

Trapping of the Cyano Radical: Does it Ever Happen?

Lennart Ebersson and Ola Persson

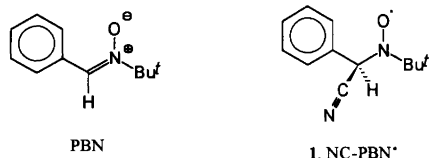
Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden

Ebersson, L. and Persson, O., 1998. Trapping of the Cyano Radical: Does it Ever Happen? – Acta Chem. Scand. 52: 608–621. © Acta Chemica Scandinavica 1998.

The possible trapping of the cyano radical by α -phenyl-*N*-*tert*-butylnitrone (PBN) has been probed by a new method for the generation of CN^\cdot , photolysis of *N*-cyanosuccinimide with PBN. Only in 1,1,1,3,3,3-hexafluoroopropan-2-ol was EPR spectral evidence obtained for the formation of a true spin adduct, namely the isocyano adduct of PBN. In other solvents, like dichloromethane or acetonitrile, the photolysis reaction took an entirely different course and gave the *N*-cyano-3-succinimidyl adduct of PBN and a second aminoxyl of unknown structure. The same pair of adducts could be obtained by photolysis of *N*-cyanomaleimide and PBN in a reductive coupling reaction. Maleimide gave a similar but clearly different pair of spectra.

The possibility that the cyano or isocyano PBN adduct might undergo spontaneous hydrolysis to give the aminoformyl or formylamino adduct, respectively, was explored. It was shown that the authentic cyano adduct does not give the aminoformyl adduct under hydrolytic conditions. Since there is no method to prepare the isocyano adduct for such experiments, the problem of its hydrolytic reactivity is still open. The aminoformyl adduct of PBN was prepared by addition of the formamide anion to PBN, followed by oxidation by nickel peroxide, and characterized by its EPR spectrum.

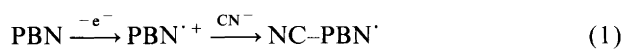
The attempted trapping of the cyano radical, CN^\cdot , by the spin trap, α -phenyl-*N*-*tert*-butylnitrone (PBN) has given two types of spin adducts, denoted **X1** and **X2**, with differing sets of hfs constants, as summarized in Table 1. One set (**X1**) has the usual 3×2 line structure, whereas the second one (**X2**) features an additional nitrogen coupling of ca. 0.15 mT. Spin adduct **X1**, formed in trapping situations in which cyanide ion or hydrogen cyanide is oxidized together with PBN, has been independently prepared by two methods using starting materials with known carbon-to-carbon connectivity between CN and the putative α -carbon of the spin adduct, and its assignment to NC-PBN^\cdot (**1**) therefore is firmly established.^{1,2}



In view of the higher redox potential of cyanide ion, $E^\circ(\text{CN}^\cdot/\text{CN}^-) = 2.0 \text{ V}$,³ in comparison with that of PBN, $E^\circ(\text{PBN}^\cdot/ \text{PBN}) = 1.5 \text{ V}$,⁴ it was suggested that these reactions might proceed via the radical cation of PBN which, being a soft electrophile, should react with the

* To whom correspondence should be addressed.

softer carbon center of cyanide ion [eqn. (1)].⁵ At least under strongly oxidizing conditions, such as oxidation by $\text{TBPA}^{+\cdot}$ or photolysis,^{6,7} this mechanism should prevail. It has also been shown that the reaction between cyanide ion and PBN might proceed via the Forrester–Hepburn mechanism,⁸ in which a hydroxylamine (as anion or neutral species) is formed by addition of cyanide ion or hydrogen cyanide to PBN and then oxidized to the spin adduct by a weak oxidant, even as weak as dioxygen [eqn. (2)].



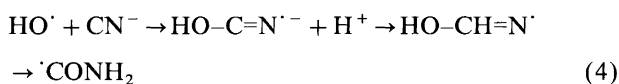
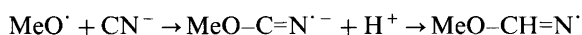
The identity of **X2** is uncertain. Initially it was assigned to **1**, but this is clearly not tenable in view of the results described above. In order to explain the results from the $\text{Mo}^{\text{V}}(\text{CN})_8^{3-} - h\nu$ experiment (Table 1), Rehorek and Janzen⁹ suggested that methoxy radicals were formed and added to cyanide ion, giving an *N*-centered radical which after protonation was trapped by PBN to give **X2** [eqn. (3)]. To prove this point, a solution of cyanide ion and H_2O_2 or peroxydisulfate ion in water was photolyzed which produced the spin adduct of the aminoformyl radical, $\text{NH}_2\text{CO-PBN}^\cdot$ ($a^{\text{N}} 1.55$, $a^{\text{N}'} 0.050$, $a^{\text{H}} 0.320$, $a^{\text{H}'}$

Table 1. Published EPR spectra assigned to NC-PBN'.

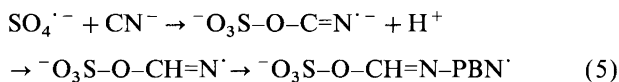
Method	Solvent	a^N/mT	a^H/mT	a^N/mT
WO ₃ /TiO ₂ /hν of PBN/CN ⁻³³	MeCN/water	1.42	0.192	—
Anodic oxidation of PBN/CN ⁻¹	MeCN	1.504	0.198	—
Ph(CN)CH' + Me ₃ CNO ¹	MeCN	1.50	0.198	—
PhCH(CN)N(Bu')OH/O ₂ ²	Hexane	1.46	0.171	—
TBPA ⁺ oxidation of PBN/CN ⁻⁶	MeCN or CH ₂ Cl ₂	1.51	0.195	—
PBN/CN ⁻ /Co ^{III} W/hν ⁷	CDCl ₃	1.51	0.23	—
Chloranil/CN ⁻ /hν ³⁴	MeOH	1.494	0.212	—
Peroxidase/PBN/CN ⁻³⁵	H ₂ O	1.60	0.24	—
PBN/HCN/O ₂ ⁸	EtOH-H ₂ O	1.52	0.24	—
γ-Radiolysis of PBN/NCCH ₂ CH ₂ CN ³⁶	PhH-NCCH ₂ CH ₂ CN (90:10)	1.44	0.55	0.12
PBN/Mo ^V (CN) ₆ ³⁻ /hν ³⁷	MeOH-CH ₂ Cl ₂ ^a	1.46	0.49	0.16
PBN/Hg(CN) ₂ /hν ³⁸	MeOH ^a	1.46	0.50	0.15

^a At 200 K.

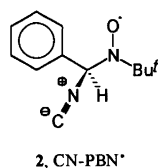
0.050 mT). The formation of the 'CONH₂ radical was believed to occur in the way shown in eqn. (4).



Also, peroxydisulfate-PBN in acetonitrile-water (6:1) was photolyzed in the presence of cyanide ion, giving an *N*-centered spin adduct with a^N 1.49, a^H 0.170, a^H 0.082 mT. This was ascribed to the process of eqn. (5).

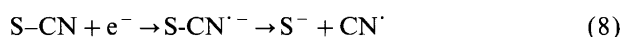
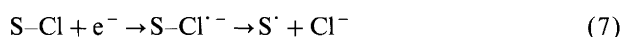
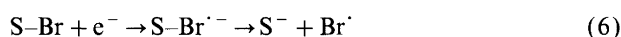


We are not convinced that it is necessary to invoke these more complex interpretations, and have therefore explored some other possibilities, to be reported below. It was shown¹⁰ in connection with the formation of cyano adducts from two other spin traps, 2-methyl-2-nitrosopropane and 3,5-dibromo-4-nitrosobenzene-sulfonate, that such adducts are hydrolyzed to amino-formyl adducts in aqueous medium, and therefore this reaction might also occur with NC-PBN'. A second possibility, not explored earlier, would be that the cyano radical is trapped by PBN forming the *N*-connected aminoxyl CN-PBN',¹¹ an isocyano adduct (**2**), which would correspond to **X2**. Such an aminoxyl might also be sensitive toward hydrolysis in aqueous media, giving rise to the formylamino adduct, HCONH-PBN'.



Results

N-Cyanosuccinimide, a possible source of cyano radical. It was desirable to use a new source of the cyano radical not involving oxidation of cyanide ion or photolysis of metal cyanides. In view of earlier studies on the cleavage of radical anions of *N*-halosuccinimides, where (*N*-bromosuccinimide)^{·-} cleaves to give succinimide anion¹² and a bromine atom [eqn. (6)] and (*N*-chlorosuccinimide)^{·-} to give succinimidyl radical and chloride ion¹³ [eqn. (7)], we anticipated that (*N*-cyanosuccinimide)^{·-} would cleave in the former fashion [eqn. (8)]. Thus photolysis of *N*-cyanosuccinimide¹⁴ with PBN should proceed according to eqn. (9). The simultaneously formed succinimide anion would be possible to neutralize efficiently by addition of a proton donor, such as 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), as shown in previous studies,¹⁵ thus leaving the cyano radical to be trapped by PBN.



S = *N*-succinimidyl



Electron transfer and cycloaddition properties of N-cyanosuccinimide. Cyclic voltammetry in acetonitrile-Bu₄NPF₆ showed that *N*-cyanosuccinimide was reduced in an irreversible process at $E_{\text{pc}} = -1.32$ V vs. Ag/AgCl, which should be compared to the corresponding values for *N*-chloro- and *N*-bromo-succinimide, -0.37 and 0.03 V, respectively, vs. SCE. (Ag/AgCl + 0.04 V).^{16,17} Thus, unlike the two haloimides,¹⁸ *N*-cyanosuccinimide should not act as a thermal oxidant toward good electron donors, as shown by the fact that 1,2,4,5-tetramethoxybenzene with $E^\circ(\text{ArH}^{\cdot+}/\text{ArH}) = 0.84$ V did not react thermally with *N*-cyanosuccinimide in HFP in the dark (EPR spectral detection, 20 h). Irradiation of the solution

immediately generated the radical cation of 1,2,4,5-tetra-methoxybenzene.

It is known that nitriles undergo cycloaddition to the 1,3-dipole of nitrones, and that the reaction is favoured by electron-withdrawing substituents.¹⁹ However, *N*-cyanosuccinimide did not undergo any discernible thermal reaction with PBN over a period of 20 h, as monitored at 290 nm by UV spectroscopy.

