 10^{-2}$ Gauss/ppm $= 3{\cdot}73 \times 10^{-2}$ MHz/ppm. Nuclei with lines shifted to low field have positive coupling constants, those with lines shifted to high field have negative coupling constants.

The basic compounds in the synthesis of the verdazyls, the formazans 1, were prepared by known procedures.[12] The verdazyls summarized in Table 1 were obtained following two known reaction pathways,[13] with modifications of the procedures in some cases:

(a) The formazans 1 and an aldehyde are cyclized in the presence of an acid to yield the verdazylium cation 2, which is subsequently reduced to the verdazyl 3 under basic conditions (verdazyls 7–18).

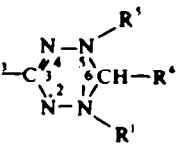
(b) The formanzan 1 is alkylated; thermal ring closure of the alkylformazan 4 yields the leucoverdazyl 5, which is subsequently dehydrogenated to the verdazyl 3 with $FeCl_3$ under basic conditions (verdazyls 19–20).

†The position of an atom relative to the radical centre is denoted in the usual way:

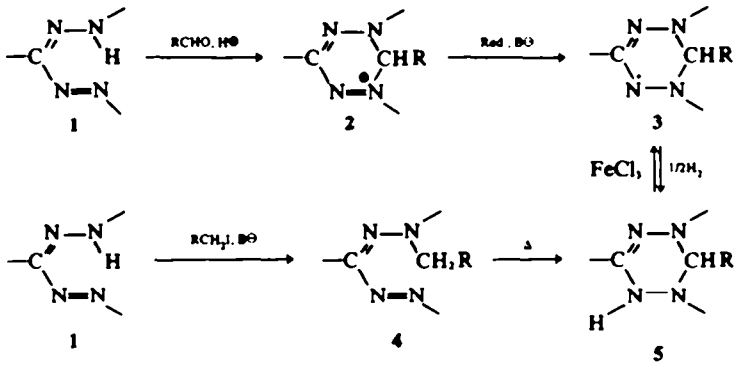


‡Presented in part at the 10*th International Symposium on Free Radicals*. Lyon, September (1971).

Table 1. Verdazyls prepared



Verdazyl	R' = R'	R³	R⁶	m.p. (dec)
6	C_6H_5	$C_6H_4OCH_3$-(4)	H	128–129°[14]
7	$C_6H_4CH_3$-(4)	$C_6H_4OCH_3$-(4)	H	116–117°
8	$C_6H_4CH_2CH_3$-(4)	$C_6H_4OCH_3$-(4)	H	127–128°
9	$C_6H_4CH(CH_3)_2$-(4)	$C_6H_4OCH_3$-(4)	H	137–138°
10	$C_6H_4C(CH_3)_3$-(4)	$C_6H_4OCH_3$-(4)	H	171–172°
11	C_6H_5	CH_2CH_3	H	59–60°
12	C_6H_5	$CH(CH_3)_2$	H	72–73°
13	C_6H_5	$CH_2C_6H_5$	H	116–117°[15]
14	C_6H_5	$CHCH_3C_6H_5$	H	127–128°
15	C_6H_5	$CH_2CH(CH_3)_2$	H	79–80°
16	C_6H_5	$CH_2CHCH_3C_2H_5$	H	64–65°
17	C_6H_5	$CH_2CHCH_3C_6H_5$	H	100–101°
18	C_6H_5	$CH{=}CHC_6H_5$	H	139–140°
19	C_6H_5	CH_3	CH_2CH_3	81–82°
20	C_6H_5	CH_3	$CH(CH_3)_2$	114–115°



The diamagnetic leucoverdazyls **5**, which can be easily obtained by hydrogenation of the verdazyls **3** with 5% Pd/$BaSO_4$ as cayalyst,[8] are the reference standards in the determination of the paramagnetic shifts.

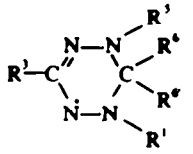
The NMR spectra of all the verdazyls studied are resolved and exhibit resonance lines of all aliphatic and aromatic protons, except for those which are covered by the intense resonance band of the solvent DBNO or which are too broadened to be certainly assigned as is often the case with the C-6 protons due to the inversion occuring in the verdazyl ring. The resonance lines were assigned by comparison of the various spectra and on the basis of ESR[16] and NMR[7-9] data obtained previously. The values of the measured paramagnetic shifts in ppm as well as in MHz and Gauss are listed in Table 2.

The NMR lines from the *o*- and *p*-protons in the N-phenyl rings are shifted to high field yielding a somewhat larger negative coupling constant for the *p*-protons than for the *o*-protons. The NMR line of the *m*-protons is shifted to low field and gives a positive coupling constant. The data of the N-phenyl ring protons of all verdazyls except **19** and **20** are fairly constant in this series and as compared to others.[8,9] In **19** and **20** the corresponding coupling constants are about 10% larger than usual. This increase indicates that aliphatic substituents at C-6 considerably influence the conformation of the verdazyl molecule.

