Low-field Photochemically Induced Dynamic Nuclear Polarization (Photo-CIDNP) of Diazanaphthalenes

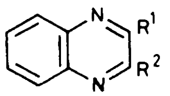
Gaston Vermeersch,* Jean Marko, and Nadine Febvay-Garot
Laboratoire de Biophysique, Faculté de Pharmacie, Université de Lille II, 59045 Lille Cedex, France
Serge Caplain and Alain Lablache-Combier
Laboratoire de Chimie Organique Physique, L.A.C.N.R.S. 351, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France

Photoreduction of some diazanaphthalenes in proton-donor solvents has been investigated by means of chemically induced dynamic nuclear polarization (CIDNP). While very few polarizations are observed during irradiation in a high magnetic field, CIDNP spectra recorded after the samples have been irradiated in a weak magnetic field demonstrate strong polarizations due to the solvent and the starting compounds. Polarizations due to addition products are also observed. Using the Den Hollander rule for low magnetic fields we affirmed that the principal radical pair of the photoreaction is formed by the abstraction of a hydrogen atom of the solvent by the nitrogen heterocycles excited in the triplet state. The validity of our results was then confirmed by a study of the photoreduction of acridine in a weak field using the experimental procedures described.

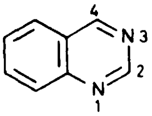
In a previous publication[1] we reported studies of the variation of the photochemical behaviour of various quinoxalines as a function of the solvent. Our CIDNP results also showed that the polarizations observed in proton-donor solvents can be basically explained by the radical pair mechanism. As in the case of acridine,[2] the origin of these polarizations seems to be the photoreduction of quinoxalines by alcohols.

In order to verify this hypothesis, we have undertaken a study of the photoreduction of several diazanaphthalenes [quinoxaline (**1**), 2-methylquinoxaline (**2**), 2,3-dimethylquinoxaline (**3**), quinazoline (**4**), phthalazine (**5**), and cinnoline (**6**)] using the CIDNP technique.

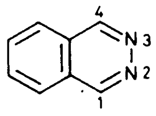
Numerous chemical and spectroscopic studies of these compounds have shown that, in every case, photosubstitution products are formed in the presence of proton-donor solvents.[3] Addition products are often formed simultaneously during these reactions. The substitution products generally derive from the unstable addition products which are self-aromatizing. Numerous e.s.r. studies have demonstrated that the photochemical reactions of most of these nitrogen heterocycles occur with the same radical intermediate, the neutral NH semiquinone radical.[4] In addition, recent work published by McLauchlan[5] has both confirmed the existence of these radicals and demonstrated the presence of chemically induced electron polarizations during the irradiation of four diazanaphthalenes in the presence of various quenchers.



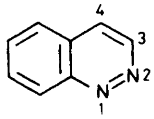
(**1**) $R^1 = R^2 = H$
(**2**) $R^1 = CH_3$, $R^2 = H$
(**3**) $R^1 = R^2 = CH_3$



(**4**)



(**5**)



(**6**)

Experimental

High-field Photo-CIDNP Experiments.—CIDNP spectra were run on a Bruker WP 80 W.G. n.m.r. spectrometer operating in the Fourier transform mode at 1.88 T. The CIDNP probe is commercially available from Bruker. A silica light pipe (length 500 mm, diameter 8 mm) leads the full emission spectrum of the collimated beam of a high-pressure Xe–Hg short arc lamp (Oriel; 1 000 W) to the level of the detection coil.

Low-field Photo-CIDNP Experiments.—For the experiments in a weak magnetic field (30 G), the n.m.r. sample tube was irradiated in an auxiliary electromagnet located near the n.m.r. spectrometer (JEOL C 60 H.L.). The light source was a high-pressure mercury lamp (Philips SP; 1 000 W). The light beam was directly focused, by a quartz condenser (*f* 75 mm), onto the tube located between the magnetic poles. The rotating samples, irradiated for 60 s, were subsequently transferred by hand to the probe of the spectrometer. Recording began 5 s after the end of the irradiation. The main problem posed by this routine was the rapid relaxation of the polarized species. For this reason, in order to record the entire CIDNP spectrum (δ 0—10), we had to pass by successive recordings of 0.5—1 p.p.m. width which were then used to construct a complete low-field spectrum. The direction of polarization (A or E) is determined by comparing the same spectral region recorded 45 s after the sample insertion into the probe (*i.e.*, after the polarized species are totally relaxed).