Irradiation of N-cyanosuccinimide and PBN in dichloromethane, acetonitrile and benzene. Over a period of 1 h, the irradiation of PBN and *N*-cyanosuccinimide in dichloromethane generated an aminoxyl **X3** with a 3×2 line spectrum, each line being split further by one hydrogen, a^N 1.44, a^H 0.765, $a^{H'}$ 0.079 mT (Fig. 1a). There was also a weak spectrum of 3×2 broad lines, a^N 1.41, a^H ca. 0.28 mT (see further below), ca. 5% of the intense one, of a second aminoxyl radical **X4**. The signal persisted for many hours afterwards. In the spectrum from α -[²H]PBN the 0.765 mT doublet was replaced by a $0.765/6.5 = 0.118$ mT 1:1:1 triplet, resulting in a 3×4 line spectrum (Fig. 1b). Since the spectrum of **X4** now was totally obscured, any changes in it were impossible to detect. The effect of cooling the sample to -30 °C was that the signal built up more slowly and was considerably weaker. At -10 °C the buildup was still slow, but the spectrum reached fairly high intensity.

Irradiation of PBN-cyanosuccinimide in acetonitrile (UV) similarly gave a 3×2 line spectrum with each line split into a doublet, a^N 1.45, a^H 0.758, $a^{H'}$ 0.079 mT, and a weak spectrum of 3×2 broad lines, a^N 1.41, a^H 0.28 mT. The spectra persisted for a long time. In benzene the same two spectra appeared, but now the weaker spectrum comprised ca. 20% of the mixture (Table 2). In both

cases it is assumed that these spectra correspond to **X3** and **X4**.

Irradiation of N-cyanosuccinimide and PBN in HFP or solvent mixtures containing HFP. In neat HFP, UV irradiation of *N*-cyanosuccinimide and PBN gave a weak spectrum of an *N*-connected spin adduct, a^N 1.51, a^H 0.474, $a^{N'}$ 0.148 mT (Fig. 2). These hfs constants are distinctly different from those of *N*-succinimidyl-PBN[·] (lit.¹⁵ a^N 1.54, a^H 0.62, $a^{N'}$ 0.133 mT). The signal could be enhanced by sensitization by 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (TAP⁺). After discontinuing irradiation, the spectrum persisted with a half-life of about 30 min. The same spectrum, although weaker, was seen during photolysis of PBN and *N*-cyanoglutarimide in HFP.

In order to see how a gradual increase of the HFP contents in dichloromethane would affect the spectra, PBN-*N*-cyanosuccinimide was irradiated in dichloromethane with 2, 5, 10 and 20% HFP added (Table 2). As seen from Fig. 3, even at 2% HFP the intensities of the spectra of **X3** and **X4** decreased significantly. The spectrum of **X4** was better resolved, a^N 1.438, a^H 0.266, $a^{N'}$ 0.140 mT. At 20% HFP, the intensities of the spectra decreased further, but there were only slight changes in the hfs constants. The use of [²H]HFP at the 2% level had no effect on the spectra; in particular, no significant change in linewidths was noticeable.

A similar experiment in acetonitrile-HFP (2%) generated a superposition of two spectra, consisting of ca. 90% of one with a^N 1.45, a^H 0.771, $a^{H'}$ 0.080 (1 H) mT (assigned to **X3**) and one with a^N 1.43, a^H 0.196, $a^{N'}$ 0.087 mT. The latter spectrum is presumably the same as the minor component seen in acetonitrile,

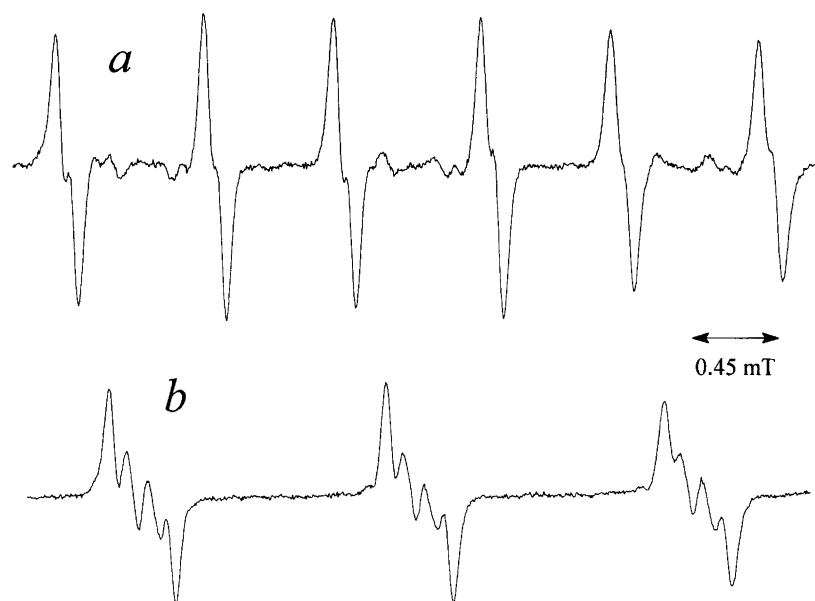


Fig. 1. EPR spectrum from a solution of *N*-cyanosuccinimide (110 mmol dm^{-3}) and (a) PBN (80 mmol dm^{-3}) or (b) PBN- α -[²H] in dichloromethane. The solution was first irradiated by UV light for 40 min, and the spectrum was then obtained by accumulation of 35 spectra during 15 min of continued irradiation.

Table 2. EPR spectra from spin adducts generated from the UV irradiation of *N*-cyanosuccinimide with PBN under various conditions.

Solvent ^a	a^{N}/mT	a^{H}/mT	Other/mT	Proportion (%)
DCM	1.44	0.765	$a^{\text{H}'} = 0.079$ (1 H)	95
	1.41	0.28	Broad	5
DCM-HFP (2% v/v)	1.469	0.779	$a^{\text{H}'} = 0.075$ (1 H)	60 ^b
	1.438	0.266	$a^{\text{N}'} = 0.104$	40
DCM-[² H]HFP (2% v/v)	1.469	0.778	$a^{\text{H}'} = 0.072$ (1 H)	60 ^c
	1.438	0.276	$a^{\text{N}'} = 0.094$	40
DCM-HFP (5% v/v)	1.461	0.788	$a^{\text{H}'} = 0.065$ (1 H)	60
	1.443	0.271	$a^{\text{N}'} = 0.098$	40
DCM-HFP (10% v/v)	1.463	0.779	$a^{\text{H}'} = 0.065$ (1 H)	50
	1.437	0.275	$a^{\text{N}'} = 0.102$	50
DCM-HFP (20% v/v)	1.478	0.781	$a^{\text{H}'} = 0.070$ (1 H)	50
	1.463	0.279	$a^{\text{N}'} = 0.097$	50
HFP	1.51	0.474	$a^{\text{N}'} = 0.148$	
AN	1.45	0.758	$a^{\text{H}'} = 0.079$ (1 H)	
	1.42	0.27	Broad	
AN-HFP (2% v/v)	1.45	0.771	$a^{\text{H}'} = 0.080$ (1 H)	90 ^d
	1.43	0.196	$a^{\text{N}'} = 0.087$	10
AN-[² H]HFP (2% v/v)	1.46	0.768	$a^{\text{H}'} = 0.080$ (1 H)	85 ^e
	1.43	0.195	$a^{\text{N}'} = 0.079$	15
[² H ₃]AN-[² H]HFP (2% v/v)	1.467	0.766	$a^{\text{H}'} = 0.080$ (1 H)	85 ^f
	1.438	0.187	$a^{\text{N}'} = 0.070$	15
AN-HFP (10% v/v)	1.45	0.771	$a^{\text{H}'} = 0.080$ (1 H)	85
	1.42	0.196	$a^{\text{N}'} = 0.090$	15
AN-HFP (20% v/v)	1.45	0.759	$a^{\text{H}'} = 0.080$ (1 H)	85
	1.42	0.196	$a^{\text{N}'} = 0.094$	15
AN-HFP (60% v/v)	1.45	0.759	$a^{\text{H}'} = 0.080$ (1 H)	85
	1.43	0.276	$a^{\text{N}'} = 0.131$	15
PhH	1.44	0.770	$a^{\text{H}'} = 0.080$ (1 H)	80
	1.42	0.274	Broad lines	20
PhH-HFP (2%)	1.44	0.764	$a^{\text{H}'} = 0.070$ (1 H)	80
	1.464	0.275	$a^{\text{N}'} = 0.070$	20

^a DCM = dichloromethane, HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol, AN = acetonitrile. ^b $\Delta H_{\text{pp}} = 0.123$ mT. ^c $\Delta H_{\text{pp}} = 0.123$ mT. ^d $\Delta H_{\text{pp}} = 0.122$ mT. ^e $\Delta H_{\text{pp}} = 0.125$ mT. ^f $\Delta H_{\text{pp}} = 0.121$ mT.

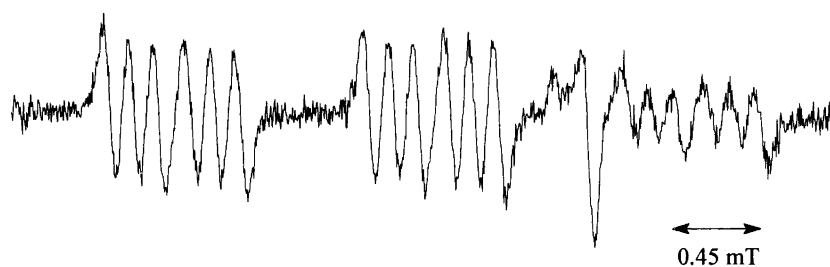


Fig. 2. EPR spectrum from a solution of *N*-cyanosuccinimide (0.20 mol dm^{-3}) and PBN (80 mmol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol. The solution had first been irradiated by UV light for 90 min, and the spectrum was then obtained by accumulation of 100 spectra during 40 min of irradiation. The extra feature between the middle and right sextet originates from irradiation of the quartz insert in the cavity.

dichloromethane and benzene, with a^{H} significantly smaller and with the a^{H} coupling resolved, and is thus assigned to **X4**. The use of acetonitrile-[²H]HFP (2%) or [²H₃]acetonitrile-[²H]HFP (2%) somewhat improved the resolution of the weaker spectrum, but did not affect

the hfs constants of any of the spectra, nor were the linewidths affected. Addition of up to 60% HFP to acetonitrile did not affect the formation of these spectra (Table 2), except that their intensity decreased and a^{H} and $a^{\text{N}'}$ increased.