The NMR line from the *o*-protons in the C-phenyl ring (**6–10**) is shifted to low field yielding a positive coupling constant. The NMR line of the corresponding *m*-protons is shifted to high field and lies under the DBNO band, but can be easily observed in other solvents. Substitution of aromatic protons by methoxy groups (**6–10**) leaves the overall spin density distribution in the verdazyls almost unchanged and replaces the aromatic proton coupling by a methoxy proton coupling of opposite sign and about one-tenth the magnitude in agreement with the literature.[7,9,17]

In DBNO the resonance line of the C-6 protons in

Table 2. ^{1}H paramagnetic shifts $\delta_p = (\nu_p - \nu_d)\nu_d$ and coupling constants a_i of the verdazyls **6–20** at 295°K



Verdazyl solvent	Assignment		Shift $\nu_p - \nu_d$ [Hz]*	Shift δ_p [ppm]	Coupling constants a_i MHz	Gauss
6	$R^1 = R^3$:	H_o	−7530	−83·7	−3·12	−1·11
DBNO		H_m	2760	30·7	1·14	0·408
		H_p	−7990	−88·8	−3·31	−1·18
	R^3:	H_o	2760	30·7	1·14	0·408
$CDCl_3$	R^5:	H_m	−1040	−11·6	−0·431	−0·154
		H_{OCH_3}	−169	−1·88	−0·070	−0·025
7	$R^1 = R^3$:	H_o	−7490	−83·2	−3·10	−1·11
DBNO		H_m	2770	30·8	1·15	0·409
		H_{CH_3}	8360	92·9	3·46	1·24
	R^3:	H_o	2770	30·8	1·15	0·409
$CDCl_3$	R^5:	H_m	−1040	−11·6	−0·431	−0·154
		H_{OCH_3}	−166	−1·84	−0·069	−0·025
8	$R^1 = R^3$:	H_o	−7430	−82·6	−3·08	−1·10
DBNO		H_m	2660	29·6	1·10	0·393
		H_{-CH_2-}	6130	68·1	2·54	0·906
	R^3:	H_o	2660	29·6	1·10	0·393
$CDCl_3$	$R^1 = R^3$:	H_{CH_3}	55	0·61	0·023	0·008
	R_5:	H_m	−1030	−11·4	−0·427	−0·152
		H_{OCH_3}	−166	−1·84	−0·069	−0·025
9	$R^1 = R^3$:	H_o	−7300	−81·1	−3·03	−1·08
DBNO		H_m	2660	29·6	1·10	0·393
		$H_{-CH<}$	3580	39·8	1·48	0·529
		H_{CH_3}	243	2·70	0·101	0·036
	R^3:	H_o	2660	29·6	1·10	0·393
$CDCl_3$	$R^1 = R^3$:	H_{CH_3}	215	2·39	0·089	0·032
	R^5:	H_m	−990	−11·0	−0·410	−0·146
		H_{OCH_3}	−173	−1·92	−0·072	−0·026
10	$R^1 = R^3$:	H_o	−7470	−83·0	−3·96	−1·10
DBNO		H_m	2710	30·1	1·12	0·400
		H_{CH_3}	242	2·69	0·100	0·036
	R^3:	H_o	2710	30·1	1·12	0·400
$CDCl_3$	$R^1 = R^3$:	H_{CH_3}	230	2·56	0·095	0·034
	R^5:	H_m	−1010	−11·2	−0·419	−0·149
		H_{OCH_3}	−172	−1·91	−0·071	−0·025
11	$R^1 = R^3$:	H_o	−7250	−80·6	−3·00	−1·07
DBNO		H_m	2710	30·1	1·12	0·400
		H_p	−7720	−85·8	−3·20	−1·14
	R^3:	H_{-CH_2-}	−11000	−122·2	−4·56	−1·63
		H_{CH_3}	1130	12·6	0·468	0·167
CCl_4	$R^1 = R^3$:	H_m	2710	30·1	1·12	0·400
	R^5:	H_{CH_3}	1140	12·7	0·472	0·168
	$R^4 = R^{4'}$:	H	−580	−6·44	−0·240	−0·086
12	$R^1 = R^3$:	H_o	−7200	−80·0	−2·98	−1·06
DBNO		H_m	2630	29·2	1·09	0·389
		H_p	−7660	−85·1	−3·17	−1·13
	R^3:	$H_{-CH<}$	−7910	−87·9	−3·28	−1·17
		H_{CH_3}	780	8·67	0·323	0·115
CCl_4	$R^1 = R^3$:	H_m	2720	30·2	1·13	0·402
	R^5:	H_{CH_3}	810	9·00	0·336	0·120
	$R^4 = R^{4'}$:	H	−576	−6·40	−0·239	−0·085
13	$R^1 = R^3$:	H_o	−7290	−81·0	−3·02	−1·08
DBNO		H_m	2650	29·4	1·10	0·392
		H_p	−7650	−85·0	−3·17	−1·13
	R^3:	H_{-CH_2-}	−9100	−101·1	−3·77	−1·34
14	$R^1 = R^3$:	H_o	−7300	−81·7	−3·05	−1·09

