

Generation of tricyanomethyl spin adducts of α -phenyl-*N*-*tert*-butylnitron (PBN) via non-conventional mechanisms

Lennart Ebersson* and John J. McCullough

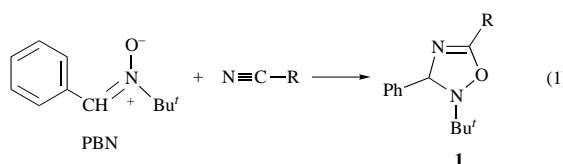
Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden

Spin adducts, formally derived from tricyanomethyl radical attachment to α -phenyl-*N*-*tert*-butylnitron (PBN; IUPAC name: *N*-benzylidene-*tert*-butylamine *N*-oxide), have been generated by various methods, such as oxidation of a mixture of tricyanomethanide ion and PBN by tris(4-bromophenyl)ammonium ion or bromine, photo-oxidation of a mixture of tricyanomethane and PBN with 2,4,6-tris(4-methoxyphenyl)pyrylium ion as a sensitizer, or photolysis of chlorotricyanomethane and PBN at -30°C , the low temperature being necessary to avoid fast concurrent cycloaddition with PBN. Both the *C*- and *N*-connected spin adducts, $(\text{NC})_3\text{C-PBN}^\bullet$ and $(\text{NC})_2\text{C}=\text{C}=\text{N-PBN}^\bullet$, have been characterized, as has an aminoxyl formed by elimination of hydrogen cyanide from the former species, $(\text{NC})_2\text{C}=\text{C}(\text{Ph})\text{N}(\text{O}^\bullet)\text{Bu}^\dagger$. For comparison, similar experiments have been performed using carbamoyldicyanomethanide ion and carbamoylchlorodicyanomethane and the spin adduct $\text{H}_2\text{NCO}(\text{CN})_2\text{C-PBN}^\bullet$ has been characterized.

The redox properties of tricyanomethanide ion, carbamoyldicyanomethanide ion, chlorotricyanomethane and carbamoylchlorodicyanomethane have been studied by cyclic voltammetry. For chlorotricyanomethane, the redox reactivity has also been evaluated by its propensity to generate radical cations from aromatic substrates ArH in 1,1,1,3,3,3-hexafluoropropan-2-ol. Tricyanomethanide ion has $E[(\text{CN})_3\text{C}^\bullet/(\text{CN})_3\text{C}^-]_{\text{rev}}$ at 1.35 V (vs. Ag/AgCl) in acetonitrile while chlorotricyanomethane with E_{pc} at about 0.6 V and a capability to oxidize compounds with redox potentials up to ca. 1.5 V to radical cations, emerges as belonging to the strongest neutral organic electron acceptors.

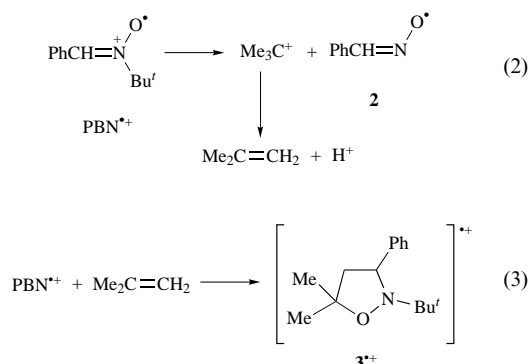
Introduction

It was recently reported that the common spin trap α -phenyl-*N*-*tert*-butylnitron (PBN) may undergo cycloadditions under certain conditions. The first report¹ dealt with spin adduct formation in systems containing PBN and cyanohalogenomethanes, where it was shown that reaction (1), giving rise to dihydro-



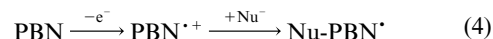
1,2,4-oxadiazoles **1**, was a complicating feature, making the use of compounds containing nitrile functions of uncertain value in spin trapping situations.

The second report² dealt with the decomposition of the radical cation of PBN ($\text{PBN}^{\bullet+}$), generated photochemically³ in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), to give first the *tert*-butyl cation and radical **2**. The loss of a proton from the *tert*-butyl cation produced 2-methylpropene [reaction (2)] which underwent cycloaddition with PBN [or, more likely, with $\text{PBN}^{\bullet+}$, as shown in reaction (3)] to give eventually the radical



cation of cycloadduct **3** characterized by its EPR spectrum. The same spectrum was obtained with 2-methylpropene or a source thereof (*tert*-butyl alcohol), and other alkenes upon similar treatment generated EPR spectra which were compatible with the isoxazolidine structure.

Our involvement with the nitrile cycloaddition problem stems from an interest in spin adduct formation via non-conventional mechanisms, such as the 'inverted spin trapping' mechanism (oxidation of the spin trap to its radical cation,⁴ followed by reaction of the latter with a nucleophile)⁵ and the Forrester-Hepburn mechanism (addition of the nucleophile to the spin trap, followed by oxidation of the hydroxylamine formed by a weak oxidant).⁶ These mechanisms are illustrated for PBN in reactions (4) and (5).



Having demonstrated the mechanistically ambiguous nature of trinitromethyl spin adduct formation from PBN,^{5e} we turned to the tricyanomethyl system in view of its electronic similarity to trinitromethyl, both as radicals and anions.⁷ The tricyanomethyl radical has been characterized by EPR spectroscopy⁸ and was shown to decay in a second-order process, presumably involving coupling, with a rate constant of ca. $5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 22°C . Thus it is more persistent than the trinitromethyl radical⁹ which presumably is a thermodynamically unstable species with access to a fast, unimolecular decay process due to the high stability of the NO_2 radical.¹⁰ In the course of this work, it became clear that a polycyanohalogenomethane such as chlorotricyanomethane reacted rapidly with PBN giving a cycloaddition product of type **1** [$\text{R} = \text{CCl}(\text{CN})_2$], τ_1 of PBN in the presence of 0.1 mol dm^{-3} chlorotricyanomethane being of the order of 1 min. The kinetic characterization of this and a few similar reactions, as well as an X-ray crystallographic study

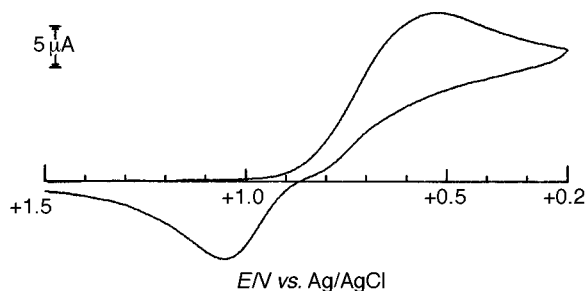


Fig. 1 Cyclic voltammetry of a solution of chlorotricyanomethane (5 mmol dm^{-3}) in acetonitrile- Bu_4NPF_6 ($0.15 \text{ mmol dm}^{-3}$) at a sweep rate of 100 mV s^{-1} . Start of sweep at 1500 mV in the negative direction.

of two cycloadducts [**1**, $\text{R} = \text{CCl}_2(\text{CN})$ and $\text{CCl}(\text{CN})_2$], is reported in the preceding paper.¹¹

In spite of the experimental difficulties caused by cycloadduct formation from electronegatively substituted nitriles, it was nevertheless possible to perform experiments aiming at the generation of tricyanomethyl spin adducts. Salts of the tricyanomethanide ion did not undergo cycloaddition with PBN,¹¹ and problems with chlorotricyanomethane and other reactive tricyanomethyl derivatives could be circumvented by working at lower temperature (0 to -30°C). In what follows, we describe the generation of the tricyanomethyl spin adducts of PBN and the problems associated with the identification of the relevant mechanisms of their formation.

Results

Cyclic voltammetry of potassium tricyanomethanide in acetonitrile

Since oxidants of various strengths are involved in non-conventional trapping mechanisms,¹² it was necessary to know the redox properties of the $(\text{CN})_3\text{C}^*/(\text{CN})_3\text{C}^-$ couple. Cyclic voltammetry of $\text{KC}(\text{CN})_3$ or $\text{Bu}_4\text{NC}(\text{CN})_3$ in acetonitrile- Bu_4NPF_6 (0.15 mol dm^{-3}) showed an anodic wave at $E_{\text{pa}} = 1.33 \text{ V}$ (vs. Ag/AgCl , Pt electrode, sweep rate 0.1 V s^{-1}) but no cathodic one. The anodic reaction was shown to be a $1e^-$ process by calibration of the peak height against a known ferrocene concentration. At 50 V s^{-1} (technical limit of the instrument) E_{pa} was 1.40 V and a small cathodic peak had developed at $E_{\text{pc}} \sim 1.32 \text{ V}$. Thus $E_{\text{rev}}[(\text{CN})_3\text{C}^*/(\text{CN})_3\text{C}^-]$ can be placed at about 1.35 V (vs. Ag/AgCl ; all potentials in the following will be given with this electrode as reference). An elongated reduction wave with E_{pc} at $-(0.4-0.5) \text{ V}$ was also seen.

