Tetrahedron. Vol. 27, pp. 3623 to 3628. Pergamon Press 1971. Printed in Great Britain

SPIN DENSITIES IN 1,3,5-TRIPHENYLVERDAZYL AN NMR STUDY

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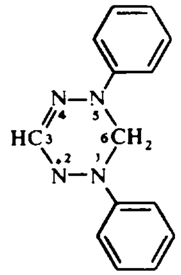
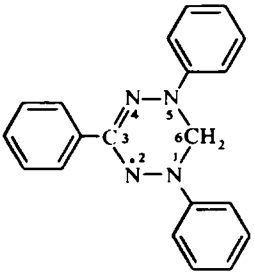
(*Received in the UK* 23 *March* 1971; *Accepted for publication* 8 *April* 1971)

Abstract—NMR spectra of 1,3,5-triarylverdazyls dissolved in DBNO yield all H hfs coupling constants and their assignment for 1,3,5-triphenylverdazyl. The experimental data are compared with McLachlan spin density calculations.

ESR[2] and NMR[1, 3] studies on a series of substituted 1,5-diarylverdazyls have revealed both the magnitude and the sign of hyperfine splitting (hfs) coupling constants in 1,5-diphenylverdazyl (I). From these data the spin density distribution in the verdazyl ring and in the N-phenyl rings of 1,3,5-triphenylverdazyl (II) can be derived. However, it is not possible to obtain dependable estimates of the spin densities in the C-phenyl ring. The significance of II as a primary verdazyl makes an experimental evaluation of its hfs coupling constants desirable.

I





II

As can easily be seen from the high number of hfs lines, 101 250 are expected for II, the ESR method is not suited to give the hfs coupling constants of II. ESR spectra of II[4] or of other 1,3,5-triarylverdazyls[2, 4] show 9 lines or 9 not highly resolved groups consistent with 4 nitrogens which are equivalent within the linewidth. We have therefore extended our ^{1}H and ^{2}D NMR studies[1] to a series of 1,3,5-triarylverdazyls.* Since the solubility of 1,3,5-triarylverdazyls is rather low, di-t-butylnitroxide (DBNO) was used as the solvent to obtain a more rapid spin exchange.[5] The compounds which were investigated are summarized in Table 1.

The NMR spectra of these verdazyls are resolved and exhibit resonance lines of all aliphatic, methoxy and aromatic protons except for those which are covered by the intense resonance band of the solvent DBNO. A representative spectrum is shown in Fig 1. Eqs (1) and (2) yield the hfs coupling constants from the observed para-

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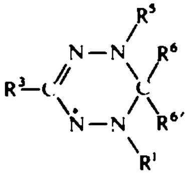
* Note added in proof: Very recently the NMR spectrum of 1,3,5-triphenylverdazyl was published.[19] The measured values and their assignment are in good agreement with the results presented here, except those concerning the methylene bridge of the verdazyl.

TABLE 1. PREPARED VERDAZYLS



	R^3	$R^1 = R^5$	$R^6 = R^{6'}$	m.p. (dec.)
II	C_6H_5	C_6H_5	H	140–141°[4]
III	C_6H_5	C_6H_5	D	160–161°[3]
IV	C_6H_5	$C_6H_4C_2H_5$—(4)	H	128–129°[3]
V	C_6H_5	$C_6H_4OCH_3$—(4)	H	143–144°[6]
VI	C_6D_5	$C_6H_4OCH_3$—(4)	H	144–145°
VII	$C_6H_4OCH_3$—(4)	$C_6H_4OCH_3$—(4)	H	124–125°[4]