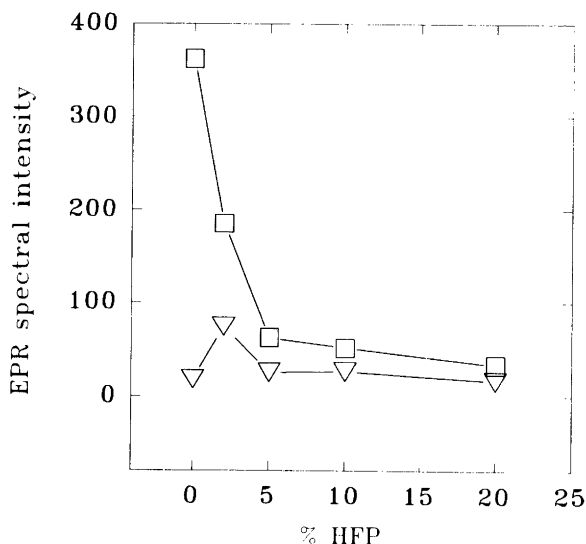
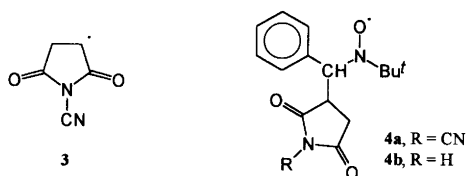


Fig. 3. Variation of EPR spectral intensity (per spectrum) with percentage of HFP in dichloromethane in a solution of *N*-cyanosuccinimide (110 mmol dm^{-3}) and PBN (80 mmol dm^{-3}). The solution had first been irradiated by UV light for 40 min, and the spectrum was then obtained by accumulation of 20–30 spectra with continued irradiation. Squares correspond to **X3** and triangles to **X4**.

Irradiation of PBN and compounds related to N-cyanosuccinimide. The species **X3** and **X4**, as characterized by their EPR spectra, did not seem to be derived from any cyano radical or cyanide ion chemistry and thus necessitated a separate and slightly diversionary study. The spectrum of at least **X3** clearly is derived from a spin adduct of PBN, whereas that of **X4** might have a more complex origin. We have not yet been able to identify the structures of **X3** and **X4** with certainty, but the following results give some clues.

An obvious possibility would be that a radical formed in the photolysis process, for example the very reactive CN^\cdot , might abstract an α -hydrogen from *N*-cyanosuccinimide and form a radical **3**, which could be trapped by PBN to form spin adduct **4a**. Since no spin adducts formed by H abstraction from the solvent were detected, this process then must be selective for the hydrogens of *N*-cyanosuccinimide. A second possibility would be that *N*-cyanosuccinimide somehow might be converted into *N*-cyanomaleimide or maleimide; it is for example known that succinimide anion reacts with *N*-bromo- or *N*-chloro-succinimide to form maleimide, which ends up as polymaleimide.²⁰

When authentic *N*-cyanomaleimide* was used in the



* Prepared in the same way as *N*-cyanosuccinimide.¹⁴

photolysis with PBN, spin adducts with spectra identical to those of **X3** and **X4** were formed, except that the higher quality of the **X4** spectrum made possible the resolution of an additional hfs constant of 0.028 mT (1 H^\cdot). Thus it appears that *N*-cyanomaleimide might be an intermediate on the route to **X3** and **X4**.

When PBN was instead photolyzed with maleimide, a second possible intermediate, in dichloromethane, two spectra with similar but not identical characteristics as those of **X3** and **X4** appeared in an equally slow process. After 1–1.5 h of photolysis or 5–10 h in diffuse daylight, the spectra were well developed and persisted for many hours after discontinuation of the irradiation. The major spectrum had $a^N = 1.44 \text{ mT}$ and a large coupling constant of 0.68 mT (0.765 mT for **X3**) to α -H and a small coupling, 0.060 mT (0.079 mT for **X3**) to one hydrogen in the attached group, whereas the minor spectrum (with ca. 40% intensity in relation to the other spectrum) was considerably more complicated. It featured couplings to four different hydrogens (0.116 , 0.099 , 0.079 and 0.059 mT , 1 H each) and two couplings to nitrogen of 1.44 and 0.060 mT . Since couplings to different nuclei of the attached group of PBN spin adducts seldom exceed one or two,²¹ the latter spectrum can hardly correspond to a PBN spin adduct. Figure 4 shows the EPR spectrum of the middle group of lines and a simulation based on the parameters. The use of α -[²H]PBN changed the major spectrum by converting the 0.68 mT doublet to a $0.68/6.5 = 0.103 \text{ mT}$ triplet, but left the minor spectrum unchanged.

By analogy with the assignment of **X3** to structure **4a**, the major spectrum of Fig. 4 is assigned to the spin adduct **4b**. The second spectrum must have more complex background, and its structural assignment, as well as those of similar spectra from other activated olefins, like *N*-phenylmaleimide, maleic anhydride and diethyl maleate, will be the subject of a separate study.²²

The photolysis of di-*tert*-butyl peroxide with various substrates is often used to produce radicals. The photolysis of a solution of PBN, succinimide and di-*tert*-butyl peroxide in dichloromethane in about 1 h generated a predominant spectrum of *tert*-BuO–PBN $^\cdot$ ($a^N 1.45$, $a^H 0.217 \text{ mT}$; lit.²¹ $a^N 1.421$, $a^H 0.183 \text{ mT}$ in benzene), accompanied by a weak spectrum (ca. 10%) with $a^N 1.45$, $a^H 0.66 \text{ mT}$ where the broad lines ($\Delta H_{pp} = 0.107 \text{ mT}$) indicated further coupling. The difference in lifetime of the two radicals was such that the weak spectrum comprised 35% after 20 h. Unfortunately, the *tert*-BuO–PBN $^\cdot$ spectrum obscured any possible contribution from the second spectrum. The similarity of the α -H couplings (0.66 mT vs. 0.68 mT in the maleimide experiment) and the mode of generation supports the assignment of the spectrum to structure **4b**.

Photolysis of PBN with persulfate and cyanide ion. As mentioned above, an earlier⁹ critical experiment involved the photolysis of potassium peroxydisulfate and PBN in acetonitrile–water (6:1) in the presence of tetra-

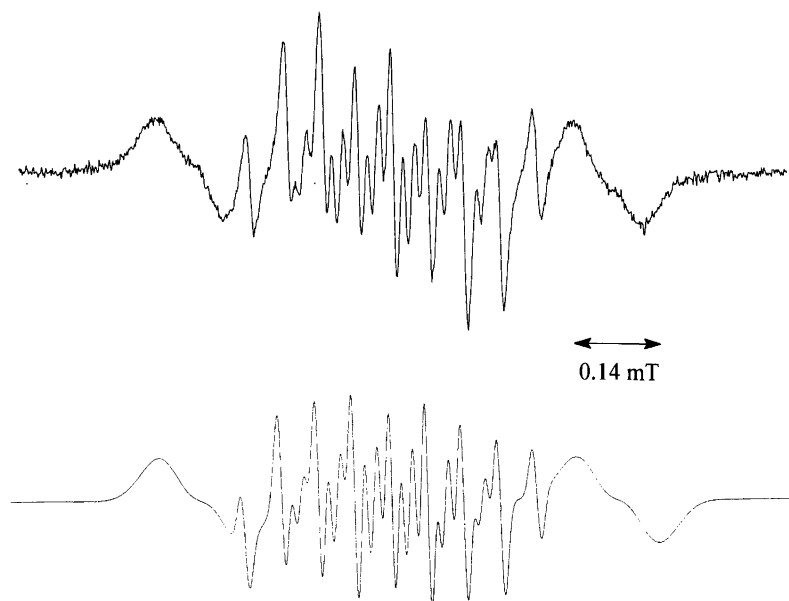


Fig. 4. The middle group of lines of the EPR spectrum of an irradiated solution of PBN (80 mmol dm^{-3}) and maleimide (0.15 mol dm^{-3}) in dichloromethane-HFP (1%). The solution was first irradiated by UV light for 30 min, and the spectrum was then obtained by accumulation of 30 spectra during 12 min of continued irradiation. The simulation is based on the parameters given in the text.

butylammonium cyanide [eqn. (3)] which gave a spectrum of three 6-line groups with a^N 1.49, $a^{N'}$ 0.170 and a^H 0.082 mT. It was assigned to $^-\text{O}_3\text{S}-\text{O}-\text{CH}=\text{N}-\text{PBN}^{\cdot}$ formed via eqn. (3).

In our hands a spectrum consisting of three 6-line groups (Fig. 5a) developed. It consisted of a superposition of two spectra, namely that of $\text{SO}_3\text{O}-\text{PBN}^{\cdot}$ (a^N 1.400, a^H 0.119 mT) and a second spectrum which in the simplest way (a detailed analysis was precluded by the masking of lines by the first spectrum) could be characterized by the following parameters: a^N 1.53, a^H 0.284, $a^{N'}$ 0.076 mT. The signal was stable and persisted after the light had been shut off. The ratio between the spectra varied between runs. It should be noted that the appearance of the spectrum of Fig. 5a is similar to the spectrum described by Rehorek, except that we assign the lower coupling constant to N' : aminoxyls with a coupling constant < 0.1 mT to the α -hydrogen of PBN are rare.²³ We checked the assignment by using α -[^2H]PBN as the spin trap, which led to the spectral characteristics expected for the latter parameter set (Fig. 5c). For a^N 0.170, $a^{2\text{H}} = 0.082/6.5 = 0.013$ mT, a triplet of triplets is expected.

Careful inspection of Fig. 5 shows that the simulated spectra do not fit altogether well with the experimental ones. As will be shown below, this is due to the fact that the $3 \times 2 \times 3$ pattern preliminarily assigned to the weaker spectrum is not correct. We will return to this problem in connection with the discussion of the spectra of Fig. 8.