The various diazanaphthalenes were Merck-Schuchardt products and were used without further purification.

Results and Discussion

High-field Experiments.—We irradiated compounds (**1**)—(**6**) in deuteriated methanol solutions. The observed polarizations are presented in Table 1. One can note that in all cases, except (**6**), the principal polarizations are due to the initial diazanaphthalenes and, except for (**4**), we were unable to detect polarizations caused by the formation of an addition product of the solvent with these compounds. The spectrum obtained during irradiation of (**4**) in [$^2H_4$]methanol contains a pattern of three emission lines at δ 4.7 and another emission pattern at δ 6.54. According to the observed chemical shifts, two of the emission

Table 1. Polarizations observed during irradiation of (**1**)—(**6**) in [$^2H_4$]methanol in a high magnetic field (spectrometer field): A, absorption; E, emission; s, singlet

Compound	Protons	Chemical shift δ	Polarization
(**1**)	H(2), H(3)	8.87	s, E
(**2**)	H(2)	8.85	s, E
	CH_3	2.75	s, A
(**3**)	CH_3	2.70	s, A weak
(**4**)	H(2)	9.40	s, A
	H(4)	9.17	s, E
		6.54	E (pattern)
		4.70	E (pattern)
		9.64	s, E
(**5**)	H(1), H(4)	9.62	s, E
(**6**)			No polarization

lines of the first pattern could correspond to solvent-addition products in positions 2 and 4, while the third high-field line might correspond to 1,2- or 1,4-dihydroquinazoline. The second pattern at δ 6.54 can be assigned to the proton of the NH group of these different compounds. It is difficult to assign these resonances unambiguously because the dihydro products which give rise to these lines are very unstable and have practically never been isolated, at least in the case of methanol and quinazoline.

During irradiation of these compounds in ethanol, we subsequently detected the same polarizations as those obtained in the aromatic part of the spectrum in the case of [$^2H_4$]methanol, as well as a first-order quadruplet near δ 9.7 for the formyl proton of acetaldehyde. Such results were obtained for all the diazanaphthalenes studied.

When using the WP 80 spectrometer in the pulse mode, we had to be very careful in exploiting the polarizations due to the multiplet effect. This effect is obtained for pulse angles of < 20°[6] but is cancelled for angles of 90° at which point only the net effect remains. Therefore we repeated the preceding experiments in ethanol using two different pulse angles. For an angle of 15° we obtained an A/E (absorption/emission) multiplet effect while for an angle of 90° we observed no net polarization for the quadruplet of acetaldehyde. Such a result, as in the case of acridine, affirms the participation in the photochemical reaction of a radical $R^\bullet$ derived from the solvent.

The few results obtained for these compounds in alcohols at high field do not enable us to propose a complete reaction path. However, we can already state that the principal pair is created by the abstraction of a hydrogen atom from the solvent by the excited diazanaphthalene. This explanation is suggested by our observation of the polarization of acetaldehyde when the photoreaction occurs in ethanol. Accordingly, by application of the Kaptein rule for the multiplet effect,[7] the A/E phase allows us to affirm that the acetaldehyde is formed by dismutation of the radical pair $\overline{R^\bullet\,R^\bullet}^{F}$ (with $R^\bullet = CH_3\dot{C}HOH$, $a_{H_\beta} > 0$ $a_{H_\alpha} < 0$,[8] $J_{\alpha\beta} > 0$, and $\sigma_{ij} > 0$, A/E→$\Gamma_m < 0$; therefore $\mu\varepsilon$ must be > 0 corresponding to $\mu > 0$, thus an F pair and $\varepsilon > 0$ which corresponds to a cage product).

