Spin-polarized (CIDEP) Neutral α-Aminoalkyl Radicals from Tertiary Amines observed in Solution by Flash-photolysis Electron Spin Resonance

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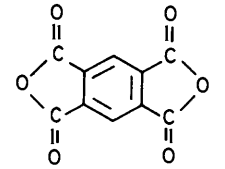
Laser flash photolysis of benzene-1,2:4,5-tetracarboxylic dianhydride in the presence of tertiary amines yielded α-aminoalkyl radicals, many of which had not been observed previously in solution. They were produced in a spin-polarized state *via* the Triplet Mechanism, to facilitate their observation by e.s.r.

Aliphatic amines act as efficient quenchers of the excited electronic states of a variety of compounds,[1-3] including carbonyl derivatives, heterocyclic molecules, aromatic hydrocarbons, and alkenes. Both photoreduction and physical quenching often occur at diffusion-controlled rates and, depending on the competing photophysical processes, either or both of the excited singlet and triplet states of the light-absorbing molecule may be involved (for example the dramatic medium effects observed with fluorenone [4,5]). The rapidity of the triplet reaction has made amines ideal quenchers in investigating the Triplet Mechanism (TM) of Chemically Induced Dynamic Electron Polarization (CIDEP) [6] observed in several flash-photolysis e.s.r. studies. The electron spin polarization which arises in the intersystem crossing (ISC) step from the excited singlet to the triplet is readily trapped in the radicals which are formed subsequently; the reaction rate competes satisfactorily at reasonable amine concentrations with the triplet spin–lattice relaxation rate. A curiosity in these studies has been that whilst the e.s.r. spectra of radicals formed from the substrate are readily observable, in no case have the spectra of the radicals derived from the tertiary amines been reported.[7] It has been assumed that they react too quickly to be observed on the microsecond timescale of current flash-photolysis e.s.r. experiments, and they have gone unreported in independent optical studies. A kinetic study of the reactions of the radical $Me\dot{C}HNEt_2$ produced by H-abstraction from triethylamine has shown it to have some of the fastest known reactions of radicals with ground state molecules.[8]

However, the reactions of amines with excited states do not always yield TM-polarized radicals: sometimes the quenching reactions are too slow and sometimes the ISC process is not spin-selective.[7l] In these situations the alternative Radical Pair Mechanism (RPM) [6,9] of electron spin polarization predominates in the short-term e.s.r. spectra of the radicals derived from the parent molecule. A knowledge of the e.s.r. parameters of the α-aminoalkyl radicals involved in the pair of radicals produced is then essential to the analysis of the precise intensity distributions that are observed. Only in this way can the polarization patterns be interpreted in detail to yield such information as the multiplicity of the radical precursor and the identities of the radicals which encounter, so as to expose the microstructure of the reaction mechanism as it unfolds with time. Furthermore the intensity distributions in RPM-polarized radicals often bear little relation to those observed in the same radicals at thermal equilibrium and this can cause difficulties in their identification. In consequence it is imperative to observe the amine radicals themselves. In solution, e.s.r. parameters for the α-aminoalkyl radical from only one tertiary amine, trimethylamine, have been reported,[10-12] although comparatively low-resolution spectra were obtained from several others in the solid state at room temperature.[13] In this paper we report the direct observation of seven related α-aminoalkyl radicals in solution.


(1)

A characteristic of α-aminoalkyl radical spectra is that they are complex, as a result of extensive hyperfine coupling, and the absolute intensity of each line is low. Indeed it has been stated that they are for the most part barely detectable, owing to the high number of hyperfine lines which are expected to have large linewidths.[10,11] As will be seen later, the linewidth suggestion is not correct, nor would it be expected to be for a carbon-centred radical under normal conditions. To overcome the intensity problem the radicals have been created deliberately in a highly polarized state *via* a TM process which leaves the relative intensities of the lines unchanged from those expected at thermal equilibrium whilst increasing the absolute intensities drastically. In the reaction systems studied the radicals disappeared rapidly by reaction (typically within 7 μs of their formation, which suggests that the mechanism is not second-order in the radical concentration) and could be detected only by using the flash-photolysis e.s.r. technique; this is one of the first reports of the detection by this method of a species which cannot also be observed in the longer timescale.