Cyclic voltammetry of chlorotricyanomethane in acetonitrile

Cyclic voltammetry of chlorotricyanomethane in acetonitrile- Bu_4NPF_6 (0.15 mol dm^{-3}) at scan rates between 0.05 and 50 V s^{-1} showed a reduction peak at $E_{\text{pc}} = 0.52 \text{ V}$ and an anodic one at $E_{\text{pa}} = 1.05 \text{ V}$ (Fig. 1), the latter nearly coinciding with the chloride ion E_{pa} determined separately under the same conditions (1.07 V ; E_{pc} of Cl_2 formed at the anodic wave was 0.87 V). Repeated cycling gave virtually identical CV traces, with no changes in peak positions or currents. The cathodic process must involve dissociative electron transfer [in this context meaning only that the intermediate radical anion, $(\text{CN})_3\text{C}-\text{Cl}^{\cdot-}$, must be very short-lived]¹³ giving initially Cl^- and $(\text{CN})_3\text{C}^*$ (see Discussion) followed by instantaneous reduction of $(\text{CN})_3\text{C}^*$ to $(\text{CN})_3\text{C}^-$ [reactions (6)–(8)]. The anodic process consists of

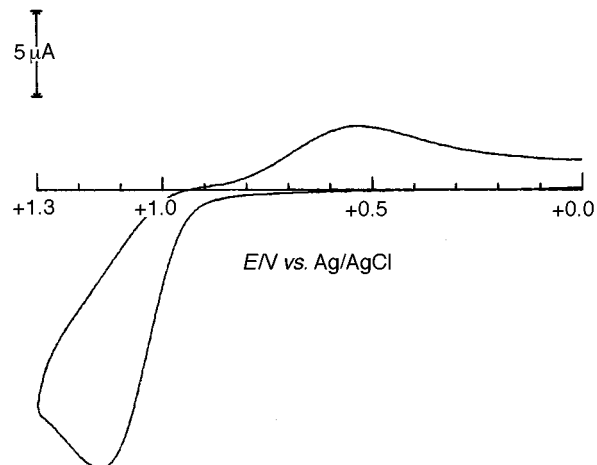
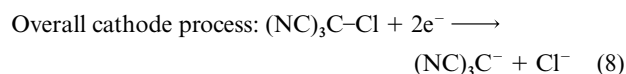
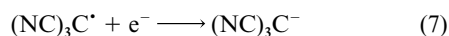
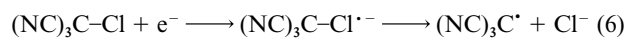
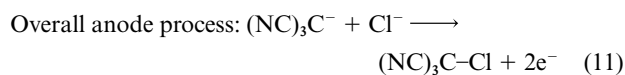
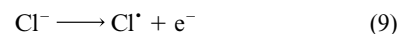


Fig. 2 Cyclic voltammetry of a solution of tetrabutylammonium tricyanomethanide (2.0 mmol dm^{-3}) and tetraethylammonium chloride (2.0 mmol dm^{-3}) in acetonitrile- Bu_4NPF_6 ($0.15 \text{ mmol dm}^{-3}$) at a sweep rate of 100 mV s^{-1} . Start of sweep at 0 mV in the positive direction.

reoxidation of Cl^- and reaction of Cl^* (or Cl_2) with $(\text{CN})_3\text{C}^-$ to re-form chlorotricyanomethane [reactions (9)–(11)].¹⁴



Similar electrode reactions should also take place upon oxidation of a solution containing chloride ion and tricyanomethanide ion. Fig. 2 shows a CV trace in which a solution of tetraethylammonium chloride (2.0 mmol dm^{-3}) and tetrabutylammonium tricyanomethanide (2.0 mmol dm^{-3}) in acetonitrile- Bu_4NPF_6 was oxidized to a potential immediately beyond the chloride oxidation peak in the first anodic scan and then upon reversal of the scan direction developed a cathodic peak at $E_{\text{pc}} = 0.54 \text{ V}$ (cf. 0.52 V when chlorotricyanomethane was reduced). Repetitive cycling (10 cycles) gave nearly identical CV traces.

Thus chlorotricyanomethane emerges as a strong oxidant, with a redox potential $E_{\text{rev}}[(\text{NC})_3\text{C}-\text{Cl}/(\text{NC})_3\text{C}-\text{Cl}^{\cdot-}]$ which should be $\geq 0.6 \text{ V}$. This conclusion was corroborated by using chlorotricyanomethane as a $1e^-$ oxidant for a range of aromatic compounds ArH in HFP and recording the EPR spectra of the corresponding $\text{ArH}^{\cdot+}$. One can then approximately determine the highest $E^\circ(\text{ArH}^{\cdot+}/\text{ArH})$ which still allows for the observation of $\text{ArH}^{\cdot+}$. We have used this method previously as a semiquantitative indicator of the redox potential of ICl ,¹⁵ Br_2 ,¹⁵ dibenzoyl peroxide,¹⁶ *N*-fluorodibenzene sulfonimide³ and nitrogen dioxide¹⁷ (upper limits were 1.7 , 1.5 , 1.4 , 1.1 and 1.5 V , respectively).

In the case of chlorotricyanomethane, compounds with $E^\circ(\text{ArH}^{\cdot+}/\text{ArH})$ up to 1.5 V (Ag/AgCl) gave radical cations in HFP. The borderline cases were 1,4-dimethoxybenzene (1.50 V) and 3,3',4,4'-tetramethylbinaphthalene (1.40 V) which gave well resolved and moderately intense EPR spectra of the corresponding radical cations persisting for 10–15 min. 1-Methoxynaphthalene (1.47 V) upon treatment with chlorotricyanomethane in HFP gave a solution of the radical cation of its dehydrodimer, 4,4'-dimethoxy-1,1'-binaphthalene, which persisted for 3–4 h. This behaviour is characteristic of 1-methoxynaphthalene.¹⁸ Finally, to exemplify with a less reactive radical cation, that of 1,4-dimethoxy-2,3-dimethylbenzene (1.22 V) generated in this way was persistent for many hours, its EPR signal decreasing in intensity by only 20% over 24 h.

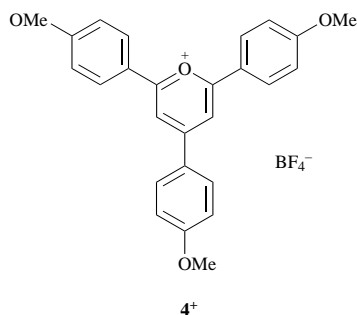
Table 1 Generation of the EPR spectrum of the tricyanomethyl radical under various conditions

Reactant	Conditions	Solvent	$T/^\circ\text{C}$	a^{N}/mT
Cl-C(CN) ₃	$h\nu$ (UV)	CH ₂ Cl ₂	22	0.235
Cl-C(CN) ₃	$h\nu$ (UV)	CH ₂ Cl ₂	-30	0.235
Cl-C(CN) ₃	$4^+-h\nu$ (>400 nm) ^a	CH ₂ Cl ₂	-30	0.235
Cl-C(CN) ₃	$h\nu$ (UV)	HFP	0	0.239
Cl-C(CN) ₃	$4^+-h\nu$ (>400 nm) ^a	HFP	0	0.239
Cl-C(CN) ₃	1-MON- $h\nu$ (>400 nm) ^b	CH ₂ Cl ₂	22	0.235
KC(CN) ₃	SO ₂ Cl ₂ - $h\nu$ (UV)	CH ₃ CN	22	0.224
KC(CN) ₃	SO ₂ Cl ₂ - $h\nu$ (UV)	HFP	22	0.241

^a [4⁺] = 1 mmol dm⁻³. ^b 1-MON = 1-methoxynaphthalene; [1-MON] = 5 mmol dm⁻³.

Generation of the tricyanomethyl radical

It was first established that the tricyanomethyl radical could be generated by photolysis of chlorotricyanomethane. These experiments are listed in Table 1. UV irradiation of chlorotricyanomethane (end absorption at $\lambda < 240$ nm¹¹) in dichloromethane at 22 or -30 °C gave a characteristic septet with $g = 2.0033$ and $a^{\text{N}}(3\text{ N}) = 0.235$ mT (lit.,⁸ in toluene, $g = 2.0033$, $a^{\text{N}} = 0.228$ mT). The intensity of the signal was enhanced by a factor of 2–4 upon addition of a sensitizer, 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (4⁺, 1 mmol dm⁻³), irradiation



being performed at $\lambda > 400$ nm. Also 1-methoxynaphthalene had a similar effect. Analogous results were obtained when the photolyses were carried out in HFP at 0 °C.

The reaction between KC(CN)₃ and sulfuryl chloride was previously established as the method of choice to prepare chlorotricyanomethane.¹⁹ Thus UV irradiation at 22 °C of these components in dichloromethane or HFP led directly to the formation of tricyanomethyl radical, presumably with the intervention of chlorotricyanomethane.

