

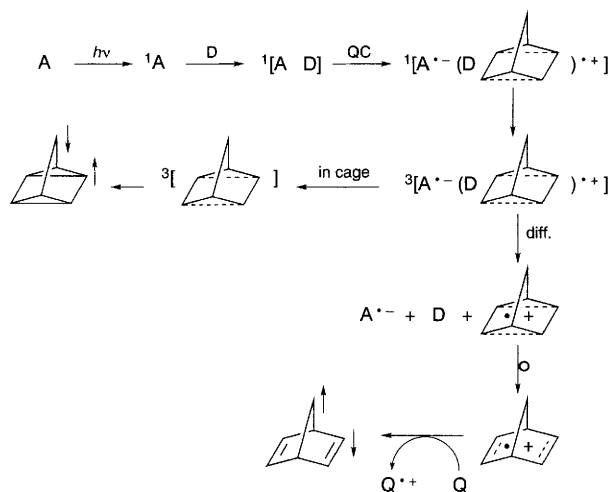


F-pair mechanism cannot explain the concurrent inversion of the polarization direction of QC, which is undoubtedly an in-cage recombination product.

In order to check the role of durene, the 1-cyanonaphthalene (CN)-sensitized QC isomerization was re-investigated. It is known that singlet excited CN and 1,4-dicyanonaphthalene (DCN) form emissive exciplexes with alkylbenzenes,<sup>10</sup> and QC quenches the exciplex fluorescence close to the diffusion-controlled limit.<sup>2</sup> Pac *et al.* have proposed that triplexes are involved in the CN- or DCN-sensitized isomerization of QC in neat arenes or in cyclohexane solvent in the presence of arenes.<sup>2</sup> In acetonitrile, the isomerization probably proceeds *via* an electron transfer pathway with a much lower quantum yield than those in non-polar solvents, presumably owing to fast back electron transfer in the singlet radical-ion pair.<sup>11</sup> In this context, however, no CIDNP effect was detected during the CN-sensitized isomerization of QC in acetonitrile. Roth and coworkers have proposed a mechanistic interpretation that both singlet and triplet recombination of the resulting ion-radical pair would regenerate QC and the complementary polarization components associated with these pathways would cancel each other.<sup>7</sup>

We confirmed the lack of polarization of the CN/QC system under conditions as reported.<sup>7</sup> However, irradiation of a ternary mixture of CN, QC and durene (D) in [<sup>2</sup>H<sub>3</sub>]acetonitrile resulted in an excellent CIDNP spectrum which is completely identical with that observed for the DBMBF<sub>2</sub>/QC/D system [Fig. 1(c)]. A similar result was obtained when DCN was used in the place of CN. In view of Roth's suggestion,<sup>7</sup> this CIDNP result clearly demonstrates that the participation of durene facilitates intersystem crossing of the ion-radical pair and/or prevents singlet back electron transfer, thus triplet recombination dominated the overall process.

Based on the above CIDNP results and in line with Pac's works,<sup>2</sup> the requirement of the modified ion-radical pair formation in generating the observed polarization dictates the intermediacy of the DBMBF<sub>2</sub>/QC/D triplexes (or ternary ion-radical pairs) as shown in Scheme 2. The oxidation potential of durene (1.79 V vs. SCE) and the diffusion-limited quenching of DBMBF<sub>2</sub> fluorescence by durene ( $2.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) enables an exothermic electron transfer with DBMBF<sub>2</sub> ( $\Delta G = -12.7 \text{ kcal mol}^{-1}$ ). In addition, the exciplex fluorescence of



Scheme 2 A = DBMBF<sub>2</sub>, CN or DCN; D = durene. Arrows denote polarization directions.

