

CIDNP EFFECTS IN NAPHTHALENE-PYRIDINIUM EXCIPLEXES

Joachim Bargon

IBM Research K33, 5600 Cottle Road, SAN JOSE CA 95193 USA

and Gian Piero Gardini

Istituto Policattedra di Chimica Organica, 43100 PARMA, ITALY

(Received in UK 11 June 1976; accepted for publication 5 July 1976)

When irradiating a solution of  $1 \times 10^{-4}$  mole of naphthalene and  $1 \times 10^{-4}$  mole of pyridine in acetic acid- $d_4$  as the solvent (0.5 ml) with the filtered light of a high pressure mercury-xenon arc (1000 W,  $2900 > \lambda > 3600$  Å), we observed the CIDNP<sup>1</sup> phenomenon in the NMR spectrum of naphthalene. Figure 1 shows the spectral region ( $8\text{ppm} > \delta_{\text{TMS}} > 7\text{ppm}$ ) recorded with a Varian HA 60 spectrometer at room temperature. The quartz probe of this spectrometer admitted UV irradiation through the paddle holes via a light guide.

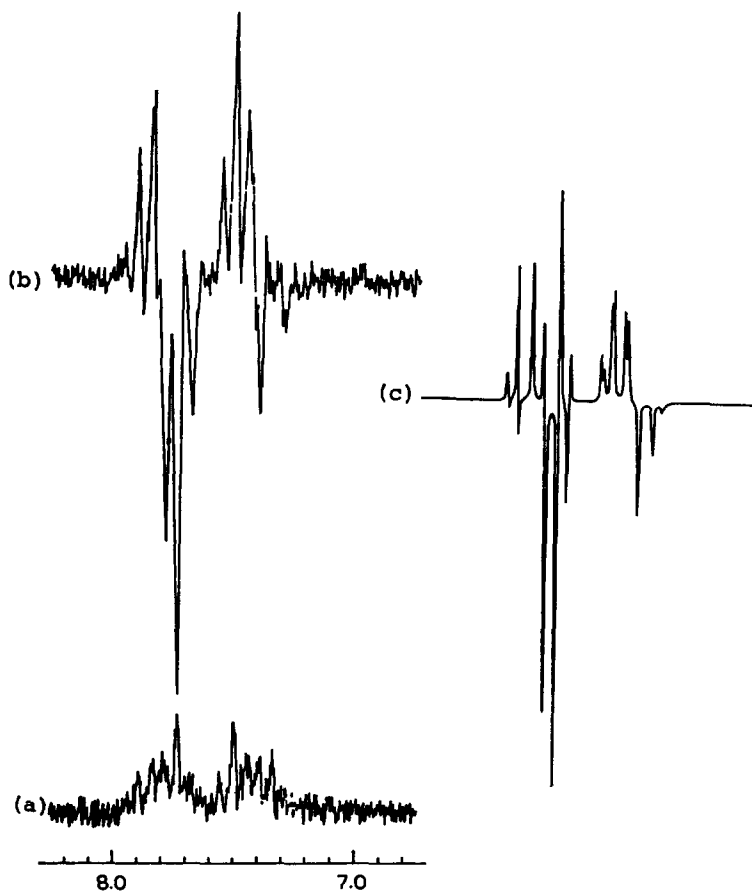
Before the irradiation, naphthalene exhibits the usual  $A_2B_2$ -type absorption pattern<sup>2</sup>, (lower trace of Fig. 1), but upon irradiation the naphthalene shows a multiplet effect<sup>3</sup> type CIDNP pattern with the low-field ( $\beta$ -protons) and the high-field ( $\alpha$ -protons) both in A/E polarization mode.<sup>3</sup>

No chemical products can be observed in the NMR spectrum. Neither pyridine, nor the solvent show CIDNP.