Table 2—*Continued*

Verdazyl solvent	Assignment		Shift $\nu_p - \nu_o$[Hz]*	Shift δ_p[ppm]	Coupling constants a, MHz	Gauss
DBNO		H_m	2690	29·9	1·11	0·398
		H_p	−7790	−86·6	−3·23	−1·15
	R^3:	$H_{-CH<}$	−7070	−78·6	−2·93	−1·04
		H_{CH_3}	835	9·28	0·346	0·123
$CDCl_3$	R^3:	H_{CH_3}	840	9·33	0·348	0·124
15	$R^1 = R^3$:	H_o	−7350	−81·7	−3·05	−1·09
DBNO		H_m	2730	30·3	1·13	0·403
		H_p	−7750	−86·1	−3·21	−1·15
	R^3:	H_{-CH_2-}	−10160	−112·9	−4·21	−1·50
		$H_{-CH<}$	1860	20·7	0·771	0·275
		H_{CH_3}	297	3·30	0·123	0·044
$CDCl_3$	R^3:	H_{CH_3}	254	2·82	0·106	0·038
16	$R^1 = R^3$:	H_o	−7420	−82·4	−3·08	−1·10
DBNO		H_m	2710	30·1	1·12	0·400
		H_p	−7840	−87·1	−3·25	−1·16
	R^3:	$H_{-CH_2-\beta}$	−11050	−122·8	−4·58	−1·63
		$H_{-CH_2-\beta}$	−9550	−106·1	−3·96	−1·41
		$H_{-CH<}$	1760	19·6	0·729	0·260
17	$R^1 = R^3$:	H_o	−7300	−81·1	−3·03	−1·08
DBNO		H_m	2670	29·7	1·11	0·395
		H_p	−7700	−85·6	−3·19	−1·14
	R^3:	$H_{-CH_2-\beta}$	−10640	−118·2	−4·41	−1·57
		$H_{-CH_2-\beta}$	−9570	−106·3	−3·97	−1·41
		$H_{-CH<}$	1910	21·2	0·792	0·282
$CDCl_3$	R^3:	H_{CH_3}	248	2·76	0·103	0·037
18	$R^1 = R^3$:	H_o	−7380	−82·0	−3·06	−1·09
DBNO		H_m	2730	30·3	1·13	0·403
		H_p	−7820	−86·9	−3·24	−1·16
	R^3:	$H_{-CH-\beta}$	−6450	−71·7	−2·67	−0·953
		$H_{-CH-\gamma}$	5630	62·6	2·33	0·832
$CDCl_3$	R^3:	H_o	916	10·2	0·380	0·135
		H_m	−346	−3·84	−0·143	−0·051
		H_p	916	11·3	0·380	0·135
19	$R^1 = R^3$:	H_o	−8130	−90·3	−3·37	−1·20
DBNO		H_m	2890	32·1	1·20	0·427
		H_p	−8550	−95·0	−3·54	−1·26
	R^3:	H_{CH_3}	−13500	−150·0	−5·60	−2·00
	R^{ω}:	H_{-CH_2-}	3520	39·1	1·46	0·520
		H_{CH_3}	530	5·89	0·220	0·078
CCl_4	$R^1 = R^3$:	H_m	2820	31·3	1·17	0·417
	R^{ω}:	H_{CH_3}	480	5·33	0·199	0·071
20	$R^1 = R^3$:	H_o	−8410	−93·4	−3·49	−1·24
DBNO		H_m	2990	33·2	1·24	0·442
		H_p	−8900	−98·9	−3·69	−1·32
	R^3:	H_{CH_3}	−13200	−146·7	−5·47	−1·95
	R^{ω}:	$H_{-CH<}$	3380	37·6	1·40	0·500
		H_{CH_3}	840	9·33	0·348	0·124
CCl_4	$R^1 = R^3$:	H_m	2950	32·8	1·22	0·436
	R^{ω}:	$H_{-CH<}$	3240	36·0	1·34	0·480
		H_{CH_3}	834	9·27	0·346	0·123

*Shift relative to the corresponding ^1H resonance in a diamagnetic leucoverdazyl; resonance frequency: H = 90 MHz.

the verdazyls are covered by the DBNO band. In other solvents the detection of this NMR signal also meets with experimental difficulties, since this resonance is considerably broadened compared to others due to the ring inversion, which is slow on the NMR time scale. Only DMR of deuterated verdazyls clearly demonstrated the location of the C-6 proton resonance.[8,9]

In summary the NMR data for the verdazyl series studied (Table 1) agree quite well in sign and magnitude with the experimental results obtained previously,[8,9,16] and show the same fair agreement with the calculated spin density distribution in 1,5-diphenylverdazyl or 1,3,5-triphenylverdazyl.[9,18]

This NMR study of verdazyls was carried out with the aim of obtaining additional information

about the origin of γ-hydrogen hyperfine splittings in aliphatic substituents. In order to facilitate the discussion we arrange the obtained data in three groups: (A, B and C).

(A) Verdazyls with aliphatic substituents in the *p*-position of the N-phenyl rings (**6–10**).

The isotropic hyperfine H coupling constants of the aliphatic substituents in **6–10** are summarized in Table 3. This table also lists data for a similar phenoxyl series and the verdazysl **21** and **22**. The spin densities at the substituted sp^2-carbons, which are given in the last column, were derived from the a_{H_α}-splittings with the McConnell equation[22]

$$a_{H_\alpha} = -23{\cdot}7\,\rho_C. \quad (2)$$

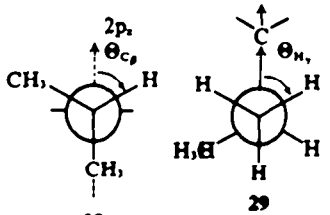
The isotropic hyperfine coupling constant of a β-hydrogen in alkyl substituents depends greatly on its orientation relative to the radical centre or relative to the substituted sp^2-carbon. The angular dependence of a_{H_β} has been approximated by

$$a_{H_\beta} = (A \times B \cdot \cos^2 \theta_{C_\beta})\,\rho_C,^{23,24} \quad (3)$$

where B is a constant with a value of about 50 Gauss and A (small and often neglected) relates the coupling constant to the spin density at the substituted C-atom, when θ_{C_β} is 90°. For freely rotating methyl groups Eq (3) reduces to Eq (4).