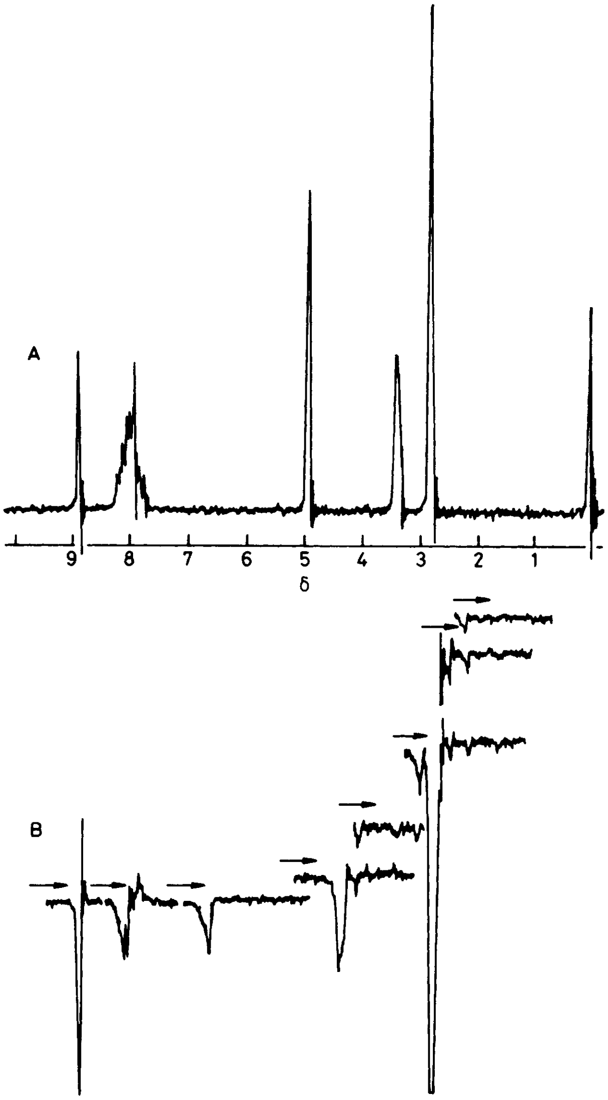


Figure 1. ^1H N.m.r. spectra of (**2**) in deuteriated methanol: A, before irradiation; B, after irradiation in a magnetic field of 30 G

Low-field Experiments.—In a previous paper where we studied the influence of the magnetic field on the intensities of the CIDNP polarizations,[1] we showed that these polarizations pass by a maximum near 30 G when the irradiation is carried out in a proton-donor solvent. Therefore we decided to complement the scanty results of the previous section with low-field CIDNP measurements. Compounds (**1**)—(**6**) were irradiated in solution in [$^2H_4$]methanol in a magnetic field of 30 G from an auxiliary magnet.

In Figure 1, we have presented an example of a reconstructed spectrum obtained of the sample after its transfer to the spectrometer. (The arrows indicate both the beginning of the recording and direction of the scan.) The observed polarizations are presented in Table 2 and the results are much more interesting than those obtained for samples irradiated in the spectrometer. In every case we can identify polarizations due to the initial diazanaphthalenes which are much stronger than those observed in high field. In the case of (**6**), we even observe polarizations which are not evident at high field. Moreover, one notes that the protonated part of the deuteriated solvent (CHD_2OD, CH_2DOD, CD_3OH) yields equally strong emissions in all cases. These polarizations, arising from the solvent, prove unambiguously that the solvent intervenes in the form of a radical ($\dot{C}D_2OH$, $\dot{C}DHOD$, $\dot{C}H_2OD$) in this photochemical reaction.

