Chemical Polarisation of ^{13}C and ^{15}N Nuclei in the Thermal Decomposition of Diazoaminobenzene (1,3-Diphenyltriazene)*

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(Received 13 February 1973; accepted 14 March 1973)

Abstract—Chemical polarisation of ^{13}C and ^{15}N nuclei in the thermal decomposition of diazoaminobenzene has been investigated. Most of the polarised products with the exception of benzene result from cage recombination processes, and both the ^{13}C and ^{15}N true nuclear polarisation coefficients are rather high, up to 10000 and more. ^{13}C CIDNP has been shown to provide a new and useful technique for the measurement of ^{13}C spin-lattice relaxation time T_1.

Free radical reactions of organic compounds and the corresponding CIDNP mechanisms can be studied very successfully using proton spectra. Since the hyperfine coupling constants with ^{13}C and ^{15}N nuclei can, however, be considerably larger, the nuclear relaxation times longer and the spectra generally much simpler and easier to interpret in detail, the study of heavier nuclei provides many advantages over ^{1}H-CIDNP, particularly in the case of σ-radicals.

INTRODUCTION

BOTH the reaction rate constant k and the nuclear relaxation time $T_1 = 1/\beta$ must be known to calculate the value of E, the true coefficient of nuclear polarisation, equal to the ratio of nuclear polarisation in the diamagnetic product molecule at the moment of its formation and at thermal equilibrium. The only actually measured enhancement factor K is determined through the signal intensities or peak values during the reaction $I(t)$ and at thermal equilibrium $I(\infty)$,

$$K = \frac{I(t) - I(\infty)}{I(\infty)} \approx \frac{I(t)}{I(\infty)}$$

If the warming up period is considerably shorter than T_1, then for first order reactions[1]

$$K = \frac{Ek - \beta}{\beta - k}\,(e^{-kt} - e^{-\beta t}) - e^{-\beta t}$$

If at the same time, as is usual in carbon-13 and nitrogen-15 polarisation, $E \gg 1$ and $(Ek - \beta) \approx Ek$, then

$$K \approx \frac{Ek}{\beta - k}\,(e^{-kt} - e^{-\beta t}).$$

At the moment of maximum polarisation

$$t_{\max} \approx \frac{\ln(\beta/k)}{\beta - k},$$

$$K_{\max} \approx \frac{Ek}{\beta - k}\left[\left(\frac{k}{\beta}\right)^{k/(\beta - k)} - \left(\frac{k}{\beta}\right)^{\beta/(\beta - k)}\right]$$

and only $K_{\max}$, k and β are necessary for the calculation of E. In some rather important cases both the reaction rate constant k and the relaxation time $T_1 = 1/\beta$ of any particular polarised line can be determined from the CIDNP experiment itself by measuring the pure absorption signal, once with a very weak and non-saturating r.f. field and then with a completely saturating strong r.f. field (difference of the necessary r.f. amplitudes is about 30 to 40 db).[2]

For fast reactions $k \gg \beta$ and $e^{-kt} \ll e^{-\beta t}$, giving a single decay tail practically totally determined by T_1 alone. In this case polarisation persists long after the end of the chemical reaction. Since the intermediate free radicals are also no longer present, the chemical polarisation phenomenon provides a good new method for the measurement of long relaxation times of even very weak spectral lines in ^{13}C, ^{15}N, ^{31}P or other spectra.[2] On the other hand, if the spectrum is registered with a saturating r.f. field that tends to destroy differences in energy level populations through saturation and consequently effectively shortens T_1 to the point where $\beta \gg k$, (the difference between equal level populations at complete saturation and a true thermal equilibrium is immaterial if $E \gg 1$), then $e^{-kt} \gg e^{-\beta t}$ and the signal decay tail is determined solely by the reaction kinetics without any interfering relaxation effects (see Fig. 1).

In the case of slow reactions $k \ll \beta$ the r.f. field amplitude has little influence on signal decay and only k can be accurately determined from the CIDNP data. In many cases k can be sufficiently increased by raising the temperature, which at the same time leads to a lengthening of T_1 if the dipole-dipole interaction provides the dominant relaxation mechanism. If $k \approx \beta$, then a strong r.f. field leads to a signal decay tail determined by k and T_1 must be determined from a separate experiment.

All this discussion applies to the CW-methods, but the Fourier transform methods are just as flexible. It is also important to note that the nuclear relaxation times during the active decomposition reaction can be significantly shorter due to the presence of significant amounts of free radicals, particularly at the peak of the reaction. This leads to irregularities in the time dependence of the ^{13}C polarisation pattern[3] and changes in the nuclear Overhauser effect of the solvent lines (see Figs. 2 and 3). This variability of the spin-lattice relaxation times is a further complication in an already very complicated situation and from this only one conclusion can be drawn, namely that the calculated nuclear polarisation coefficients E are actually only the minimum values. The true values are certainly larger in all cases where the time dependence of nuclear polarisation shows any irregularities during the reaction.

EXPERIMENTAL

We studied the thermal decomposition reaction of 1,3-diphenyltriazene (diazoaminobenzene) in various solvents at 155° to 179°C, using both natural and ^{15}N-labelled (44% enrichment) compounds. The ^{13}C and ^{15}N CIDNP spectra were registered at 15·09 MHz and 6·08 MHz, respectively on a universal frequency-sweep, spin stabilised, NMR double resonance spectrometer, using stationary

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* Paper presented at the International Symposium on Chemically Induced Dynamic Polarisation of Nuclei and Electrons, Tallinn, Estonian SSR, 13th to 16th August 1972.