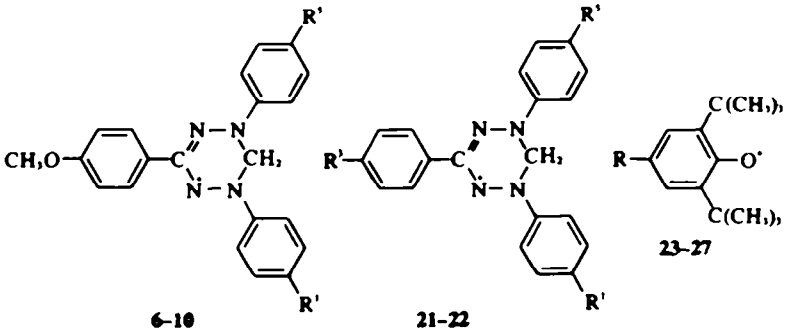
$$a_{H_\beta} = (A + 1/2\,B)\,\rho_C. \quad (4)$$

Using the data from the verdazyls **6** and **7**, and neglecting A, a B value of 49·6 Gauss is obtained, which lies in the expected range. The observed variation of a_{H_β} in the verdazyls **7**, **8** and **9** indicates that the rotation around the bond between the substituted C-atom and C_α is hindered yielding different equilibrium conformations. On the time average the β-hydrogens of **8** and **9** are closer to the nodal plane of the π-system (phenyl ring) than in the freely rotating methyl group. The a_{H_β} value of **9** suggests an equilibrium conformation (**28**) with $\theta_{C_\beta} \approx 60°$ for the single β-hydrogen.



28 **29**

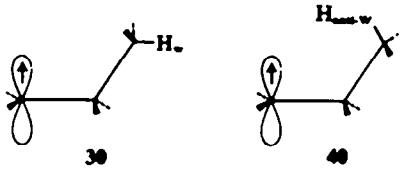
Table 3. Isotropic hyperfine H coupling constants (Gauss) of aliphatic substituents in the verdazyls **6–10**, **21**, **22** and in the 2,6-di-t-butylphenoxyls **23–27**



6–10 **21–22** **23–27**

			a_{H_α}	a_{H_β}	a_{H_γ}	ρ_C*
6	R' = R²:	H	−1·18			0·050
7	R' = R²:	CH_3		1·24		
8	R' = R²:	CH_2CH_3		0·91	0·010	
9	R' = R²:	$CH(CH_3)_2$		0·53	0·036	
10	R' = R²:	$C(CH_3)_3$			0·036	
21[a]	R' = R²:	H	−1·11			0·047
	R²:	H	0·27			−0·011
22[a]	R' = R²:	$C(CH_3)_3$			0·035	
	R²:	$C(CH_3)_3$			−0·007	
23[19]	R:	H	(−)9·6			0·405
24[20]	R:	CH_3		(+)10·7		
25[20]	R:	CH_2CH_3		(+)9·0		
26[21]	R:	$CH(CH_3)_2$		(+)4·6		
27[11,21]	R:	$C(CH_3)_3$			+0·385	

*Spin density at the substituted sp^2-carbon derived from $a_{H_\alpha} = -23{\cdot}7\,\rho_C$.[22]



30 40

The experimental data of the verdazyls **6–10**, and particularly of **21** and **22** in Table 3 show, that the γ-hydrogen hyperfine splitting and the spin density at the substituted sp^2-carbon have the same sign, and substitution of the *p*-hydrogen by a t-butyl group replaces the α-hydrogen splitting by a γ-hydrogen splitting opposite in sign and about 30 times smaller in magnitude. The remarkable increase of a_H, going from ethyl to isopropyl (**8–9**) reflects a considerable change in the conformation. According to the β-hydrogen splitting in the equilibrium conformation **28** of the isopropyl verdazyl **9** one methyl group eclipses on the time average the p_z-orbital containing the unpaired spin ($\theta_{C_\beta} = 0°$).

As is well known from a number of ESR studies, especially on bicyclic radicals, where geometrical requirements are fulfilled by a rigid molecular framework,[25,26] optimal long range interactions in γ-positions are observed in a W-plan arrangement[25] (**30**, $\theta_{C_\beta} = 0°$, $\theta_{H_\gamma} = 180°$). In agreement with the experimental findings, SCF-MO-INDO[2] and *ab inito* investigations[3] also demonstrate that γ-hydrogen splittings reach their optimal positive values in the W-conformation, which permits a cumulative effect of spin-delocalization and spin-polarization contributions. In various other conformations ($\theta_{C_\beta} > 30°$, $\theta_{H_\gamma} < 120°$) the contributions of spin-delocalization and of spin-polarization may cancel each other or yield negative values with respect to a positive spin density at the substituted radical site.[2,3] Since in the aliphatic *p*-substituents of this verdazyl series (**8–10**) all γ-hydrogen splittings have the same sign as the spin density at the sp^2-carbon to which they are attached, the contribution of one γ-hydrogen in a W-plan arrangement seems to dominate all other γ-hydrogen contributions on the time average. This view is supported by the increase of the γ-hydrogen splitting, which is observed going from ethyl to isopropyl. These experimental findings are not restricted to this verdazyl series. The phenoxyl series listed in Table 3 shows quite a similar behaviour, and the situation seems to be rather typical for *p*-substituted aryl groups at a radical centre.

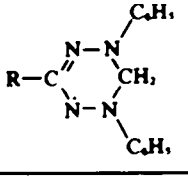
(B) Verdazyls with aliphatic substituents at C-3 (**11–18**, **31–33**).

Table 4 lists the H coupling constants of the aliphatic substituents at C-3 in these verdazyls and also presents data of several similarly substituted nitronylnitroxides (**34–39**)[27,28] for comparison.

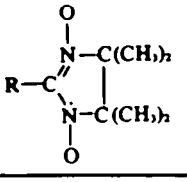
The most striking feature of the data in this series is the size of the β-hydrogen coupling constants as compared to the α-hydrogen splitting. The β-hydrogen splittings are about twice as large as usual.