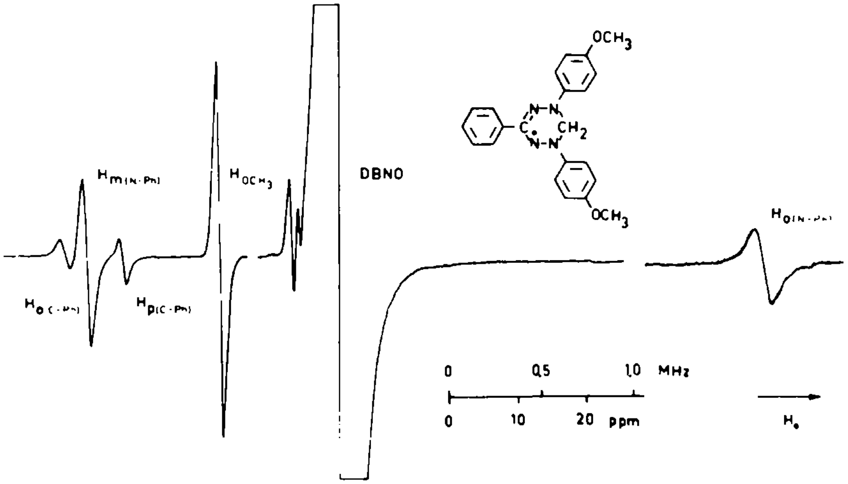


FIG 1. NMR spectrum of 3-phenyl-1,5-bis(4-methoxyphenyl) verdazyl in DBNO

magnetic shifts $\delta_p = (\nu_p - \nu_d)\,\nu_d$ [ppm] for protons and deuterons respectively at 295°K.[1,7]

$$a_H = 3{\cdot}73\,\delta_{p(295°K)}\cdot 10^{-2}\,[\mathrm{MHz}] \tag{1a}$$

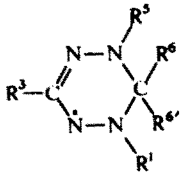
$$a_H = 1{\cdot}33\cdot 10^{-2}\,\delta_{p(295°K)}\,[\mathrm{G}] \tag{1b}$$

$$a_D = 5{\cdot}73\,\delta_{p(295°K)}\cdot 10^{-3}\,[\mathrm{MHz}] \tag{2a}$$

$$a_D = 2{\cdot}05\cdot 10^{-3}\,\delta_{p(295°K)}\,[\mathrm{G}] \tag{2b}$$

The values of the measured paramagnetic shifts and the calculated hfs coupling constants are listed in Table 2. The NMR lines have been assigned on the basis of verdazyl NMR data obtained previously[1] and by comparison of the various spectra. The ^{2}D NMR spectra of the verdazyls III and VI yield the ^{1}H NMR lines of the

TABLE 2. ^{1}H AND ^{2}D PARAMAGNETIC SHIFTS $\delta_p = (\nu_p - \nu_d)\nu_d$ AND COUPLING CONSTANTS a_i OF THE VERDAZYLS *II–VII* IN DBNO AT 295° K



Verdazyl	Assignment		Shift $\nu_p - \nu_d$ [Hz]^a	Shift σ_p [ppm]^b	Coupling Constants a_i	
					MHz	Gauss
II	$R^1 = R^5$:	H_o	−7050	−78·5	−2·93	−1·05
		H_m	2610	29·0	1·04	0·39
		H_p	−7520	−83·5	−3·11	−1·11
	R^3:	H_o	2610	29·0	1·04	0·39
		H_m	^{c}	^{c}	^{c}	^{c}
		H_p	1840	20·4	0·76	0·27
	$R^6 = R^{6'}$:	H	^{c}	^{c}	^{c}	^{c}
III	$R^6 = R^{6'}$:	D	−10·5	−0·8	−0·0046	−0·002
IV	$R^1 = R^5$:	H_o	−7520	−83·5	−3·11	−1·11
		H_m	2780	30·9	1·15	0·41
		H_{CH_2}	6370	71·0	2·65	0·95
		H_{CH_3}	57	0·63	0·024	0·008
	R^3:	H_o	2780	30·9	1·15	0·41
		H_m	^{c}	^{c}	^{c}	^{c}
		H_p	2050	22·8	0·85	0·30
	$R^6 = R^{6'}$:	H	^{c}	^{c}	^{c}	^{c}
V	$R^1 = R^5$:	H_o	−6670	−74·0	−2·76	−0·99
		H_m	2180	24·2	0·90	0·32
		H_{OCH_3}	810	9·0	0·34	0·12
	R^3:	H_o	2710	30·1	1·12	0·40
		H_m	^{c}	^{c}	^{c}	^{c}
		H_p	1790	19·9	0·74	0·27
	$R^6 = R^{6'}$:	H	^{c}	^{c}	^{c}	^{c}
VI	R^3:	D_o	430	31·1	0·178	0·064
		D_m	−160	−11·6	−0·067	−0·024
		D_p	300	21·7	0·124	0·044
VII	$R^1 = R^5$:	H_o	−7150	−79·5	−2·96	−1·06
		H_m	2440	27·1	1·01	0·36
		H_{OCH_3}	810	9·0	0·34	0·12
	R^3:	H_o	2670	29·7	1·11	0·40
		H_m	^{c}	^{c}	^{c}	^{c}
		H_{OCH_3}	−175	−1·95	−0·073	−0·026
	$R^6 = R^{6'}$:	H	^{c}	^{c}	^{c}	^{c}