With the amine spectra expected to be complex the molecule irradiated, benzene-1,2:4,5-tetracarboxylic dianhydride (BTDA) (1), was chosen so as to yield a counter-radical with small hyperfine couplings to ensure that spectral overlap with the other radical would not be severe. The radicals are emissively polarized, which is consistent with selective population of the upper triplet sublevel of BTDA in the ISC process, as has been reported previously in a solid-state study of the charge-transfer complex of BTDA with anthracene.[14] The chemistry of the BTDA molecule and its derived radicals in this system is quite complicated, as is the associated polarization behaviour; it will be reported separately.

Experimental

The flash-photolysis e.s.r. method and broad-banding modifications to the basic Bruker ER 200D spectrometer have been described in detail elsewhere.[15] The spectra were obtained without field modulation using a sampling method which involved the time-integration of transient signals, obtained at a series of digitally advanced magnetic field settings, resulting from a train of photolysis pulses from a Lambda Physik EMG 101 excimer laser operating at 308 nm. The integration periods and the sampling times were recorded

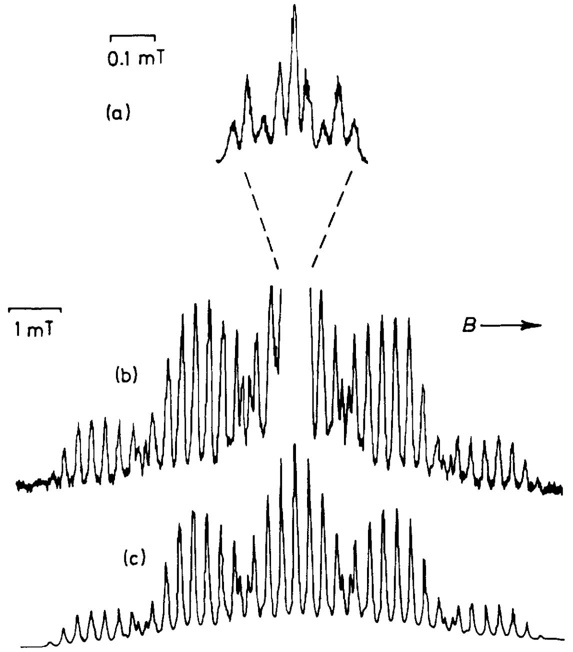


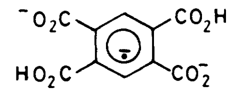
Figure 1. The spectra of (a) the radical obtained from BTDA, (b) the TEA$^{\cdot}$ radical, and (c) the simulation of the latter using the coupling constants in the Table and values of $T_1 = 5$ μs and $T_2 = 0.17$ μs. The TEA$^{\cdot}$ spectrum (low and high field) was recorded using 20 mW of incident microwave power (IMP), 64 averages, and an integration window between 1 and 4 μs after the flash. For the BTDA spectrum 20 μW of IMP, 16 averages, and a post-flash integration window of 3—12 μs were employed

carefully for subsequent use in the calculation of the lineshape functions applied to the spectra simulated for comparison with those observed. The *g* values of the radicals were obtained by absolute measurement of the frequency of the klystron, with simultaneous measurement of the magnetic field *via* an n.m.r. probe; a correction was applied for differences between the probe and sample positions by calibration using a radical of known *g* value (the 2,3,5,6-tetramethyl-1,4-benzoquinone anion,[16] *g* 2.004 915). The *g* values are believed accurate to ±0.000 03.

All solutions were degassed by passage of nitrogen, although its effect was not apparent, and were caused to flow slowly through the irradiation region. The purest chemicals available commercially were used as supplied. Solutions in dimethylformamide–propan-2-ol (2 : 1 v/v) were typically 0.15M in BTDA and 1M in amine.

Results

In all the spectra recorded shortly after the photolysis flash the spectrum from a BTDA-derived radical [Figure 1(a)] was observed. It consisted of a triplet of triplets with hyperfine couplings of 0.103 mT and 0.033 mT, with *g* 2.003 85. The couplings are close to those observed previously by Fessenden *et al.*[17] and assigned to the radical (2), although the *g* value is considerably different. An unidentified radical with coupling constants almost identical with those observed, but with its *g* value not reported, was observed as a secondary species in the electrolytic generation of the radical anion from BTDA.[18] The assignment remains a matter of conjecture, particularly since a preliminary study of the time-dependence of the spectrum suggests that two radicals might be formed from BTDA. However, this uncertainty does not affect the interpretation of the spectra of the α-aminoalkyl radicals. The simplicity of the BTDA-derived spectrum, together with its longer lifetime, caused the line intensities to be very high as compared with those of the α-aminoalkyl radicals. In consequence, it was necessary to avoid recording the complete spectra of both radicals simultaneously so as to overcome dynamic range problems in the dedicated microprocessor used in the experiment and the experimental spectra were recorded in two independent halves to either side of the strong signal.


