Tetrahedron. Vol 23, pp 4661 to 4676. Pergamon Press Ltd. 1967. Printed in Great Britain

STABILITY AND EQUILIBRIA OF FREE RADICALS—III*

PREPARATION OF STABLE, STERICALLY SHIELDED, DIARYLNITROGEN RADICALS WITH DONOR AND ACCEPTOR ARYL GROUPS IN THE SAME MOLECULE

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(*Received* 29 *March* 1967; *accepted for publication* 4 *April* 1967)

Abstract Diarylamines ArNHAr′ (Ar = 2,4,6-tri-, 2,6-di- or 2,4-dinitrophenyl, and Ar′ = phenyl or a phenyl with electron-donating substituents) were prepared; their IR and UV spectra, electrooxidation and electroreduction potentials were studied. Oxidation of picryl- and 2,6-dinitrophenyl-substituted compounds with Ag_2O affords paramagnetic solutions giving ESR signals when Ar′ has MeO or NR_2 substituents. Radicals IVi and Vi are stable even in crystalline state.

INTRODUCTION

IN THE preceding parts of this series[1,2] we tried to bring experimental evidence to the problem of the uncommon stability of diphenylpicrylhydrazyl (I). In contrast to triarylmethyl free radicals where both electron-donating and electron-accepting *para*-substituents increase the stability,[3a] in diarylnitrogen free radicals electron-donating substituents increase, and electron accepting substituents decrease, their stability as evidenced by the dissociation of tetrarylhydrazines.[3b–7] This difference between triarylmethyl, tetra-arylhydrazinium or triarylaminium free radicals (class S with no unshared electron pair on the C or N atom, non-Hammett behaviour)[8] and between diarylnitrogen, triarylhydrazyl or diarylnitroxide free radicals (class O with a lone pair on the N atom, Hammett behaviour),[8] has been rationalized theoreti-

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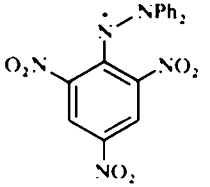
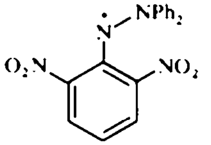
cally[8 10] and is in agreement with studies on tetrazanes.[11] However, diphenylpicrylhydrazyl I which possesses three nitro groups does not dimerize even at very low temperatures.[12]

The ESR spectra of 1,1-diphenyl-2-picrylhydrazyl and related free radicals were analyzed by many investigators,[13a 13o] but until now only coupling constants with the two hydrazylic nitrogen atoms were unambiguously assigned; coupling constants with the nitro group nitrogen atoms or with the protons have not yet been assigned, although degassed solutions present hyperfine structure due to interactions with the latter atoms.[13p]

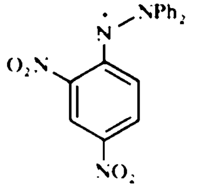
We advanced the hypothesis that the nitro groups exert a steric effect, along with their electronic effect, and proved this hypothesis by synthesizing two hydrazyl free radicals II and III, with dinitrophenyl groups,[1] in positions 2,6 and 2,4 respectively.



I



II



III

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Phenyl groups are manifest in the ν8a and ν19a bands at 1600 and 1500 cm^{-1}. Specific substitution patterns appear in compounds e–g (symmetrical CH_3 stretching band at 2840–2845 cm^{-1} of anisyl groups) and h (the same band at 2815–2830 cm^{-1} in dimethylaniline groups); in compounds a and i (out-of-plane CH deformation vibrations in monosubstituted phenyl groups at 695–700 and 740–765 cm^{-1}) and in *p*-substituted compounds d, g, h, i at 840–850 cm^{-1}.

Electrochemical reduction and oxidation potentials of diarylamines, on the dropping mercury electrode in ethanol, and on the rotating platinum electrode in acetonitrile, respectively, are presented in Table 4. A fairly good correlation between the oxidation potentials and the electronic absorption spectra is apparent: with the same substituents R, the $E_{\frac{1}{2}}$ value is lowest for VH, higher for VIH and highest for IVH (in spectra the last order is reversed); with a given polynitrophenyl group, the oxidation potentials decrease in the sequence a > g > j > i > h, which is the same as that observed in electronic spectra. This similarity can be accounted for, because the highest occupied molecular orbital is involved in both these processes. The electro-oxidation is probably the following monoelectronic process:

TABLE 4. REDUCTION POTENTIALS (ON THE DROPPING MERCURY ELECTRODE IN ETHANOL WITH 0·1N LiCl, VOLTS VS. S.C.E.) AND OXIDATION POTENTIALS (ON THE ROTATING PLATINUM ELECTRODE IN ACETONITRILE WITH 0·2N $NaClO_4$, VOLTS VS. THE Ag/0·01N Ag^+ ELECTRODE) OF DIARYLAMINES

Comp. (R)	IVH (2,4,6-Trinitro)		VH (2,6-Dinitro)		VIH (2,4-Dinitro)	
	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$
a (H)	1·28	0·57, 0·75, 0·95	1·18	0·69, 0·84	1·24	0·67, 0·90
g (*p*-MeO)	0·97	0·52, 0·68, 0·88	0·90	0·62, 0·80	0·90	0·62, 0·87
h (*p*NMe_2)	0·40	0·45, 0·66, 0·82	0·28	0·62, 0·82	0·40	0·63, 0·87
i (*p*NPh_2)	0·66	0·62, 0·84, 1·10	0·60	0·60, 0·80	0·66	0·62, 0·82
j [3,4 $(MeO)_2$]	0·95		0·84		0·90	
IH IIIH	0·82	0·70, 0·92*	0·69	0·84	0·81	0·60, 0·86

* The wave at −0·70 V is twice higher than the wave at −0·92 V.

$$Ar_2NH - e^- \rightarrow Ar_2\dot{\underset{\cdot\cdot}{N}} + H^+$$

On the other hand, the electroreduction potentials depend little on the nature of the substituent R; the dependence on the number of nitro groups is determinant (their position also influences but little the $E_{\frac{1}{2}\,red}$ values, as shown by comparing the data for VH and VIH). In the picryl compounds IVH there appear three polarographic waves, while in the dinitrophenyl compounds VH and VIH only two are present. It appears, therefore, that the reduction involves the nitro groups.

