Magnetic Field and Polarized Light Dependence of Chemically Induced Dynamic Nuclear Polarization (CIDNP) of Acridines and Quinoxalines in Various Solvents

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Acridine and quinoxalines exhibit nuclear polarizations during irradiation in various solvents. In order to elucidate the origin of these polarizations, we have studied the magnetic field and polarized light dependence of the nuclear polarizations in different solvents. The results are interpreted in terms of two different mechanisms. The effects observed in proton-donor solvents are ascribed to a radical-pair mechanism with contribution from what could be a triplet Overhauser mechanism. This last mechanism explains the polarizations observed in benzene solution.

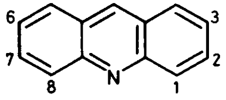
The photoreduction of acridine in alcohols and ethers is well known and polarizations obtained by CIDNP studies of this reaction are perfectly explained by the radical-pair theory.[1]

The same photoreduction process occurs during irradiation of quinoxalines in alcohols, as shown recently.[2] However, in both cases, the interpretation of the polarizations of the starting materials presents some difficulty. Furthermore these polarizations are the only ones which take place in the case of acridines [3] when biacetyl is used as sensitizer or when irradiation of acridine [4] and quinoxalines [5] is done in benzene or acetonitrile, no photoreduction occurring in these solvents. Similar observations were made with benz- and dibenzacridines.[3]

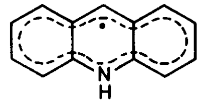
The radical-pair mechanism fails to interpret these polarizations as well as those mentioned by Bargon for quinones [6] and Kalibabchuk for phenazine.[7] Nevertheless they could be explained by a triplet Overhauser mechanism [8] as in the case of some other nuclear polarizations.[9] We have studied the magnetic field and polarized light dependence of these polarizations to verify this assumption. Indeed, as shown by Adrian,[10] these two factors are proof of the triplet Overhauser mechanism, if some experimental precautions are taken.

Roth [11] demonstrated that there is no relationship between nuclear spin polarization intensities and magnetic field strength, specifically since the observed effects may be composed of several independent contributions. So this magnetic-field dependence cannot be considered as the only criterion of the intervention of the triplet mechanism. However, it does provide valuable indications, when allied to other experimental tests. Similarly, on the basis of polarized light experiments, Roth [12] has also pointed out that a particular irradiation system must be used to avoid experimental artefacts.

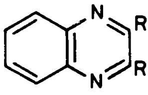
These conditions lead us to define a rigorous experimental procedure to study acridine (1), quinoxaline (2), 2-methylquinoxaline (3), and 2,3-dimethylquinoxaline (4).



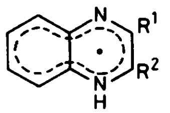
(1)



(1r)



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



(2r) $R^1 = R^2 = H$
(3r$_1$) $R^1 = CH_3$, $R^2 = H$
(3r$_2$) $R^1 = H$, $R^2 = CH_3$
(4r) $R^1 = R^2 = CH_3$

Experimental

For the field-dependent experiments, the n.m.r. sample tube was irradiated, while spinning for 60 s in an auxiliary electromagnet whose field can be varied, and transferred manually to a JEOL C-60 HL continuous wave n.m.r. spectrometer. We used a Philips SP 1000 high-pressure mercury lamp, whose beam was directly focused through a quartz lens (*f* 75 mm) on the sample. A saw-tooth unit always sweeping the same spectral width (0.25 p.p.m.) was used for recordings which started 5 s after the end of irradiation. We measured the polarization–time variation from a given signal. For each magnetic field value, we can compare the intensities of the signal after either transfer and irradiation or transfer without irradiation, which took into account the time necessary for probe tuning in putting the sample in the spectrometer. The difference between these two intensities gave the value of the polarization after the same transfer time.

For polarized-light experiments, we used the same experimental device. An Oriel far-u.v.–visible linear polarizer was put just behind the quartz lens.

The polarized beam fell on the n.m.r. sample tube after only crossing two interfaces (air–quartz and quartz–solvent) instead of the eight in the classical irradiation setting of spectrometers. Thus, the light intensity reaching the sample was practically the same (at *ca.* 2%) for light polarized perpendicular or parallel to the incident plane. The sample was irradiated for 45 s and then transferred manually to the n.m.r. probe. Recording started 5 s after the end of irradiation.