(2)

The α-aminoalkyl radicals were observed in the inert solvent cyanomethane and in various other protic and aprotic solvents. In both cyanomethane and propan-2-ol BTDA was soluble to an appreciable extent only in the presence of the amine. In tetrahydrofuran no radicals were detected from BTDA despite a previous report that photolysis yields an ion pair,[19] nor were any radicals detected in dimethylformamide.

The previous study [12] of α-aminoalkyl radicals produced by *X*-irradiation in an adamantane matrix poisoned with the amines yielded an important source of hyperfine coupling constants which aided the initial identification of the radicals. Subsequent analysis necessitated some reassignment and yielded small changes in magnitude, mainly in the smallest coupling constant quoted; no literature values were available for the radicals formed from tripropylamine or tributylamine. The couplings used in the spectral simulations are given in the Table. To the stick spectra calculated from these values were applied lineshape functions obtained by integration of the analytical solutions of the relevant Bloch equations between the integration limits set experimentally. As always the lineshapes are quite sensitive functions of T_2, and in the simulations this was varied to produce optimum fits. It is realised that, with the exception of the trimethylamine radical for which all of the couplings were measured directly, T_2 has been used here to introduce a line-broadening effect for which the smallest (unresolved) δ-couplings are responsible.

In Figure 1 is shown the entire spectrum observed in the presence of triethylamine, together with the spectral simulation of the $\mathrm{Me\dot{C}HNEt_2}$ (TEA$^{\cdot}$) radical. In all other diagrams, for reasons of space, only the low-field halves of the α-aminoalkyl radical spectra are shown. In Figure 2 the radicals are $\mathrm{\dot{C}H_2NMe_2}$ (TMA$^{\cdot}$) from trimethylamine, $\mathrm{\dot{C}H_2N(Me)Et}$ from dimethylethylamine (DMEA), and $\mathrm{\dot{C}H_2NEt_2}$ from diethylmethylamine (DEMA). The spectra of $\mathrm{Et\dot{C}HNPr_2}$ from tripropylamine (TPA) and of $\mathrm{Pr^n\dot{C}HNBu_2}$ from tributylamine (TBA) are given in Figure 3. Each spectrum displayed a small emission/absorption distortion (from low to high field) typical of a RPM contribution to the polarization from a geminate radical pair originating from a triplet precursor. A recent method for obtaining the whole spectrum,[20] including the few lines obscured by the spectrum of the BTDA radical, could not be used because of the very short lifetimes of the α-aminoalkyl radicals.

The results from DEMA and DMEA confirm that H-abstraction occurs preferentially from the methyl group rather than from the methylene of the ethyl group.[12] Extensive efforts were made to detect the alternative radicals whose spectra should be some 4 mT wider. Some very weak lines were observed in the outlying regions and also small distortions in the line intensities of the main radicals were evident. It is apparent that other radicals were present in these systems but sufficient information to characterize them could not be

Table. E.s.r. parameters for α-aminoalkyl radicals

			Hyperfine coupling constants (mT) *			
Amine	Radical	g Value	a_α	a_β	a_γ	a_N
TMA	$\dot{C}H_2NMe_2$	2.003 18	1.295		0.41	0.709
DMEA	$\dot{C}H_2N(Et)Me$	2.003 24	1.3		0.422 (CH_3) 0.33 (CH_2)	0.73
DEMA	$\dot{C}H_2NEt_2$	2.003 26	1.281		0.351	0.702
TEA	$Me\dot{C}HNEt_2$	2.003 32	1.396	1.924	0.254	0.518
TPA	$Et\dot{C}HNPr_2$	2.003 14	1.374	1.865	0.254	0.528
TBA	$Pr^n\dot{C}HNBu_2$	2.003 13	1.38	1.79	0.254	0.52
HDEA	$Et_2N\dot{O}$	2.005 47	1.064			1.567

* Radical coupling constants refer to radical of general type $RC_\beta H_2-\dot{C}_\alpha H-N(C_\gamma H_2R')_2$ (R, R′ = H, Me, Et, Pr).