Table 4 also includes data for 1,1-diphenylpolynitrophenylhydrazines IH, IIH and IIIH. The first polarographic wave for IH ($E_{\frac{1}{2}\,red}$ = −0·70 V vs SCE) is twice as high as the second (−0·92 V), therefore we consider that the first wave results from the superposition of two waves.

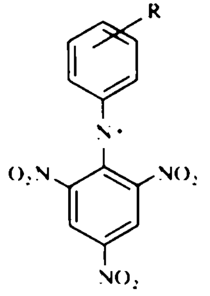
By comparing the electroxidation potentials of hydrazines IH–IIIH with those

The ESR spectra of II and III are practically identical,[2] providing that the electronic factors in these two radicals are similar, but only II which has the same steric screening as I can be isolated in solid state and is stable in solution.

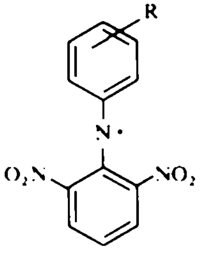
Independently the same two radicals II and III were afterwards reported in three other laboratories,[14–16] from which the last had obtained them since 1958.[*]

An X-ray diffraction analysis[17a] recently evidenced the importance of the steric shielding in diphenylpicrylhydrazyl. In N-picryl-*p*-iodoaniline, the two aryl groups are tilted with 65° relatively to one another,[17b] as seen from X-ray diffraction spectra, and in picramide the *ortho*-nitro group is tilted with 21° as seen from the UV spectrum.[17c]

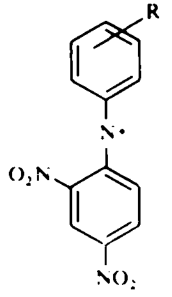
In continuation of the above studies, we wished to apply the same idea of the combined steric and electronic effects to diarylnitrogen free radicals. Until now, no crystalline diarylnitrogen free radical was reported, in other words the tetraarylhydrazines so far described are symmetrical and dissociate only in solution and at elevated temperatures, even those with stabilizing electron-donating substituents.[18a] Taking into account that the stability of free radicals is governed by steric as well as by electronic factors,[18b] as it is well established in the carbon and oxygen series,



IV



V



VI

R

a H

b *o*-Me

c *m*-Me

d *p*-Me

e *o*-Me

f *m*-OMe

g *p*-OMe

h *p*-NMe_2

i *p*-NPh_2

j 3,4 $(OMe)_2$

one can expect that diaryl nitrogen free radicals with formulae IV and V should be more stable than VI. With R = *p*-NPh_2 radicals IVi–VIi are the "*p*-phenylogues" of I–III. This prediction has been fulfilled and radicals IVi and Vi (R = *p*-NPh_2) have been isolated in crystalline state.

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[*] The preliminary reports[16b,c] had not, however, been included in *Chem. Abstr.*

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TABLE 1. ELEMENTARY ANALYSES AND M.PS OF DIARYLAMINES (UPPER ROW, CALC VALUES; LOWER ROW, FOUND)

Comp (R)	IVH (2,4,6-Trinitro)			VH (2,6-Dinitro)					VIH (2,4-Dinitro)		
	M.p.	Lit. m.p.	Ref.	M.p	Formula	C	H	N	M.p.	Lit. m.p.	Ref.
a (H)	179	180	19	106[a]					156	156	21
b (*o*-Me)	163	163	22	119	$C_{13}H_{11}N_3O_4$	57·14	4·05	15·38	-		—
						57·22	4·38	15·23			
c (*m*-Me)	129	129	22, 23	107	$C_{13}H_{11}N_3O_4$	57·14	4·05	15·38			
						57·34	4·40	15·13			
d (*p*-Me)	168	165	23, 24	135	$C_{13}H_{11}N_3O_4$	57·14	4·05	15·38			
						57·40	4·33	14·94	137	131	25
e (*o*-OMe)	143	143	23	163	$C_{13}H_{11}N_3O_5$	53·98	3·83	14·53			
						54·0	3·6	14·6	164	164	26
f (*m*-OMe)	126[b]		–	140	$C_{13}H_{11}N_3O_5$	53·98	3·83	14·53			
						54·25	4·21	14·20	137	138	27
g (*p*-OMe)	172	172	23, 24	169	$C_{13}H_{11}N_3O_5$	53·98	3·83	14·53			
						54·00	4·19	14·79	140	140	28
h (*p*-NMe$_2$)	185	183	24, 29	155	$C_{14}H_{14}N_4O_4$	56·62	4·66	18·54			
						56·30	5·00	18·78	169	170	30
i (*p*-NPh$_2$)	179[c]	—		222	$C_{24}H_{18}N_4O_4$	67·60	4·25	13·14			
						67·75	4·17	13·57	163[d]		
j [3,4-(OMe)$_2$]	156[e]		—	171	$C_{14}H_{13}N_3O_6$	52·67	4·10	13·16			
						53·00	3·98	13·06	175[f]		

[a] Lit m.p[20] 107–108°.

[b] Found: C, 47·02; H, 3·29; N, 17·27. $C_{13}H_{10}N_4O_7$ requires: C, 46·71; H, 3·02; N, 16·76%.

[c] Found: C, 61·40; H, 3·75; N, 14·70. $C_{24}H_{17}N_5O_6$ requires: C, 61·14; H, 3·64; N, 14·85%.