Acridine and the various diazanaphthalenes were Merck–Schuchardt products and were used without further purification.

Results and Discussion

Field-dependent Experiments.—We study polarizations of (1)—(4) for magnetic field values varying from 0 to 12 000 G either in alcohol (CD_3OD) or ether [dioxane for (1)] and in

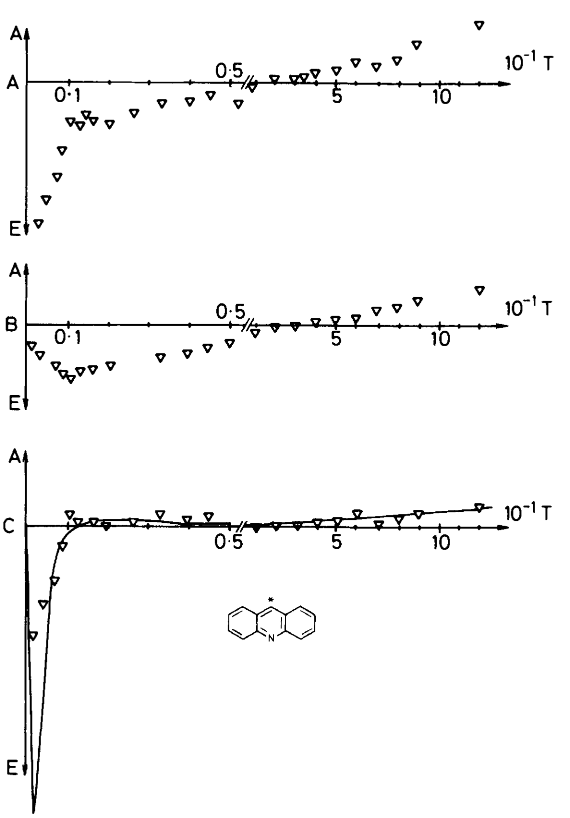


Figure 1. Polarization *versus* magnetic field: A, in the RH solvent; B, in deuteriated benzene; C, triangles represent the experimental difference A − B for a given field. The full curve represents computer calculations and has been scaled to the experimental points (an asterisk denotes the proton studied)

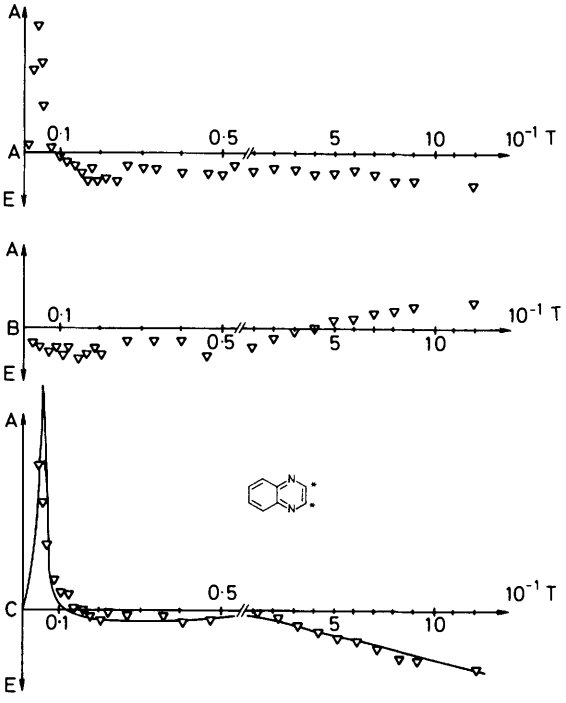


Figure 2. As Figure 1

deuteriated benzene. Only the most intense polarizations are of interest, *i.e.* 9-H of (1), 2- or 3-H of (2), 3-H and 2-Me of (3), 2- and 3-Me of (4). Figures 1 and 2 summarize our results in the case of (1) and (2). The main difference between the curves obtained in RH solvent and benzene is at very low-field values (between 0 and 200 G).