Oxidation of PBN and cyanide ion by tris(4-bromophenyl)-aminium ion. The oxidation of PBN–cyanide ion was also performed thermally by treatment of a PBN–tetra-

butylammonium cyanide solution in acetonitrile–water (6:1) with tris(4-bromophenyl)aminium hexachloroantimonate. A weak spectrum similar to that obtained by photochemical persulfate oxidation was obtained: a^N 1.49, a^H 0.26, $a^{H'}$ 0.067, $a^{N'}$ 0.075 mT.

Generation of authentic aminoformyl spin adducts, $\text{R}_2\text{NCO}-\text{PBN}^{\cdot}$ ($\text{R}=\text{H}$ and/or alkyl). The a^N 1.494, a^H 0.284, $a^{N'}$ 0.076 mT spectrum detected in the persulfate experiment might be suspected to belong to $\text{H}_2\text{NCO}-\text{PBN}^{\cdot}$, formed by hydrolysis of initially formed $\text{NC}-\text{PBN}^{\cdot}$. Nitriles substituted by electron-withdrawing groups, as for example *N*-acetylglucynonitrile, are easily hydrolyzed.²⁴ Cyano adducts from two other spin traps, namely 2-methyl-2-nitrosopropane and 3,5-dibromo-4-nitrosobenzenesulfonic acid, have been suggested to be converted into $\text{H}_2\text{NCO}^{\cdot}$ adducts in aqueous medium.¹⁰ For comparison we therefore looked for other ways to produce the EPR spectrum of $\text{H}_2\text{NCO}-\text{PBN}^{\cdot}$. It has been shown²⁵ that thermal treatment of HCONR_2 , $\text{R}=\text{H}$ or Me, with di-*tert*-butyl peroxalate in benzene is a useful method to make spin adducts $\text{R}_2\text{NCO}-\text{PBN}^{\cdot}$ via abstraction of the formyl hydrogen by *t*-BuO $^{\cdot}$. We used the photolysis of di-*tert*-butyl peroxide as a source of *t*-BuO $^{\cdot}$ and generated spin adducts of this type (Table 3) from a range of HCONR_2 .

Control experiments first showed that the use of benzene as the solvent in the case of formamide and *N*-methylformamide created difficulties due to phase separation, the lower, polar phase being rich in the formamide and low in di-*tert*-butyl peroxide. These conditions resulted in weak spectra for which the exact environment was difficult to determine, but probably was predomi-

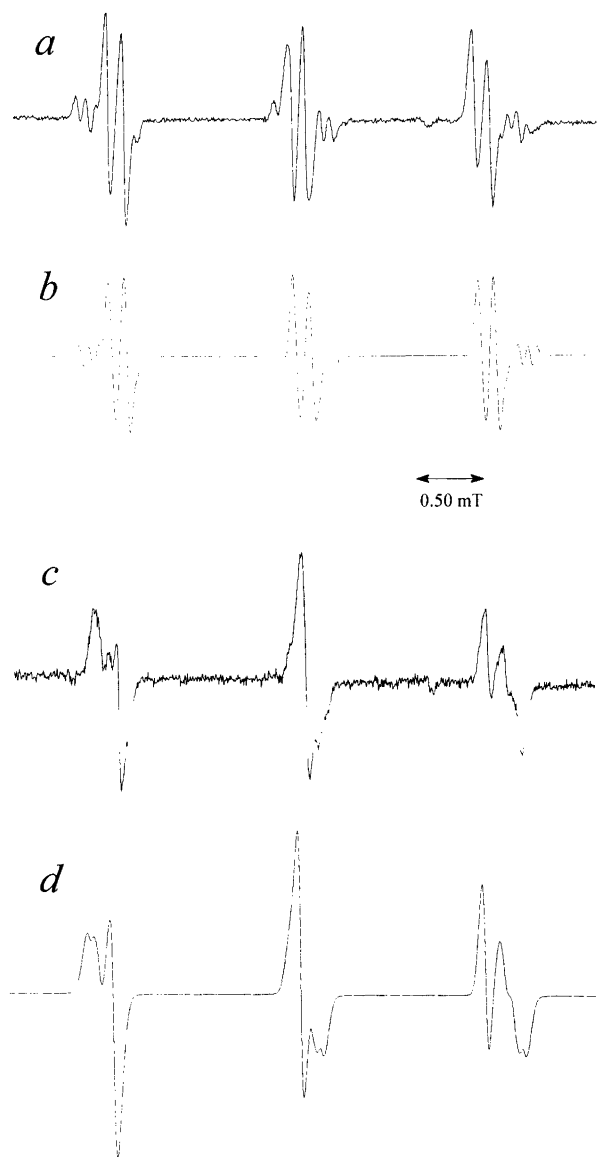


Fig. 5. (a) EPR spectrum of a solution of PBN (80 mmol dm⁻³), Bu₄NCN (60 mmol dm⁻³) and K₂S₂O₈ (50 mmol dm⁻³) in acetonitrile-H₂O (6:1 v/v). The solution was first irradiated by UV light for 30 min, and the spectrum was then obtained by accumulation of 30 spectra during 12 min of continued irradiation. The more intense 3 × 2 line spectrum (a^N 1.384, a^H 0.119 mT) was assigned to SO₃O-PBN[•] (lit.²² a^N 1.390, a^H 0.123 mT). The second spectrum had a^N 1.494, a^H 0.284 and $a^{N'}$ 0.076 mT. (b) Simulation of the spectrum in (a) using the parameters given and with a center field difference of 0.050 mT and an area ratio of 7:3 between the spectra. (c) EPR spectrum recorded as in (a), except that PBN- α -[²H] was used. (d) Simulation of the spectrum in (c) using the parameters given, except that the two a^D were set at 0.119/6.5 = 0.018 mT and 0.284/6.5 = 0.044 mT, and with a center field difference of 0.050 mT and an area ratio of 7:3 between the spectra.

nantly composed of formamide. It was therefore necessary to use polar solvents, such as acetonitrile or acetic acid, in order to maintain homogeneous solution conditions.

Irradiation of an 0.1 mol dm⁻³ solution of PBN in acetonitrile-formamide-di-*tert*-butyl peroxide (ratio 7:1:1) by unfiltered light from a mercury lamp generated the EPR spectrum of an aminoxyl radical, a^N 1.485, a^H 0.187, $a^{N'}$ 0.077, $a^{H'}$ 0.063 and $a^{H''}$ 0.022 (2 H) mT. The middle group of signals is shown in Fig. 6a, together with a simulation in Fig. 6b. Thus the aminoxyl radical shows three couplings from the attached group, one to nitrogen, one to a hydrogen and one to two equivalent hydrogens. It is not immediately obvious that such a coupling pattern can belong to NH₂CO-PBN[•], and we therefore extended the study to isotopomers of both formamide and PBN.

The use of HCON²H₂ as the substrate gave a 3 × 5 line spectrum, the middle group of which is shown in Fig. 6c and simulated in Fig. 6d by a^H 0.187, $a^{N'}$ 0.077, $a^{D'}$ 0.0097 and $a^{D''}$ 0.0034 (2 D) mT. Thus the replacement of two protons by deuterium atoms caused the three extra hydrogen couplings to disappear. The use of α -[²H]PBN and HCONH₂ and HCON²H₂, respectively, gave spectra the middle groups of which are shown in Figs. 7a and 7c, simulated in Figs. 7b and 7d by the parameter sets a^{2H} 0.029, $a^{N'}$ 0.080, $a^{H'}$ 0.063 and $a^{H''}$ 0.022 (2 H) mT, and a^{2H} 0.029, $a^{N'}$ 0.080, $a^{2H'}$ 0.0097 and $a^{2H''}$ 0.0034 (2 D) mT.

In order to avoid any possibility that H abstraction from acetonitrile might interfere, the photolysis of PBN and di-*tert*-butyl peroxide was performed in benzonitrile, which gave an aminoxyl with a similar spectrum, a^N 1.46, a^H 0.160, $a^{N'}$ 0.076, $a^{H'}$ 0.074 and $a^{H''}$ 0.021 (2 H) mT. In acetic acid, the corresponding spectrum had a^N 1.485, a^H 0.160, $a^{N'}$ 0.077, $a^{H'}$ 0.065 and $a^{H''}$ 0.021 (2 H) mT and in trimethylacetic acid a^N 1.485, a^H 0.160, $a^{N'}$ 0.077, $a^{H'}$ 0.072 and $a^{H''}$ 0.021 (2 H) mT.

Returning now to the solvent mixture used in the critical experiment above, photolysis of PBN-HCONH₂-*tert*-butyl peroxide in 6:1 acetonitrile-water produced the spectrum shown in Fig. 8a, and simulated by the following parameters a^N 1.485, a^H 0.205, $a^{N'}$ 0.069, $a^{H'}$ 0.063 and $a^{H''}$ 0.020 (2 H) mT in Fig. 8b. The spectrum responded in the expected way when α -[²H]PBN was used with HCONH₂ in acetonitrile-H₂O and PBN with HCON²H₂ in acetonitrile-²H₂O (Figs. 8c and 8d).

The behaviour of H₂NCO-PBN[•] is curious in at least two respects: its EPR spectrum exhibits three couplings $a^{H'}$ and $a^{H''}$ (2) to hydrogens from the CONH₂ group instead of the maximally two expected, and the coupling to the α -H changes drastically with the polarity of the solvent, from 0.280 mT in formamide-water (3:2) to 0.165 mT in benzonitrile and benzene-acetonitrile (3:2). We assume that this behaviour is connected with the rotation around the C(O)-N bond, coupled to the strong hydrogen-bonding properties of the CONH₂ group. Similar behaviour was shown by aminoxyls generated from *N*-methyl-, *N*-ethyl- and *N*-isopropyl-formamide (Table 4): in all cases the solvent effect on $a^{\alpha-H}$ was strong, and two couplings $a^{H''}$ of about 0.02 mT were sometimes required to simulate the spectra properly. The

Table 3. Spin adducts formed from various amides and PBN upon UV irradiation with di-*tert*-butyl peroxide or thermal treatment with di-*tert*-butyl peroxalate.