In addition, for compounds (**1**)—(**4**), we observed additional polarizations, namely an emission pattern at δ 6.5 for (**1**)—(**3**) and at δ 7 for (**4**) which can be assigned to the NH groups of the

Table 2. Assignments of CIDNP signals observed during irradiation of (**1**)—(**6**) in deuteriated methanol in a weak magnetic field (30 G): A, absorption; E, emission; s, singlet; p, pattern; d doublet

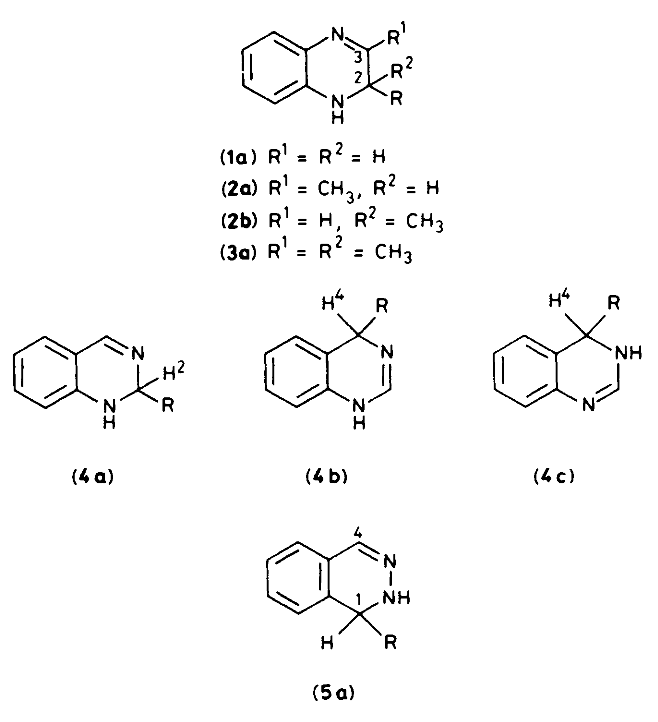
Compound	Observed polarizations	Assignments	
(**1**)	δ 9, s, A	H(2), H(3)	(**1**)
	δ 8, p, A	aromatic protons	
	δ 6.5, p, E		
	δ 4.5, s, E	OH (solvent)	
	δ 4.4, s, E		
	δ 3.35, p, E	$CHD_2 + CH_2D$ (solvent)	
(**2**)	δ 8.8, s, E	H(2)	(**2**)
	δ 8, p, E	aromatic protons	
	δ 6.6, p, E		
	δ 4.3, s, E	OH (solvent)	
	δ 4, s, E		
	δ 3.35, p, E	$CH_2D + CD_2H$ (solvent)	
	δ 2.75, s, E	CH_3 (**2**)	
	δ 2.15, s, E		
(**3**)	δ 7.9, p, E	aromatic protons (**3**)	
	δ 6.5, p, E		
	δ 4.5, s, E	OH (solvent)	
	δ 3.35, p, E	$CH_2D + CHD_2$ (solvent)	
	δ 2.7, s, E	CH_3 (**3**)	
(**4**)	δ 9.6 s, E	H(2)	(**4**)
	δ 9.3, s, E	H(4)	
	δ 8, p, E	aromatic protons	
	δ 7, p, E		
	δ 4.8, s, E		
	δ 4.5, s, E	OH (solvent)	
	δ 3.35, s, E	$CH_2D + CHD_2$ (solvent)	
(**5**)	δ 9.6, s, E	H(1), H(4)	(**5**)
	δ 8.1, p, E	aromatic protons	
	δ 4.6, s, E	OH (solvent)	
	δ 4.55 s, E		
	δ 3.35, p, E	$CH_2D + CHD_2$ (solvent)	
(**6**)	δ 9.4, d, E	H(3)	(**6**)
	δ 8.2, p, E	aromatic protons	
	δ 4.5, s, E	OH (solvent)	
	δ 3.35, p, E	$CH_2D + CHD_2$ (solvent)	

addition products, whose probable structures are presented in Scheme 1.