Table 4. Isotropic hyperfine H coupling constants (Gauss) of the C-3 substituent (R) in the verdazyls **11–18** and **31–33** and of the C-2 substituent (R) in the nitronylnitroxides **34–39**

11–18, **31–33**



34–39



Compound	R	a_{H_α}	a_{H_β}	a_{H_γ}	a_{H_δ}	ρ_C*
31[a]	H	0·72				−0·030
32[a]	CH_3		−2·03			
11	CH_2CH_3		−1·63	0·168		
12	$CH(CH_3)_2$		−1·17	0·120		
33[a]	$C(CH_3)_3$			0·105		
13	$CH_2C_6H_5$		−1·34			
14	$CHCH_3C_6H_5$		−1·04	0·124		
15	$CH_2CH(CH_3)_2$		−1·50	0·275	0·038	
16	$CH_2CHCH_3C_2H_5$		−1·63; −1·41	0·260		
17	$CH_2CHCH_3C_6H_5$		−1·57; −1·41	0·282	0·037	
18	$CH{=}CHC_6H_5$		−0·953	0·832		
34[27]	CH_3		(−)3·3			
35[27]	CH_2CH_3		(−)2·00			
36[27]	$CH_2C_6H_5$		(−)1·8			
37[27]	$CH_2CH(CH_3)_2$		(−)1·99			
38[28]	$CH_2CHCH_3C_6H_5$		−2·93; −1·41	0·18	−0·038	
39[27]	$CH{=}CHC_6H_5$		(−)1·4	(+)1·4		

*Spin density at the substituted sp^2-carbon derived from $a_{H_\alpha} = -23·7\,\rho_C$.[23]

Using the data from the verdazyls **31** and **32**, and neglecting A, Eq (4) yields a B value of 135 Gauss, which greatly deviates from the usual value of about 50 Gauss. The remarkably large values is probably brought about by the special situation at C-3, which represents a node in this extended allyl system.† The observed decrease of the β-hydrogen splittings in the verdazyls **32**, **11** and **12** agrees with a hindered rotation around the C-α, C-3 bond yielding different equilibrium conformations as has been found in many other examples. In these equilibrium conformations the β-hydrogens of **11** and **12**, also in **13–17**, are closer to the nodal plane of the π-system (verdazyl ring) than in the freely rotating methyl group (**32**). The a_{H_β} values of **12** and **14** suggest an equilibrium conformation with $\theta_{C_\beta} \approx 60°$ (figure **28**). Due to the asymmetric β-carbon the β-hydrogens in **16** and **17** are diastereotopic.[29] They should differ, therefore, in their paramagnetic shifts, and this behaviour has already been demonstrated in the nitronylnitroxide **38**.[28] As one expects the NMR spectra of **16** and **17** yield two different β-hydrogen splittings. The mean value of a_{H_β} and a_{H_β} corresponds to the β-hydrogen splitting in a similar compound with a symmetric β-carbon (**15**).

According to the experimental data summarized in Table 4 the γ-hydrogen splittings have the *opposite* sign as compared to the spin density at the substituted C-3 carbon. In addition the γ-hydrogen splittings *decrease* going from ethyl to t-butyl (**11** > **12** > **33**). The largest γ-hydrogen splitting, which stems from only one hydrogen, is observed in the NMR spectra of **15–17**. These findings are completely different from the results obtained in the series (A). Since the γ-hydrogen splittings decrease going from ethyl to t-butyl the major contribution to these splittings comes from a methyl group, which on the time average is close to the p_z-orbital plane through C-6, C-3 and C-α perpendicular to the verdazyl ring ($\theta_{C_\gamma} \approx 0°$). Due to steric hindrance in the favoured conformations of **15–17** the single γ-hydrogen predominantly points to the verdazyl ring ($\theta_{H_\gamma} \to 0°$). The extreme view of this situation gives the conformation shown in figure **40**, which exactly represents the long known anti-W arrangement. Anti-W arrangements are usually associated with only small hyperfine interactions. In this series, however, the contribution of only one γ-hydrogen in a position, which is close to an anti-W arrangement, apparently dominates the contributions of all other γ-hydrogens. This unusual result might be attributed to the strongly polar situation (inductive interaction) in the special molecular fragment (alkyl substituted amidine carbon), which seems to increase considerably the contribution of the spin polarization to the γ-hydrogen splitting in question.

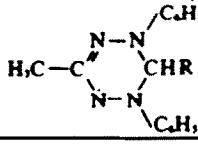
The NMR spectra of **15**, **16** and **17** show, in addition, positive δ-hydrogen splittings of about 0·04 Gauss. The δ-hydrogen NMR lines of **16**, however, cannot be certainly assigned to the δ-H_{CH_3} or δ-H_{-CH_2-} for the present, therefore these data have not been presented in Table 4. Contrary to the findings in the verdazyls **15–17** the δ-hydrogens of the similarly substituted nitronylnitroxide **38** yield a negative splitting of comparable size. The long range interaction in the δ-position is expected to depend strongly on the appropriate arrangement of bonds. Therefore any conclusion from the observed δ-hydrogen splittings on the bond arrangement in non rigid systems meets with considerable difficulties.

The data of the 3-styrylverdazyl **18** (Table 4) again illustrate that the C-3 substituent in the verdazyls and C-2 substituent in the nitronylnitroxides[27,28] show a quite similar behaviour.

(C) Verdazyls with aliphatic substituents at C-6 (**42**, **19** and **20**).