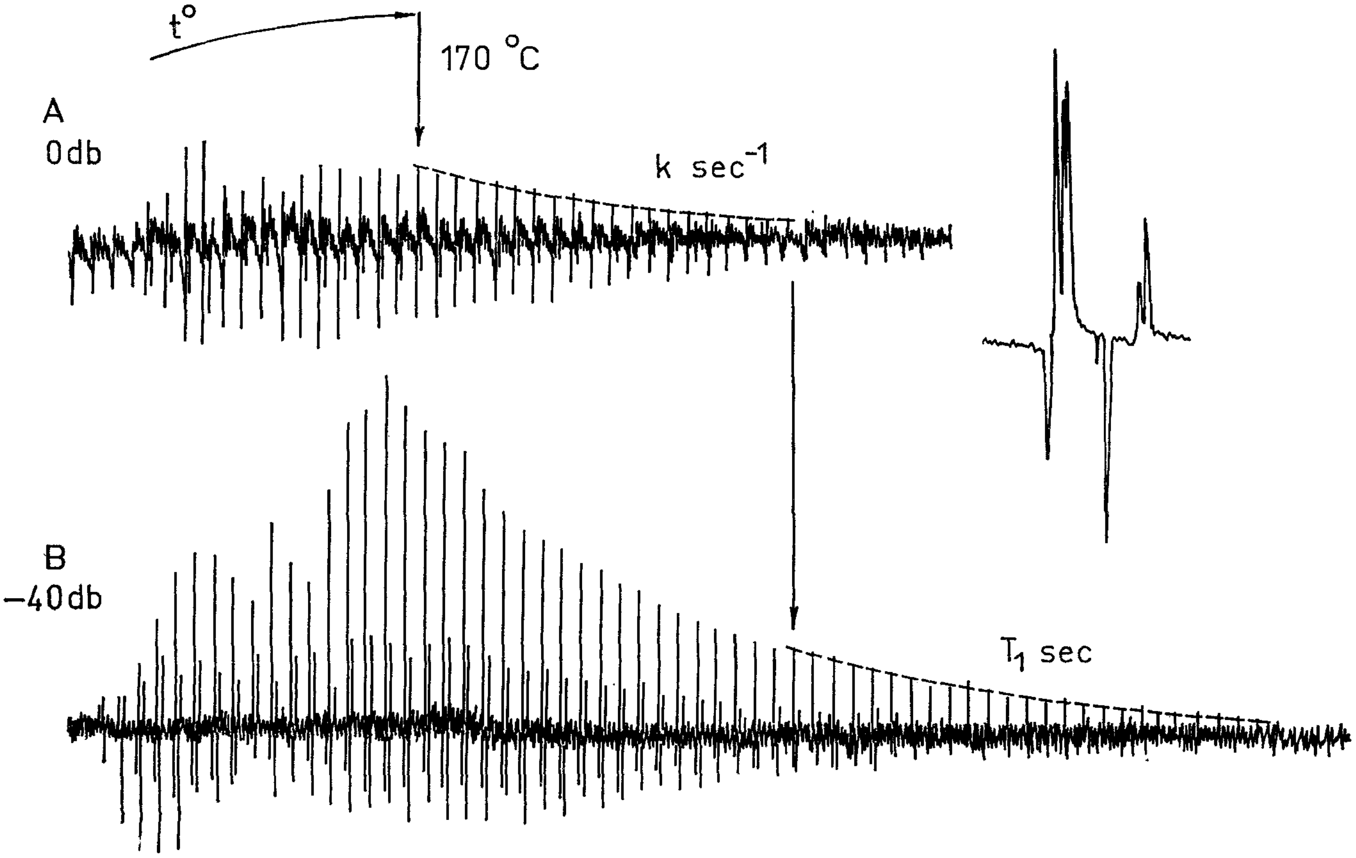


Fig. 1. Determination of both the reaction rate constant k and the ^{13}C nuclear relaxation time T_1 from the CIDNP data. Thermal decomposition of diazoaminobenzene in cycloheptanone. (A) r.f. amplitude 0 db; (B) r.f. amplitude −40 db.

