Photochemically Induced Dynamic Nuclear Polarization (Photo-CIDNP) of Angular Dibenzacridines

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Photoreduction of angular dibenzacridines in proton-donor solvents has been investigated by means of chemically induced dynamic nuclear polarization (CIDNP). The results show that the position of the angular benzo-group directly influences the reaction scheme. Polarization of the starting materials has been observed during irradiation in benzene solution. The origin of these polarizations is discussed.

In previous papers, we have reported CIDNP studies of the photochemical reactions of acridine (1)[1,2] and benz[*a*]- (1a) and benz[*c*]-acridines (1c)[3] in hydrogenated solvents RH. The observed polarizations showed us that in proton donor solvents the first step of the reaction is the formation of the radical pair acridinyl$^\cdot$(2)R$^\cdot$ in the singlet state. Then radical recombination leads to adduct (3) by two different ways depending on the acridine derivative, either directly from the initial radical pair or after diffusion. This last pathway is not observed for (1), but is responsible for the polarization in the case of (1a). On the other hand, for (1c) both recombinations take place. The position of the angular benzo-groups (*a* or *c*) influences the reaction path of the photoreduction of acridines in hydrogenated solvents as well as the reaction rate.

To prove this statement we have studied several dibenzacridines: dibenz[*a,j*]acridine (1a,j), dibenz[*a,h*]acridine (1a,h) and dibenz[*c,h*]acridine (1c,h). These compounds depict the three possible positions of both angular benzo-groups in relation to the nitrogen atom and the *para*-carbon atom of acridines (C-13). As yet, no photochemical studies of these compounds have been carried out and we assigned the observed CIDNP signals by comparison with those obtained during irradiation of the angular benzacridines (1a) and (1c). In addition, incremental calculations due to benzo-groups and literature data on these dibenzacridines[4] confirm our assignments.

Results and Discussion

Spectra obtained during Irradiation of Ethereal Solutions of (1a,h), (1a,j), *and* (1c,h).—Chemical shifts, assignments, and CIDNP polarizations are summarized in Table 1. The spectrum obtained on irradiation of (1a,j) in tetrahydrofuran is shown in the Figure. Polarizations of 13-H in adduct (3) and of 13-H and aromatic protons in the starting dibenzacridines are observed as for the other acridines. Furthermore, polarizations of adduct (3) are much weaker than in the other cases while the polarizations of starting materials (1a,j), (1a,h), and (1c,h) are always strong. It must also be noted with (1c,h) that only 13-H gives rise to CIDNP and no evidence of adduct polarizations is shown. This is related to the rate of appearance of the signals, instantaneous in the case of (1a,j) and slower in the case of (1c,h).

Spectra obtained during Irradiation of Ethereal Solutions of (1a,h), (1a,j), and (1c,h) *in the Presence of* CCl_4.—CCl_4, acting as a radical scavenger, enables us to determine the identity of the partners in the radical pair. The coresults are summarized in Table 2. For (1a,j) and (1a,h) they confirm those obtained with other acridines, *i.e.* formation of chloroform, the solvent chlorinated derivative (proof of the existence of radical R$^\cdot$) and 13-trichloromethyldibenzacridane (4) [proof of the existence of dibenzacridinyl radical (2)]. During these irradiations a yellow precipitate appeared in the n.m.r. sample tube. In the case of (1c,h), neither polarizations nor precipitate were observed. That means either that the photochemical reaction does not occur or that the polarized species are present in too small a quantity to give rise to CIDNP effects.

CIDNP Interpretation.—First we discuss the case of (1a,j) and (1a,h). Indeed they are the only products which show polarizations for (3) and (4) corresponding to the photoreduction. Radicals (2a,j) and (2a,h) are formed, as with acridine, by hydrogen-atom abstraction from the solvent by the excited dibenzacridine. Furthermore, the observed polarizations (A) for 13-H of adducts such as (3) confirm, by application of Kaptein's rules,[5],†,‡ that the radical pairs leading to these addition products are in an *F* state as in the case of benz[*a*]acridine.[3] Results obtained with CCl_4 confirm this statement since no more polarizations are seen for (3a,j) and (3a,h): the radicals are scavenged before radical-pair formation.