Indeed, a maximum polarization between 30 and 50 G is always observed with the RH solvent. In benzene, polarizations are weaker and the maximum is spread out by *ca.* 100 G for the aromatic protons and 40 G for methyl groups.

Similar curves are drawn when (2) is irradiated in CD_3OD, CH_3OH, or ethanol (different RH solvents) and also with degassed solutions in RH solvent as well as in deuteriated benzene.* To verify that the radical-pair theory explains the reactions in RH solvents, the theoretical curve is calculated according to a program developed by Kaptein and Den Hollander. All the nuclear spin-state polarizations of the protons of a product from a radical pair are determined by these calculations (diffusion model) for 27 values of the magnetic field.

As the number of protons in the radical pairs under study is very high, we only take into account those which possess the larger hyperfine coupling constants.[13] Thus we introduce a *J* value different from 0 and try to obtain a theoretical curve as close as possible to the experimental one (A) in the case of the RH solvent. No calculation gives a satisfying result. But when we take the difference between the experimental curves obtained with an RH solvent (A) and those with benzene (B), a plot of C = A − B exactly fits our calculations. Curves C are shown in Figures 1 and 2 in the case of (1) and (2). The input data are summarized in the Table.

The following remarks can be made.

(a) For acridine (1) irradiated in dioxane, 9-H polarization is explained by formation of acridine by diffusion from the singlet radical pair.

(b) For the diazanaphthalenes (2)—(4) irradiated in methanol, H and Me polarizations can be explained by the formation of these products by diffusion from a corresponding triplet radical pair. It must be noted that with 2-methylquinoxaline (3), two radicals can be involved in the reaction [($3r_1$) and ($3r_2$)]. The simulation curve is calculated by averaging the polarizations of each case.

(c) As the best interpretation of the experimental results involves the difference between A and B, it seems that two polarization mechanisms intervene in the reaction in an RH solvent, the radical-pair mechanism and another one which only occurs with benzene.

To verify this assumption, we study the photoreaction of acridine (1) in a particular alcohol, t-butyl alcohol, which does not possess hydrogen atoms easily abstractable by the excited acridine as in other alcohols. In this system, the radical-pair mechanism is supposed to be inoperative. We can summarize our results in the following manner. No polarization of acridine or adduct is detected in t-butyl or [$^2H_9$]t-butyl alcohol.† In degassed solutions, evidence is shown for strongly enhanced absorption for 9-H of (1).† When biacetyl is added to the solution and without previous degassing, only 9-H exhibits enhanced absorption.† We plot the curve of

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* This result seems to be inconsistent with those reported in ref. 4*b*. It only reveals that the optical device used transmits much more energy to the system than that in the C-60 HL spectrometer. Thus the excited intermediate species concentration is higher and less sensitive to the oxygen concentration in the solvent and only the appearance rate and the intensity of the polarizations are affected by degassing.

† These irradiations are carried out inside the spectrometer.[1]

Table. Input data used in computer simulations

Radicals	Acridine in dioxane (1r) and dioxanyl (α and β)	(2r)	(3r₁)	(2)—(4) in methanol (3r₂)	(4r)	$\dot{C}H_2OH$
Hyperfine coupling constants (rad s^{-1})	$a_{H_4} = a_{H_5} = -6.370 \times 10^7$ a_{H_9} -1.961×10^8 a_{NH} -6.250×10^7 a_{H_α} -3.060×10^8 a_{H_β} $+8.100 \times 10^8$	a_{H_2} -7.000×10^7 a_{H_3} -5.100×10^7 a_{NH} -1.355×10^8	a_{H_2} -0.824×10^8 a_{CH_3} 0.521×10^8 a_{NH} -1.350×10^8	a_{CH_3} 0.705×10^8 a_{H_3} -0.634×10^8 a_{NH} -1.233×10^8	$a_{(CH_3)_\alpha}$ 0.834×10^8 $a_{(CH_3)_\beta}$ 0.651×10^8 a_{NH} -1.224×10^8	a_{H_α} -3.222×10^8
g factor	2.0025 2.0036	2.0028	2.0028	2.0028	2.0028	2.0033
J (rad s^{-1})	3.000×10^8	4.200×10^8	-3.000×10^8	-3.000×10^8	-3.000×10^8	
Multiplicity of the pair	Singlet			Triplet		
Type of product	Escape			Escape		