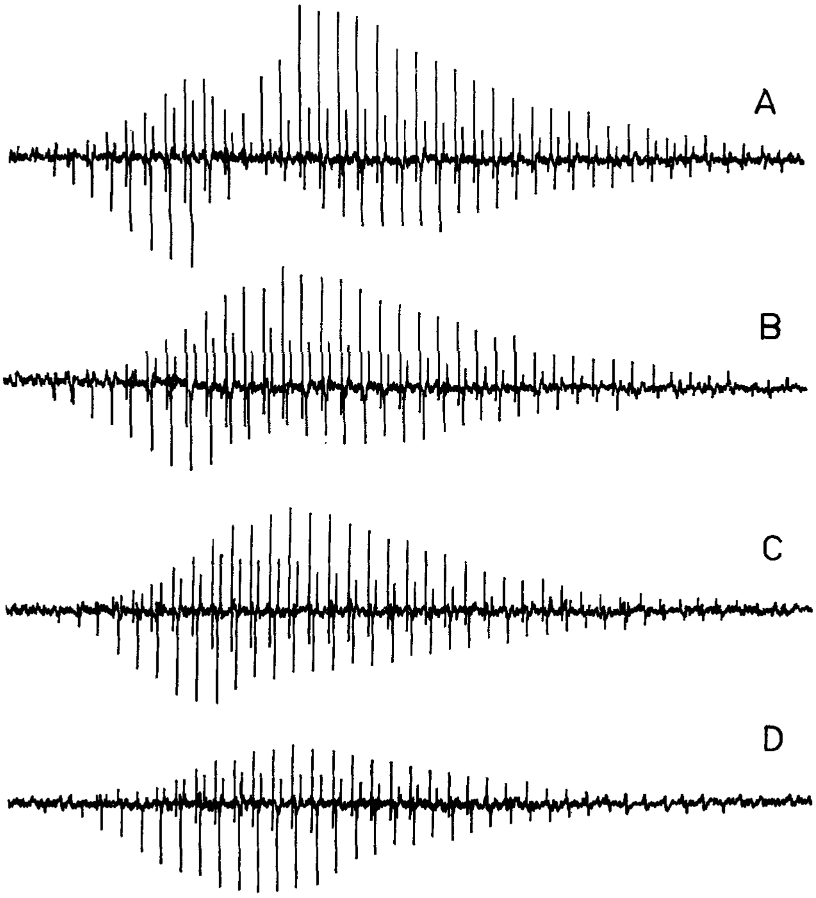


Fig. 2. Changes in the reaction kinetics and the ^{13}C relaxation times during rapid reactions with high concentrations of free radicals. Thermal decomposition of diazoaminobenzene in cycloheptanone at 170°C. (A) 1·0 g, (B) 0·7 g, (C) 0·5 g, and (D) 0·3 g of DAAB per 3 ml of cycloheptanone, respectively.

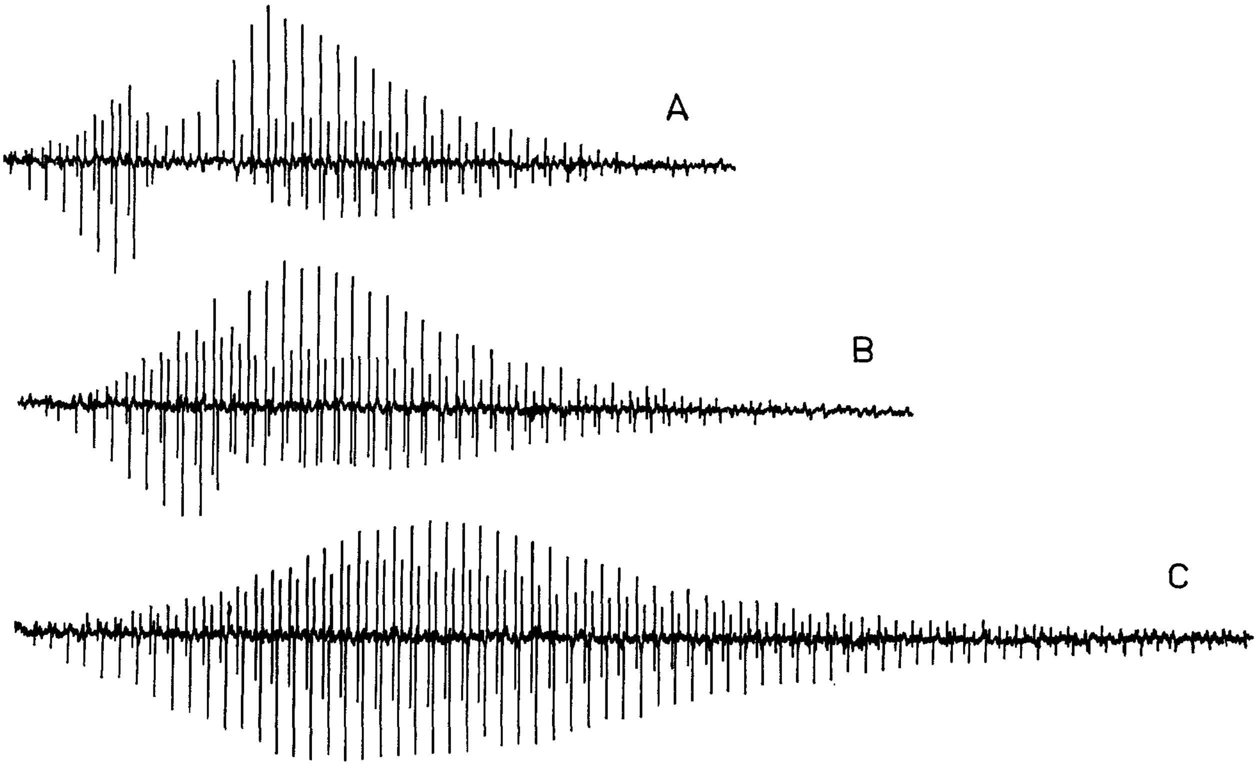


FIG. 3. Thermal decomposition of 1·0 g of diazoaminobenzene in 3 ml of cycloheptanone at various temperatures. ^{13}C double resonance spectrum. (A) 179°C; (B) 166°C; (C) 155°C.

15 mm O.D. sample tubes. Time sharing was used to decouple the receiver circuit from the transmitter and proved to be very effective, even in the case of very fast reactions with rapid gas evolution or with boiling samples. All spectra were accumulated, using a 512-channel CAT (Nokia LP 4050). The chemical shifts are given in ppm on the δ-scale downfield from external tetramethylsilane for ^{13}C and from aqueous Na^{15}NO$_3$ for the ^{15}N shifts. The ^{13}C chemical shift of benzene from external TMS is 128·0 ppm on this scale and that of carbon disulphide 193·1 ppm. The ^{15}N chemical shift of nitrobenzene is taken to equal -5 ppm from external NO$_3^-$.