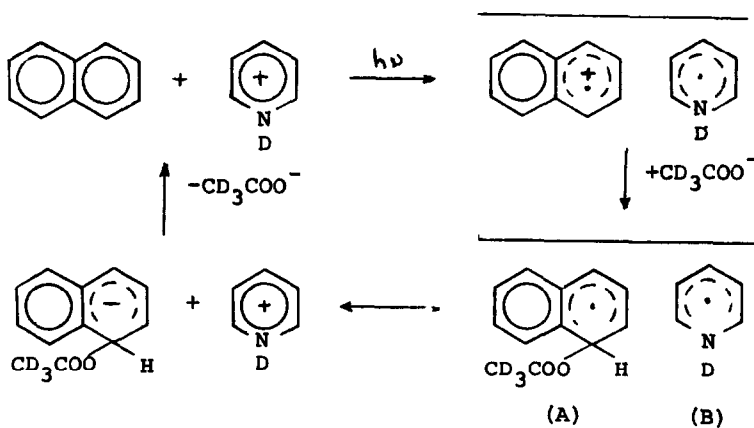
We explain this observation as follow: pyridine in acetic acid is protonated to about 100% and thus occurs in form of the pyridinium ion.<sup>4</sup> This species apparently acts as an acceptor, but it is not sufficiently powerful an acceptor to form a charge transfer complex with naphthalene in its ground state. With the photoexcited naphthalene, however, protonated pyridine forms an exciplex; pyridinium itself does not absorb the light in the range provided by our lamp.<sup>4</sup>

Scheme I summarizes the proposed sequence of steps leading to the polarization of naphthalene.

Fig. 1 - CIDNP spectrum (60 MHz) of naphthalene (b) and simulated spectrum (c)



SCHEME I



The radical pair which give rise to the observed CIDNP consists of pyridyl (B) and cyclohexadienyl-type naphthyl (A) radicals. From the known  $g$ -values of these radicals<sup>5</sup> and the known signs of the hyperfine coupling constants of the protons in cyclohexadienyl-type radicals<sup>6</sup> we conclude using the Kaptein rules for CIDNP<sup>7</sup> that this radical pair has electronic triplet character.

The fact that only naphthalene shows CIDNP is somewhat puzzling but appears to be due to efficient nuclear relaxation in the free paramagnetic species escaping the solvent cage which surrounds the pair. The chemical exchange outlined in Scheme I appears to be rather instrumental in inducing fast nuclear spin relaxation in the free paramagnetic species, which competes favorably with their decay.

This photoinitiated process appears to be reversible to a very high degree, because we were unable to detect any photoproduct by gas-liquid chromatography in a sample irradiated for 24 hours.

Similarly, we observed CIDNP effect in naphthalene and substituted naphthalenes during UV irradiation of their solutions in dipolar aprotic solvents in the presence of known acceptors, namely *ortho*- or *para*-disubstituted benzenes, with cyano, carboxyl or carboxyalkyl substituents, but *only* if a suitable nucleophile was provided to generate (A) from the originally formed naphthalene radical cation.

Computer simulations of the naphthalene CIDNP patterns using a computer program written by J. den Hollander<sup>8</sup> gave agreement with the experimental spectra only if the parameters for  $\dot{A}$ -type radicals were used as opposed to those which apply for the naphthalene radical cation.<sup>9</sup> This was taken as an additional evidence in favor of Scheme I. Further details of these photoreactions including discussions of the solvent effect in a large number of D/A systems, will be outlined later. We feel that CIDNP could give interesting suggestions on many intermediates formed during photoreactions and which cannot be monitored chemically (lack of photoproduct) nor spectroscopically (lack of fluorescence and/or phosphorescence).

## REFERENCES

- <sup>1</sup> For a review, see R. Kaptein in *Adv. Free Radical Chem.*, Vol. 5, G. H. Williams ed., Academic Press, N.Y., 1975, p. 319.
- <sup>2</sup> J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.* 35, 1060 (1957).
- <sup>3</sup> Reference 1, p. 324.
- <sup>4</sup> S. Bruchenstein and I. M. Kolthoff, *J. Am. Chem. Soc.* 78, 10 (1956).
- <sup>5</sup> R. W. Fessenden and P. Neta, *Chem. Phys. Letters* 18, 14 (1973); S. Di Gregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.* 95, 8455 (1973) and references cited therein.
- <sup>6</sup> U. R. Bohme and H. C. Wolf, *Chem. Phys. Letters* 17, 582 (1972).
- <sup>7</sup> R. Kaptein, *Chem. Comm.* 732 (1971).
- <sup>8</sup> J. A. den Hollander, Leiden Univ., private communication.
- <sup>9</sup> J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.* 90, 4201 (1968).