[d] Found: C, 67·81; H, 4·58; N, 13·07. $C_{24}H_{18}N_4O_4$ requires: C, 67·60; H, 4·25; N, 13·14%.

[e] Found: C, 46·06; H, 3·20; N, 15·35. $C_{14}H_{12}N_4O_8$ requires: C, 46·16; H, 3·32; N, 15·38%.

[f] Found: C, 52·33; H, 4·12; N, 13·20. $C_{14}H_{13}N_3O_6$ requires: C, 52·67; H, 4·10; N, 13·16%.

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TABLE 2. ELECTRONIC ABSORPTION SPECTRA OF DIARYLAMINES IVH VIH IN 1,2-DICHLOROETHANE SOLUTION (UPPER ROW, λ_{max} IN mμ; LOWER ROW, MOLAR ABSORPTIVITIES)

Amine (R)	IVH (2,4,6-Trinitro)				VH (2,6-Dinitro)			VIH (2,4-Dinitro)			
a (H)	250 sh		363ᵃ		266·5		427	262 sh		356ᵇ	
	10,500		9100		21,500		6200	7800		14,000	
b (*o*-Me)	247 sh		358		261		430			—	
	13,800		12,600		13,600		4680				
c (*m*-Me)	245 sh		367		258		430			—	
	17,000		12,000		25,000		6050				
d (*p*-Me)	252 sh		382		260		434	264		358	
	16,550		13,800		25,300		7200	7900		17,200	
e (*o*-OMe)	253 sh		383·5		258		434			—	
	10,500		11,800		28,700		8900				
f (*m*-OMe)	251 sh		367		257		428	267		356	
	14,150		12,300		20,500		6100	7500		11,800	
g (*p*-OMe)	242 sh		381		257		436	264		358	
	17,800		11,200		15,500		5200	10,500		15,100	
h (*p*-NMe$_2$)	262	316	380 sh	465	254 sh	282 sh	470	263		367	
	21,000	11,000	8000	10,200	16,300	15,100	5600	19,800		12,000	
i (*p*-NPh$_2$)		303	340 sh	464	249 sh	306	454	267 sh	303	342 sh	393 sh
		25,300		10,500	18,100	25,000	7000	13,000	25,500	16,900	13,500
j [3,4-(OMe)$_2$]	247 sh	266 sh	370 sh	409	263		440	264 sh		360	
	13,800	4600	8300	8800	14,700		5500	12,200		16,400	
IH–IIIH	260 sh		322			260 sh	394	267			338
	11,800		11,000			15,000	3700	14,000			12,800

[a] Lit.[31a] 233·5 mμ (ε 19,500), 367 mμ (ε 13,200) in ethanol.

[b] Lit.[31a] 231·5 mμ (ε 12,800), 350·5 mμ (ε 17,000) in ethanol.

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Preparations and properties of diarylamines

The diarylamines IVH, VH and VIH* whose oxidation should lead to diarylnitrogen free radicals IV–VI were prepared by nucleophilic substitution of activated halogen atoms in halo-polynitrobenzenes (2,4-fluoro- or -chlorodinitrobenzene, 2,6-chlorodinitrobenzene and picryl chloride, respectively) with substituted aniline derivatives (aniline, *o*-, *m*- and *p*-toluidine, *o*-, *m*- and *p*-anisidine, N,N-dimethyl- and -diphenyl-*p*-phenylenediamine, 4-aminoveratrole). The reactions were carried out in absolute ethanol under reflux with 2–2·5 moles amine for one mole halopolynitrobenzene in the case of aniline, toluidines and anisidine; with equimolar ratios in the case of 3,4-dimethoxyaniline; and with an excess of halonitrobenzene in the presence of solid sodium hydrogen carbonate for the *p*-dimethyl- or -diphenylaminoanilines. The yields were over 70%, and the products were recrystallized from benzene–ethanol ($R = p\text{-}NPh_2$) or ethanol (for the other amines). In some cases ($R = p\text{-}NMe_2$) chromatography on alumina from chloroform was necessary. The properties and elementary analyses of the diarylamines IVH–VIH are presented in Table 1. Some compounds of this class had been obtained in several crystalline forms and their chromoisomerism has been studied.[22-24]

Electronic absorption maxima of diarylamines in ethylene dichloride are presented in Table 2. It can be seen that from the diarylamines with the same substituents R, the longest-wave length band appears in VH at the lowest frequencies; then come compounds IVH, while in VIH the frequencies are the highest. This situation was encountered in the 1,1-diphenyl-2-polynitrophenylhydrazines[1, 32a] and in the polynitrophenylhydrazones of furyl alkyl ketones.[32b] Although the bathochromic and hyperchromic effects of this band in the sequence VIHa, e g, and j are quite small indicating little interaction between the 2,4-dinitrophenyl and polymethoxyphenyl groups in diarylamines, these effects are larger in compounds VHa, e g, j and in IVHa, e g, j. Moreover, appreciable bathochromic effects are observed in all cases with compounds h and i, with the strongly donor groups NMe_2 and NPh_2, proving that there exists an interaction between the two aryl groups in diarylamines across the amino nitrogen atom.[33]

Methyl and methoxy substituents cause about the same shifts of the longest-wavelength bands. These shifts are more pronounced in the picrylderivatives IVH than in the dinitroderivatives VH or VIH. Interestingly, *m*-methoxy derivatives f absorb at lower wavelengths than *o* or *p*-methoxy (e or g), owing to conjugative effects, but a steric effect probably operates in IVHb (*o*-methyl) which absorbs at lower wavelength than *m*- or *p*-methyl derivatives.

In ethanol, all maxima are hipsochromically shifted relatively to the dichloroethane solution. In the case of the longest-wavelength band, the shift is 24 mμ for IVHi, 17 mμ for VHi and only 3 mμ for VIHi. This negative solvatochromy is normal for such polar compounds.