[a] Shift relative to the corresponding H or D resonance of the diamagnetic leucoverdazyls

[b] Resonance frequencies: H = 90 MHz, D = 13·81 MHz

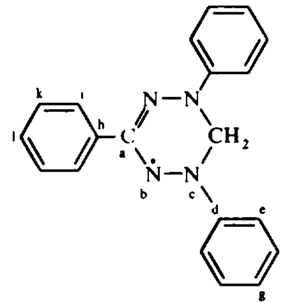
[c] The NMR lines of these protons are covered by the very intense DBNO resonance band

verdazyls II and V which were covered by the intense DBNO band, and confirm the assignment of the C-phenyl ring protons.

The NMR lines from the o- and p-protons in the N-phenyl rings are shifted to high yield and yield 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. The coupling constants of the N-phenyl ring protons are fairly constant in this series and others.[1,2] The NMR lines from the o- and p-protons in the C-phenyl ring are shifted to low field and yield a larger coupling constant for the o- than for the p-protons in contrast to the normal situation in the N-phenyl rings. The NMR line from the m-protons of the C-phenyl ring is shifted to high field and lies under the DBNO line, as the spectrum of the deuterated verdazyl VI clearly shows. Substitution of aromatic protons by methoxy groups results in a small change of the overall spin density distribution in the verdazyls (V, VII) and replaces the aromatic proton coupling by a methoxy proton coupling of opposite sign and about one-tenth of the magnitude in agreement with the literature.[8,9] The resonance line of the C-6 protons in the verdazyls likewise lies under the DBNO resonance, as the spectrum of the verdazyl III shows. The ^{2}D NMR line of III is unusually broad compared to others and again[1] indicates a ring inversion in C-6 unsubstituted verdazyls which is slow on the NMR time scale.

The measured proton hfs coupling constants and their assignment in the primary 1,3,5-triphenylverdazyl (II) allows one to compare spin densities (table 3) calculated from the experimental data by use of the McConnell[10] equation $a_H = -23{\cdot}7\ \rho_C^\pi$[11] and the Stone and Maki[12] equation $a_N = 28{\cdot}6\ \rho_N^\pi$ and spin densities (Table 3) obtained by McLachlan[13] molecular orbital calculations. A calculation has been performed[14] using the following parameters: $\beta_{C_aN_b} = \beta_{N_cC_d} = 1{\cdot}2\ \beta_{CC}$, $\beta_{N_bN_c} = \beta_{CC}$, $\alpha_N = \alpha_C + 1{\cdot}2\ \beta_{CC}$, $\lambda = 1{\cdot}2$. As table 3 shows, the agreement between these two series of spin

TABLE 3. CALCULATED SPIN DENSITIES FOR 1,3,5-TRIPHENYLVERDAZYL (II)



Position	Experimental			Calculated		
	a [G]	I	ρ_i^π	$\rho_i^{\pi a}$	$\rho_i^{\pi b}$	$\rho_i^{\pi c}$
a	—	C	—	−0·0461	−0·0526	−0·0562
b	6·0 (N)	N	0·21	0·1944	0·2301	0·2485
c	6·0 (N)	N	0·21	0·2040	0·2295	0·2421
d	—	C	—	−0·0345	−0·0353	−0·0355
e	−1·05 (H)	C	0·044	0·0791	0·0572	0·0461
f	0·39 (H)	C	−0·016	−0·0313	−0·0254	−0·0224
g	−1·11 (H)	C	0·047	0·0723	0·0489	0·0363
h	—	C	—	0·0032	0·0039	0·0042
i	0·39 (H)	C	−0·016	−0·0077	−0·0086	−0·0091
k	−0·155 (H)	C	0·0065	0·0002	0·0003	0·0003
l	0·27 (H)	C	−0·011	−0·0066	−0·0073	−0·0078