The reaction scheme which explains the photoreduction of (1a,j) and (1a,h) is quite similar to the one propounded for (1a). The *j* or *h* position of the second benzo-group does not influence the reaction path, but only the appearance rate of the CIDNP signals, *i.e.* the formation rate of the polarized species. In the case of (1a,h) this rate is slowest and the same as during irradiation of (1c). Hence the *c* or *h* (equivalent) benzo-group positions influence the formation rate of the polarized products.

Compound (1c,h), among the three benzacridines studied giving no CIDNP signals for products such as (3), (4), and RCl, corroborates this statement. The first step of the reaction in this case, which is hydrogen-atom abstraction from the solvent by the nitrogen atom of the excited singlet state of dibenzacridine, is strongly inhibited by the presence of the *c* and *h* benzo-groups. All these considerations and previous results[1,3] lead us to the general Scheme for the photoreduction of acridine and its angular homologues in proton-donor

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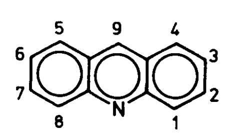
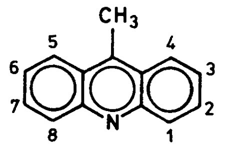
† The following parameters were used in Kaptein's rules: g_2 2.0030, $g(R^\bullet)$ 2.0038, $g(CCl_3^\cdot)$ 2.0091 (ref. 6), in (2) $a_{H-13} < 0$, in R$^\cdot$ $a_{H_\alpha} < 0$.
‡ We are indebted to J. P. Quaegebeur, C. E. A. Saclay, for the measurement of $g(R^\cdot)$.

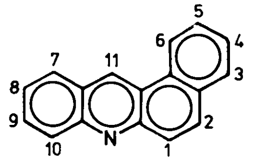
(1)

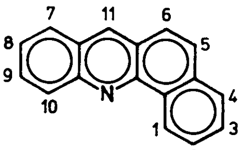




(1Me)

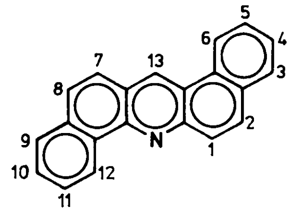
(1a)

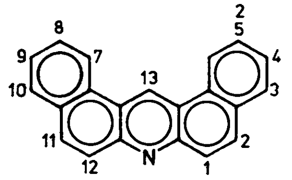




(1c)

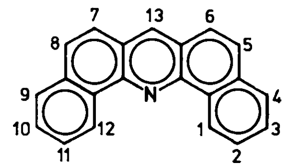
(1ah)

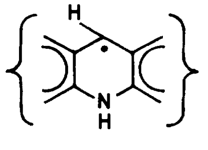




(1aj)

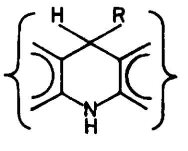
(1ch)

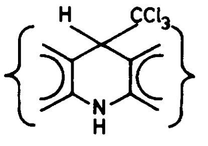




(2)

(3)





(4)

R =

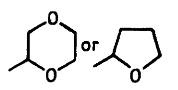


Table 1. Assignments of CIDNP signals observed during irradiation of (1a,j), (1a,h), and (1c,h) in ethereal solution (A, enhanced absorption; E, emission) (chemical shifts in p.p.m. relative to Me_4Si)

Compound		Dioxane	[$^2H_8$]Dioxane	THF	[$^2H_8$]THF
	(1a,j) 13-H	10.2 (A)	10.2 (A)	10.1 (A)	10.2 (A)
(1a,j)	6-, 7-H	9 (E)	9 (E)	9 (E)	9 (E)
	1-, 12-H	8 (A)	8 (A)	7.9 (A)	7.9 (A)
	(3a,j) 13-H	doublet 5.80 (A) *J* 5 Hz	singlet 5.8 (A)	doublet 5.9 (A)	singlet 5.9 (A)
	(1a,h) 13-H	9.6 (A)	9.6 (A)	9.6 (A)	9.6 (A)
(1a,h)	6-H	9 (E)	9 (E)	9 (E)	9 (E)
	(3a,h) 13-H	doublet 5.25 (A) very weak	5.2 (A) (weak)	doublet 5.2 (A) (weak)	
(1c,h)	(1c,h) 13-H	8.7 (A)	8.7 (A)	8.7 (A)	

solvents. In the Scheme, acridine mainly reacts *via* (a), (1c) *via* both (a) and (b), and (1a), (1a,j), and (1a,h) only *via* (b).