Generation of (NC)₃C-PBN[•] and related spin adducts under conditions favouring inverted spin trapping

Inverted spin trapping takes place when a nucleophile and PBN are oxidized in acetonitrile or dichloromethane with an oxidant strong enough to remove an electron from PBN ($E_{\text{pa}} = 1.53$ V), giving the reactive PBN^{•+}. Either tris(4-bromophenyl)ammonium hexachloroantimonate (TBPA^{•+}, $E_{\text{rev}} = 1.10$ V) or tetraphenylphosphonium hexachloroosmate(v) ($E_{\text{rev}} = 1.24$ V) was previously used as the oxidant.^{5a,b} Photochemical oxidation of PBN was also feasible.^{5c,d}

TBPA^{•+}, in an amount corresponding to a ca. 8 mM solution, was added to a solution of potassium tricyanomethanide (0.17 mol dm⁻³) and PBN (0.10 mol dm⁻³) in acetonitrile. The blue colour of the ammonium salt disappeared within 10–20 s, and a red–brown colour remained but faded to almost colourless in 3–4 min. The first recording of an EPR spectrum was started 1 min after mixing and consisted of a six-line spin adduct spectrum ($a^{\text{N}} = 1.43$, $a^{\text{H}} = 0.64$ mT) and a second, weak spectrum with the characteristics of a 1:1:1 triplet of broad lines with some signs of further resolution. The latter spectrum disappeared rapidly and was associated with a product formed from the ammonium ion as shown by a control experiment involving

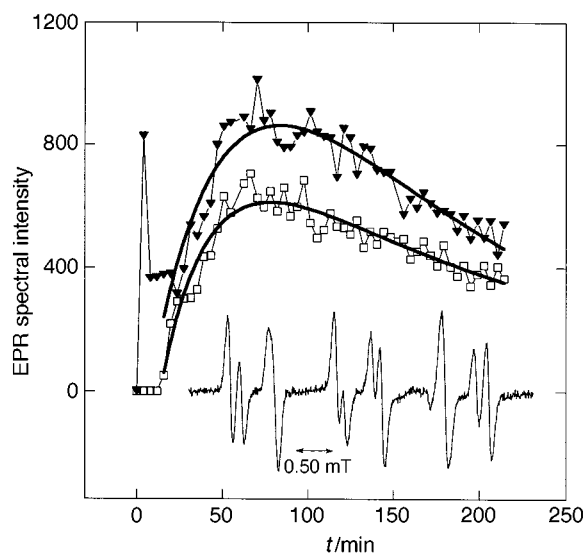


Fig. 3 EPR spectral intensities (leftmost line of each adduct) of spin adducts detected in the reaction between PBN (100 mmol dm⁻³), potassium tricyanomethanide (170 mmol dm⁻³) and tris(4-bromophenyl)ammonium ion (~8 mmol dm⁻³) in acetonitrile at 22 °C. ▼ (NC)₃C-PBN[•]; □ X1. Thin lines are included to improve readability. Thick curves, see text.

only KC(CN)₃ and TBPA^{•+} which gave a weak spectrum of the same appearance. The spin adduct spectrum decayed (Fig. 3, triangles) to a lower intensity in the first 10–15 min and then increased slowly to a maximum in ca. 1.5 h and then decayed again. In parallel, a second spin adduct started to appear ca. 15 min after mixing ($a^{\text{N}} = 1.40$, $a^{\text{H}} = 0.39$ mT; Fig. 3, □), reached a maximum after ca. 1.5 h and then decayed.

The behaviour shown in Fig. 3 indicates that the 1.43, 0.64 mT spin adduct is formed in two different phases: (i) one process involving fast initial formation during the first few seconds after mixing, followed by rapid decay, and (ii) one process involving slow formation beginning 15 min after mixing and proceeding for a considerable time. The 1.40, 0.39 mT species has the same slow time development. The thick curves of Fig. 3 represent the best fits to the intensities of the two spin adducts in the slow phase of the reaction, using as a kinetic model a double-exponential function ($k_{\text{up}} = 0.020$, $k_{\text{down}} = 0.0078$ min⁻¹ for the 1.43, 0.64 mT species and $k_{\text{up}} = 0.035$, $k_{\text{down}} = 0.0053$ min⁻¹ for the 1.40, 0.39 mT species).

An increase in [TBPA^{•+}]₀ to about 16 mmol dm⁻³ doubled the initial concentration of the 1.43, 0.64 mT spin adduct 1 min after mixing (Fig. 4), whereas the concentrations of the two spin adducts in the slow phase was much lower (Fig. 4, triangles). At a lower [TBPA^{•+}]₀ of ca. 4 mmol dm⁻³, the reverse behaviour was observed: a low intensity of the 1.43, 0.64 mT spin adduct in the first phase and higher intensities of both spin adducts later (Fig. 4, squares). Only in the latter experiment was it possible to fit the experimental points in the slow phase to the same kinetic model as above (Fig. 4, thick lines; $k_{\text{up}} = 0.08$, $k_{\text{down}} = 0.0019$ min⁻¹ for the 1.43, 0.64 mT species and $k_{\text{up}} = 0.13$, $k_{\text{down}} = 0.0015$ min⁻¹ for the 1.40, 0.39 mT species).

When Ph₄POsCl₆ (a dark brown–red solution) was used instead as the oxidant of PBN–KC(CN)₃ in acetonitrile, the solution was instantaneously decolourized, but no EPR signal of any spin adduct appeared. With Fe^{III}(phenanthroline)₃(PF₆)₃ as the oxidant, no signal appeared.

These experiments and several repeats show that spin adducts appear upon oxidation of a KC(CN)₃-PBN solution in acetonitrile with TBPA^{•+}. However, there was a curious two-phase behaviour, as shown in Figs. 3 and 4, not seen before in similar experiments with other nucleophiles.⁵ Also two spin adducts appeared, of which the one with the larger a^{H} (0.64 mT) was assigned to (NC)₃C-PBN[•], based on the analogy with

Table 2 Formation of $(\text{CN})_3\text{C-PBN}^{\bullet}$ from $\text{MC}(\text{CN})_3$ and PBN under conditions favouring the inverted spin trapping or Forrester–Hepburn mechanism. $[\text{Salt}] = 0.17 \text{ mol dm}^{-3}$; $[\text{PBN}] = 0.10 \text{ mol dm}^{-3}$.

M	Oxidant (mmol dm^{-3})	Additive (mmol dm^{-3})	Solvent	a^{N}/mT	a^{H}/mT
K^+	$\text{TBPA}^{\bullet+}$ (8)	—	CH_3CN	1.45	0.64 ^a
K^+	Br_2 (5–50)	—	CH_3CN	1.43	0.63
K^+	Br_2 (5–50), $h\nu$ ($\lambda > 40 \text{ nm}$) ^b	—	CH_3CN	1.43	0.63
K^+	$\text{Ph}_4\text{POsCl}_6$	—	CH_3CN	No signal	
K^+	$\text{Fe}^{\text{III}}(\text{phen})_3(\text{PF}_6)_3$	—	CH_3CN	No signal	
Bu_4N^+	$\text{TBPA}^{\bullet+}$ (8)	—	CH_2Cl_2	1.45	ca. 0.55 ^c
Bu_4N^+	Br_2 (50)	—	CH_2Cl_2	1.43	0.56
Bu_4N^+	Br_2 (50), $h\nu$ ($\lambda > 400 \text{ nm}$) ^d	—	CH_2Cl_2	1.43	0.56
Bu_4N^+	Br_2 (50) ^e	—	CH_2Cl_2	1.43	0.086
Bu_4N^+	Br_2 (50), $h\nu$ ($\lambda > 400 \text{ nm}$) ^{e,f}	—	CH_2Cl_2	1.43	0.086
K^+	$\text{TBPA}^{\bullet+}$ (8)	—	HFP	No signal ^g	
K^+	Cl_4Q (20), $h\nu$ (UV)	TFA (20)	CH_3CN	1.42	0.63
Bu_4N^+	Cl_4Q (20), $h\nu$ (UV)	TFA (20)	CH_2Cl_2	1.42	0.60
H^+ ^h	4^+ (1)	—	CH_2Cl_2	1.40	0.58 ^c
H^+ ^h	4^+ (1), $h\nu$ ($\lambda > 430 \text{ nm}$)	—	CH_2Cl_2	1.40	0.58

^a Formed in the initial, fast phase of the reaction. Also a signal with $a^{\text{N}} = 1.40$ and $a^{\text{H}} = 0.39$ mT developed in the second, slow phase. ^b After the light had been shut off, a weak signal of $a^{\text{N}} = 0.80$ (1 N) and 0.078 (2 N) mT persisted for 20–30 min. ^c Weak signal. ^d After the light had been shut off, two weak spectra of $a^{\text{N}} = 0.80$ (1 N) and 0.074 (2 N) mT and $a^{\text{N}} = 1.35$ (1 N), $a^{\text{N}} = 0.37$ (1 N) and $a^{\text{H}} = 0.13$ (1 H), respectively, persisted for 10–30 min. ^e $[\alpha\text{-}^2\text{H}]\text{PBN}$ was used, which gave a triplet of triplets. ^f After the light had been shut off, two weak spectra of $a^{\text{N}} = 0.80$ (1 N) and 0.076 (2 N) mT and $a^{\text{N}} = 1.35$ (1 N) and $a^{\text{N}} = 0.37$ (1 N) mT, respectively, persisted for 10–30 min. ^g The $\text{TBPA}^{\bullet+}$ signal persisted for > 20 h. ^h $[\text{HC}(\text{CN})_3] = 22 \text{ mmol dm}^{-3}$.