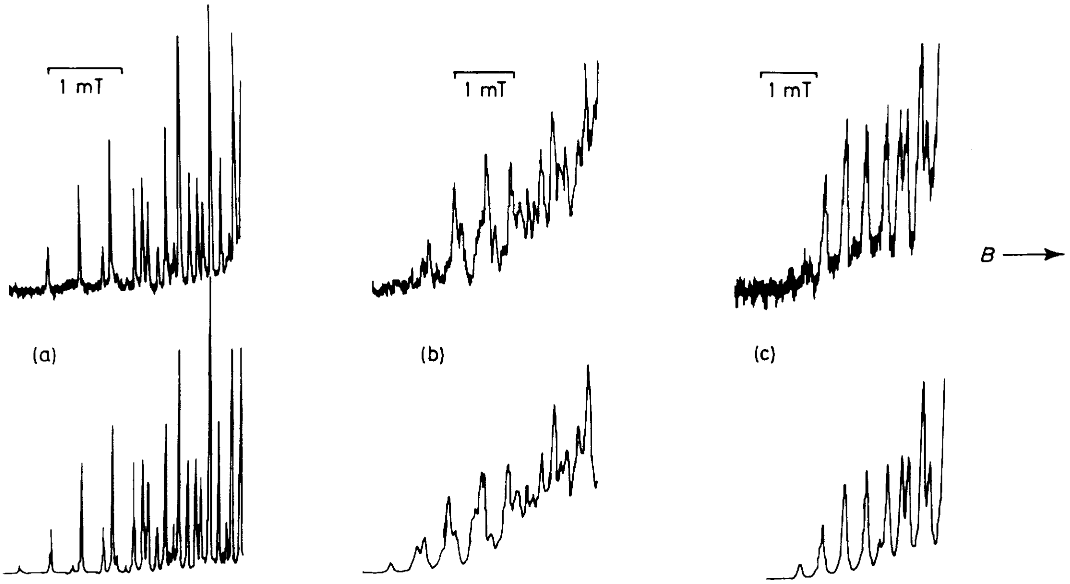


Figure 2. The low-field half spectra of (a) TMA˙ and the radicals derived from (b) DMEA and (c) DEMA. The spectra were recorded using 20 mW of IMP, 48 or 64 averages, and integration windows of 1 and 4 μs following the flash. In each case the calculated spectrum appears below the observed one. Values of T_1 = 5 μs and T_2 = (a) 0.25 μs, (b) 0.16 μs, (c) 0.16 μs were used. Under the conditions of the experiment none of these values represents the absolute relaxation time of the system

obtained. No independent information on the reaction-site selectivity of these molecules is available.

Attempts to extend the methods to other amines met with limited success. With tripentylamine a BTDA-derived radical was observed but no amine radical was detected. Tribenzylamine yielded a narrow, rather structureless, α-aminoalkyl spectrum which has not been analysed. Another tertiary amine, hydroxydiethylamine (HDEA), gave the $Et_2N\dot{O}$ radical,[21] parameters for which are included in the Table, and it seems likely that related molecules would behave similarly. Primary and secondary amines, on the other hand, reacted with BTDA to yield products which were insoluble in the normal solutions used. Dissolving these products in various solvents and irradiating them yielded no detectable radicals.

Discussion

Amine photoreduction is believed to occur usually *via* a charge-transfer process involving the formation of an exciplex which may dissociate into a radical ion pair or into a radical pair formed by H-abstraction within the exciplex;[1,2] this latter stage may also occur between the members of an initially formed ion pair. However, some recent discussions still invoke direct hydrogen abstraction without the intermediacy of an exciplex.[22,23] The relative importance of these four processes leading to reaction intermediates has been investigated in detail for reactions between carbonyl compounds and amines using CIDNP methods,[24,25] but no information exists for the reaction system reported here. In four of the reaction systems studied no evidence was obtained for any radicals other than the α-aminoalkyl but it is possible that the unassigned weak lines observed when DEMA and DMEA were used as the amines originated in the appropriate cations. An attempt to confirm this in a time-resolved study was thwarted by the extremely short lifetime of all the radicals observed. As stated already, the neutral α-aminoalkyl radicals react very rapidly with many ground-state substrate molecules and their rate of disappearance suggests that this was their fate here.