In a typical experiment a 0·5 g diazoaminobenzene sample was dissolved in 3 ml of solvent, mostly cycloheptanone, although *n*-octanol, *n*-octyl iodide, aniline and N-dimethylaniline were also used. The sample was rapidly warmed up to the decomposition temperature, and both the polarisation kinetics and the polarisation pattern were registered, using a recorder and the above-mentioned CAT.

A typical thermal decomposition experiment of diazoaminobenzene in cycloheptanone gives the following products: gaseous nitrogen 13·9%; free aniline 9·5%; aniline as Schiff base 37·0%; diphenylamine 2·1%; diphenyl 1·3%; benzene 30·4%; other 4·7%. Some *p*- and possibly *o*-aminodiphenyl may also be formed, but was difficult to determine by GLC. The major part of aniline formed is converted to the Schiff base in a secondary reaction with the cycloheptanone solvent.

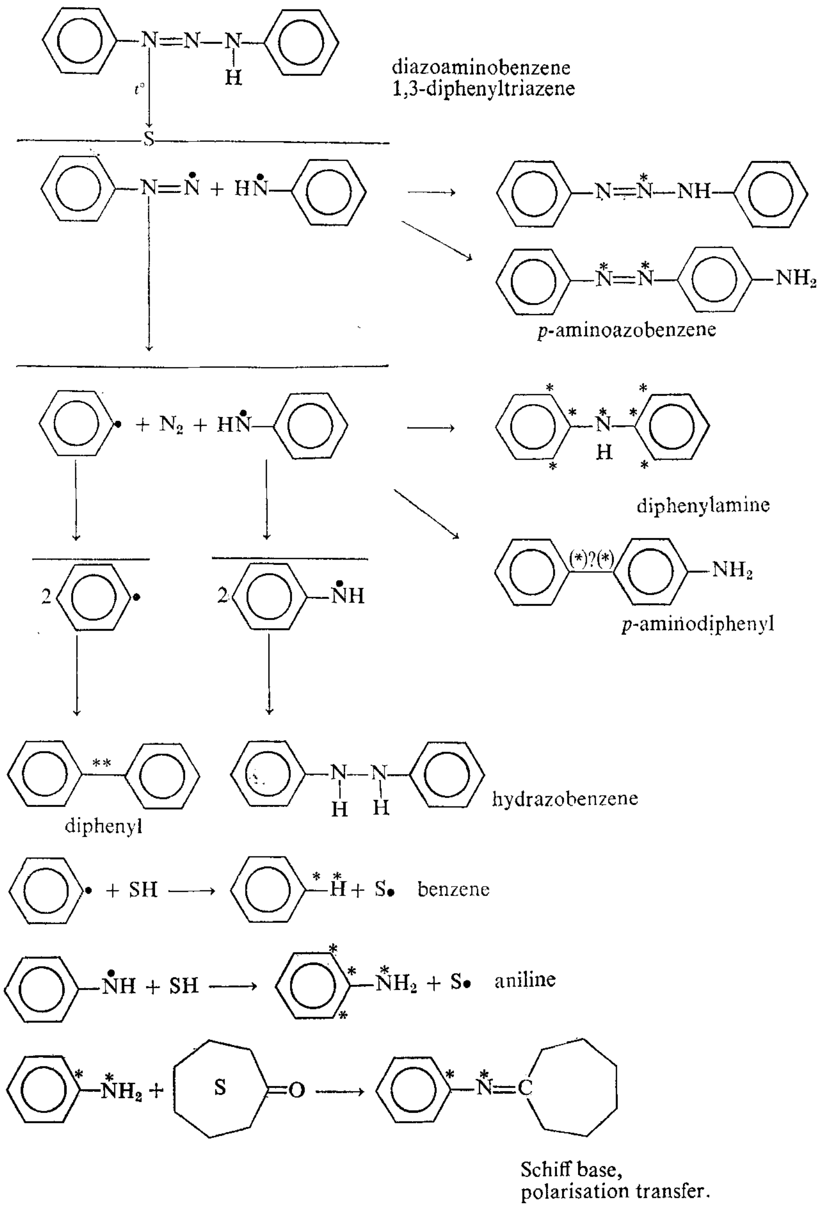
RESULTS AND DISCUSSION

The decomposition reaction sequence, including the formation of at least two different cage radical pairs, regeneration of polarised diazoaminobenzene, formation of cage recombination products and hydrogen abstraction reactions with the solvent, is shown in Scheme 1.

While only polarised benzene has been reported[4] in the proton spectrum of the diazoaminobenzene decomposition reaction, the ^{13}C spectrum also reveals the presence of polarised aniline, diphenylamine and diphenyl[2] (or *p*-aminodiphenyl), and the ^{15}N-CIDNP spectrum makes the presence of small amounts of polarised *p*-aminoazobenzene very probable. In the ^{13}C NMR spectrum (see Fig. 4) both C-1 and C-2, 6 of aniline and diphenylamine are polarised. The C-1 polarisations of aniline and diphenylamine have opposite signs in accordance with their different formation in a hydrogen abstraction and a cage recombination reaction, respectively. Some of the C-1 polarisation in aniline is carried over to the Schiff base in a secondary reaction with the cycloheptanone solvent, giving a weak emission line at 151·8 ppm. Benzene gives a strong emission line at 128·0 ppm that is replaced by the iodobenzene emission lines if the decomposition is carried out in *n*-octyl iodide. The presence of alkyl iodide does not cause any other significant changes in the polarised spectrum (see Fig. 5).