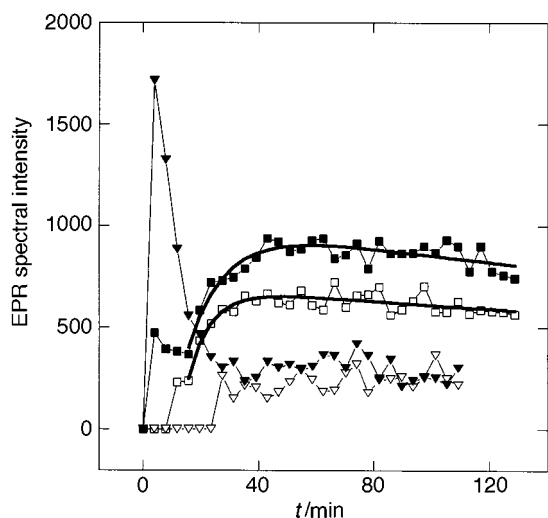


Fig. 4 EPR spectral intensities (leftmost line of each adduct) of spin adducts detected in the reaction between PBN (100 mmol dm^{-3}), potassium tricyanomethanide (170 mmol dm^{-3}) and tris(4-bromophenyl)aminium ion (triangles: $\sim 16 \text{ mmol dm}^{-3}$; squares: $\sim 4 \text{ mmol dm}^{-3}$) in acetonitrile at 22°C . Filled symbols: $(\text{NC})_3\text{C-PBN}^{\bullet}$; empty symbols: **X1**. Thin lines are included to improve readability. Thick curves, see text.

the large a^{H} of similar spin adducts containing electron-withdrawing groups [$(\text{NO}_2)_3\text{C-PBN}^{\bullet}$ 0.44 mT,^{5c} $(\text{CN})_2\text{CH-PBN}^{\bullet}$ 0.50 mT,²⁰ $\text{CF}_3\text{CO-PBN}^{\bullet}$ 0.54 mT,²¹ $\text{R}_2\text{NCO-PBN}^{\bullet}$ 0.59 mT;²¹ cf. also discussion below]. The nature of the second spin adduct, denoted **X1**, will be discussed below.

The experiment was also performed with a more redox active spin trap, 4- $\text{CH}_3\text{O-PBN}$ ($E_{\text{rev}} 1.29 \text{ V}$). This experiment gave no spin adduct immediately after mixing, but two spin adducts started to appear after about 5 min and went through a maximum intensity after about 35 min (see Fig. 5). The thick lines of Fig. 5 again correspond to the best fits to a double exponential, the first order rate constants k_{up} being 0.070 and 0.092 min^{-1} and k_{down} 0.014 and 0.013 min^{-1} , respectively. The hfs constants were nearly the same as for the PBN adducts, $a^{\text{N}} = 1.45$, $a^{\text{H}} = 0.64$ mT and $a^{\text{N}} = 1.40$, $a^{\text{H}} = 0.37$ mT, and the structure of the former was assigned similarly. A 1:1:1 triplet of broad unresolved lines appeared with low intensity and disappeared within 15 min.

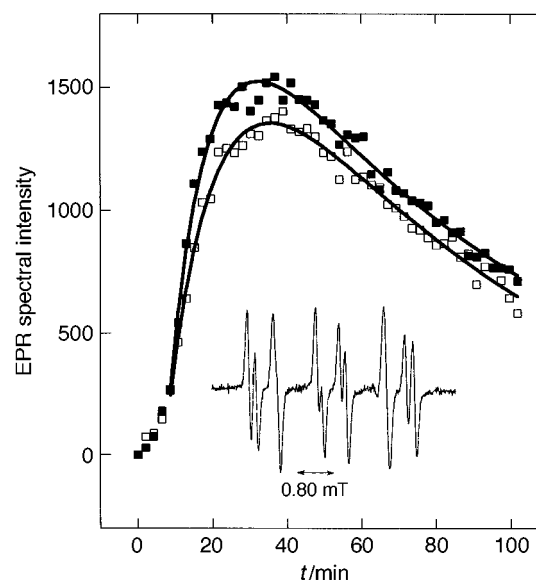


Fig. 5 EPR spectral intensities (leftmost line) of spin adducts detected in the reaction between 4-MeOPBN (100 mmol dm^{-3}), potassium tricyanomethanide (170 mmol dm^{-3}) and tris(4-bromophenyl)aminium ion ($\sim 10 \text{ mmol dm}^{-3}$) in acetonitrile at 22°C . \square $(\text{NC})_3\text{C-MeO-PBN}^{\bullet}$; \blacksquare MeO-**X1**. Thick curves, see text.

As amply demonstrated, HFP strongly decreases the reactivity of many nucleophiles in comparison with dichloromethane or acetonitrile.²² This means that inverted spin trapping is prohibited in HFP except for certain neutral nucleophiles, like phosphorus compounds^{5c} and carboxylic acids.¹⁶ $\text{TBPA}^{\bullet+}$, in an amount corresponding to $\sim 4 \text{ mM}$ solution was added to a solution of potassium tricyanomethanide (0.17 mol dm^{-3}) and PBN (0.10 mol dm^{-3}) in HFP. Now the blue colour of $\text{TBPA}^{\bullet+}$ persisted for at least 20 h, and the only EPR spectra seen at any time were that of $\text{TBPA}^{\bullet+}$ and the triplet. Thus nucleophilic reactivity appears to be required for spin adduct formation.

The tetrabutylammonium salt of the tricyanomethanide ion was used in experiments of the same type as described above in dichloromethane where the potassium salt was not soluble. In acetonitrile and dichloromethane only a very weak spin adduct spectrum with similar characteristics to $(\text{CN})_3\text{C-PBN}^{\bullet}$ could be recorded from PBN or 4-MeO-PBN, using $\text{TBPA}^{\bullet+}$ as the oxidant (Table 2).

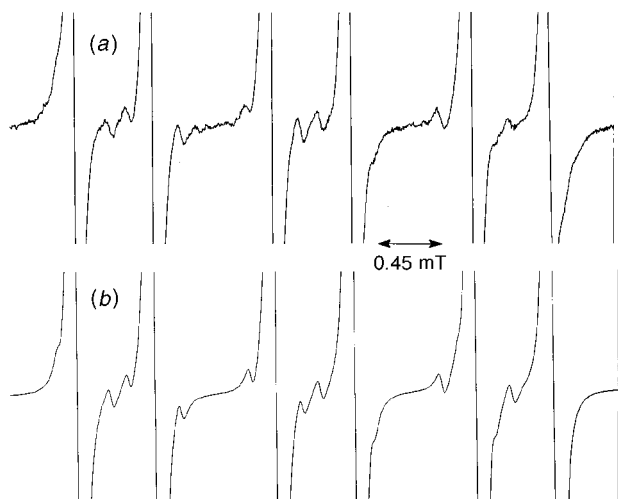
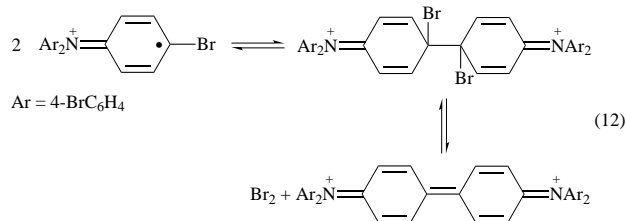


Fig. 6 (a) EPR spectrum from an irradiated (UV) solution of PBN (0.10 mol dm^{-3}), $\text{Bu}_4\text{NC}(\text{CN})_3$ (0.17 mol dm^{-3}) and bromine (50 mmol dm^{-3}) in dichloromethane. (b) A simulated superposition of the spectra assigned to $(\text{NC})_3\text{C-PBN}^\bullet$ and $(\text{NC})_2\text{C}=\text{C}=\text{N-PBN}^\bullet$ in the ratio of 20:1, using hfs constants given in Table 2.