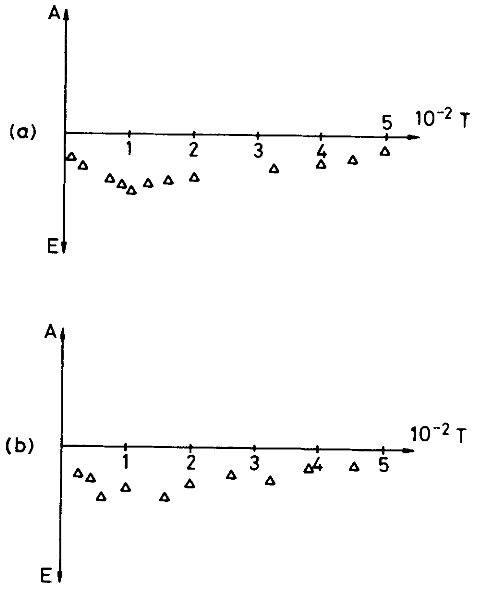

Figure 3. Polarization of 1-H of (1) *versus* magnetic field: (a) in deuteriated benzene; (b) in t-butyl alcohol

polarization *versus* magnetic field values for 0—500 G for the t-butyl alcohol–acridine system. The results are quite similar to those obtained for the C_6D_6–acridine system (Figure 3). So we can conclude that the only mechanism operating in t-butyl alcohol is the same as in benzene. This could be the triplet mechanism as we tried to demonstrate it by polarized-light experiments.

Polarized-light Experiments.—We only study the strongest polarizations which occur principally at low field, as seen above, *i.e.* at 100 G for 2-H of (2) and 30 G for methyl of (3). The products are irradiated in [$^2H_4$]methanol and then in [$^2H_6$]benzene to establish the participation of the triplet mechanism in each case.

The following remarks can be made. In [$^2H_4$]methanol the polarization intensities for 2-H of (2) and methyl of (3) are not significantly modified by the orientation of the incident light plane of polarization. On the other hand, similar experiments in [$^2H_6$]benzene show a 10% weaker polarization for 2-H of (2) when the electric vector E of the exciting light is perpendicular to the magnetic field B than when E is parallel to B. The same result is obtained for methyl of (3), but with a 15% decrease. So, in both cases $P_\parallel$ (polarization when E is parallel to B) is higher than $P_\perp$ (polarization when E is perpendicular to B). Some signals in C_6D_6 are presented in Figure 4.

Several interesting conclusions proceed from these results. First, the experimental set-up seems to be valid since a significant difference is seen in the case of benzene, none being measured with alcohol. So it cannot be due to an artefact as described by Roth. However, these differences between the CIDNP effects are in agreement with those calculated by Adrian[10] (10% decrease of the polarization when the angle between E and B varies from 0 to 90°) and show evidence for the intervention of the triplet mechanism and, in addition, that the dipolar transition moments of quinoxaline and 2-methylquinoxaline are perpendicular to the z-axis of these molecules.

It is surprising that, as the participation of the triplet mechanism in alcohols was proved by field-dependent experiments, no difference in the CIDNP effects in relation to the orientation of the polarization plane of the light is