A full interpretation of the polarised ^{13}C spectrum is difficult because of the presence of many closely-spaced lines with shift differences well in the range of possible solvent shifts and temperature effects. A list of the observed lines is given in Table 1 and ^{13}C chemical shifts of the possible decomposition products are shown in Table 2.

Only the benzene line and the two most diamagnetic lines of the ^{13}C spectrum give doublets in a single resonance spectrum, and thus must correspond to CH-groups. All the other lines remain singlets and must therefore correspond to carbons that do not carry hydrogen atoms. This simplifies the difficult line assignment, but some ambiguity nevertheless remains. It is immediately clear that no ^{13}C polarisation appears in the parent compound, diazoaminobenzene itself. The assignment of some lines, such as C-1 of aniline is unambiguous, because of the very characteristic ^{13}C shift value of this singlet line and the fact that the nitrogen atom in aniline is also very strongly polarised (see Fig. 6). By analogy with the dibenzoyl peroxide



SCHEME 1

decomposition,[3] the strongly polarised line at 141·7 ppm can be assigned to the central atoms of diphenyl. The 0·2 ppm experimental shift difference may easily be caused by solvent and temperature effects. C-1′ in *p*-aminodiphenyl is a much less likely choice, especially since C-1 in the same compound is not polarised. The line at 144·4 ppm belongs to the central carbon atoms of diphenylamine. The ^{13}C chemical shift coincides exactly with the expected value and just as in the case of aniline, the central nitrogen atom in diphenylamine is also polarised (see Fig. 6). The third peak in the group of three lines with strongly enhanced absorption in the carbon spectrum is difficult to assign. The ^{13}C shift value, 139·6 ppm, does not coincide with any values listed in Table 2. The mechanistic origin of this singlet line must also be different. In contrast to those at 141·7 ppm and 144·4 ppm, it reverses its sign during diazoaminobenzene decomposition in aniline, but shows enhanced absorption just as the other two in dimethylaniline, cycloheptanone, *n*-octyl alcohol and *n*-octyl iodide. The line corresponds to a $>\overset{*}{C}—C$ or $>\overset{*}{C}—N$ type of carbon in a compound that must be structurally related to aniline.

TABLE 1. ^{13}C CIDNP IN THE THERMAL DECOMPOSITION OF DIAZOAMINOBENZENE IN CYCLOHEPTANONE AT 170°C

^{13}C chemical shift, ppm		Signal multiplicity in the ^{13}C single resonance spectrum[a]	Assignment	Polarisation		
from ext. TMS	from ext. CS_2			sign	T_1 s[b]	calculated polarisation coefficient *E*
151·8	41·3	s	Schiff base C-1	E		
147·5	45·6	s	Aniline C-1	E		
147·0	46·1	d, v.w.	?	A		
144·4	48·7	s	Diphenylamine C-1, C-1′	A	53	28000
141·7	51·4	s	Diphenyl C-1, C-1′	A	60	20000
139·6	53·5	s	?	A		
130·8	62·3	s, w.	?	E		
128·0	65·1	d	Benzene	E		
117·5	75·6	d	Diphenylamine C-2, 6	A		
114·9	78·2	d	Aniline C-2, 6	A		

[a] s—singlet, d—doublet, v.w.—very weak.
[b] at 170°C in cycloheptanone.

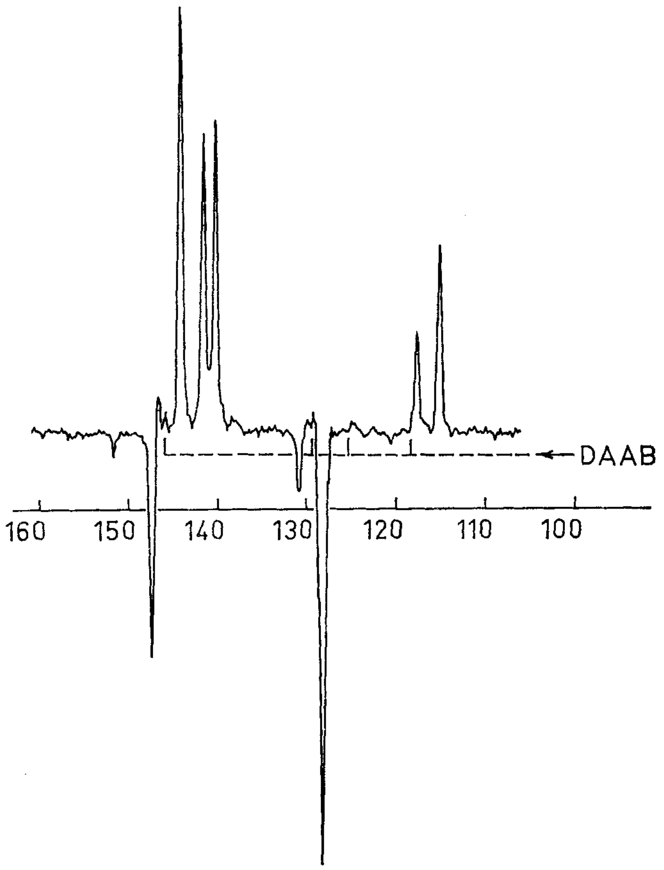
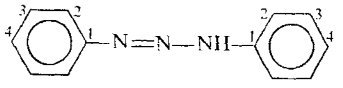
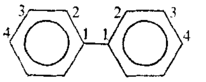
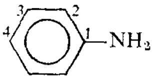
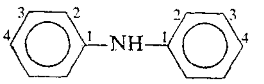
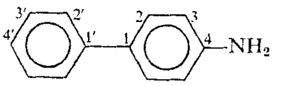
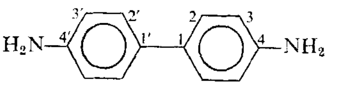
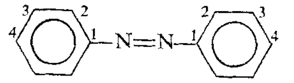
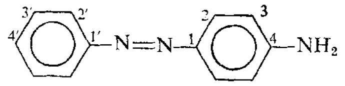


FIG. 4. ^{13}C CIDNP during the thermal decomposition of 1·0 g of diazoaminobenzene in 3 ml of cycloheptanone at 170°C. Accumulated double resonance spectrum.