It is known that TBPA^{++} has radical reactivity in addition to its electrophilic and electron transfer reactivities.²³ The former is reflected in a dimerization process, in which two TBPA^{++} ions couple at the positions *ipso* to bromine [equilibrium (12)] giving



a dication which can act as an oxidizing species, either as such or by elimination of bromine or donation of Br^+ .²³ This reaction is favoured in a polar solvent such as acetonitrile. Thus it is possible that the spin adduct formation observed from $\text{PBN-KC}(\text{CN})_3\text{-TBPA}^{++}$ might actually be induced by a bromine-containing species formed according to equilibrium (12), which would act as an oxidant in the Forrester–Hepburn mechanism. This assumption could be substantiated by addition of bromine ($5\text{--}50 \text{ mmol dm}^{-3}$) to a solution of PBN and $\text{KC}(\text{CN})_3$ in acetonitrile or PBN and $\text{Bu}_4\text{NC}(\text{CN})_3$ in dichloromethane which gave a signal of $(\text{CN})_3\text{C-PBN}^\bullet$ (Table 2) but not of **X1**. Irradiation ($h\nu > 400 \text{ nm}$) of the sample for 4 min amplified the $(\text{CN})_3\text{C-PBN}^\bullet$ spectrum by a factor of 20. A weaker spectrum (*ca.* 20 times less intense) of what looked like a second spin adduct [denoted **X2**, see Fig. 6(a)] was also detectable but could not be fully analysed due to overlapping lines, $a^{\text{N}} = 1.36 \text{ mT}$ being the only hfs coupling easily discernible. When the light was shut off, the $(\text{CN})_3\text{C-PBN}^\bullet$ signal almost disappeared within 20 s, and a mixture of two weak spectra became visible. One (assigned to species **X3**) was a 1:1:1 triplet of 1:2:3:2:1 quintets and was obtained both in acetonitrile [$a^{\text{N}} = 0.80$ (1 N), 0.078 (2 N) mT] and dichloromethane [$a^{\text{N}} = 0.80$ (1 N), 0.074 (2 N) mT], whereas the partly hidden spectrum had $a^{\text{N}} = 1.37$ (1 N), $a^{\text{N}'} = 0.37$ (1 N) and $a^{\text{H}} = 0.13$ (1 H) mT and was seen only in dichloromethane. A more detailed analysis indicated that the latter spectrum belonged to species **X2**, substantiated by the simulation shown in Fig. 6(b).

Photolysis experiments with $\text{PBN}[\alpha\text{-}^2\text{H}]$, $\text{Bu}_4\text{NC}(\text{CN})_3$ and Br_2 in dichloromethane gave a strong signal of $(\text{CN})_3\text{C-}[\alpha\text{-}^2\text{H}]\text{PBN}^\bullet$ which disappeared within 30 s after discontinuation of irradiation, giving two weaker spectra: the same triplet of

quintets [$a^{\text{N}} = 0.80$ (1 N), 0.076 (2 N) mT] as above and a triplet of triplets [$a^{\text{N}} = 1.35$ (1 N), 0.37 (1 N) mT]. In the latter spectrum, the coupling to deuterium, expected to be $0.13/6.5 = 0.020 \text{ mT}$, could not be resolved due to the low intensity of the signal.

The inverted spin trapping mechanism can be induced by photochemical oxidation.^{5c,d} To test this possibility, a solution of potassium tricyanomethanide (0.17 mol dm^{-3}), PBN (0.10 mol dm^{-3}) and chloranil (tetrachlorobenzoquinone, Cl_4Q , *ca.* 20 mmol dm^{-3}) in acetonitrile was irradiated by UV light at 22°C , a low concentration of trifluoroacetic acid being added to suppress the otherwise strongly dominating EPR signal of $\text{Cl}_4\text{Q}^{\bullet-}$. A strong spin adduct signal with $a^{\text{N}} = 1.42$ and $a^{\text{H}} = 0.63 \text{ mT}$ and a weak signal of $\text{Cl}_4\text{Q}^{\bullet-}$ appeared within 30 s of the onset of irradiation. Both signals disappeared within 1 min when irradiation was discontinued. Also with this method of generation the Bu_4N^+ salt gave a spin adduct signal in dichloromethane ($a^{\text{N}} = 1.42$ and $a^{\text{H}} = 0.60 \text{ mT}$). In addition, $\mathbf{4}^+$ was used as a sensitizer in a photochemical experiment analogous to the one described above, a strong signal of $(\text{CN})_3\text{C-PBN}^\bullet$ being obtained. The signal associated with **X3** was also seen in this experiment.

Generation of $(\text{NC})_3\text{C-PBN}^\bullet$ under conditions favouring the Forrester–Hepburn mechanism

Since several of the experiments described in the previous section might lead to the production of strong acid, the Forrester–Hepburn mechanism [reaction (5), with $\text{NuH} = \text{HC}(\text{CN})_3$] might also be involved in the formation of spin adducts. As shown for several NuH ,^{1,3,6,12,16} this mechanism makes possible spin adduct generation under mild oxidizing conditions.

The preparation of $\text{H-C}(\text{CN})_3$ or, rather, its dicyanoketenimine tautomer, $\text{HN}=\text{C}=\text{C}(\text{CN})_2$, has been described.²⁴ It is a reactive compound, prone to polymerize in the solid state or in solution to an orange-coloured material. Here it was prepared *in situ* by adding an equivalent amount of methanesulfonic acid to a solution of $\text{Bu}_4\text{NC}(\text{CN})_3$ (22 mmol dm^{-3} in dichloromethane) which gave a yellow–orange solution. PBN was added, whereupon immediate addition of $\mathbf{4}^+$ (1 mmol dm^{-3}) gave a very weak signal of $a^{\text{N}} = 1.40$ and $a^{\text{H}} = 0.58 \text{ mT}$, presumably induced by the laboratory light.¹⁶ The spectrum was strongly amplified upon irradiation with light of $\lambda > 430 \text{ nm}$, $a^{\text{N}} = 1.40$ and $a^{\text{H}} = 0.58 \text{ mT}$. With chloranil as the sensitizer, similar behaviour was seen. A control experiment with methanesulfonic acid, $\mathbf{4}^+$ and PBN in acetonitrile gave no EPR signal under thermal conditions, but a six-line spin adduct signal ($a^{\text{N}} = 1.51$; $a^{\text{H}} = 0.45 \text{ mT}$) appeared upon irradiation. A signal with similar hfs constants ($a^{\text{N}} = 1.52$; $a^{\text{H}} = 0.476 \text{ mT}$) has previously³ been assigned to $\text{PhSO}_2\text{O-PBN}^\bullet$, generated from toluene-*p*-sulfonic acid and PBN in the same way.

The reaction between $\text{H-C}(\text{CN})_3$ and PBN has a second pathway available, namely cycloaddition to give the dihydro-1,2,4-oxadiazole derivative **1**, $\text{R} = \text{CH}(\text{CN})_2$. The above generation of $\text{HC}(\text{CN})_3$ was repeated, PBN was added and the mixture allowed to react for 10 min. A simple workup was performed in order to remove any remaining source of tricyanomethanide ion. The material formed was treated with PBN and TBPA^{++} in acetonitrile which led to the slow formation of a mixture of the $1.43, 0.64 \text{ mT}$ and $1.40, 0.39 \text{ mT}$ adducts, discussed in connection with Figs. 3 and 4.

Table 2 lists the experiments designed to lead to the formation of $(\text{CN})_3\text{C-PBN}^\bullet$ *via* the inverted spin trapping or Forrester–Hepburn mechanism.

Generation of $(\text{NC})_3\text{C-PBN}^\bullet$ *via* photolysis of chlorotri-cyanomethane

The results given in Table 1 show that the irradiation of chlorotri-cyanomethane by UV light produces a low concentration of the tricyanomethyl radical in acetonitrile, dichloromethane or HFP, probably by homolytic dissociation of the C–Cl bond

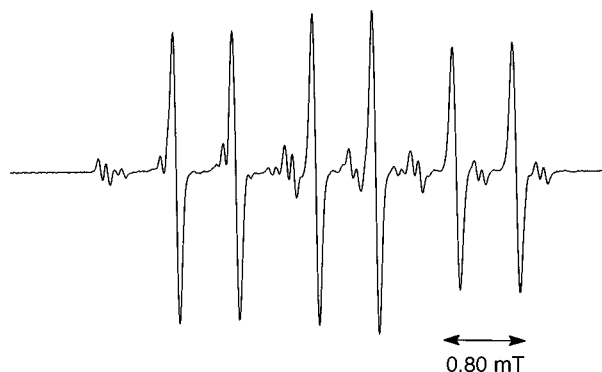
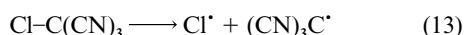
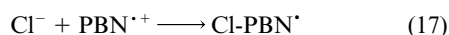
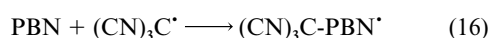


Fig. 7 EPR spectrum of a solution of chlorotricyanomethane (110 mmol dm⁻³) and PBN (50 mmol dm⁻³) in dichloromethane at -30 °C, irradiated by UV light

[reaction (13)]. The introduction of PBN into a solution of



chlorotricyanomethane introduces two complications. (i) The cycloaddition, reaction (1), $\text{R} = \text{C(CN)}_3$, which has a half-life of 0.5–5 min at ambient temperature,¹¹ depending upon the solvent used ($k = 0.14 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ in acetonitrile at 26 °C; $0.3 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ in dichloromethane; $0.032 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ in HFP). (ii) The possibility of exciting PBN to a strongly reducing excited state PBN* at 295 nm which will reduce chlorotricyanomethane to chloride ion and tricyanomethanide radical²⁵ yielding PBN^{•+}. Thus it is predicted that both the chloro and tricyanomethyl spin adducts should be formed in the photochemical experiment [see reactions (14)–(17)],



provided the cycloaddition can be avoided. The cycloaddition can be slowed down by lowering the temperature, whereas the photochemistry is more difficult to influence in an unambiguous way.