In the absence of independent information it is unclear why the α-aminoalkyl radicals could be observed in this study. BTDA is a powerful electron acceptor [26] which forms a wide range of ground-state charge-transfer complexes,[27-29] and it is probable that the aliphatic tertiary amines conform with this behaviour. It has been reported that charge-transfer in the benzophenone–aromatic amine system enhanced the photo-

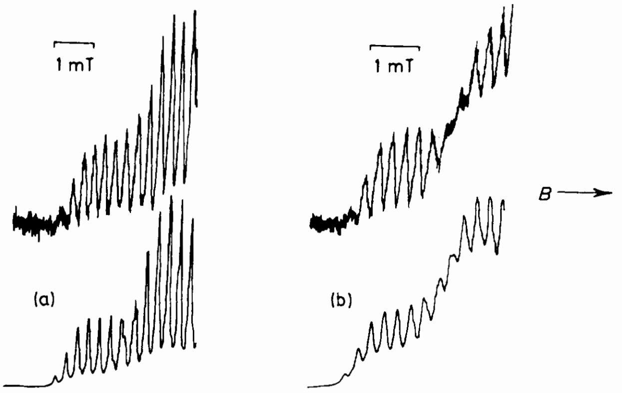


Figure 3. The low-field half spectra of (a) TPA˙ and (b) TBA˙. Recording conditions were the same as those for Figure 2. The simulations were calculated using T_1 = 5 µs and T_2 = (a) 0.13 µs, (b) 0.08 µs

reactivity of the benzophenone and increased the lifetimes of the radicals[30] produced, and it may be that similar considerations apply here. Alternatively, the association of BTDA with the amine may limit the concentration of free BTDA and consequently slow the α-aminoalkyl-radical-removing reaction. Some support for this view lies in the observation that BTDA is soluble in cyanomethane and propan-2-ol only in the presence of the amines. Also, the reaction of the radicals with the solvent appears to be slow. Dissociation of the anhydride to form the dianion before irradiation would also rationalise the observations. Further studies with two molecules closely related in chemical structure to BTDA, phthalic anhydride and naphthalic dianhydride, yield copious radicals from the parent molecules but no α-aminoalkyl radicals could be detected.[31]

However, it is difficult to form firm conclusions on this matter, for re-examination of reaction systems in which the α-aminoalkyl radicals were thought not to be observable shows that, in the photolysis of both benzophenone and acetophenone[31] in the presence of triethylamine, the outermost lines from these radicals can in fact be observed, although the centres are obscured by the spectrum from the counter-radical. On the other hand in the photolysis of either 2,3,5,6-tetramethyl-1,4-benzoquinone or a wide range of nitrogen heterocyclics the TEA radical cannot be observed.

It has been shown that, despite previous statements to the contrary, the radical from trimethylamine has no particular characteristics of its own which differentiate it from its close relatives. In particular, the spectra all display normal linewidths. The difficulty in observing these radicals lies rather in the complexity of their spectra and in their high reactivity in many situations. This reactivity causes their absolute intensities to be much less, at feasible observation times, than those of their counter-radicals, although the initial concentrations of both species were equal.

The spectral parameters reported are generally in good agreement with those already in the literature; the smaller ones reported in the adamantane matrix are probably slightly in error owing to the broader linewidth. The exception is found in the TMA˙ results where our values differ substantially from those reported by Neta and Fessenden[10] for aqueous solution, whilst being in good agreement with those reported for solution in cyclopropane.[11] Throughout, the hyperfine couplings observed in closely related radicals are sensibly similar, including those from the hitherto unreported radicals from tripropylamine and tributylamine.

In this study calculated lineshapes have been used for the first time in reproducing highly resolved spectra from flash-photolysis e.s.r. experiments using time-integration methods. These shapes are unusual in being non-Lorentzian and it is gratifying that they yield excellent resolution and that they can be calculated accurately. This is shown more clearly here than in a previous study of some rather complex spectra from nitrogen heterocyclic radicals.[71]

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