The NMR signal of the C-6 methylene protons was detected with some difficulty.[8] Due to the inversion of the verdazyl ring this signal is broad and highly temperature dependent. The small coupling constant (~ −0·06 Gauss) of the C-6 protons, which are protons in the β-position to nitrogen atoms with high positive spin densities, can be explained by the Whiffen[30] rule. The π-orbital coefficients at N-1 and N-5 have opposite signs, and a zero coupling constant is predicted for the C-6 methylene protons. When one of these protons is substituted by a methyl group (**42**), the signal of the methyl protons is easily found, and the corresponding splitting of 0·86 Gauss can even be demonstrated in the ESR specturm.[8] Replacement of the methyl hydrogens by methyl groups (**19**, **20**) seems to influence or partly block the ring inversion, since going from **42** to **19** a considerable increase (about 10%) of the N-phenyl proton splittings is observed, which indicates that a more rigid structure of the

Table 5. Isotropic hyperfine H coupling constants (Gauss) of the C-6 substituent (R) in the verdazyls **41**, **42**, **19** and **20**



Verdazyl	R	a_{H_α}	a_{H_β}	a_{H_γ}
41[a]	H	−0·06[a]		
42[a]	CH_3	−0·06	0·86	
19	CH_2CH_3	[b]	0·52	0·071
20	$CH(CH_3)_2$	[b]	0·48	0·123

[a] Derived from the corresponding deuterated compound.
[b] Not measured.

†Note added in proof. This position can be compared with the C-2 position in the allyl radical, for which calculations indicate that B should be about twice as large as usual. G. Underwood, personal communication.

molecule has been achieved. In **42**, **19** and **20** all β- and γ-hydrogen splittings have a positive sign. These findings suggest that the major contributions to these splittings come from hydrogens (β- or γ-), which are close to a W-plan arrangement with respect to the p_z-orbital of N-1 and N-5.

In summary the prepared verdazyls with aliphatic substituents show considerably large γ-hydrogen splittings depending on the position of the substituent, and in several examples even δ-hydrogen splittings can be demonstrated; all γ- and δ-hydrogen splittings have a positive sign. The experimental data obtained fit into the empirical picture of W-plan long range interactions[25] and agree with the theoretical concepts.[2,3]

EXPERIMENTAL

The NMR studies were made with a Bruker-Spectrospin HX-90 MHz high resolution spectrometer. The proton spectra were measured mainly using the broad line technique (30 Hz modulation, phase sensitive detection and linear field sweep). Each spectrum was recorded several times with linear sweep and checked by 2 kHz control distances. Some spectra were measured using the high resolution technique with frequency sweep.

1,5 - *Bis*(4 - *ethylphenyl*) - 3 - (4 - *methoxyphenyl*)*formazan*. The mixture of 4-ethylaniline (6 g, 50 mmole) in H_2O (25 ml) + conc HCl (15 ml) was cooled to 0° and kept at this temp while the soln of $NaNO_2$ (3·5 g) in H_2O (15 ml) was added dropwise with stirring. A soln of $SnCl_2 \cdot 2\,H_2O$ (35 g) in conc HCl (40 ml) was added to the stirred diazonium soln at 0°. The separated tin salt was removed, dissolved in 4N KOH and the mixture extracted with ether. The ether soln was washed with H_2O and filtered. Evaporation of the solvent in vacuum yielded 4-ethylphenylhydrazine (4·7 g).

The soln of this residue and 4-methoxybenzaldehyde (4·7 g) in EtOH (15 ml) was heated to the b.p., cooled, diluted with DMF (80 ml) and pyridine (40 ml) and kept at 0° while the diazonium salt soln [prepared as above from 4-ethylaniline (4·26 g) in H_2O (20 ml) + conc HCl (10 ml), $NaNO_2$ (2·5 g) in H_2O (10 ml)] was added in small portions with stirring. After 2 h the mixture was partitioned between benzene and H_2O. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue yielded from EtOH violet crystals (6·2 g), m.p. 83–84° (dec). (Found: C, 74·54; H, 6·72; N, 14·62. $C_{24}H_{26}N_4O$ requires: C, 74·58; H, 6·78; N, 14·50%).

3 - (4 - *Methoxyphenyl*) - 1,5 - *bis*(4 - *i* - *propylphenyl*)*formazan* was prepared as above starting with 4-i-propylaniline (50 mmole). From EtOH violet crystals (5·9 g), m.p. 122–123° (dec). (Found: C, 75·15; H, 7·13; N, 13·59. $C_{26}H_{30}N_4O$ requires: C, 75·33; H, 7·30; N, 13·52%).

1,5 - *Bis*(4 - *t* - *butylphenyl*) - 3 - (4 - *methoxyphenyl*)*formazan* was prepared as above starting with 4-t-butylaniline (50 mmole). From acetone/MeOH violet crystals (5·2 g), m.p. 152–153° (dec). (Found: C, 76·17; H, 7·67; N, 12·90. $C_{28}H_{34}N_4O$ requires: C, 75·98; H, 7·74; N 12·66%).

1,5 - *Diphenyl* - 3 - (1' - *phenylethyl*)*formazan*. A mixture of aniline (4·65 g) in H_2O (10 ml) + conc HCl (15 ml) was cooled to 0° and kept at this temp while a soln of $NaNO_2$ (3·5 g) in H_2O (10 ml) was added dropwise with stirring. A soln of phenylhydrazine (5·4 g) and 2-phenylpropionaldehyde (6·7 g) in EtOH (15 ml) was heated to the b.p., cooled, diluted with DMF (80 ml) and pyridine (40 ml) and kept at 0° while the diazonium salt soln was added in small portions with stirring. After 2 h the mixture was partitioned between cyclohexane and H_2O. The cyclohexane layer was washed 3 times with H_2O and evaporated in vacuum. The residue dissolved in cyclohexane was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane a red fraction, which yielded from MeOH red crystals (9·7 g), m.p. 81·82° (dec). (Found: C, 76·97; H, 6·35; N, 16·79. $C_{21}H_{20}N_4$ requires: C, 76·80; H, 6·14; N, 17·06%).