PBN (to make a final concentration of 50 mmol dm⁻³) was added at -10 °C to a solution of chlorotricyanomethane (0.10 mol dm⁻³) in dichloromethane. Irradiation (UV) for 2 min in the EPR cavity at -30 °C gave a strong signal composed of two spectra belonging to Cl-PBN^{•+}^{5a,d} and (CN)₃C-PBN[•] ($a^{\text{N}} = 1.40$ and $a^{\text{H}} = 0.60$ mT; Fig. 7). When the light was turned off, the chloro adduct signal disappeared within 2 min whereas the (CN)₃C-PBN[•] signal lasted somewhat longer. Monitoring the decay of the signal after the irradiation had been discontinued gave $k = 0.18(3) \text{ min}^{-1}$ at -30 °C.

A similar experiment to the previous one but with 4⁺ (1 mmol dm⁻³) present as sensitizer was performed, again at -30 °C. Irradiation with light which can excite 4⁺ ($\lambda > 400$ nm, 4⁺ absorbs at 422 nm) but not PBN ($\lambda_{\text{max}} = 295$ nm) gave an intense spectrum of (CN)₃C-PBN[•], but no chloro adduct was detectable.

Similar experiments were performed in acetonitrile, excellent spectra of (CN)₃C-PBN[•] being obtained at low temperature. The highest temperature which could be used with advantage to obtain the spin adduct was 0 °C, but then only 15–20 min were available for spectral recording. In HFP (mp -5 °C), no signal whatsoever was obtained upon photolysis of chlorotricyanomethane-PBN in HFP at 0 °C, with or without 4⁺ present.

Table 3 Formation of (CN)₃C-PBN[•] from solutions of PBN and chlorotricyanomethane under various conditions. $[\text{Cl-C(CN)}_3] = 0.1 \text{ mol dm}^{-3}$; $[\text{PBN}] = 0.05 \text{ mol dm}^{-3}$.

Conditions and other reactants (conc./mmol dm ⁻³)	Solvent	T/°C	a^{N}/mT	a^{H}/mT
$h\nu$ (UV)	CH ₂ Cl ₂	-30	1.40	0.60 ^a
4 ⁺ (1), $h\nu$ ($\lambda > 400$)	CH ₂ Cl ₂	-30	1.41	0.60 ^a
4 ⁺ (1), $h\nu$ ($\lambda > 400$)	CH ₃ CN	0	1.43	0.633
$h\nu$ (UV)	HFP	0	No signal	
4 ⁺ (1), $h\nu$ ($\lambda > 400$ nm)	HFP	0	No signal	

^a Cl-PBN[•] was also formed.

Table 3 summarizes experiments with PBN and chlorotricyanomethane under different conditions.

Control experiments with carbamoylchlorodicyanomethane and potassium carbamoyldicyanomethanide

Chlorotricyanomethane can undergo a relatively fast side reaction during storage and handling, namely hydrolysis of one cyano group with moisture to give carbamoylchlorodicyanomethane (**5**).²⁶ An authentic sample of **5** was therefore prepared by a new method¹⁹ and characterized by cyclic voltammetry and generation of spin adducts in reactions with PBN.



5

Attempts to detect the neutral radical in experiments with **5**, analogous to those described in Table 1, were unsuccessful.

The CV trace of **5** in acetonitrile was almost identical to that shown in Fig. 1, except that the peak potentials were displaced to lower potentials ($E_{\text{pc}} = 0$ mV and $E_{\text{pa}} = 965$ mV at 100 mV s⁻¹). The anodic oxidation of a solution of potassium carbamoyldicyanomethanide (this species has $E_{\text{pa}} = 1033$ mV and showed no cathodic peak at scan rates up to 50 V s⁻¹) and tetraethylammonium chloride likewise produced a CV trace nearly identical to that of Fig. 2, with $E_{\text{pc}} = 20$ mV and $E_{\text{pa}} = 1020$ mV. Thus **5** and chlorotricyanomethane exhibit similar electrochemical behaviour, being reduced at 0.0 and 0.52 V, respectively, and re-formed by anodic oxidation of chloride ion and the appropriate cyano substituted ion at about 1.0 V.

Photolysis of **5** with PBN-4⁺ in dichloromethane with light of $\lambda > 400$ nm gave an intense signal of a spin adduct, assigned to (CN)₂(CONH₂)C-PBN[•], with $a^{\text{N}} = 1.44$ and $a^{\text{H}} = 0.55$ mT. It persisted for about 20 min after the light had been shut off, the half-life being *ca.* 3 min. The same spectrum was also obtained, very intensely and with no time delay, upon treatment of a solution of potassium carbamoyldicyanomethanide and PBN in acetonitrile with TBPA^{•+} ($a^{\text{N}} = 1.43$ and $a^{\text{H}} = 0.57$ mT). With [α -²H]PBN, a similar reaction gave a triplet of triplets, $a^{\text{N}} = 1.43$ and $a^{\text{D}} = 0.088$ (calculated: $0.57/6.5 = 0.088$) mT. Also with Ph₄POsCl₆ or Fe^{III}(phenanthroline)₃(PF₆)₃ as the oxidant was an intense spectrum obtained ($a^{\text{N}} = 1.44$ and $a^{\text{H}} = 0.57$ mT) with no time delay. Bromine worked well as the oxidant, thermally as well as photochemically (UV).

When the photolysis of PBN and **5** was carried out in HFP, where nucleophilic reactions are strongly suppressed, a weak spectrum of a spin adduct with $a^{\text{N}} = 1.52$ and $a^{\text{H}} = 0.66$ mT was detected. In view of the known effect of HFP to increase hfs coupling constants of spin adducts by 5–10% in relation to less polar solvents,^{5e} this spectrum is assigned to (CN)₂(CONH₂)C-PBN[•].

Discussion

Redox and nucleophilic properties of tricyanomethanide ion

Cyclic voltammetry demonstrated that the oxidation of tricyanomethanide ion takes place at $E_{\text{rev}} = 1.35$ V in acetonitrile,

Table 4 Redox properties of the various reagents used

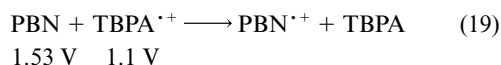
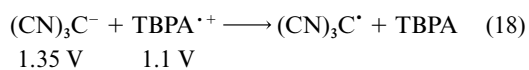
Redox couple	E_{rev} or E_p/V vs. Ag/AgCl	$E(A^{*+}/A^*)/V^a$ vs. Ag/AgCl	$E(A^*/A^{*-})/V^a$ vs. Ag/AgCl	Ref.
Cl ⁺ /Cl ⁻	1.6; 1.9			38
Br ⁺ /Br ⁻	1.4–1.5			38
(CN) ₃ C ⁺ /(CN) ₃ C ⁻	1.35			This work
(CONH ₂)(CN) ₂ C ⁺ / (CONH ₂)(CN) ₂ C ⁻	1.03			This work
ClC(CN) ₃ /ClC(CN) ₃ C ⁻	0.52			This work
ClC(CONH ₂)(CN) ₂ / ClC(CONH ₂)(CN) ₂ C ⁻	0.0			This work
4 ⁺ /4 ^{•+} (A = 4 ⁺)	-0.6	-0.7	1.8	39
Cl ₄ Q/Cl ₄ Q ⁻ (A = Cl ₄ Q)	0.0		2.0	40
1-Methoxynaphthalene		-1.1		18
TBPA ^{•+} /TBPA	1.10			38
Os ^v Cl ₆ ⁻ /Os ^{iv} Cl ₆ ²⁻	1.24			41
Fe ⁱⁱⁱ (phen) ₃ ³⁺ /Fe ⁱⁱ (phen) ₃ ²⁺	1.1			42
Br ₂ /Br ₂ ⁻	0.1			38
PBN ^{•+} /PBN	1.53			5e
4-MeO-PBN ^{•+} /4-MeO-PBN	1.29			5e
R ₂ NO ⁺ /R ₂ NO [•]	0.5–0.8			43
RNHOH ^{•+} /RNHOH	0.6–0.9			16, 44

^a See ref. 38, p. 156.