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* The notation of radicals and amines consists in a roman numeral corresponding to a formula, followed (in the case of amines only) by the letter H or D which designates the hydrogen or deuterium atom linked to the nitrogen, and lastly by a letter a–j indicating the aryl substituent bonded to the polynitrophenylamino group.

[32] [a] J. A. Weil and G. A. Janusonis, *J. Org. Chem.* **27**, 1248 (1962);
[b] A. T. Bălaban, P. T. Frangopol and E. Keplinger, *Spectrochim. Acta* **19**, 367 (1963).

[33] R. S. Tsekhansky, *Zh. Org. Khim.* **1**, 1909 (1965) and lit cited therein.

In the older literature [22b, 24a, 31b] the spectra of amines IVHa-i were studied in neutral and alkaline medium in connection with their chromoisomerism.

The infrared absorption spectra confirm the structure of the diarylamines IVH–VIH. All spectra present one strong NH stretching band at about 3300 cm^{-1} (cf. Table 3). The low frequency of this band is due to intramolecular association with the *o*-nitro groups, which also causes the usually weak NH deformation vibration to appear as a medium or strong band at 1430–1470 cm^{-1}. These assignments are substantiated by N-deuteration experiments: recrystallization of VHi and VIHi from CH_3COOD afforded VDi and VIDi. In the IR spectra of these compounds in potassium bromide pellet, νND bands at 2490 and 2450 cm^{-1}, respectively, replace the νNH bands at 3371 and 3301 cm^{-1}; δNH bands at 1465 cm^{-1} are no longer visible in these N-deuterated compounds. The data in Table 3 show that the νNH vibration presents irregularities in KBr pellet, but in CCl_4 solution it always appears at 3315 ± 5 cm^{-1} in the picrylderivatives IVH, at ca. 3340 cm^{-1} in the 2,6-dinitroderivatives VH, and at ca. 3345 cm^{-1} in the 2,4-dinitroderivatives VIH. These higher frequencies seem to indicate weaker intramolecular hydrogen bonds in the dinitroderivatives than in the picryl derivatives, and in the 2,4- than in the 2,6-dinitroderivatives. A similar situation occurs in the hydrazines IH–IIIH, included in Table 3.

TABLE 3. IR NH STRETCHING BANDS OF DIARYLAMINES IN CARBON TETRACHLORIDE SOLUTION AND POTASSIUM BROMIDE PELLET

Comp. (R)	IVH(2,4,6-Trinitro)		VH(2,6-Dinitro)		VIH(2,4-Dinitro)	
	KBr	CCl_4	KBr	CCl_4	KBr	CCl_4
a (H)	3310	3320	3326	3342	3325	3343
b (*o*-Me)	3331	3310	3325	3339		
c (*m*-Me)	3390	3315	3324	3341		
d (*p*-Me)	3329	3315	3322	3342		
e (*o*-OMe)	3331	3315	3351	3350		
f (*m*-OMe)	3296	3320	3330	3345	3350	3343
g (*p*-OMe)	3330	3321	3335	3342	3325	3350
h (*p*-NMe_2)	3278	3310	3331	3340	3345	3351
i (*p*-NPh_2)	3340	3310	(D 2490)		(D 2450)	
			3371	3340	3301	3345
j [3,4-$(OMe)_2$]	3320	3310	3330	3340	3320	3350
IH IIIH	3265	3301	3310	3316	3343	3346

The C_{arom} - N stretching vibrations appear at ca. 1300 and 1230 cm^{-1}, since these bands of VHi were replaced in VDi by shoulders at 1380 and 1340 cm^{-1}. These displacements are consistent with literature data.[33, 34]

The asymmetrical and symmetrical νN—O bands appear in the usual ranges[35] at 1520–1540 and 1340–1360 cm^{-1}, respectively, as very strong bands. In the picryl derivatives IVH these bands are doublets separated by ca. 20 cm^{-1}.

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[34] D. Hadži and M. Skrbljak, *J. Chem. Soc.* 843 (1957); C. Toma and A. T. Balaban, *Tetrahedron* Suppl. 7, 9 (1966)

[35] A. R. Katritzky and P. Simmons, *Quart. Rev.* 13, 353 (1959); *Rec. Trav. Chim.* 79, 361 (1960); G. Varsanyi, S. Holly and L. Imre, *Spectrochim. Acta*, 23A, 1205 (1967).

Phenyl groups are manifest in the ν8a and ν19a bands at 1600 and 1500 cm^{-1}. Specific substitution patterns appear in compounds e–g (symmetrical CH_3 stretching band at 2840–2845 cm^{-1} of anisyl groups) and h (the same band at 2815–2830 cm^{-1} in dimethylaniline groups); in compounds a and i (out-of-plane CH deformation vibrations in monosubstituted phenyl groups at 695–700 and 740–765 cm^{-1}) and in *p*-substituted compounds d, g, h, i at 840–850 cm^{-1}.

Electrochemical reduction and oxidation potentials of diarylamines, on the dropping mercury electrode in ethanol, and on the rotating platinum electrode in acetonitrile, respectively, are presented in Table 4. A fairly good correlation between the oxidation potentials and the electronic absorption spectra is apparent: with the same substituents R, the $E_{\frac{1}{2}}$ value is lowest for VH, higher for VIH and highest for IVH (in spectra the last order is reversed); with a given polynitrophenyl group, the oxidation potentials decrease in the sequence a > g > j > i > h, which is the same as that observed in electronic spectra. This similarity can be accounted for, because the highest occupied molecular orbital is involved in both these processes. The electro-oxidation is probably the following monoelectronic process:

TABLE 4. REDUCTION POTENTIALS (ON THE DROPPING MERCURY ELECTRODE IN ETHANOL WITH 0·1N LiCl, VOLTS VS. S.C.E.) AND OXIDATION POTENTIALS (ON THE ROTATING PLATINUM ELECTRODE IN ACETONITRILE WITH 0·2N $NaClO_4$, VOLTS VS. THE $Ag/0{\cdot}01N\ Ag^+$ ELECTRODE) OF DIARYLAMINES

Comp. (R)	IVH (2,4,6-Trinitro)		VH (2,6-Dinitro)		VIH (2,4-Dinitro)	
	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$	$E_{\frac{1}{2}\,ox}$	$-E_{\frac{1}{2}\,red}$
a (H)	1·28	0·57, 0·75, 0·95	1·18	0·69, 0·84	1·24	0·67, 0·90
g (*p*-MeO)	0·97	0·52, 0·68, 0·88	0·90	0·62, 0·80	0·90	0·62, 0·87
h (*p*NMe_2)	0·40	0·45, 0·66, 0·82	0·28	0·62, 0·82	0·40	0·63, 0·87
i (*p*NPh_2)	0·66	0·62, 0·84, 1·10	0·60	0·60, 0·80	0·66	0·62, 0·82
j [3,4 $(MeO)_2$]	0·95		0·84		0·90	
I H III H	0·82	0·70, 0·92*	0·69	0·84	0·81	0·60, 0·86

* The wave at −0·70 V is twice higher than the wave at −0·92 V.

$$Ar_2NH - e^- \rightarrow Ar_2\dot{\underset{..}{N}} + H^+$$

On the other hand, the electroreduction potentials depend little on the nature of the substituent R; the dependence on the number of nitro groups is determinant (their position also influences but little the $E_{\frac{1}{2}\,red}$ values, as shown by comparing the data for VH and VIH). In the picryl compounds IVH there appear three polarographic waves, while in the dinitrophenyl compounds VH and VIH only two are present. It appears, therefore, that the reduction involves the nitro groups.

Table 4 also includes data for 1,1-diphenylpolynitrophenylhydrazines IH, IIH and IIIH. The first polarographic wave for IH ($E_{\frac{1}{2}\,red} = -0{\cdot}70$ V vs SCE) is twice as high as the second (−0·92 V), therefore we consider that the first wave results from the superposition of two waves.

By comparing the electroxidation potentials of hydrazines IH–IIIH with those of diarylamines IVH VIH, one can see that the latter $E_{\frac{1}{2}\alpha}$ values cover a wider range including the values for hydrazines.

Preparation and properties of free radicals

Attempts to oxidize with lead dioxide the diarylamines IVHi, VHi and VIHi failed, therefore recourse was had to silver oxide as oxidizing agent. Busch and Kögel[31b] mentioned that N-picryl-α-naphthylamine and N-picrylaniline (IVHa) are oxidized by silver oxide to products which were not further investiagted. By stirring solutions of diarylamines in benzene, chloroform, tetrahydrofuran or diethyl ether with silver oxide, deeply-coloured solutions were obtained which yielded an ESR spectrum in the case of compounds IV g–j and V g–j. No electron paramagnetic resonance absorption was observed on similar oxidation of amines VIH a j, IVH a f and VH a–f. The deep violet solutions of IVi and Vi yielded on evaporation dark crystals which were paramagnetic; their solution yielded and ESR spectrum identical with that of the oxidized solution. By reduction with hydroquinone[36] they could be converted back into the corresponding diarylamines (identified by mixed m.p. and by IR spectra). Their elementary analyses and absorption bands at ca. 530 mμ (Table 5) are consistent with structures IVi and Vi (hydrazyls I–III absorb at practically the same wavelength[1]). In the IR spectra of IVi and Vi (KBr pellets or CCl_4 solution) there are no NH stretching bands; the other major bands in the spectra of the corresponding diarylamines are also present in the spectra of the free radicals. These compounds seem to be the first crystalline diarylnitrogen radicals so far reported.

TABLE 5. FREE RADICALS IVi AND Vi

Compound		IVi			Vi	
Formula		$C_{24}H_{16}N_5O_6$			$C_{24}H_{17}N_4O_4$	
		Calc.	Found		Calc.	Found
Elementary analysis	C	61·27	61·46		67·76	67·81
(Calc.; Found)	H	3·43	3·75		4·00	4·20
	N	14·88	14·54		13·17	13·07
M.p.	°C	85°			131°	
Absorption	λ, mμ	530;	300·5;	263	532;	266
bands in $C_2H_4Cl_2$	ε	2000	20,900	21,400	2500	25,700

Attempts to oxidize dipicrylamine by the same method failed. However, by treating with silver oxide solutions of picryl-methoxyamine VII or the related 2,6- or 2,4-dinitrophenyl-methoxyamine, paramagnetic species were obtained, giving ESR

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[36] S. Tazuke, K. Uno and S. Okamura, *Bull. Chem. Soc. Japan* **38**, 1218 (1965).

TABLE 6. ESR SPECTRA OF DIARYLNITROGEN FREE RADICALS IN BENZENE SOLUTION

R	IV (2,4,6-Trinitro)					V (2,6-Dinitro)				
	g-Value[a]	No of lines	Spacing gauss	Intensity ratios[b]	a_N gauss	g-Value[a]	No. of lines	Spacing gauss	Intensity ratios[b]	a_N gauss
g (p-OMe)	2·0032	7[c]	4·6	1:3:1:**2**:1:...	9·6	2·0032	7	4·6	1:3:1:**2**:1:...	9·6
h (p-NMe$_2$)	2·0032	23	2·6	5:0:10:1:20:4:40:8: 50:20:55:**22**:55...	9·6	2·0032	13	4·6	1:2:1:2:3:4:**2**:4 ...	9·6
i (p-NPh$_2$)	2·0031	8[d]	3·5	1:2:3:**2**:2 ...	7·0	2·0032	9[e]	3·6	1:2:3:4:**4**:4: ...	7·2
j [3,4-(OMe)$_2$]	2·0036	3	8·0	1:**1**:1	8·0	2·0035	3	8·0	1:**1**:1	8·0

[a] Estimated by means of potassium peroxylamindisulphonate, error +0·004.