FIG. 5. ^{13}C CIDNP during the thermal decomposition of diazoaminobenzene. (A) in *n*-octyl alcohol; (B) in *n*-octyl iodide.

TABLE 2. ^{13}C CHEMICAL SHIFTS OF SOME POSSIBLE DIAZOAMINOBENZENE DECOMPOSITION PRODUCTS (AT 160° AND 170°C IN CYCLOHEPTANONE)

Compound	^{13}C chemical shifts[a]				
	C-1	C-2,6	C-3,5	C-4	Remarks
	146·0 s	117·9 d	128·9 d	124·7 d	
	128·0 d				
	141·5 s	127·0 d	128·5 d	127·0 d	
	147·6 s	115·0 d	128·8 d	117·6 d	
	144·4 s	118·4 d	129·1 d	120·8 d	
	131·6 s 141·1 s	127·8 d 126·1 d	115·2 d 128·6 d	145·6 s 126·1 d	C1-6 C1′-6′
	131·7 s	127·1 d	115·8 d	146·1 s	
	153·1 s	122·6 d	128·8 d	130·5 d	
	151·0 s 153·7 s	124·9 d 122·3 d	114·7 d 128·8 d	145·6 s 129·2 d	C1-6 C1′-6′

[a] In ppm downfield from external TMS.

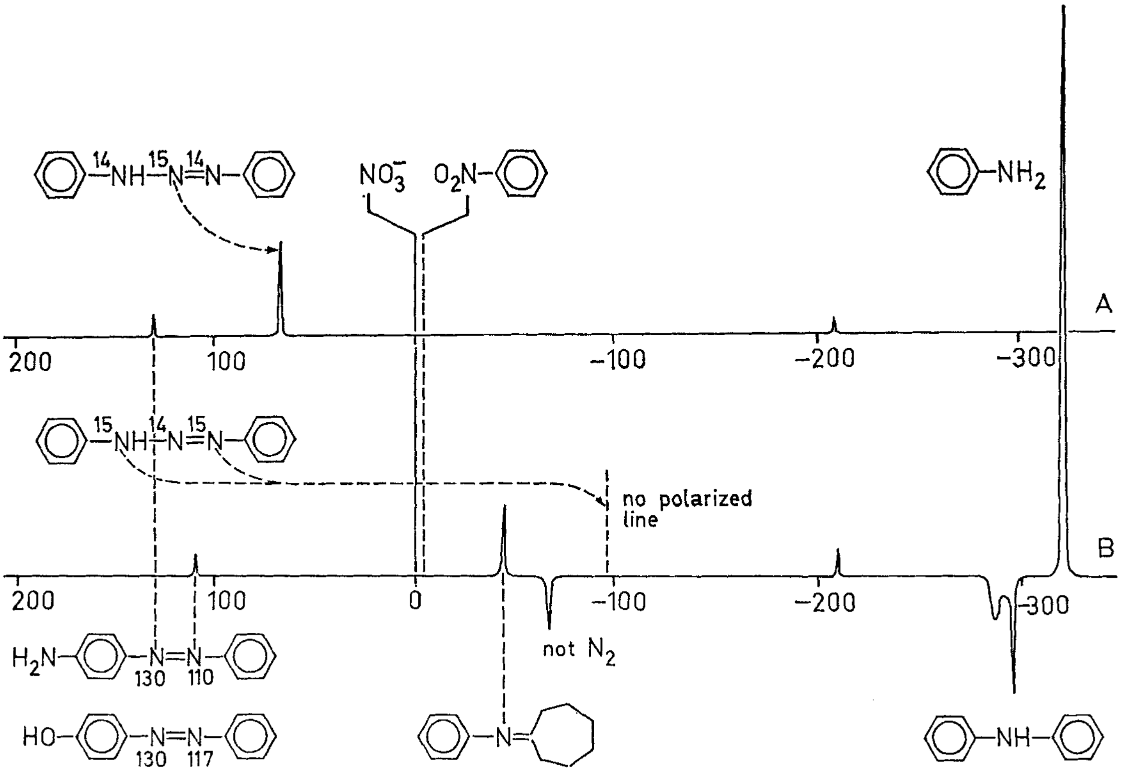


FIG. 6. ^{15}N CIDNP during the thermal decomposition of ^{15}N-enriched diazoaminobenzene in cycloheptanone at 170°C. Accumulated single resonance spectra. (A) Ph—^{14}NH—^{15}N=^{14}N—Ph; (B) Ph—^{15}NH—^{14}N=^{15}N—Ph.

The assignment of the doublet lines at high field is fairly straightforward. The line at 117·5 ppm corresponds to C-2,6 in diphenylamine. The 0·9 ppm deviation from the expected 118·4 ppm is rather large, but may be caused by some accidental noise peak, incomplete decoupling, etc. Some confirmation of this assignment is provided by experiments in other solvents, where this difference is smaller (0·1 ppm in *n*-octanol and 0·2 ppm in aniline). The line at 114·9 ppm corresponds to C-2,6 in aniline. The shift value coincides almost exactly with that of pure aniline. The difference is <0·1 ppm in cycloheptanone and 0·17 ppm in *n*-octanol.