Amide	Solvent	a^N /mT	a^H /mT	Other/mT ^a	Assigned to
HCONH ₂ ^b	PhH	1.529	0.284	$a^N = a^H = 0.052$	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂ ^c	HCONH ₂ -H ₂ O	1.529	0.287	$a^N = a^H = 0.052$	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂ ^d	AN	1.485	0.187	$a^N = 0.077, a^H = 0.063,$ $a^{H''} = 0.022$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCON ² H ₂ ^e	AN	1.485	0.187	$a^N = 0.077, a^{2H'} = 0.0097,$ $a^{2H''} = 0.0034$ (2)	$\dot{\text{C}}\text{ON}^2\text{H}_2$
HCONH ₂ ^{f,g}	AN	1.485	0.029 ^h	$a^N = 0.080, a^H = 0.063,$ $a^{H''} = 0.022$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCON ² H ₂ ^{f,i}	AN	1.485	0.029 ^h	$a^N = 0.080, a^{2H'} = 0.0097,$ $a^{2H''} = 0.0034$ (2)	$\dot{\text{C}}\text{ON}^2\text{H}_2$
HCONH ₂	HCONH ₂ -AN (2.5:1)	1.50	0.240	$a^N = 0.062, a^H = 0.065$	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂ ^j	AN-H ₂ O (6:1)	1.485	0.205	$a^N = 0.069, a^H = 0.063,$ $a^{H''} = 0.020$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂ ^{f,k}	AN-H ₂ O (6:1)	1.485	0.032 ^h	$a^N = 0.069, a^H = 0.063,$ $a^{H''} = 0.020$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCON ² H ₂ ^l	AN- ² H ₂ O (6:1)	1.483	0.205 ^h	$a^N = 0.069, a^{2H'} = 0.0097$ (1), $a^{2H''} = 0.0037$ (2)	$\dot{\text{C}}\text{ON}^2\text{H}_2$
HCONH ₂	PhCN	1.472	0.165	$a^N = 0.077, a^H = 0.062,$ $a^{H''} = 0.021$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂	HOAc	1.485	0.175	$a^N = 0.076, a^H = 0.064,$ $a^{H''} = 0.021$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂	Me ₃ CCO ₂ H	1.485	0.175	$a^N = 0.076, a^H = 0.064,$ $a^{H''} = 0.22$ (2 H)	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂	HCONH ₂ -H ₂ O (3:2)	1.523	0.280	$a^N = 0.050, a^H = 0.064,$ $a^{H''} = 0.015$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCONH ₂	PhH-AN (3:2)	1.472	0.165	$a^N = 0.077, a^H = 0.062,$ $a^{H''} = 0.021$ (2)	$\dot{\text{C}}\text{ONH}_2$
HCONH(Me) ^b	PhH	1.484	0.271	$a^N = 0.065$	$\dot{\text{C}}\text{ONH}(\text{CH}_3)$
HCONH(Me) ^c	Neat	1.484	0.271	$a^N = 0.065$	$\dot{\text{C}}\text{ONH}(\text{CH}_3)$
HCONH(Me)	AN	1.490	0.344		HCONHCH ₂ $\dot{\text{C}}$
		1.490	0.185	$a^N = 0.081, a^{H''} = 0.023$ (2)	$\dot{\text{C}}\text{ONH}(\text{CH}_3)^m$
HCONH(Et)	Neat	1.470	0.276	$a^N = 0.069$	$\dot{\text{C}}\text{ONH}(\text{Et})$
HCONH(Et)	AN	1.472	0.185	$a^N = 0.081, a^{H''} = 0.022$ (2)	$\dot{\text{C}}\text{ONH}(\text{Et})$
HCONH(Et)	DCM	1.490	0.148	$a^N = 0.097, a^{H''} = 0.018$	$\dot{\text{C}}\text{ONH}(\text{Et})$
HCONH(iPr)	Neat	1.470	0.290	$a^N = 0.072$	$\dot{\text{C}}\text{ONH}(\text{iPr})$
HCONH(iPr)	AN	1.494	0.176	$a^N = 0.090, a^{H''} = 0.018$	$\dot{\text{C}}\text{ONH}(\text{iPr})$
HCONH(iPr)	DCM	1.496	0.131	$a^N = 0.102, a^{H''} = 0.018$	$\dot{\text{C}}\text{ONH}(\text{iPr})$
MeCOCH(Me)	AN	1.46	0.331		MeCONHCH ₂ $\dot{\text{C}}$
HCON(CH ₃) ₂ ^b	PhH	1.467	0.583		$\dot{\text{C}}\text{ON}(\text{CH}_3)_2$
		1.454	0.258		HCON(CH ₃)CH ₂ $\dot{\text{C}}$
HCON(CH ₃) ₂	Neat	1.44	0.606		$\dot{\text{C}}\text{ON}(\text{CH}_3)_2^m$
		1.43	0.256		HCON(CH ₃)CH ₂ $\dot{\text{C}}$
HCON(CH ₃) ₂	AN	1.45	0.600		$\dot{\text{C}}\text{ON}(\text{CH}_3)_2^m$
		1.44	0.28		HCON(CH ₃)CH ₂ $\dot{\text{C}}$
MeCON(CH ₃) ₂	AN	1.44	0.253	$a^N = a^H$ (2) = 0.064	MeCON(CH ₃)CH ₂ $\dot{\text{C}}$
Ph-CON(CH ₃) ₂	AN	1.45	0.275	$a^N = a^H$ (2) = 0.070	Ph-CON(CH ₃)CH ₂ $\dot{\text{C}}$
HCON(Et) ₂ ^b	PhH	1.451	0.593		$\dot{\text{C}}\text{ON}(\text{Et})_2$
		1.470	0.100		HCON(Et)CH $\dot{\text{C}}$ CH ₃
		1.470	0.240		
HCON(Et) ₂	Neat	1.434	0.597	$a^N \approx 0.05$	$\dot{\text{C}}\text{ON}(\text{Et})_2$
HCON(Et) ₂	AN	1.455	0.587	$a^N \approx 0.05$	$\dot{\text{C}}\text{ON}(\text{Et})_2^m$
		1.438	0.216		HCON(Et)CH $\dot{\text{C}}$ CH ₃
HCON(Et) ₂	PhH	1.42	0.547	$a^N = 0.095$	$\dot{\text{C}}\text{ON}(\text{Et})_2^m$
		1.42	0.190		HCON(Et)CH $\dot{\text{C}}$ CH ₃
HCON(iPr) ₂	Neat	1.438	0.619	$a^N \approx 0.04$	$\dot{\text{C}}\text{ON}(\text{iPr})_2^m$
		1.450	0.331		HCON(iPr)C $\dot{\text{C}}$ (Me) ₂
HCON(iPr) ₂	AN	1.450	0.623	$a^N \approx 0.04$	$\dot{\text{C}}\text{ON}(\text{iPr})_2^m$
		1.480	0.371		HCON(iPr)C $\dot{\text{C}}$ (Me) ₂
HCON=(CH ₂) ₄ ⁿ	Neat	1.460	0.584	$a^N \approx 0.05$	$\dot{\text{C}}(\text{O})=(\text{CH}_2)_4^m$
		1.440	0.210		HCON=[CH $\dot{\text{C}}$ (CH ₂) ₃]
HCON=(CH ₂) ₄ ⁿ	AN	1.440	0.564	$a^N \approx 0.05$	$\dot{\text{C}}(\text{O})=(\text{CH}_2)_4^m$
		1.438	0.194		HCON=[CH $\dot{\text{C}}$ (CH ₂) ₃]

^a Multiplicity = 1, unless otherwise noted. ^b Ref. 25b. ^c Ref. 25a. ^d Fig. 6a. ^e Fig. 6c. ^f PBN-*d* was used. ^g Fig. 7a. ^h Coupling to deuterium. ⁱ Fig. 7c. ^j Fig. 8a. ^k Fig. 8c. ^l Fig. 8d. ^m This radical comprised >80% of the two aminoxyls. ⁿ *N*-Formylpyrrolidine.

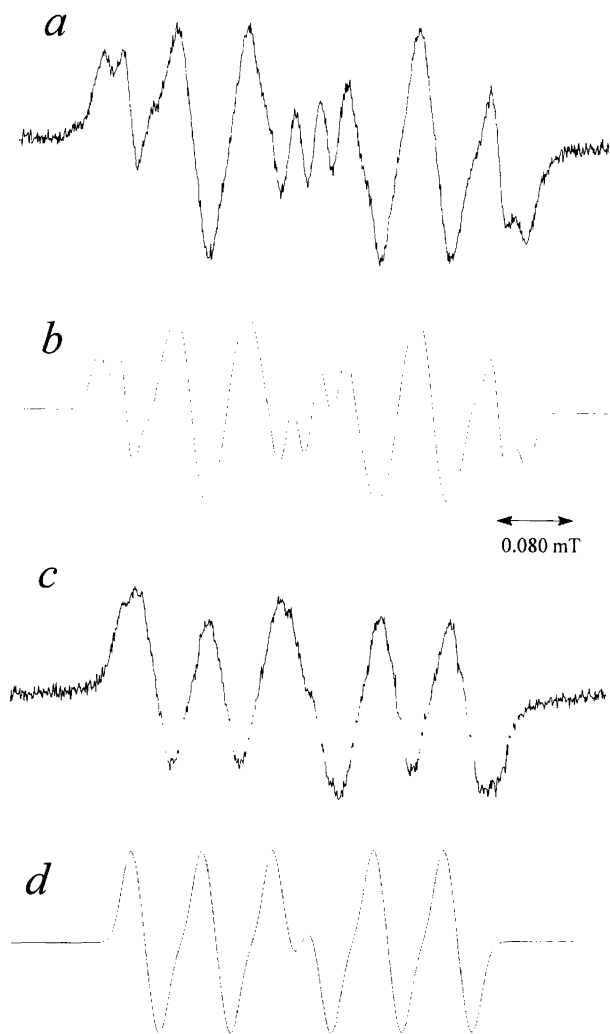


Fig. 6. (a) EPR spectrum of the middle group of lines of the spin adduct formed by UV photolysis of a solution of PBN (60 mmol dm^{-3}), HCONH_2 (2.5 mol dm^{-3}) and di-*tert*-butyl peroxide (0.7 mol dm^{-3}) in acetonitrile. The spectrum was recorded after 20 min irradiation by accumulation of 20 spectra. (b) Simulation of the spectrum in (a), using parameters listed in Table 3. (c) Same as (a), except that HCOND_2 was used. (d) Simulation of the spectrum in (c), using parameters listed in Table 3.

a^{H} coupling around 0.06 mT however disappeared in the EPR spectra of these aminoxyls. In one case, *N*-methylformamide, the aminoxyl formed from the second radical possible, HCONHCH_2^{\cdot} , was detected; its EPR spectrum exhibited only two couplings, $a^{\text{N}}=1.49$ and $a^{\text{H}}=0.344$ mT. *N*-Methylacetamide, expected to give only $\text{MeCONHCH}_2^{\cdot}$, gave an aminoxyl with similar EPR spectral parameters, $a^{\text{N}}=1.46$ and $a^{\text{H}}=0.331$ mT.