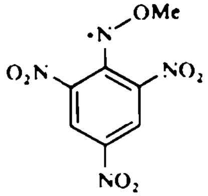
[b] The middle line is in bold-face character; the intensity ratios are approximate.

[c] After 24 hr four weaker lines appear as shoulders on the remaining three lines

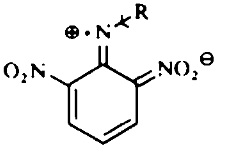
[d] After 48 hr only five lines are visible

[e] After 480 hr three major lines with three shoulders are visible.

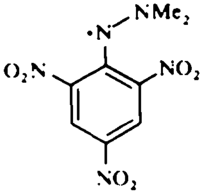
signals with hyperfine structure.[37a] It seems therefore that the requirements for the stability of nitrogen free radicals are[2] a steric shielding around the nitrogen atom (which can be ensured for instance by a picryl or a 2,6-dinitrophenyl, but less by a 2,4-dinitrophenyl group) and a dipolar structure leading to a strong electron displacement. These conditions are fulfilled by the general formula VIII, which includes the stable free radicals I, II, IV, V and VII. Data on free radicals with structures similar to IV–VI, but with nitro groups partly replaced by sulphonic groups, will be reported at a later date.[37b] The failure of Poirier and Benington[38] to prepare a radical IX was confirmed by our unsuccessful attempts to oxidize IXH either with PbO_2 or with Ag_2O.



VII



VIII



IX

Electronic paramagnetic resonance spectra

Solutions of the diarylamines in benzene were degassed by bubbling argon in special vials with two protruding tubes: one fitting into the cavity of the ESR spectrometer, the other containing powdered silver oxide. The vials were sealed off in argon atmosphere. Alternatively, the solutions were degassed by freezing and evacuating several times and sealing the evacuated vial with the solution frozen by liquid nitrogen. Immediately before taking the ESR spectra the vials were tilted and the solution was brought into contact with the silver oxide. The spectra were run several times at room temperature in order to ascertain the stability of the radicalic species. Results are presented in Table 6 and in Figs. 1 and 2.

Even in carefully degassed solutions, no supplementary splittings besides those indicated in Table 6 appear. The fairly broad lines and their superpositions preclude an unambiguous assignment of coupling constants. However, one can make the assumption that the major splitting constant is due to the diarylamino nitrogen atom, and this is indicated in Table 6. For the mono and dimethoxy compounds IVg and Vg, or IVj and VIj, respectively, the ESR spectra are pairwise identical, and the assignment of the three major lines to a triplet due to ^{14}N (nuclear spin 1) is straightforward. The ESR spectra of IVh, IVi, Vh and Vi are more complicated and the a_N values are tentative.

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[37] [a] A. T. Balaban, P. T. Frangopol, M. Frangopol and N. Negoiţă, paper to be published.

[b] P. T. Frangopol, M. Frangopol, N. Negoiţă, E. Romas and M. Paraschiv, to be published.

[38] R. H. Poirier and F. Benington, *J. Org. Chem.* **19**, 1157 (1954).

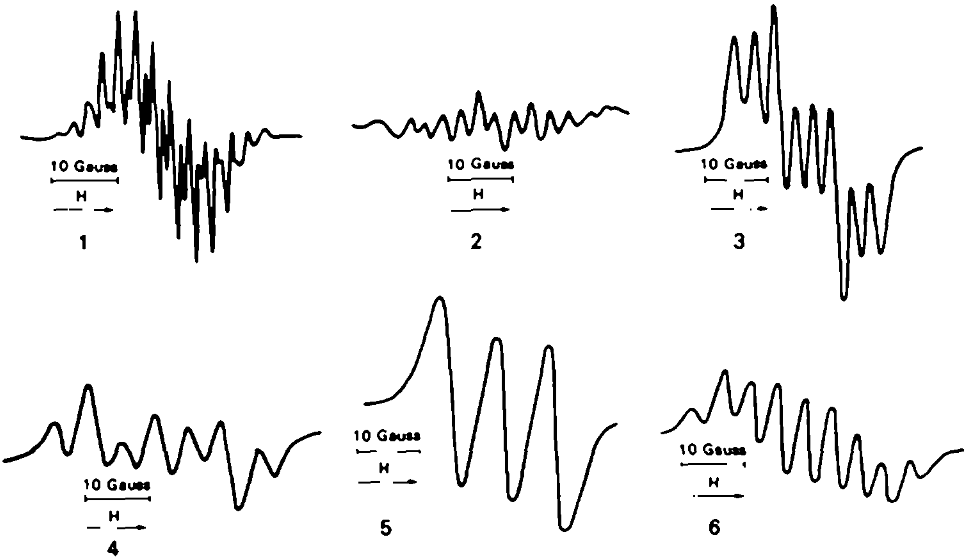

FIG. 1. ESR spectra of diarylnitrogen free radicals in benzene:
1, picryl-*p*-dimethylaminophenyl-nitrogen, IVh;
2, 2,6-dinitrophenyl-*p*-dimethylaminophenyl-nitrogen, Vh;
3, picryl-*p*-diphenylaminophenyl-nitrogen, IVi;
4, picryl-*p*-anisyl-nitrogen, IVg;
5, picryl-3,4-dimethoxyphenyl-nitrogen, IVj;
6, 2,6-dinitrophenyl-*p*-diphenylaminophenyl-nitrogen, Vi.