to be compared with trinitromethanide ion at $E_{\text{pa}} = 1.95$ V, chloride ion at $E^\circ = 1.6$ – 1.9 V, bromide ion at $E^\circ = 1.4$ – 1.5 V and thiocyanate ion at $E^\circ = 1.3$ V. Thus, somewhat surprisingly, tricyanomethanide is a moderately redox active ion, as indicated by its ready potentiometric titration in aqueous solution by hypochlorite, permanganate or cerium(IV) according to a two-electron reaction.²⁷ Also, it engages as a donor in the formation of charge transfer salts with triarylpyrylium cations.²⁸

Tricyanomethanide ion was previously described as a poor nucleophile,²⁶ being the anion of an acid with $\text{p}K = -5$.²⁹ In the form of its potassium salt it is alkylated only with difficulty, requiring reflux for long periods in acetonitrile with reactive alkyl halides, such as iodomethane, iodobutane and benzyl bromide for good yields to be obtained.³⁰

The implications of the reactivities mentioned above is that inverted spin trapping with tricyanomethanide ion might be feasible, but that the possible competition between PBN and tricyanomethanide oxidation [as exemplified in reactions (18) and (19); the pertinent redox properties of the various reagents



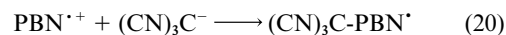
used are listed in Table 4] makes it difficult to establish the mechanism with certainty in a solvent like acetonitrile or dichloromethane, as previously noted for thiocyanate ion.^{5a} In HFP, where nucleophilic reactivity is strongly suppressed, inverted spin trapping takes place only with certain neutral nucleophiles.^{5e,16}

A second problem with (CN)₃C-PBN[•] is its low intrinsic stability, its half-life at ambient temperature being estimated at 7 s (see below). If a trapping mechanism proceeds by establishing a high initial concentration of (CN)₃C-PBN[•] 'in one shot', as both reaction (18) and (19) are expected to do, it will be technically difficult to detect (CN)₃C-PBN[•] after the period required for sample preparation. This problem does not pertain to methods of continuous generation, such as photolysis.

Spin adduct formation with tricyanomethanide ion as the source of (CN)₃C

The oxidation of KC(CN)₃ and PBN in acetonitrile with TBPA^{•+} in an initial, rapid phase gave a spin adduct of

$a^N = 1.43$ and $a^H = 0.64$ mT (Figs. 3 and 4) which was assigned to (CN)₃C-PBN[•] on the basis of its method of formation and the large a^H of 0.64 mT, analogously to that exhibited by the dicyanomethyl adduct, 0.50 mT, in malononitrile.²⁰ In dichloromethane, similar oxidation of the tetrabutylammonium salt gave a spin adduct of $a^N = 1.43$ and $a^H = 0.56$ mT, the smaller a^H in a non-polar solvent being in agreement with known solvent effects.³¹ No signal was seen in HFP. This behaviour may suggest an inverted spin trapping mechanism [reaction (20)],



PBN^{•+} being formed as a transient intermediate *via* reaction (19). A problem with this suggestion is that neither hexachlorosmate(v) nor Feⁱⁱⁱ(phen)₃³⁺ gave any spin adduct, in spite of their redox potentials being closely similar to that of TBPA^{•+} (Table 4). An alternative is that the formation of (CN)₃C-PBN[•] in the initial phase proceeds *via* the Forrester–Hepburn mechanism, where the hydroxylamine derivative already formed during the mixing procedure is exhausted completely when TBPA^{•+} is added, now exerting its oxidizing action as a consequence of equilibrium (12) (see below).

Photochemical oxidation of tricyanomethanide–PBN in acetonitrile or dichloromethane by an added sensitizer, chloranil, proceeded according to expectations (Table 2). The triplet state of chloranil is a strong oxidant (Table 4) and should sustain inverted spin trapping with ease.

Bromine acted as an efficient oxidant of tricyanomethanide–PBN in acetonitrile or dichloromethane, giving in the former solvent a medium strong signal of (CN)₃C-PBN[•] which was strongly amplified by irradiation. Analogous results were earlier found for bromine oxidation of RCOOH–PBN mixtures,¹⁶ and were interpreted in terms of the Forrester–Hepburn mechanism [reaction (5), NuH = RCOOH]. Bromine is considered to be weak as a one-electron oxidant (Table 4), and thus should not sustain the radical cation mechanism. The effect of light can have several origins, an obvious one being that bromine reacts with tricyanomethanide to give bromotriacyanomethane³² which would then behave analogously to chlorotriacyanomethane upon photolysis with PBN present (see below). In such a case, the photo-induced process giving the spin adduct might constitute true trapping of tricyanomethyl radical by PBN, as shown in reaction (16).

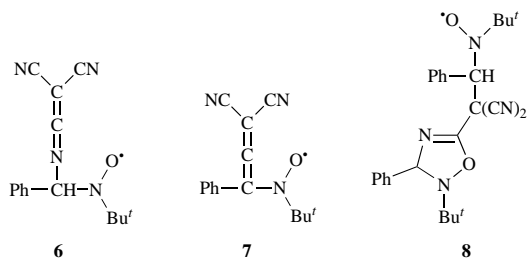
Two other aminoxyl radicals appeared in low concentration during the photochemical experiments with bromine as the

oxidant. One (**X2**) was partly hidden behind the spectrum of $(\text{CN})_3\text{C-PBN}^\bullet$ during photolysis in dichloromethane [Fig. 6(a)] but persisted for a longer time after the light had been shut off and thus could be completely analysed. The EPR signal of $(\text{CN})_3\text{C-PBN}^\bullet$ had largely disappeared within 20 s from switching off the light. The coupling constants, $a^{\text{N}} = 1.35$ (1 N), $a^{\text{N}'} = 0.37$ (1 N) and $a^{\text{H}} = 0.13$ (1 H) mT, suggested the structure of **X2** to be an N-to-C connected spin adduct, in all probability $(\text{CN})_2\text{C}=\text{C}=\text{N-PBN}^\bullet$ (**6**). The use of $[\alpha\text{-}^2\text{H}]\text{PBN}$ eliminated the doublet coupling to hydrogen and the small coupling to deuterium, estimated to be <0.02 mT, was not seen. It is known that α -cyanoalkyl radicals can react both *via* C or N in radical coupling and spin trapping.¹ Spin adducts in which the trapped radical is connected *via* nitrogen are well known, and their hfs constants are in ranges compatible with the ones given above.^{5,33}

The second aminoxyl radical (**X3**) also appeared with low intensity after the illumination period in both acetonitrile and dichloromethane and had $a^{\text{N}} = 0.80$ (1 N) and $a^{\text{N}'} = 0.078$ (2 N), unchanged when $[\alpha\text{-}^2\text{H}]\text{PBN}$ was used instead of PBN. We assign the structure of $\text{Ph}[\text{C}(\text{CN})_2\text{N}(\text{O}')\text{Bu}^\bullet]$ (**7**) to **X3**, formed by elimination of hydrogen cyanide from $(\text{CN})_3\text{C-PBN}^\bullet$.³⁴ The larger a^{N} is almost the same as that of $\text{Ph}(\text{C}=\text{O})\text{N}(\text{O}')\text{Bu}^\bullet$ (PBNO_x , **8**).^{5a}

Let us now return to the second, slow phase of the TBPA^{++} oxidations of $\text{PBN-KC}(\text{CN})_3$ (Figs. 3 and 4) where a slow buildup of $(\text{CN})_3\text{C-PBN}^\bullet$ and a second aminoxyl **X1** took place. This reaction most likely proceeds *via* the Forrester-Hepburn mechanism where a slow step precedes the oxidation of the hydroxylamine formed in reaction (5), $\text{NuH} = (\text{CN})_3\text{CH}$, to give $(\text{CN})_3\text{C-PBN}^\bullet$. Reactions of TBPA^{++} are accompanied by the generation of strong acid which accounts for the presence of cyanoform. It is suggested that the slow step is composed of both the initial attack of tricyanomethanide ion upon PBN and the release of bromine or Br^+ from the dimer of TBPA^{++} [reaction (6)],²³ leading to the establishment of low 'steady-state' concentrations of $(\text{CN})_3\text{C-PBN}^\bullet$ and **X1**.

The nature of **X1** is less obvious, but one idea is that cyanoform will undergo cycloaddition to PBN, forming **1**, $\text{R} = \text{CH}(\text{CN})_2$, which in turn may participate in the Forrester-Hepburn mechanism, resulting in the assignment of structure **8**



to **X1**. The experiment in which cyanoform and PBN were allowed to react for an extended time before the spin trapping reaction is however not fully conclusive on this point, and in the light of the earlier discussion, a^{N} is a little smaller than might have been expected.

Redox properties of chlorotricyanomethane

Cyclic voltammetry of chlorotricyanomethane established this compound to be among the strongest neutral organic acceptor molecules, with $E_{\text{rev}} \geq 0.6$ V in acetonitrile. This was corroborated by the finding that ArH of $E^\circ(\text{ArH}^{++}/\text{ArH})$ up to 1.5 V produce the corresponding radical cations by oxidation by chlorotricyanomethane in HFP.