The calculated ^{13}C nuclear polarisation coefficients E are very high, of the order of 20000 to 30000 for the fully substituted central carbon atoms in diphenyl and diphenylamine. The net polarisation of the C-2,6 doublets is somewhat less, and no polarisation could be detected for the *m*- and *p*-carbons in these compounds. These two polarised doublets and the benzene doublet also show multiplet effects superimposed upon the net polarisation, E/A for benzene, E/A for C-2,6 diphenylamine and A/E for C-2,6 in aniline. The general ^{13}C polarisation pattern is in agreement with the proposed decomposition scheme, but at present too many lines remain unassigned for meaningful quantitative calculations. Additional information is of course provided by the ^{15}N polarisation experiments.

0·5 g labelled samples of diazoaminobenzene with 44% of ^{15}N in either the central or the adjacent 1,3-positions were used for the experiments with ^{15}N chemical polarisation. Cycloheptanone was used as the solvent and the decomposition temperature was 170°C. The general ^{15}N polarisation pattern is shown in Fig. 6 and the accumulated ^{15}N CIDNP spectra in Fig. 7. A list of the observed polarised ^{15}N lines is given in Table 3 and nitrogen chemical shifts of the possible decomposition products in the following Table 4.

It is immediately clear that the most intense polarised lines in the ^{15}N spectrum result from the compounds that were also strongly polarised in the ^{13}C spectrum, namely aniline and diphenylamine.

TABLE 3. ^{15}N CIDNP IN THE THERMAL DECOMPOSITION OF LABELLED DIAZOAMINOBENZENE IN CYCLOHEPTANONE AT 170°C

^{15}N chemical shift[a]	Assignment	Polarisation sign	T_1 s	calculated polarisation coefficient E
−322	Aniline	A	60[b]	10000[c]
−296	Diphenylamine	E		
−282	?	E		
(−208)	?	A		
−65	? (not N_2)	E		
−44	Schiff base	A		
68	Diazoaminobenzene N-2	A		
110	Aminoazobenzene	A		
131	Aminoazobenzene	A		

[a] In ppm downfield from external aqueous NO_3^-.

[b] see Ref. 5.

[c] Reaction rate constant was determined from the ^{13}C data (see Fig. 1).

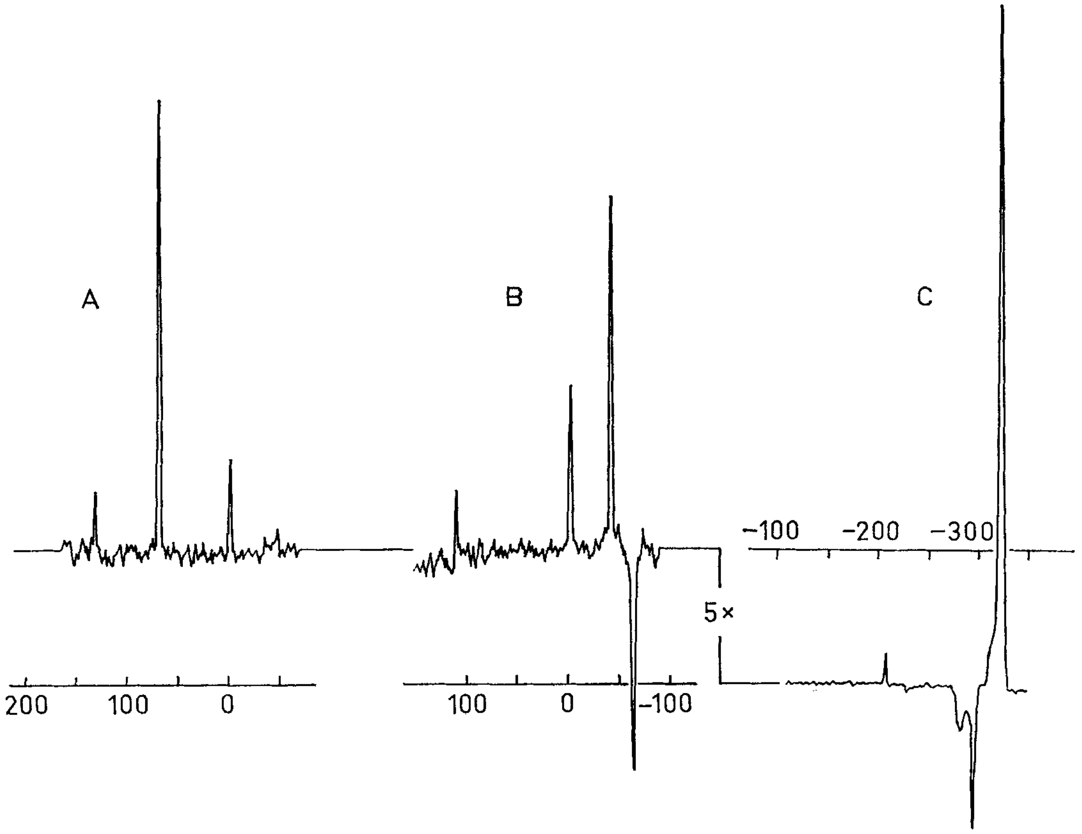


FIG. 7. ^{15}N CIDNP during the thermal decomposition of ^{15}N-enriched diazoaminobenzene in cycloheptanone at 170°C. Accumulated single resonance spectra, measured with nitrobenzene reference at −5 ppm. (A) Ph—^{14}NH—^{15}N=^{14}N—Ph; (B) Ph—^{15}NH—^{14}N=^{15}N—Ph; (C) Ph—^{15}NH—^{14}N=^{15}N—Ph.