[a] $\beta_{N_cC_d} = 1{\cdot}2\ \beta_{CC}$ [b] $\beta_{N_cC_d} = \beta_{CC}$ [c] $\beta_{N_cC_d} = 0{\cdot}9\ \beta_{CC}$

densities is correct in the signs, but only fair in the values. As demonstrated by the X-ray structural analysis[15] and the verdazyl ring inversion, the N-phenyl rings are not in the same plane with the verdazyl ring. It should therefore be reasonable to assume a somewhat lower value for $\beta_{N_cC_d}$, e.g. $\beta_{N_cC_d} = \beta_{CC}$ as in the tetrazolinyls[16] or phototetrazolinyls[17] or even lower. Spin densities from calculations with $\beta_{N_cC_d} = \beta_{CC}$ and $\beta_{N_cC_d} = 0{\cdot}9\ \beta_{CC}$, which are also listed in table 3, show a little better agreement with the experimental data than previously.[14]

The interaction of the C-6 methylene bridge with the π-system has been neglected in these calculations. For a methylene group interacting with two spin sites, Whiffen[18] has proposed within the framework of simple π-electron theory that the hfs coupling constant is proportional to the square of the sum of the π-orbital coefficients rather than the sum of the corresponding squared terms. The π-orbital coefficients of N-1 and N-5 (N_c) in the verdazyl ring are equal but of opposite sign, therefore a zero hfs coupling constant for the C-6 methylene protons is predicted. This prediction is well substantiated by the vanishingly small experimental coupling constant for the C-6 methylene protons. Consequently, the spin density at C-6 does not affect the spin density distribution in the π-electron system of the verdazyls.

The NMR spectra of this 1,3,5-triarylverdazyl series reveal the magnitude and the sign of all proton hfs coupling constants and their assignment and substantiate experimentally the calculated spin density distribution in 1,3,5-triphenylverdazyl.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker HX spectrometer using the technique described in the preceding paper.[1]

3-Pentadeuterophenyl-1.5-bis(4-methoxyphenyl)formazan. The mixture of *p*-anisidine (7·4 g) in H_2O (20 ml) + conc HCl (15 ml) was cooled to 0° and kept at this temp. while the soln of $NaNO_2$ (4·15 g) in H_2O (20 ml) was added dropwise under stirring. This diazonium salt soln was added in small portions to the stirred soln of pentadeuterobenzaldehyde-4-methoxyphenylhydrazone (prepared from pentadeuterobenzaldehyde + 4 methoxyphenylhydrazine in EtOH, m.p. 124–125° (dec)) in DMF (150 ml) and pyridine (75 ml) kept at 0°. After 4 hr the separated product was collected and recrystallized from acetone–MeOH to yield violet black needles (13·4 g), m.p. 162–163° (dec). (Found: C, 69·20: H + D, 7·28; N, 15·57. $C_{21}H_{15}D_5N_4O_2$ requires: C, 69·02; H + D, 6·90; N, 15·33%).

3-Pentadeutero-1.5-bis(4-methoxyphenyl)verdazyl (VI). 3-Pentadeuterophenyl-1.5-*bis*(4-methoxyphenyl) formazan (2 g) + $KHSO_4$ (5 g) + 38% aqueous formaldehyde (5 ml) in DMF (100 ml) were stirred for 1 hr. 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. Crystallized twice from DMF–MeOH green black crystals (1·4 g), m.p. 144–145° (dec). (Found: C, 69·43; H + D, 6·86; N, 15·02. $C_{22}H_{16}D_5N_4O_2$ required: C, 69·82; H + D, 6·92; N, 14·80%).

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