As noted before,²⁵ two types of aminoxyls are formed from *N,N*-dialkylacetamides and PBN upon thermal treatment with di-*tert*-butyl peroxalate (Table 3). The aminoxyl derived from $\cdot\text{CONR}_2$ exhibited different EPR spectral characteristics relative to those from $\cdot\text{CONHR}$ ($\text{R}=\text{H}$ or alkyl), in that no coupling to the trapped group was detectable and the coupling constant to the

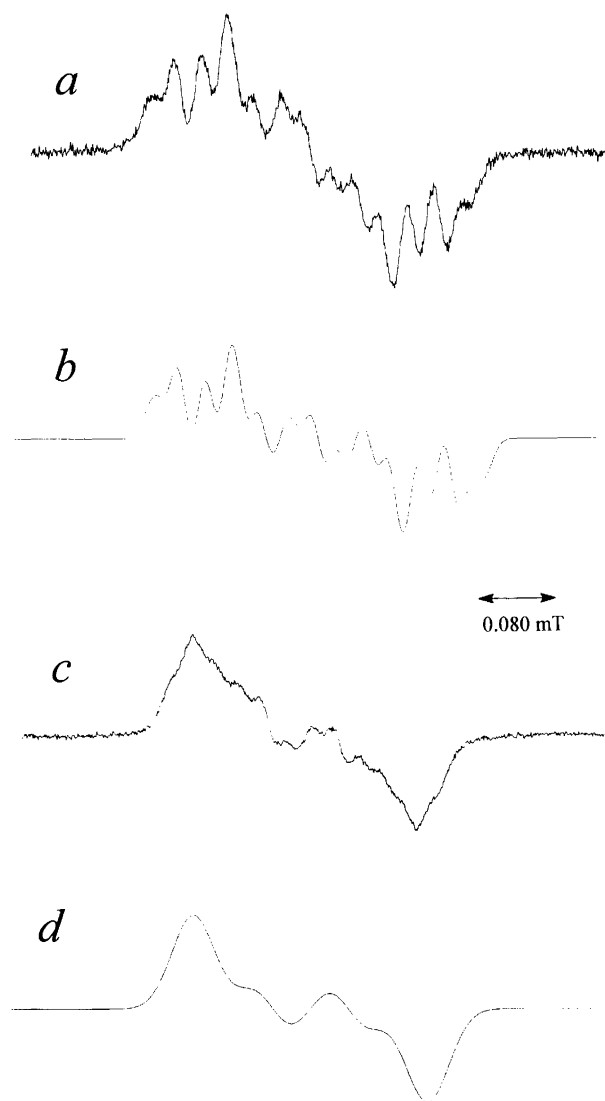


Fig. 7. (a) EPR spectrum of the middle group of lines of the spin adduct formed by UV photolysis of a solution of PBN- $\alpha^{[2}\text{H}]$ (60 mmol dm^{-3}), HCONH_2 (2.5 mol dm^{-3}) and di-*tert*-butyl peroxide (0.7 mol dm^{-3}) in acetonitrile. The spectrum was recorded after 20 min irradiation by accumulation of 20 spectra. (b) Simulation of the spectrum in (a), using parameters listed in Table 3. (c) Same as (a), except that HCOND_2 was used. (d) Simulation of the spectrum in (c), using parameters listed in Table 3.

α -hydrogen was considerably larger, around 0.6 mT. This was ascribed to the fact that the favourable pseudo-coplanar arrangement of $\text{H-N-C(=O)-C-N-O}^{\cdot}$ possible in $\text{H}_2\text{NCO-PBN}^{\cdot}$ and RNHCO-PBN^{\cdot} could not be upheld in $\text{R}_2\text{NCO-PBN}^{\cdot}$ due to the steric bulk of the R groups.^{25a}

Similar results were obtained in the present study. As shown in Table 3, HCONR_2 ($\text{R}=\text{methyl, ethyl, isopropyl}$ and tetramethylene), the dominant aminoxyl species was derived from trapping of $\text{R}_2\text{NCO}^{\cdot}$, the EPR spectrum of which is characterized by a ca. 0.6 mT coupling to α -H. There also was indication of an N' splitting of

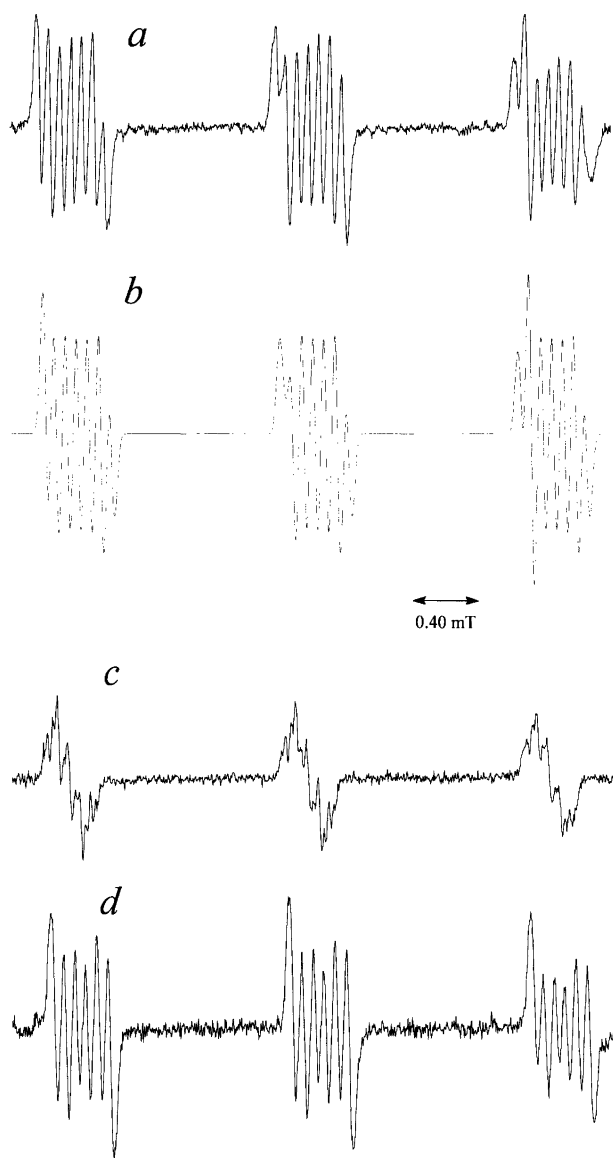


Fig. 8. (a) EPR spectrum of the spin adduct formed by UV photolysis of a solution of PBN (60 mol dm^{-3}), HCONH_2 (2.5 mol dm^{-3}) and di-*tert*-butyl peroxide (0.7 mol dm^{-3}) in acetonitrile- H_2O (6:1 v/v). The spectrum was recorded after 20 min irradiation by accumulation of 20 spectra. (b) Simulation of the spectrum in (a), using parameters listed in Table 3. (c) Same as (a), except that PBN- α - ^{2}H was used. (d) Same as (a), except that HCOND_2 was used in combination with acetonitrile- D_2O (6:1, v/v).

Table 4. EPR spectral properties of $\text{HCON(H)-PBN}^{\cdot}$.

Solvent	a^{N}/mT	a^{H}/mT	$a^{\text{N}^{\cdot}}/\text{mT}$	$a^{\text{H}^{\cdot}}/\text{mT}$
Benzene ^a	1.47	0.23	0.147	0.073
DMSO	1.50	0.205	0.165	0.145
Acetonitrile ^a	1.48	0.188	0.188	0.081
HCONH_2	1.52	0.238	0.192	0.096
HCOND_2	1.52	0.242	0.190	0.100
$\text{HCONH}_2^{\text{b}}$	1.52	0.038 ^c	0.192	0.098

^aWeak spectrum. ^b α - ^{2}H PBN was used. ^cCoupling to deuterium.

0.04–0.05 mT. The radical formed by hydrogen abstraction at the carbon adjacent to the amide nitrogen had a smaller $a^{\alpha\text{-H}}$, 0.2–0.35 mT. The lines were relatively broad (except for the radical from *N,N*-diisopropylformamide), indicating small couplings to the hydrogens in the alkyl group.

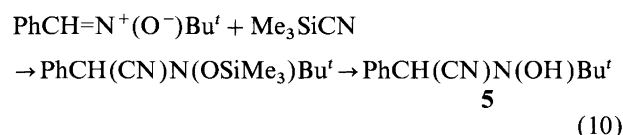
Attempts to obtain evidence for the existence of several rotamers of $\text{H}_2\text{NCO-PBN}^{\cdot}$ were made by recording spectra in the temperature range 333–223 K. Only at temperatures around 228 K (the freezing temperature of acetonitrile) were significant changes seen, and it is therefore difficult to ascertain the origin of this effect.

Preparation and EPR spectrum of the formylamino adduct $\text{HCON(H)-PBN}^{\cdot}$. If at any time the isocyano adduct CN-PBN^{\cdot} (2) were formed in the presence of water, hydrolysis to give the corresponding formylamino adduct $\text{HCON(H)-PBN}^{\cdot}$ might take place. It was therefore desirable to obtain information about the EPR spectral properties of this aminoxyl, which so far has not been characterized.

Adduct $\text{HCON(H)-PBN}^{\cdot}$ could be generated by allowing sodium to react with PBN and formamide in benzene (or DMSO) solution. The sodium slowly reacted with the amide to give the amide anion which added to the nitron according to the Forrester–Hepburn mechanism of eqn. (2), with HCON(H)^- as the nucleophile instead of cyanide ion. The best oxidant for conversion of the hydroxylamine species into the aminoxyl radical was found to be nickel peroxide which gave a spin adduct with the EPR spectral characteristics listed in Table 4. The reaction was also performed with neat formamide and *N,N*- $^{2}\text{H}_2$ formamide, which gave identical spectra showing that the H coupling to the formylamino group is to the formyl hydrogen. Sodium hydride could also be used to generate the amide anion. The use of α - ^{2}H PBN led to the expected change in the spectrum. The change in the EPR spectrum with change in solvent is fairly large, presumably due to the hydrogen-bonding properties of solvent and spin adduct, as in the case of the aminoformyl adduct.