Nuclear Polarizations during Irradiation in Benzene Solution.—All observed polarizations for (3) and RCl are compatible with this Scheme. On the other hand those of starting materials (1) seem to have a different origin. Indeed there is no photoreaction of (1c,h) while 13-H exhibits polarization, confirming this assumption.

Such polarizations are observed during photoreduction of (1), (1a), and (1c), and are the only ones to appear when the photochemical reaction in alcohol and ethers is sensitized by biacetyl (triplet-state sensitizer). Furthermore when these products are irradiated in degassed [$^2H_6$]benzene (very bad proton-donor solvent) solutions, the same polarizations take place. Results for (1), 9-methylacridine (1Me), (1a), (1c), and dibenzacridines are summarized in Table 3.

Enhanced absorption is established for *para*-hydrogen

Table 2. Assignments of polarizations observed during irradiation of (1a,j), (1a,h), and (1c,h) in ethereal solution in the presence of CCl_4 (0.1M)

Compound		Dioxane	$[^2H_8]$Dioxane	THF	$[^2H_8]$THF
(1a,j)	$CHCl_3$	7.6 (A)	7.6 (A)	7.6 (A)	
	(4a,j) 13-H	6.9 (A)	6.8 (A)	6.8 (A)	6.8 (A)
	RCl	5.9 (A + A/E)		6.2 (E + A/E)	
(1a,h)	$CHCl_3$	7.7 (A) (weak)		7.7 (A) (weak)	
	(4a,h) 13-H	6.15 (A)	6.15 (A)	6.10 (A)	6.10 (A)
	RCl	5.9 (E + A/E)		6.30 (E)	
(1c,h)	$CHCl_3$ RCl (4c,h)		no polarization		

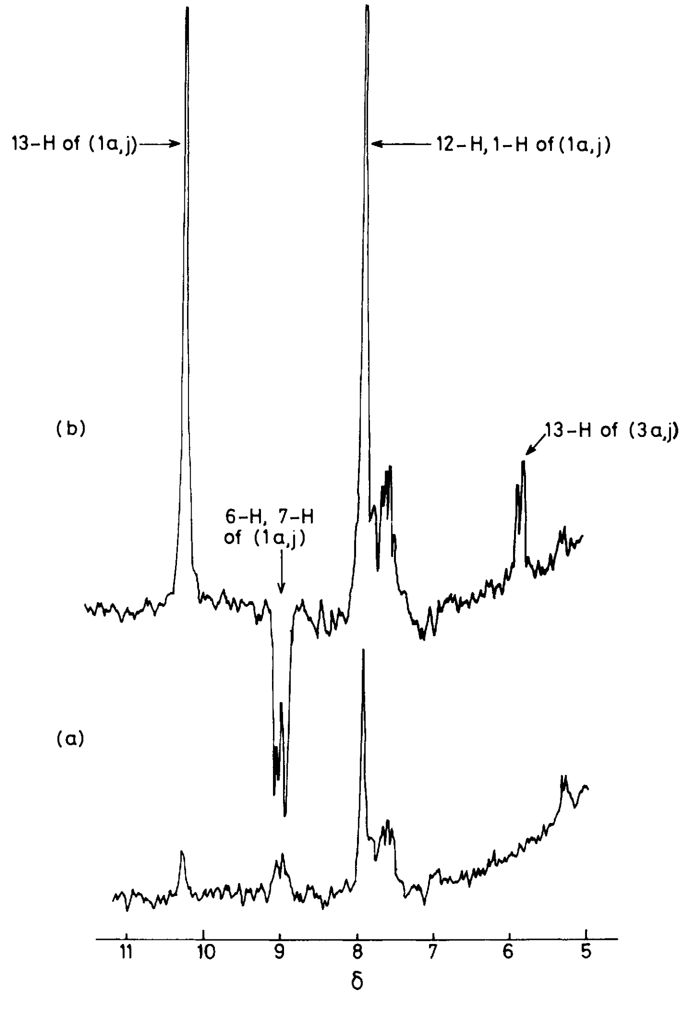
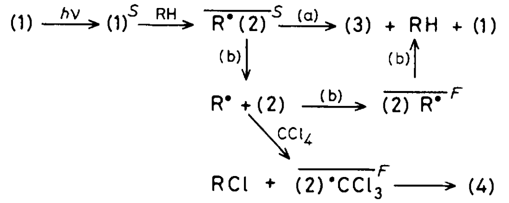


Figure. 60 MHz ^1H N.m.r. spectra of (1a,j) in THF: (a) before irradiation; (b) during irradiation



Scheme.