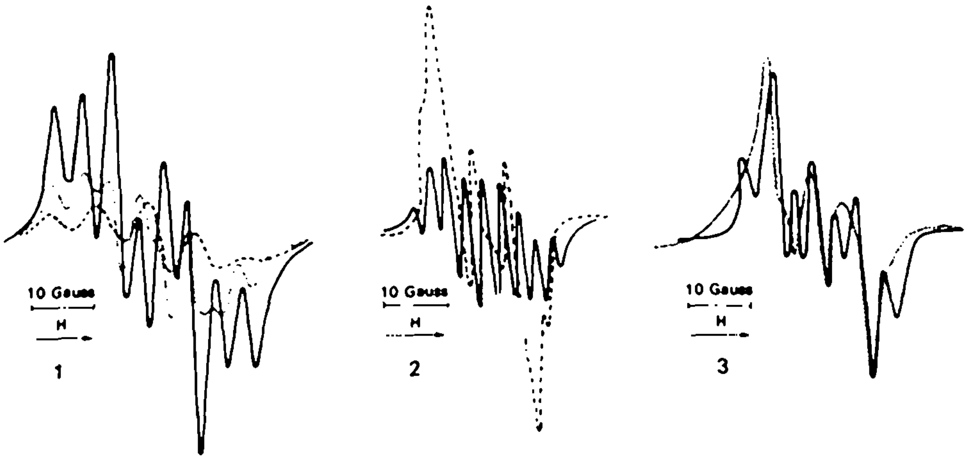

FIG. 2. ESR spectra of diarylnitrogen free radicals in benzene at room temp in argon atmosphere:

1, picryl-*p*-diphenylaminophenyl-nitrogen, IVi (full line, initially; dotted line, after two hours; dashed line, after 24 hrs);
2, 2,6-dinitrophenyl-*p*-diphenylaminophenylnitrogen, Vi (full line, initially; dashed line, after 24 hr);
3, picryl-*p*-anisyl-nitrogen, IVg (full line, initially; dotted line, after 24 hr).

The total width of the ESR spectrum is in cases g, i and j practically constant, ca. 28 gauss, as seen from Table 6 by multiplying the smallest spacing with the number of lines. This is in agreement with theoretical expectations assuming all spin densities to be positive.[39] However, the ESR spectra IVh and Vh are broader (about 50 gauss).

An important conclusion from the investigation of ESR spectra concerns the isotropic g-values of the free radicals in solution, which were estimated relatively to potassium peroxylamindisulphonate[40] (Frémy salt), $g = 2{\cdot}0055$.[41] As seen from Table 6, all g-values lie in the range 2·0031–2·0036. Since the g factors of diarylnitrogen free radicals have the same values 2·0031–2·0034,[18] whereas diarylnitroxides have higher g-values* (2·0055–2·0068),[42 43] it is apparent that the oxidizing agent (Ag_2O) did not convert the diarylamine into a diarylnitroxide, in agreement with the above chemical investigations. Oxygen or peroxides were reported[45] to convert diphenylaralkyl-amines $Ph_2N\ CH_x{}^5Ar_{3\ x}$ (x = 0 or 2) into tetraphenylhydrazinium and diphenylnitroxide free radicals.

The number of paramagnetic centers of solid IVi was determined by comparing its ESR spectrum with that of standard samples of carbon and diphenylpicrylhydrazyl. It was found that, although IVi did not reveal an NH stretching band, the signal had an integrated intensity corresponding to a number of spins equal to only 7% of the number of molecules of IVi present in the sample. Attempts to purify the radical by thin-layer chromatography on silica-gel in order to free it from diamagnetic impurities gave the opposite result.

EXPERIMENTAL

Starting materials. Halopolynitrobenzenes were prepared as described.[1] The substituted anilines required for the preparation of diarylamines IVH VIH were commercial compounds with the following three exceptions.

m-Anisidine was prepared from *m*-aminophenol by N-acetylation with Ac_2O, methylation with Me_2SO_4 in alkaline soln,[27] and acid hydrolysis of the Ac group; the base was set free by alkalinization and purified by distillation b.p.$_{760}$ 251°, and recrystallization, m.p. 126° from EtOH.

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* Spin-orbit coupling with atoms heavier than N increases the value of the g-factor.[44]

[39] H. S. Jarrett, *J. Chem. Phys.* **25**, 1289 (1956).

[40] E. Fremy, *Ann. Chim. Phys.* **15**, 459 (1845); G. Harvey and R. G. W. Hollingshead, *Chem. & Ind.* 244 (1953); J. P. Lloyd and G. E. Pake, *Phys. Rev.* **94**, 579 (1954); G. Brauer (Editor), *Handbuch der präparativen anorganischen Chemie* (2nd Edition) Vol. I, p. 452. Enke Verlag, Stuttgart (1960); R. P. Singh, *Canad. J. Chem.* **44**, 1994 (1966).

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[42] F. A. Neugebauer and P. H. H. Fischer, *Z. Naturforschung* **21b**, 1036 (1966); P. H. H. Fischer and F. A. Neugebauer, *Ibid.* **19a**, 1514 (1964).

[43] E. G. Rozantsev, *Usp. Khim.* **35**, 1549 (1966); R. M. Dupeyre and A. Rassat, *J. Am. Chem. Soc.* **88**, 3180 (1966) and previous papers in the series.

[44] A. J. Stone, *Mol. Phys.* **6**, 509 (1963); K. Scheffer and H. B. Stegmann, *Ber. Bunsenges. physik. Chem.* **67**, 864 (1963); B. G. Segal, M. Kaplan and G. K. Fraenkel, *J. Chem. Phys.* **43**, 4191 (1965); O. H. Griffith, D. W. Cornell and H. M. McConnell, *Ibid.* **43**, 2909 (1965); J. R. Thomas, *J. Am. Chem. Soc.* **86**, 1446 (1964).

[45] G. A. Abakumov, A. A. Abramova and G. A. Razuvaev, *Dokl. Akad. Nauk S.S.S.R., Khim.* **169**, 579 (1966).