The EPR spectrum of $\text{HCON(H)-PBN}^{\cdot}$ in formamide is shown in Fig. 9, together with a simulation.

Synthesis and properties of authentic NC-PBN^{\cdot} . The trimethylsilyl ether of the cyano adduct of PBN was prepared by treatment of PBN by trimethylsilyl cyanide.²⁶ It was hydrolyzed by treatment with hydrochloric acid. Base treatment and extractive workup afforded the corresponding hydroxylamine 5 [eqn. (10)].



Oxidation of the hydroxylamine in various solvents afforded NC-PBN^{\cdot} (Table 5). The coupling constants increase with increasing polarity of the solvent. The

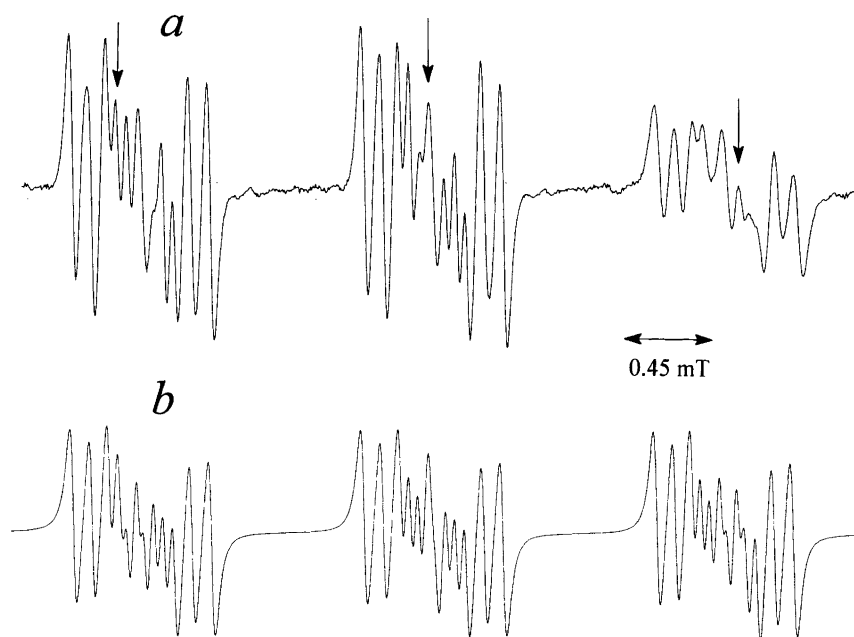


Fig. 9. (a) EPR spectrum of the formylamino PBN spin adduct, obtained by oxidation of a mixture of formamide anion and PBN in neat formamide. The peaks indicated by the arrows are due to the presence of a small proportion of $\text{Bu}_2\text{NO}^\cdot$ ($a^{\text{N}} = 1.62$ mT). (b) Simulation of the spectrum, using the parameters of Table 4. The proportion of the $\text{Bu}_2\text{NO}^\cdot$ spectrum was ca. 2%.

Table 5. EPR spectral properties of authentic NC-PBN $^\cdot$, prepared by oxidation of the corresponding hydroxylamine.

Oxidant ^a	Solvent	a^{N}/mT	a^{H}/mT
O_2	Hexane	1.46	0.171
Tl^{III}	Hexane	1.47	0.175
$\text{Co}^{\text{III}}\text{W}$	Dichloromethane	1.50	0.199
$(\text{PhCOO})_2$	Dichloromethane	1.51	0.199
Tl^{III}	Acetonitrile	1.51	0.193
Br_2	Acetonitrile	1.51	0.199
Br_2	Acetonitrile-H $_2\text{O}$ (6:1, v/v)	1.525	0.209
$\text{TAP}^+ - h\nu$ (> 400 nm)	Acetonitrile-H $_2\text{O}$ (6:1, v/v)	1.525	0.209
Br_2	Formamide	1.54	0.216
Tl^{III}	HFP	1.60	0.245

^a Tl^{III} = thallium trifluoroacetate; $\text{Co}^{\text{III}}\text{W}$ = tetrabutylammonium 12-tungstocobalt(III)ate; TAP^+ = tris-2,4,6-(4-methoxyphenyl)pyrylium tetrafluoroborate.

lifetime of NC-PBN $^\cdot$ was dependent upon the strength of the oxidant, so that for example bromine in acetonitrile-water oxidized the spin adduct further to diamagnetic species within minutes. On the other hand, photo-oxidation by TAP^+ in acetonitrile-water (6:1) produced a strong spectrum of NC-PBN $^\cdot$ which persisted for long periods ($k_{\text{decay}} = 0.021 \text{ min}^{-1}$). No other spectrum appeared during this time. This shows that the spontaneous hydrolysis of NC-PBN $^\cdot$ does not take place, at least not with formation of $\text{H}_2\text{NCO-PBN}^\cdot$.

The persistence of NC-PBN $^\cdot$ when generated by photo-oxidation by TAP^+ in acetonitrile-water (6:1) made possible experiments in which the effect of some added reagents upon the rate of disappearance of NC-PBN $^\cdot$ could be studied. With acid (trifluoroacetic

acid 0.2 mol dm^{-3}) added no rate change was noted ($k_{\text{decay}} = 0.018 \text{ min}^{-1}$), whereas addition of sodium hydroxide (4 mmol dm^{-3}) and hydrogen peroxide (4 mmol dm^{-3}) increased k_{decay} to 0.067 min^{-1} . In neither case was the EPR spectrum of $\text{H}_2\text{NCO-PBN}^\cdot$ detectable during the kinetic run.

Discussion

General about spin trapping under oxidizing conditions. It has been amply demonstrated^{6,7,15} that the exposure of a mixture of a spin trap and a nucleophile Nu^- to a strong oxidant in many cases leads to the phenomenon of 'inverted' spin trapping, namely that the spin trap is oxidized to its radical cation which then captures the nucleophile to give the spin adduct. The reaction is exemplified by PBN-cyanide ion in eqn. (1). This mechanism prevails when the nucleophile is more difficult to oxidize than the spin trap, and the competition between spin trap and Nu^- oxidation can be analyzed by the Marcus theory of electron transfer (ET) reactions.¹¹ In the case of cyanide ion, we are dealing with an oxidation-resistant species [$E^\circ(\text{CN}^\cdot/\text{CN}^-) = 2.0 \text{ V}$],³ which is more difficult to oxidize than for example PBN [$E^\circ(\text{PBN}^\cdot/\text{PBN}) = 1.5 \text{ V}$]. Thus the cyanide ion should be a favourable candidate for inverted spin trapping, as shown previously.⁶

Even under weakly oxidizing conditions a spin adduct can be formed without the intervention of any radical, as shown earlier by Forrester and Hepburn⁸ and lately in the case of fluoro²⁷ and acyloxy²⁸ spin adducts and spin adducts derived from heterocyclic N-H bases.²⁹ This mechanism is again exemplified by the cyanide ion

and PBN in eqn. (2). Since hydroxylamines and their anions are easily oxidized [$E_{pa}(\text{PhNHOH}^+/\text{PhNHOH})=0.61\text{ V}$; $E_{pa}(\text{PhNHO}^{\cdot-}/\text{PhNHO}^-)=-0.75\text{ V}$],²⁸ it is sometimes possible to use as weak an oxidant as dioxygen to convert the adduct into the spin adduct.

The carbon-to-carbon connected spin adduct of cyano radical, NC-PBN. This spin adduct has been prepared by two methods giving unambiguously determined connectivity between CN and PBN (Table 1). Our method involved the reaction shown in eqn. (10), which provided the hydroxylamine 7. The latter was then the starting material for obtaining NC-PBN \cdot by oxidation with various reagents (Table 5), thus providing its hfs constants in a range of solvents.

Comparison of the data in Table 5 with data for the spin adducts formed in the reactions of Table 1 shows that NC-PBN \cdot is invariably formed when mixtures of PBN and cyanide ion are oxidized in some way. This is best explained by recognizing that the nucleophilicity of cyanide ion is the important factor in establishing the connectivity between the cyano group and PBN: the softer carbon atom of cyanide ion attacks the soft α -carbon of PBN \cdot^+ or PBN and gives NC-PBN \cdot via eqns. (1) or (2). The formation of this spin adduct can presumably be considered as diagnostic of either of these nucleophilic mechanisms.

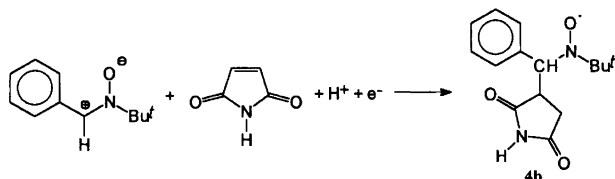
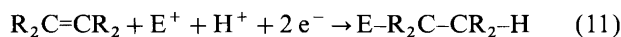
The nitrogen-to-carbon connected spin adduct of cyano radical, CN-PBN. The second spin adduct listed in Table 1 has the characteristics expected of a nitrogen-to-carbon connected adduct between the cyano radical and PBN, CN-PBN \cdot . The reactions in which it was formed do not involve oxidation of cyanide ion but instead involve exposure of NC-C or NC-metal bonds to high-energy reaction conditions, γ -radiolysis or photolysis, which are expected to favour the generation of CN \cdot .

As pointed out already, irradiation of PBN and *N*-cyanosuccinimide should proceed overall according to eqn. (9). Based on earlier work on the formation of succinimidyl spin adducts, one would then expect that succinimidyl-PBN \cdot would be prominent among the aminoxyls formed in dipolar aprotic solvents, but for unknown reasons this species was not detected under any conditions tried. If the reactivity of the succinimide anion could be curtailed, the system would be set up for the trapping of CN \cdot . This situation could be created by conducting the photolysis in HFP, the pK of which is 9.3 and thus sufficient to neutralize succinimide anion ($pK=9.7$). The weak EPR spectrum obtained by irradiation in HFP (Table 2) had hfs constants similar to those reported for X2, and we therefore suggest that the same species, CN-PBN \cdot , is responsible for this EPR spectrum.