Table 3. CIDNP Effects for reactions of various acridines in degassed, deuteriated benzene solution

Product	Protons	δ	Polarization
(1)	9-H	8.05	A
(1Me)	CH_3	2.50	E
(1a)	11-H	8.80	A
	6-H	8.20	E
	5-H	7.45	A
(1c)	11-H	8.00	A
	5- or 6-H	7.30	E
(1a,h)	13-H	8.80	A
	6-H	8.20	E
	8- or 7-H	7.40	E
(1a,j)	13-H	9.70	A
	6-, 7-H	8.40	E
	2-, 11-H	7.65	A
	3-, 10-H	7.50	A
	5-, 8-H	7.42	A
(1c,h)	13-H	7.90	A
	5- or 6-H and 7- or 8-H	7.38	E

atoms [9-H for (1), 11-H for (1a) and (1c), and 13-H for (1a,h), (1a,j), and (1c,h)]. A methyl group (1Me) which replaces a *para*-hydrogen atom exhibits emission.

Moreover, some additional polarizations characterize the type of structure studied: 6-H (E) of (1a), (1a,h), and (1a,j) for the benzo[*a*]-type, 5-H (E) or 6-H (E) of (1c), 7-H (E) or 8-H (E) of (1a,h), and 5-H (E) or 6-H (E) and 7-H (E) or 8-H (E) of (1c,h) for the benzo[*c*]-type.

These assignments were made by comparison with literature data.[4,7] The other signals are unaffected and no polarization was shown either by the solvent or by an adduct.

Further experiments were done to elucidate this phenomenon and the main results are in Table 3. Polarizations only appear during irradiation of degassed solution. The non-reactive T_1 π-π^* triplet state of acridines is probably responsible for these polarizations as shown by sensitization and quenching experiments. Indeed the same polarizations are observed when biacetyl (E_{t_1} 57 kcal mol^{-1} [8]) is used as sensitizer (for acridine E_{t_1} 42 kcal mol^{-1} [9]). On the other hand, the presence of rubrene (E_t 25 kcal mol^{-1},[10] triplet quencher) cancels all the polarizations. These polarizations do not seem to be due to radical-pair formation; Kaptein's rules can only be applied to the pair $\overline{(2)\ C_6D_5^{\cdot}}$ and polarizations predicted in this case are opposite to that observed: $\{\mu > 0,\ \varepsilon > 0,\ a_i < 0,\ g_2 > g^{\cdot}{}_{C_6D_5}{}^{11} \Rightarrow \Gamma_n < 0 \Rightarrow E\}$. These polarizations seem to depend upon the hyperfine coupling constant, for enhanced absorption is observed for 9-H in (1) and emission for the methyl group in (1Me).

Thus, the photoreduction process previously described cannot be responsible for these polarizations. But we can affirm that, during irradiation of these acridines in alcohols and ethers, the polarizations of the starting materials result from two different mechanisms. The same phenomenon takes place during irradiation of diazanaphthalenes[12] and is in part explainable by the triplet mechanism theory. Further experiments are presented in the following paper in order to elucidate this phenomenon. We studied the magnetic field and polarized light orientation dependence of nuclear spin polarizations.

Experimental

Experiments were conducted with a JEOL C-60 HL spectrometer, whose probe was specially modified to allow *in situ* irradiation of the sample.[13] The full emission spectrum of an SP 1000 Philips lamp was used as light source. Sensitizing and quenching experiments required liquid filters. In the presence of rubrene, the filter was a 3 cm thick solution of chromium alum (6.2 g l^{-1}), cobalt sulphate (8 g l^{-1}), and nickel sulphate (2 g l^{-1}). In the presence of biacetyl, the filtering solution contained potassium chromate (0.09 g l^{-1}) and sodium carbonate (0.33 g l^{-1}). Solutions were degassed through three freeze–pump–thaw cycles (10^{-5} mmHg) in special quartz n.m.r. sample tubes. Dibenzacridines were synthesized by the method described in ref. 4*b*. Acridine and benzacridines are commercially available from Merck–Schuchardt.

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