4-Aminoveratrole was prepared from catechol by methylation with Me_2SO_4 in aqueous alkaline soln,[46] nitration and reduction with $SnCl_2$ in HCl.[47]

p-Aminotriphenylamine (N,N-diphenyl-*p*-phenylenediamine) was prepared from Ph_3N by mononitration and reduction. The nitration with HNO_3 in AcOH[48] always gives mixtures of mono- and polynitroderivatives (cf.[49]), therefore a different procedure was adopted, namely the reaction with $NaNO_2$ (3 moles for one mole Ph_3N) in AcOH at 70° for 1 hr, in conditions which differ slightly from those described.[50] *p*-Nitrotriphenylamine, m.p. 142°,[48, 51, 52] was reduced with Zn powder in AcOH[52] to *p*-aminotriphenylamine, m.p. 145°.[48, 52]

Ag_2O was prepared from $AgNO_3$ and NaOH.[53]

Preparation of polynitrophenyl-aryl-amines IVH VIH

The reaction of halopolynitrobenzenes (1 mole) with 2 2·5 moles aniline (a), toluidines (b d) or anisidines (e g) was effected by heating under reflux for 2 8 hr in EtOH followed by cooling and filtering off the red, orange or yellow diarylamine, which was recrystallized from EtOH (yield 90 98%). Longer heating periods were necessary for the reaction with 1-chloro-2,6-dinitrobenzene.

2,4,6-Trinitro-2'-methoxydiphenylamine (IVHe) had been prepared by a different method,[23] from methyl-picryl-nitramine and *o*-anisidine.

The reaction with 4-aminoveratrole was carried out with equimolar amounts of reagents in EtOH, in the presence of solid $NaHCO_3$. The reaction failed with 1-chloro-2,4-dinitrobenzene; with 1-fluoro-2,4-dinitrobenzene after 10 hr heating under reflux in EtOH, it afforded a product which was chromatographed on a column packed with alumina from $CHCl_3$ benzene (1:1). The pure product VIHj is yellow. The reaction proceeded normally with the two other halonitrobenzenes affording the red VHj and IVHj which were recrystallized from EtOH or AcOH. Deuterations were performed by recrystallization from CH_3COOD obtained from Ac_2O and D_2O.

The reactions with N,N-dimethyl- or -diphenyl-*p*-phenylenediamine were effected with equimolar amounts of amine, halopolynitrobenzene and $NaHCO_3$ in EtOH at reflux temp. The crude products IVh VIh were chromatographed on alumina from $CHCl_3$. The products IVi VIi were recrystallized from benzene EtOH or from AcOH. N-Deuterations were effected by recrystallization from CH_3 COOD.

Preparation of free radicals

In the special vial (Fig. 3), a weighed amount of diarylamine was introduced at B (outer diameter 5 mm, fitting into the cavity of the ESR spectrometer). A 20 times larger amount of freshly prepared Ag_2O was introduced at A, and a volume of abs benzene was introduced from a tipped microburet into B in order to give a 10^{-1} molar soln; O_2-free argon was bubbled through the soln through the Cu capillary D for 30 min, then this capillary was raised through the stopper E above point C, and with argon still flowing, the vial was sealed off at C. Alternatively, the vial was attached to a high vacuum line, the benzene soln at B was frozen in liquid N_2 and the vial was evacuated, then the vacuum tap was turned off, the Dewar flask was removed and the soln was allowed to warm up to room temp; the freezing and pumping were repeated several times.

Before recording the ESR spectrum, the vial is tilted so that the soln flows into A, and after a few min the supernatant dark-coloured soln is decanted back into B, then the ESR spectrum is recorded.

For preparing the free radicals IVi and Vi, the amines IVHi and VHi (0·1 g) were stirred with 2 g of freshly prepared dry Ag_2O and with 0·1 g anhyd Na_2SO_4 in 10 ml dry benzene. After 2 hr stirring, the violet soln was filtered off, the soln was chromatographed (preparative TLC on silica-gel using a mixture

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[46] F. Ullmann, *Liebigs Ann.* **327**, 115 (1903); W. Perkin, Jr. and C. Weizmann, *J. Chem. Soc.* **89**, 1649 (1906)

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of CCl_4 and toluene (1:2) as eluent). After evaporating the solvent in vacuum, the violet-black product was stored in the cold.

Regeneration of IVHi *from* IVi.[36, 54] A soln of the free radical IVi in CCl_4 was shaken with an equivalent amount of quinol in water. After washing with water, the CCl_4 soln was dried over $CaCl_2$, then the IR spectrum of the soln showed the product to be identical with IVHi.

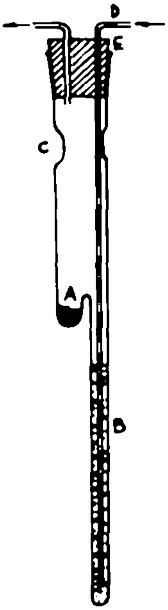

FIG. 3. Seal vial for ESR spectra in inert atmosphere.

Apparatus. UV absorption spectra were recorded with an Optica (Milan) CF4 spectrophotometer. IR absorption spectra were recorded with a Jena UR-10 spectrophotometer. Electroreduction and electro-oxidation potentials were registered with a Heyrovsky LP 55 polarograph; the rotating Pt electrode was described previously.[55] The ESR spectrometer operates in the X-band and has a high-field modulation.[56]

Acknowledgements. The collaboration of Dr. I. Pascaru for the ESR spectra, of Mrs. M. Paraschiv for the UV spectra, of Mrs. E. Romas for the IR spectra, of Mrs. C. Bratu for the electroreduction potentials, of Mrs. M. Roman and C. Popescu for elementary analyses, and the technical assistance of D. Papae are gratefully acknowledged.

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