Spin adducts derived from N-cyanosuccinimide. The use of *N*-cyanosuccinimide as a photochemical source of CN \cdot led to an unexpected diversion of the study. In nominally neutral solvents like benzene, dichloromethane

and acetonitrile, the irradiation of PBN and *N*-cyanosuccinimide generated two aminoxyls (X3 and X4) with EPR spectra consisting of $3 \times 2 \times 2$ lines, the predominant one (corresponding to X3) showing an unusually large coupling to the α -hydrogen, 0.77 mT. Since none of these aminoxyls is formed in HFP but is replaced by NC-PBN \cdot , it is logical to assume that X3 and X4 are formed via further reactions of *N*-cyanosuccinimide under 'neutral' conditions.

While a fair number of ideas regarding the nature of X3 and X4 can be put forward, it eventually became clear that a spin adduct 4a involving the C-connected *N*-cyano-3-succinimidyl radical 3 must be the most likely one for X3. For X4, it is not yet possible to assign a structure. The fact that maleimide upon photolysis with PBN gave a pair of spectra with similar characteristics as the spectra from *N*-cyanosuccinimide suggest a common origin of these aminoxyls, the one with the characteristics of X3 being analogously assigned to structure 4b. The synthetic principle of reductive coupling of an activated olefin and two electrophiles according to eqn. (11) is an established one,³⁰ and is formally applicable to a nitron like PBN (Scheme 1). Here one electron is sufficient to balance the reaction. This new reaction will be the subject of a separate study.²²



Scheme 1.

The fate of the cyano adduct of PBN under hydrolytic conditions. As stated above and based on analogies with other cyano spin adducts,¹⁰ we surmised that NC-PBN \cdot might be hydrolyzed to give the aminofornyl adduct, H₂NCO-PBN \cdot , and that this species would for example be responsible for the EPR spectra recorded under the following conditions:

(i) photolysis of CN \cdot + S₂O₈²⁻ + PBN in water⁹ (a^N 1.55, a^H 0.320, a^N 0.050, a^H 0.050 mT), (ii) photolysis of CN \cdot + S₂O₈²⁻ + PBN in acetonitrile-water⁹ (6:1) (a^N 1.49, a^H 0.082, a^N 0.170 mT), (iii) photolysis of CN \cdot + S₂O₈²⁻ + PBN in acetonitrile-water (6:1) (Fig. 5) [a^N 1.494, a^H 0.284, a^N 0.076 mT, partly obscured by the spectrum of SO₃O-PBN \cdot (a^N 1.384, a^H 0.119 mT)], and (iv) oxidation of CN \cdot + PBN in acetonitrile-water (6:1) by tris(4-bromophenyl)aminium ion (a^N 1.49, a^H 0.26, a^H 0.067, a^N 0.075 mT).

In view of the high sensitivity of the coupling constants of the EPR spectrum of H₂NCO-PBN \cdot to the α -hydrogen and to the nitrogen of the attached group to changes in the medium, especially a hydrogen bonding one, this assumption is a reasonable one. In acetonitrile,

each group of the authentic spectrum has the more complex appearance of Fig. 6a, whereas in acetonitrile–water (6:1) the simpler spectrum of Fig. 8a results. In fact, when the simulated spectrum of Fig. 8b is superimposed upon a simulation of the spectrum of $\text{SO}_3\text{O}-\text{PBN}^\cdot$ in the appropriate proportions, the spectrum in Fig. 5a can be nearly perfectly reproduced.

However, the hypothesis that $\text{NC}-\text{PBN}^\cdot$ might undergo facile hydrolysis to $\text{H}_2\text{NCO}-\text{PBN}^\cdot$ in water-containing media was refuted by the fact that no such reaction was observed when authentic $\text{NC}-\text{PBN}^\cdot$ was generated in acetonitrile–water (6:1) and subjected to acid or low concentrations of peroxide plus base, the latter an efficient procedure for the hydrolysis of nitriles to amides, with no $\text{H}_2\text{NCO}-\text{PBN}^\cdot$ detectable.

The possible fate of the isocyano adduct of PBN under hydrolytic conditions. Isonitriles undergo hydrolysis with ease,³¹ and one can therefore speculate that the cases where assignments have been based on the assumption that aminoformyl adducts are formed^{9,10} instead might depend on the hydrolysis of isocyano adducts to give the formylamino adduct. The EPR spectra of both the aminoformyl and formylamino adduct of PBN are fairly complex and vary significantly with solvent (Tables 3 and 4). It cannot be excluded that these spectra can be assigned wrongly, especially when spectra of authentic spin adducts are not known under similar conditions.

Conclusions

Trapping of the cyano radical. The results obtained provide additional evidence that the formation of the cyano spin adduct of PBN in most cases occurs by a mechanism in which the cyano radical is not trapped; instead the reaction proceeds via the PBN radical cation [eqn. (1)] or the Forrester–Hepburn mechanism [eqn. (2)]. Methods of generation of CN^\cdot are of high-energy type, such as photolysis or radiation chemistry, and lead to formation of the isocyano adduct.

Possible hydrolysis of the cyano and isocyano adduct. It does not seem likely that the cyano adduct of PBN can be hydrolyzed spontaneously in water-containing media and thus be responsible for the EPR spectral detection of aminoxy radicals with the assumed structure of $\text{H}_2\text{NCO}-\text{PBN}^\cdot$. The problem whether the isocyano adduct can undergo spontaneous hydrolysis to give the formylamino adduct is still an open one.

Experimental

Instruments and methods. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 or Bruker 400 MHz spectrometer. Cyclic voltammetry was performed by the BAS-100 instrument, using an Ag/AgCl electrode as the reference, and with *iR* compensation. Potentials given and discussed in the text are given with the Ag/AgCl

electrode as reference. All measured potentials were calibrated against the internal ferricinium–ferrocene couple (0.43–0.44 V vs. Ag/AgCl in acetonitrile).

EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using light from the 50 W high-pressure Hg lamp from Bruker (ER 202). The EPR experiments were performed as described earlier (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.01–0.04 mT). Simulations were carried out by the public domain programme WINSIM³² or by Simfonia (Bruker AG).

Materials. PBN was obtained from Aldrich or Lancaster, whereas α -[^2H]PBN, $(\text{Bu}_4\text{N})_5\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}$ ($\text{Co}^{\text{III}}\text{W}$), 1,2,4,5-tetramethoxybenzene and *N*-formylpyrrolidine were available from earlier studies. Acetonitrile and HFP were of UVASOL quality and dichloromethane of SupraSolv quality. 2,4,6-Tris(4-methoxyphenyl)pyrylium tetrafluoroborate (TAP^+) was a gift from Professor Dr. Eberhard Steckhan, University of Bonn. All other chemicals were of highest commercial quality available.

N-Cyanosuccinimide. This compound was prepared as described.¹⁴ Its spectral properties agreed with those reported.

N-Cyanomaleimide. This compound was prepared from maleimide and cyanogen bromide using the same method as for *N*-cyanosuccinimide.¹⁴ After workup, recrystallization from ethyl acetate–hexane gave a pale brown solid which gave white crystals after treatment with activated carbon in refluxing dichloromethane, m.p. 104–106 °C. ^1H NMR (DMSO): δ 7.39 (s); ^{13}C NMR (DMSO): δ 103.12, 137.64, 165.77.

*N-tert-Butyl- α -cyanobenzylhydroxylamine (7).*²⁶ Trimethylsilyl cyanide (0.56 g, 5.6 mmol) and PBN (0.50 g, 2.8 mmol) in benzene were refluxed for 20 h. The solvent was evaporated, providing the trimethylsilyl ether of **7**, m.p. 73–74 °C (lit.²⁶ 75–76 °C). ^1H NMR (^2H]chloroform): δ –0.22 (s, 9 H), 1.31 (s, 9 H), 5.15 (s, 1 H), 7.39 (m, 3 H), 7.56 (m, 2 H). ^{13}C NMR (^2H]chloroform): δ 0.61 [$\text{Si}(\text{CH}_3)_3$], 27.00 [$\text{C}(\text{CH}_3)_3$], 57.74 [$\text{C}(\text{CN})\text{H}$], 61.60 [$\text{C}(\text{CH}_3)_3$], 117.71 (CN), 128.83, 128.86, 129.12, 135.44 (Ph carbons). The ether was dissolved in ethanol and hydrolyzed by treatment with 10% hydrochloric acid. Evaporation of the solvent gave the hydrochloride **7-HCl** of the hydroxylamine. When needed, compound **7** was obtained by treatment of its aqueous solution with a slight excess of dilute sodium hydroxide solution, extraction with dichloromethane and evaporation of the organic phase. This procedure afforded **7** in admixture with a small proportion of $\text{NC}-\text{PBN}^\cdot$. M.p. 95–97 °C. ^1H NMR (^2H]chloroform): δ 1.34 (s, 9 H), 4.70 (s, 1 H), 5.05 (s, 1 H), 7.42 (m, 3 H), 7.57 (m, 2 H). ^{13}C NMR (^2H]chloroform): 26.55 [$\text{C}(\text{CH}_3)_3$], 56.22 [$\text{C}(\text{CN})\text{H}$],

60.73 [C(CH₃)₃], 118.23 (CN), 128.73, 129.22, 129.40, 135.67 (Ph carbons).

Preparation of HCONH-PBN. Ten microlitres of formamide were stirred with PBN (10–15 mg) in benzene (0.70 ml). A small piece of sodium (1–2 mg) was added and the mixture was stirred at 23 °C for 15–20 min, after which time the sodium piece was removed. Nickel peroxide (10 mg) was added and allowed to react with stirring for 1–2 min. The benzene solution was decanted into an EPR tube which was deaerated by Ar bubbling for 2 min. The experiment in DMSO or neat formamide was performed in the same way. The spectrum in acetonitrile was obtained by first carrying out the above procedure in benzene, decanting the benzene phase and dissolving the remainder in acetonitrile. Sodium hydride could also be used as the base to generate the amide anion.

Acknowledgement. Financial support from the Swedish Natural Science Research Council, the Knut and Alice Wallenberg Foundation and the Crafoord Foundation is gratefully acknowledged.

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Received September 15, 1997.