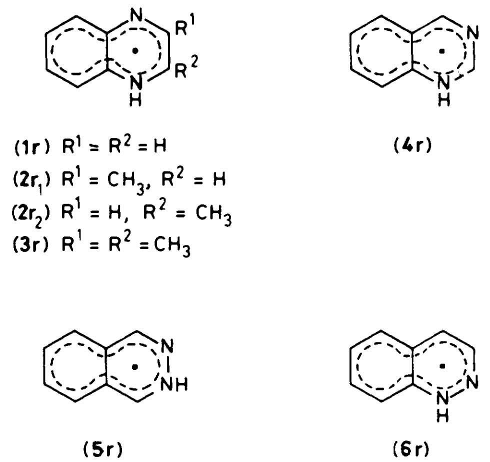
On considering these structures, we can assign the remaining polarizations as follows: H(2) of (**1a**) at δ 4.4 (E), H(2) of (**2a**) at δ 4.0 (E), CH_3 of (**2b**) at δ 2.15 (E), H(2) of (**4a**) or H(4) of (**4b**) or H(4) of (**4c**) at δ 4.8 (E), H(1) of (**5a**) at δ 4.55 (E). The values of the observed chemical shifts correspond to those calculated by incrementation.

Our results lead us to the conclusion that the photochemical reaction of diazanaphthalenes in alcohol occurs because of the presence of a radical pair which is formed, as with acridine, by hydrogen-atom abstraction from the solvent by the excited diazanaphthalenes. The radicals resulting from these products are shown in Scheme 2. All of these radicals except (**6r**) were detected by e.s.r. during the irradiation of these diazanaphthalenes in a glassy matrix of $[^2H_4]$methanol, and their parameters (*g* factors and spin densities) were determined.[4] In the case of quinazoline, the CIDEP experiments[5b] proved the existence of a semiquinone-type radical [like (**4r**)]. However it was not possible to identify unambiguously the nitrogen atom to which the hydrogen is attached. For the other diazanaphthalenes electronic polarizations were observed for the radicals (**1r**), (**5r**), and (**6r**).

At this point one is ready to try to determine the multiplicity of the radical pair using the Den Hollander rule for weak fields.[9] This rule, which is very similar to the Kaptein rule for the net effect, can be stated as $\Gamma = \mu\varepsilon a_i$ ($\Gamma > 0$, absorption; $\Gamma < 0$, emission). The parameters μ, ε, and a_i are defined in the same way as for the Kaptein rules.[7]



Scheme 1.



Scheme 2.

If we consider the emission of the various adducts mentioned above, then for $\mu\varepsilon a_i < 0$ with $a_i < 0$,[4] we have $\mu\varepsilon > 0$. In addition, the formation of these adducts arises from recombination in the main radical pair ($\varepsilon > 0$); thus this pair is formed in a triplet state ($\mu > 0$).

This result agrees quite well both with those obtained from our CIDNP study on quinoxalines as a function of the magnetic field,[1] and with the CIDEP data published by McLauchlan.[5] In this latter work, the observed electronic polarizations can be explained both by the radical pair and by the triplet mechanism. The one exception is for phthalazine for which only the radical pair mechanism is efficient. It might seem surprising that we did not use the intervention of the triplet mechanism in the analysis of the polarizations reported in this article. But our experiments