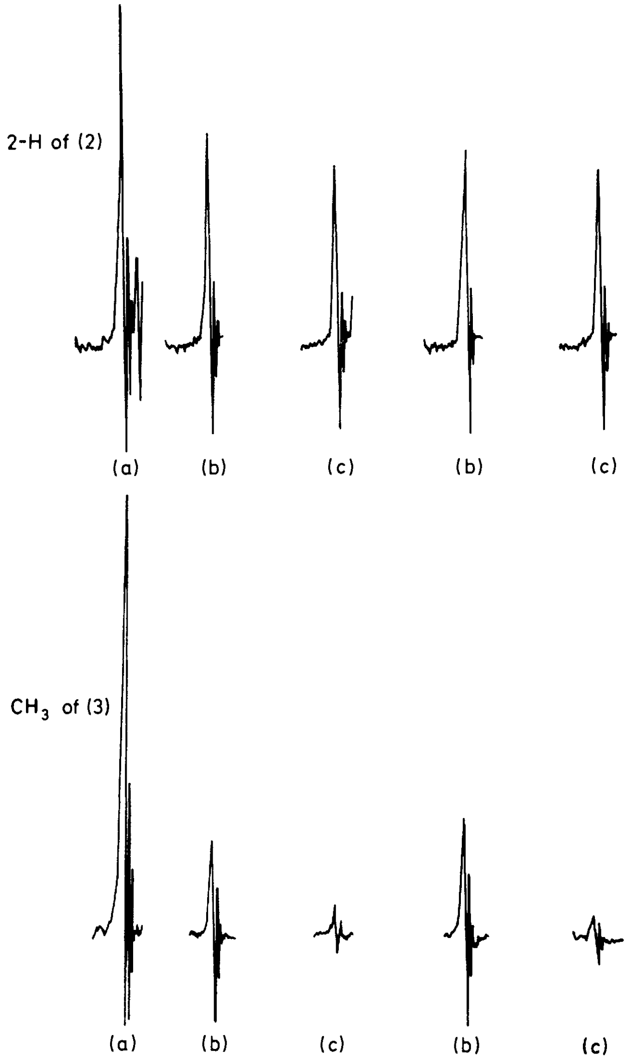

Figure 4. Plane of polarization dependence of CIDNP effects observed during the reaction of (2) and (3) in deuteriated benzene: (a) signal before irradiation; (b) signal after transfer and irradiation with polarized light with E perpendicular to B; (c) signal after transfer and irradiation with polarized light with E parallel to B

observed in methanol. This can be explained by the low value (30 G) of the magnetic field used in our experiments. At this value, the radical-pair mechanism at low field (mixing S–T) becomes preponderant.

Polarized-light experiments also show that nuclear polarizations recorded in benzene arise from the electronic polarizations of the irradiated products. This assumption is supported by recent work of McLauchlan,[14] which indicates that quinoxaline, according to the solvent, can react either by both mechanisms or by the triplet mechanism alone. By CIDEP experiments, McLauchlan clearly demonstrates that polarizations from the triplet mechanism result from anisotropic intersystem crossing from a singlet excited state to the sublevels of a non-degenerate triplet state. Then, electronically polarized radicals appear by rapid trapping of the polarized triplet.

These arguments also invalidate the mechanism proposed by Steiner[15] which explains the lack of a triplet sublevel population in an intermediate exciplex by a selective 'depopulation' rather than a selective population process. This initial step must be followed by a transfer from the radical electronic polarization to the nuclei. According to the CIDNP triplet mechanism, it occurs by transverse electron–nucleus relaxation. However, we could, in benzene or acetonitrile, neither scavenge neutral radicals from irradiated products nor observe solvent polarizations.

Excimer formation between a triplet state excited molecule of the aza-aromatic heterocycle and another one in the ground state is a tempting explanation. That is that the excimer can lead by electron transfer, in such polar solvents as acetonitrile (ε 40), to a radical-ion pair in which one of the electronically polarized partners transfers its polarization to the nuclei by electron–nucleus transverse relaxation. Then this pair leads to the starting heterocycle, polarized in the nucleus. Nevertheless, this explanation cannot be satisfactory since in benzene (a weakly polar solvent, ε 2) polarizations are likewise observed. As no ionization occurs in this case, the excimer comes back to its ground-state either by fluorescence or non-radiative transition.

On the basis of our experimental results, Pouzard and Thevand entered upon a theoretical study of this problem. Their explanation is still based upon the electronic spin polarization in a triplet state as demonstrated by Wong[16] and which governs the CIDEP triplet-state mechanism.

A nuclear polarization in a triplet state from dipole–dipole interactions between electrons and nuclei is then created. Pouzard and Thevand[17] calculate this polarization in the simplest case of a single $\frac{1}{2}$ nuclear spin coupled with electrons in the triplet state. Enhanced absorption can be predicted for 2-H of quinoxaline according to their results which is consistent with our experimental observations. In spite of its extreme simplification, this model can reflect the nuclear polarization observed in benzene or acetonitrile. A more general treatment must take into account all the simplifying hypotheses and needs to be computed.

Acknowledgements

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