1,5 - *Diphenyl* - 3 - *styrylformazan* was prepared as above using cinnamic aldehyde (6·6 g). From EtOH/ligroin red crystals (4·2 g), m.p. 150–151° (dec). (Found: C, 77·49; H, 5·64); N, 17·32. $C_{21}H_{18}N_4$ requires: C, 77·27; H, 5·56; N, 17·17%).

1,5 - *Diphenyl* - 3 - (2' - *phenylpropyl*)*formazan* was prepared as above using 3-phenylbutyraldehyde (7·4 g). From EtOH red crystals (9·2 g), m.p. 120–121° (dec). (Found: C, 77·26; H, 6·51; N, 16·30. $C_{22}H_{22}N_4$ requires: C, 77·16; H, 6·48; N, 16·36%).

1,5 - *Diphenyl* - 3 - (2' - *methylbutyl*)*formazan* was prepared as above using 3-methylpentenal (3 g). From MeOH red crystals (2·8 g), m.p. 92–93° (dec). (Found: C, 73·75; H, 7·77; N, 19·17. $C_{18}H_{22}N_4$ requires: C, 73·43; H, 7·53; N, 19·03%).

1,5 - *Diphenyl* - 3 - (2' - *methylpropyl*)*formazan* was prepared as above using 3-methylbutyraldehyde (5 g). From MeOH red crystals (3·8 g), m.p. 98–99° (dec). (Found: C, 72·85; H, 7·00; N, 19·92. $C_{17}H_{20}N_4$ requires: C, 72·82; H, 7·19; N, 19·99%).

3 - (4 - *Methoxyphenyl*) - 1,5 - *bis*(4 - *methylphenyl*)*verdazyl* (**7**). 3-(4-Methoxyphenyl)-1,5-bis(4-methylphenyl)-formazan (3 g) + $KHSO_4$ (5 g) + paraformaldehyde (1 g) in DMF (50 ml) were stirred for 16 h. The mixture was filtered, the filtrate cooled to 0°, 38% aqueous formaldehyde (5 ml) was added and then dropwise 2N NaOH until the colour of the mixture changed to green. The product was separated by addition of H_2O. The filtered product yielded crystallized from acetone/MeOH green black crystals (1·6 g), m.p. 116–117° (dec). (Found: C, 74·20; H, 6·17; N, 15·26. $C_{25}H_{27}N_4O$ requires: C, 74·37; H, 6·42; N, 15·08%).

1,5 - *Bis* - (4 - *ethylphenyl*) - 3 - (4 - *methoxyphenyl*)*verdazyl* (**8**). 1,5-Bis-(4-ethylphenyl)-3-(4-methoxyphenyl)-formazan (3 g) + $KHSO_4$ (5 g) + paraformaldehyde (1 g) in DMF (100 ml) were treated as above (**7**). From DMF/MeOH green black crystals (1·9 g), m.p. 127–128° (dec). (Found: C, 75·30; H, 6·84; N, 14·09. $C_{25}H_{27}N_4O$ requires: C, 75·16; H, 6·81; N, 14·02%).

3 - (4 - *Methoxyphenyl*) - 1,5 - *bis*(4 - *i* - *propylphenyl*)*verdazyl* (**9**). 3-(4-Methoxyphenyl)-1,5-bis(4-i-propylphenyl)formazan (3 g) + $KHSO_4$ (5 g) + paraformaldehyde (1 g) in DMF (100 ml) were treated as above (**7**). From acetone/MeOH dark green crystals (1·2 g), m.p. 137–138° (dec). (Found: C, 75·74; H, 7·50; N, 12·94. $C_{27}H_{31}N_4O$ requires: C, 75·85; H, 7·31; N, 13·10%).

1,5 - *Bis*(4 - *t* - *butylphenyl*) - 3 - (4 - *methoxyphenyl*)*verdazyl* (**10**). 1,5-Bis(4-t-butylphenyl)-3-(4-methoxyphenyl)formazan (3 g) + $KHSO_4$ (5 g) + paraformaldehyde (1 g) in DMF (100 ml) were treated as above (**7**). From DMF/MeOH green crystals (1·8 g), m.p. 171–172° (dec). (Found: C, 76·35; H, 7·52; N, 12·38. $C_{29}H_{35}N_4O$ requires: C, 76·45; H, 7·74; N, 12·30%).

3 - *Ethyl* - 1,5 - *diphenylverdazyl* (**11**). BF_3-ethyl etherate (10 ml) + 38% aqueous formaldehyde (10 ml) in DMF (20 ml) were stirred for 10 min; 3-ethyl-1,5-

diphenylformazan (2 g) was added and the mixture stirred for 2 h. The mixture was diluted with benzene (150 ml), cooled to 10° and kept at this temp while 2N NaOH was added until the colour of the vigorously stirred mixture had changed to green. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. This residue yielded from MeOH green crystals (1·2 g), m.p. 59–60° (dec). (Found: C, 72·65; H, 6·69; N, 21·45. $C_{16}H_{17}N_4$ requires: C, 72·43; H, 6·46; N, 21·12%).

1,5 - *Diphenyl* - 3 - *i* - *propylverdazyl* (12). BF_3-ethyl etherate (10 ml) + 38% aqueous formaldehyde (10 ml) in DMF (20 ml); 1,5-diphenyl-3-i-propylformazan (3 g) were treated as above (11). The residue yielded from MeOH green crystals (1·8 g), m.p. 72–73° (dec). (Found: C, 73·32; H, 6·97; N, 20·10. $C_{17}H_{18}N_4$ requires: C, 73·09; H, 6·86; N, 20·06%).