TABLE 4. ^{15}N CHEMICAL SHIFTS OF SOME POSSIBLE DIAZOAMINOBENZENE DECOMPOSITION PRODUCTS AND THEIR ANALOGUES (IN CYCLOHEPTANONE)

Compound	Temperature °C	^{15}N chemical shifts[a] N-1	N-2	N-3
Nitrobenzene	40	−4·3		
	170	−3·8		
Diazoaminobenzene	40	−96·5	65·6	−96·5
	70		65·6	
	107	−96·0	66·1	−96·0
	128		67·1	
	150	−93·9	68·0[b]	−93·9
Aniline		−322		
Diphenylamine[c]		−290		
Nitrogen gas[d]		−70		
p-Hydroxyazobenzene[e]	35	130	117	

[a] From external aqueous NO_3^- or at higher temperatures from the secondary standard, external nitrobenzene. The ^{15}N chemical shift of nitrobenzene is remarkably constant and changes only by 0·5 ppm to low field if the sample temperature is raised from 40°C to 170°C.

[b] Slow decomposition without significant polarisation.

[c] Determined from ^{14}N spectra, ±10 ppm.

[d] $^{15}N_2$ gas at about 20 atm pressure.

[e] In water, N-1 adjacent to the phenol ring.

The calculated nitrogen ^{15}N polarisation coefficient $E \approx 10000$ in aniline and is certainly higher in diphenylamine, where the exact value could not be calculated because of the difficulties with line assignment. The line at −296 ppm is the most probable one but the other at −282 ppm is also possible because of the very inaccurate nitrogen shift determination from ^{14}N spectra. The enhanced absorption line at −44 ppm corresponds to the Schiff base that is formed from the polarised aniline and the cycloheptanone solvent in a secondary reaction. Contrary to our preliminary assignment,[2] the ^{15}N emission signal at −65 ppm does not belong to polarised molecular nitrogen and must at present be left unassigned. A rapid helium or argon flow through the sample during the reaction had no effect on the signal intensity as it should if it were caused by an evolving gas. In a similar experiment with dibenzoyl peroxide at 110°C both the polarised CO_2 and even the benzene line could be eliminated by a moderate helium flow. The enhanced absorption line at 68 ppm from aqueous NO_3^- has a very high probability of being caused by the initial diazobenzene itself. The chemical shifts of the polarised line and that of N-2 in diazobenzene measured under the same conditions coincide exactly. Polarisation of the initial material is usual in reactions where any compound undergoes a reversible free radical decomposition reaction accompanied by some other parallel and irreversible free radical reactions. If the polarised ^{15}N line at 68 ppm can indeed be assigned to the initial compound, then the free radicals that still contain two nitrogen atoms and are formed in the thermal decomposition of diazoaminobenzene and in the decomposition of benzenediazonium fluoborate at high pH, must be very different. In the case of the diazo compounds C-1, N-1 and N-2 are all about equally polarised, showing that there must be significant delocalisation in the possible intermediate radical Ph—N═N—O•, but in the diazoaminobenzene decomposition reaction only one nitrogen is strongly polarised. No polarised line could be detected in the vicinity of −96 ppm or in the ^{13}C spectra. Since only the Ph—N═N• radical can be formed in this case, it must be a σ-radical with very unequal hyperfine coupling constants to the two nitrogen atoms.

The two comparatively weak polarised ^{15}N absorption lines at 110 ppm and 131 ppm may be caused by *p*-aminoazobenzene, the rearrangement product of diazoaminobenzene. The nitrogen shifts of this compound have not been measured, but the ^{15}N shifts of *p*-hydroxyazobenzene (see Table 4) are so close to the observed values that little doubt remains about this assignment. No ^{15}N lines can be detected in this shift range in the diamagnetic reaction product and so only a minute amount of this compound must be involved.

The general pattern of ^{15}N polarisation agrees with that of ^{13}C and with the proposed reaction scheme. At the same time ^{15}N CIDNP is a welcome addition to both ^{1}H and ^{13}C CIDNP. Both the possible diazoaminobenzene polarisation and the formation of a very small amount of polarised *p*-aminoazobenzene could be detected only by this method. It is also important to note that ^{15}N CIDNP is not confined to enriched compounds only. Figure 8 shows the ^{15}N line of polarised aniline, formed in the thermal decomposition of unlabelled diazoaminobenzene with natural abundance of all nuclei.

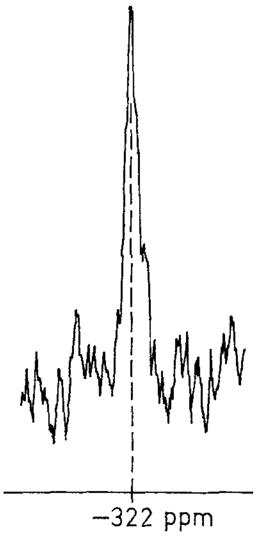


FIG. 8. ^{15}N CIDNP at natural abundance. Polarisation of the aniline —NH_2 signal in the thermal decomposition of diazoaminobenzene. Enhanced absorption signal, accumulated during 10 successive decompositions of 0·5 g DAAB in 3 ml of cycloheptanone.

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