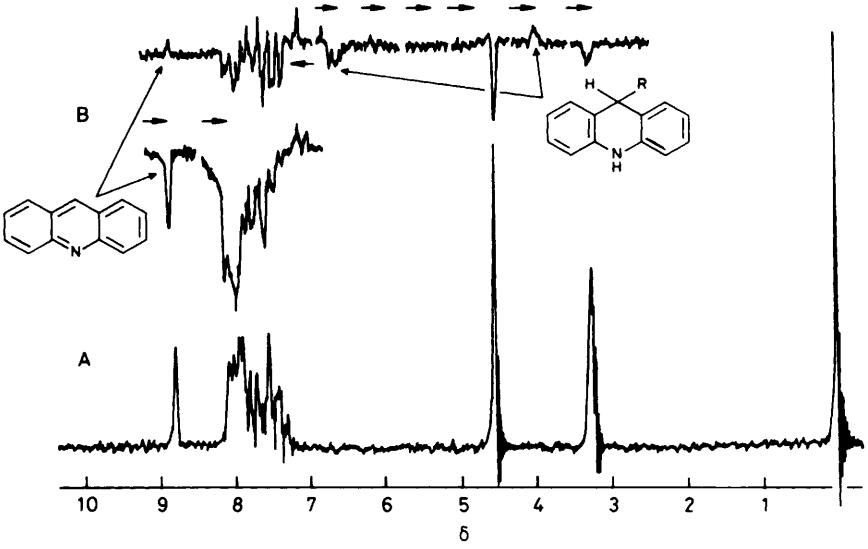


Figure 2. ^{1}H N.m.r. spectra of acridine in deuteriated methanol (see text)

were conducted in a weak magnetic field (30 G) and only the radical pair mechanism is efficient (mixing S–$T_{\pm}$) with such fields. In a previous publication we had already cited the intervention of the triplet mechanism during the irradiation of the various quinoxalines in proton-donor solvents.[1]

In order to confirm the information obtained from the low-field experiments, we repeated measurements of the photoreaction of acridine in methanol.[2]

In Figure 2 we have presented two spectra: the first (A) obtained before irradiation and the second (B) obtained after irradiation of the sample in a magnetic field of 30 G. Polarizations due to the solvent (E) are found as in the preceding cases. We note emissions for all the protons of acridine as well as an enhanced absorption for H(9) of the solvent adduct (δ 4). Special attention might be called to an emission pattern at δ 6.6 which corresponds to the NH group of the resulting acridanes. This last polarization has never been reported for high-field irradiations. The application of the Den Hollander rule for the polarizations observed for the acridine adduct (A) allows us to affirm that the main radical pair of the reaction occurs in a singlet state ($a_i < 0$,[10] $\varepsilon > 0$, $\Gamma n > 0$, thus $\mu < 0$). This conclusion is in agreement with those of experiments run in the spectrometer field.[2] In addition, this experiment has allowed us to verify the reliability of the experimental procedures we followed in the low-field experiments.

Hence we have definitely determined that the photoreduction of diazanaphthalenes in alcohols yields polarizations which can be interpreted perfectly well using the radical pair theory.

References

1 G. Vermeersch, J. Marko, N. Febvay-Garot, S. Caplain, and A. Lablache-Combier, *J. Chem. Soc., Perkin Trans. 2*, 1984, 43.

2 G. Vermeersch, N. Febvay-Garot, S. Caplain, and A. Lablache-Combier, (*a*) *Tetrahedron Lett.*, 1974, 3127; (*b*) *Tetrahedron*, 1975, **31**, 867.

3 For a revue see A. Lablache-Combier in 'Elements de Photochimie Avancée,' ed. P. Courtot, Hermann E.d., Paris, 1972, p. 289.

4 (*a*) A. Castellano, J. P. Catteau, A. Lablache-Combier, and B. Plankaert, *Tetrahedron*, 1972, **28**, 3511; (*b*) J. P. Catteau, Thesis, University of Lille, 1973; (*c*) A. Castellano, J. P. Catteau, A. Lablache-Combier, and B. Tinland *J. Chem. Res.* (*M*), 1979, 0901; (*d*) A. Castellano, Thesis, University of Lille, 1981.

5 (*a*) S. Basu, K. A. McLauchlan, and G. R. Sealy, *Chem. Phys. Lett.*, 1982, **88**, 1, 84; (*b*) S. Basu, K. A. McLauchlan, and A. J. D. Ritchie, *Chem. Phys.*, 1983, **79**, 95.

6 S. Schaublin, A. Wokaun, and E. E. Ernst, *J. Magn. Reson.*, 1977, **27**, 273.

7 R. Kaptein, *Chem. Commun.*, 1971, 732.

8 R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 3, 1245.

9 J. A. Den Hollander, Thesis, Leiden, 1976, p. 84.

10 A. Castellano, J. P. Catteau, A. Lablache-Combier, and G. Allan, *Can. J. Chem.*, 1973, **51**, 21, 3508.

Received 6*th February* 1984; *Paper* 4/200