The radical anion of chlorotricyanomethane was assumed to cleave in the usual fashion,²⁵ namely that the anion formed corresponds to the redox couple with the highest E° . As seen from the redox potentials listed in Table 4, this leads to the situation depicted in reaction (15).

Spin adduct formation with chlorotricyanomethane as the source of $(\text{CN})_3\text{C}$

Straight UV photolysis of chlorotricyanomethane in acetonitrile, dichloromethane or HFP gave low steady-state concentrations of tricyanomethyl radical, most likely by homolysis of the C-Cl bond. The use of a sensitizer in combination with light of $\lambda >$ than 400 nm increased the intensity of the signal, even if the net effect on the intensity was rather moderate due to the fact that the tricyanomethyl radical disappears in a fast second-order self-coupling reaction.⁸

The photolysis of chlorotricyanomethane-PBN solutions must be performed at low temperature, preferably below -20°C , if possible, in order to avoid the fast cycloaddition of reaction (1).¹¹ With this precaution, UV irradiation in dichloromethane gave strong EPR spectra of a mixture of Cl-PBN^\bullet and $(\text{CN})_3\text{C-PBN}^\bullet$ (Fig. 6), presumably by reactions (14)–(17). In acetonitrile, only $(\text{CN})_3\text{C-PBN}^\bullet$ was detected, in line with the higher reactivity of Cl-PBN^\bullet in polar media. It is not clear why the signal of $(\text{CN})_3\text{C-PBN}^\bullet$ was not seen in HFP; generally, trapping of radicals by PBN in this solvent seems to take place without problems.^{5e} It may either be that the extremely polar properties of this solvent makes the cleavage of the chlorotricyanomethane radical anion proceed to Cl^\bullet and $(\text{CN})_3\text{C}^\bullet$ instead of the mode shown in reaction (15) or that any $(\text{CN})_3\text{C-PBN}^\bullet$ formed is not persistent enough for EPR detection. The tricyanomethyl group should be a good leaving group, and spin adducts containing groups with this property undergo S_N reactions with ease.³⁵ The explanation may also simply be that the cycloaddition is too fast at temperatures at or slightly below 0°C , the lower limit dictated by the mp of HFP, -5°C .

This brings us to the problem of judging the 'intrinsic stability' of $(\text{CN})_3\text{C-PBN}^\bullet$. The disappearance of the spin adduct after the light had been shut off in the photochemical experiment followed approximate first-order kinetics with $k = 0.18(3)$ min^{-1} in dichloromethane at -30°C . According to the usual rule of thumb, with the rate constant changing by a factor of 2 for each 10 K, the half-life of $(\text{CN})_3\text{C-PBN}^\bullet$ should then be *ca.* 7 s at 20°C , in agreement with the observation of its fast disappearance after the photochemical oxidation by bromine at 22°C . As a consequence of this estimate, all sightings of $(\text{CN})_3\text{C-PBN}^\bullet$ for longer periods, as in the slow phase of Figs. 3 and 4, must be caused by the occurrence of one or several slow steps preceding the step leading to the formation of $(\text{CN})_3\text{C-PBN}^\bullet$.

Generation of spin adducts involving $(\text{H}_2\text{NCO})(\text{CN})_2\text{C}$

Originally experiments involving the carbamoyldicyanomethyl system were performed to check that no leakage to this occurred from tricyanomethyl substituted derivatives, particularly by hydrolysis of chlorotricyanomethane.^{11,26} Generally, no indication of this side reaction was obtained. However, since the carbamoyldicyanomethyl system is less extreme in its properties, its reactions can also be used to complement those from the tricyanomethyl system. As an example, the cycloaddition of carbamoylchlorodicyanomethane to PBN is slow, making experimentation at 20°C feasible.

Table 5 shows a comparison between the various reactivities observed. From the lower acidity of the acid, carbamoyldicyanomethanide ion should be a better nucleophile than tricyanomethanide. It is oxidized at a 0.3 V lower potential, meaning that inverted spin trapping experiments with TBPA^{++} , $\text{Os}^{\text{V}}\text{Cl}_6^-$ or $\text{Fe}^{\text{III}}(\text{phen})_3^{3+}$ cannot be interpreted unambiguously. Both oxidation of carbamoyldicyanomethanide ion and PBN can take place in competition and thus both true and inverted spin trapping can be invoked to explain the strong EPR signals observed for all three oxidants. The fact that carbamoyldicyanomethyl radical could not be detected under conditions where tricyanomethyl radical was, suggests that the former has a higher reactivity which presumably underlies its trapping by PBN in HFP.

Table 5 Outcome of various reactions involving either the (CN)₃C or (H₂NCO)(CN)₂C system

Reaction	(CN) ₃ C system	(H ₂ NCO)(CN) ₂ C system
pK _a of the corresponding acid ²⁹	-5.1	-2.8 ^a
Detection of the neutral radical by photolysis of the Cl compound	Yes	No
E _{pa} in CV voltammetry of anion	1.35 V	1.03 V
E _{pc} in CV of chloro compound	0.52 V	0.0 V
Oxidation of ion with PBN in DCM or AN with TBPA ⁺⁺ or Br ₂	Spin adduct observed <i>a</i> ^N 1.43, <i>a</i> ^H 0.63 mT	Spin adduct observed <i>a</i> ^N 1.44, <i>a</i> ^H 0.55 mT
Oxidation of ion with PBN in DCM or AN with Os ^V Cl ₆ or Fe ^{III} (phen) ₃	No spin adduct observed	Spin adduct observed
Photolysis of PBN and the chloro compound in DCM	Spin adduct observed	Spin adduct observed
Photolysis of PBN and the chloro compound in HFP	No spin adduct observed	Spin adduct observed <i>a</i> ^N 1.52, <i>a</i> ^H 0.66 mT
Half-life of spin adduct at 22 °C	7 s	3 min

^a Taken to be the same as that of (EtOCO)(CN)₂CH.

Experimental

Materials

Published methods were used to prepare KC(CN)₂CONH₂²⁶ and KC(CN)₃.²⁶ The latter was recrystallized from acetonitrile or 1,2-dimethoxyethane, and material from either solvent gave the same results where this was checked. Chlorotricyanomethane and carbamoylchlorodicyanomethane were prepared by improved modifications of literature procedures, which are described elsewhere.¹⁹ Their properties agreed with previous literature reports.^{19,26} Tetrabutylammonium tricyanomethanide has been reported previously,³⁶ but very little physical data was given for the compound. Our methods of preparation and characterization are given below. PBN and TBPASbCl₆ were obtained from Aldrich, whereas [α -²H]PBN, MeO-PBN, Ph₄POsCl₆, Fe^{III}(phen)₃(PF₆)₃ and the ArH used for calibration of the redox properties of chlorotricyanomethane were available from earlier studies.¹⁵ Acetonitrile and HFP were of Merck UVASOL quality and dichloromethane of SupraSolv quality. 2,4,6-Tris(4-methoxyphenyl)pyrylium tetrafluoroborate (4⁺BF₄⁻) was a gift from Professor Dr Eberhard Steckhan, University of Bonn. All other chemicals were of the highest commercial quality available.

Tetrabutylammonium tricyanomethanide

Tetrabutylammonium hydrogen sulfate (3.39 g, 0.01 mol) in water (25 ml) was neutralized to pH 7.0 with aqueous sodium hydroxide. Potassium tricyanomethanide (1.29 g, 0.01 mol) was added with stirring to the resulting solution (volume *ca.* 50 ml). The cloudy solution was extracted with 2 × 25 ml dichloromethane and the combined extracts gravity filtered and evaporated. The resulting colourless oil was left in a desiccator over P₂O₅ for 2 days and further dried at 20 mmHg to afford 2.0 g of crystalline material, mp 50–55 °C. Recrystallization from ethanol–diethyl ether at -70 °C gave 1.6 g (48%) of crystals, mp 51–54 °C (C₂₀H₃₆N₄ requires C, 72.3; H, 11.3; N, 16.8. Found: C, 72.2; H, 10.9; N, 16.9%); δ_{H} (300 MHz; [²H₆]acetone) 0.99 (t, 3 H, *J* 7.36, 4-H), 1.44 (sextet, 2 H, *J* 7.35, 3-H), 1.81 (m, 2 H, 2-H) and 3.42 (m, 2 H, 1-H); δ_{C} (75.4 MHz; [²H₆]acetone) 13.77, 20.27, 24.29 and 59.26 (Bu₄N⁺); 5.51, 121.74 [(CN)₃C⁻, α -C and CN, respectively], lit.,²⁷ for KC(CN)₃ 4.94 and 121.1.

Instruments and methods

¹H and ¹³C NMR spectra were recorded on a Varian XL-300 spectrometer (*J* values are given in Hz). 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).^{3,5,16} Simulations were carried out by the public domain programme WINSIM.³⁷

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