DBMBF<sub>2</sub>/durene can be efficiently quenched by QC, implying the involvement of the triplex. The concentrations used in the CIDNP experiments (*ca.* 0.02 mol dm<sup>-3</sup> for each component) are high enough to ensure effective combination of the three components. Therefore, formation of an intermediate triplex is a logical conclusion. The participation of durene in the triplex may significantly stabilize the IRP by delocalizing the positive charge, and the insertion of durene between the sensitizer and QC in the IRP must facilitate the circumvention of the singlet back electron transfer, hence promoting the intersystem crossing that makes the triplet recombination pathway predominant.

In view of the fact that triplex emission is hardly observed in polar solvents, CIDNP experiments may afford a new approach for probing the intermediacy of triplexes in electron transfer reactions conducted in polar solvents. In addition, the triplex-mediated photoinduced electron transfer reaction is expected to be used in other reactions to alter reaction channels.

The authors from Lanzhou University are grateful to the National Natural Science Foundation of China and the State Education Commission of China for financial support. Y. L. C. gratefully acknowledges generous financial support from the Natural Science and Engineering Council of Canada, in the form of operating and travel grants (Canada-PRC scientific exchange program, 1991).

Received, 16th February 1995; Com. 5/009491

## Footnote

† DBMBF<sub>2</sub> is a singlet sensitizer,<sup>6</sup> thus  $\mu$  is negative. The  $g$  value of QC<sup>+</sup> (*ca.* 2.0025<sup>12</sup>) is smaller than that of DBMBF<sub>2</sub><sup>-</sup> (2.0033<sup>5</sup>), thus  $\Delta g$  is negative. The hyperfine splitting constants (hfc) of the cyclobutane protons and bridgehead protons of QC<sup>+</sup> are -10.5 and 7.9 gauss, respectively.<sup>5</sup> Therefore, the emission of the cyclobutane protons and the enhanced absorption of the bridgehead ones mean that the polarized QC must be an in-cage product ( $\epsilon$  is positive). The opposite polarization direction of the alkenic and bridgehead protons of NBD predict that the polarized NBD must derive from escaped QC<sup>+</sup> ( $\epsilon$  is negative) with a singlet exit channel ( $\gamma$  is positive).

## References

- 1 J.-I. Kim and G. B. Schuster, *J. Am. Chem. Soc.*, 1992, **114**, 9309 and references cited therein.
- 2 C. Pac, *Pure Appl. Chem.*, 1986, **58**, 1249; Y. Masaki, Y. Uehara, S. Yangagida and C. Pac, *Chem. Lett.*, 1990, 1339; Y. Masaki, S. Yangagida and C. Pac, *Chem. Lett.*, 1988, 1305.
- 3 A. T. Soltermann, J. J. Cosa and C. M. Previtali, *J. Photochem. Photobiol. A: Chem.*, 1991, **60**, 111.
- 4 For an unique emissive triplex in acetonitrile, see: J. Saltiel, D. E. Townsend, B. D. Watson and P. Shannon, *J. Am. Chem. Soc.*, 1975, **97**, 5688.
- 5 Z. L. Liu, M. X. Zhang, L. Yang, Y. C. Liu, Y. L. Chow and C. I. Johansson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 585.
- 6 Y. L. Chow and X. E. Cheng, *Can. J. Chem.*, 1991, **69**, 1331.
- 7 H. D. Roth, M. L. M. Schilling and G. Jones, II, *J. Am. Chem. Soc.*, 1981, **103**, 1246; H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.*, 1981, **103**, 7210.
- 8 R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 1971, 731.
- 9 G. L. Closs and M. S. Czeropski, *J. Am. Chem. Soc.*, 1977, **99**, 6127.
- 10 H.-F. Davis, S. K. Chattopadhyay and P. K. Das, *J. Phys. Chem.*, 1984, **88**, 2798.
- 11 G. Jones, II, S. H. Chiang, W. G. Becker and J. A. Welch, *J. Phys. Chem.*, 1982, **86**, 2805.
- 12 R. Kaptein, in *Advances in Free Radical Chemistry*, ed. G. H. Williams, Elek Science, London, 1975, vol. 5, p. 319.