1,5 - *Diphenyl* - 3 - (1' - *phenylethyl*)*verdazyl* (14). BF_3-ethyl etherate (10 ml) + paraformaldehyde (2 g) in benzene (50 ml) were stirred for 10 min; 1,5-diphenyl-3-(1'-phenylethyl)formazan (5 g) dissolved in benzene (250 ml) was added and the mixture stirred for 6 h. The mixture was cooled to 10° and kept at this temp while 2N NaOH was added until the colour of the vigorously stirred mixture had changed to green. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue was chromatographed with cyclohexane on Al_2O_3 (Brockmann) to give upon elution with cyclohexane/benzene (1 : 1) green fractions, which yielded crystallized from benzene/ligroin dark green crystals (2·2 g), m.p. 127–128° (dec). (Found: C, 77·13; H, 6·49; N, 16·06. $C_{22}H_{21}N_4$ requires C, 77·39; H, 6·20; N, 16·41%).

1,5 - *Diphenyl* - 3 - (2' - *methylpropyl*)*verdazyl* (15). 1,5-Diphenyl-3-(2'-methylpropyl)formazan (2 g) + $KHSO_4$ (5 g) + paraformaldehyde (0·5 g) in DMF (100 ml) were stirred for 16 h. The mixture was filtered, the filtrate cooled to 10°, 38% aqueous formaldehyde (10 ml) was added and then dropwise 2N NaOH until the colour of the mixture changed to green. The mixture was partitioned between benzene and H_2O. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane/benzene (3 : 1) green fractions, which yielded crystallized twice from MeOH green needles (0·68 g), m.p. 79–80° (dec). (Found: C, 73·59; H, 7·36; N, 19·08. $C_{18}H_{21}N_4$ requires: C, 73·69; H, 7·21; N, 19·10%).

1,5-*Diphenyl* - 3 - (2' - *methylbutyl*)*verdazyl* (16). 1,5-Diphenyl-3-(2'-methylbutyl)formazan (2 g) + $KHSO_4$ (5 g) + paraformaldehyde (0·5 g) in DMF (100 ml) were treated as above (15). The residue dissolved in ligroin was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane green fractions, which yielded crystallized from MeOH green crystals (0·74 g), m.p. 64–65° (dec). (Found: C, 74·49; H, 7·40; N, 18·42. $C_{19}H_{23}N_4$ requires: C, 74·23; H, 7·54; N, 18·23%).

1,5 - *Diphenyl* - 3 - (2' - *phenylpropyl*)*verdazyl* (17). 1,5-Diphenyl-3-(2'-phenylpropyl)formazan (2 g) + $KHSO_4$ (5 g) + paraformaldehyde (0·5 g) in DMF (100 ml) were treated as above (15). The residue yield crystallized twice from EtOH dark green crystals (0·64), m.p. 100–101° (dec). (Found: C, 77·53; H, 6·63; N, 15·82. $C_{23}H_{23}N_4$ requires: C, 77·71; H, 6·52; N, 15·76%).

1,5 - *Diphenyl* - 3 - *styrylverdazyl* (18). BF_3-ethyl etherate (5 ml) + paraformaldehyde (1 g) in $CHCl_3$ (50 ml) were stirred for 10 min; 1,5-diphenyl-3-styrylformazan (1 g) dissolved in $CHCl_3$ (200 ml) was added and the mixture stirred for 1 h. The mixture was cooled to 10° and kept at this temp while 1N NaOH was added until the colour of the vigorously stirred mixture had changed to green. The $CHCl_3$ layer was washed 3 times with H_2O and evaporated in vacuum. The residue yielded from acetone/EtOH dark green crystals (0·64 g) m.p. 139–140° (dec). (Found: C, 78·00; H, 5·77; N, 16·50. $C_{22}H_{19}N_4$ requires: C, 77·85; H, 5·64; N, 16·51%).

6 - *Ethyl* - 3 - *methyl* - 1,5 - *diphenylverdazyl* (19). 3-Methyl-1,5-diphenylformazan (5 g) in DMF (100 ml) + BaO (10 g) + $Ba(OH)_2 \cdot 8\,H_2O$ (1 g) + propyl iodide (10 ml) were stirred for 24 h. The mixture was partitioned between benzene and H_2O. The benzene layer was washed 5 times with H_2O and evaporated in vacuum. The residue in DMF (100 ml) was heated to 150° (brown → green) and cooled to room temp. A soln of $FeCl_3 \cdot 6\,H_2O$ (6 g) in 1N Na_2CO_3 (40 ml) was added, the violet mixture was stirred for 1 min and then partitioned between benzene and 0·2N Na_2CO_3. The benzene layer was washed 4 times with H_2O and evaporated in vacuum. The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane green fractions, which yielded green crystals, (crystallized twice from ligroin) (2·3 g), m.p. 81–82° (dec). (Found: C, 73·13; H, 7·10; N, 20·17. $C_{17}H_{18}N_4$ requires: C, 73·09; H, 6·86; N, 20·06%).

3 - *Methyl* - 1,5 - *diphenyl* - 6 - *i* - *propylverdazyl* (20). 3-Methyl-1,5-diphenylformazan (5 g) in DMF (100 ml) + BaO (10 g) + $Ba(OH)_2 \cdot H_2O$ (1 g) + 1-iodo-2-methylpropane (10 ml) were treated as above (19). The residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with cyclohexane/benzene (4 : 1) green fractions, which yielded green crystals, crystallized twice from MeOH, (1·1 g), m.p. 114–115° (dec). (Found: C, 73·59; H, 7·37; N, 19·27. $C_{18}H_{21}N_4$ requires: C, 73·68; H, 7·22; N, 19·10%).

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