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^{1}H NMR Conformational Study of Viologen-Linked Porphyrins (*p*-PC*n*V)

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Synopsis. Conformation of viologen-linked porphyrins (*p*-PC*n*V, n=4—7), which are capable of intramolecular electron transfer, was studied by ^{1}H NMR in order to gain insight into the relative geometry of the donor and acceptor during the electron transfer process. The orientation of the viologen with respect to the porphyrin was interpreted in terms of the rate of the intramolecular electron transfer between the two π-systems.

The viologen-linked porphyrins (Fig. 1) exhibit the intramolecular electron transfer process from the porphyrin to the viologen.[1–5] The rate of this process depends crucially on the length of the methylene chain intervening between the two π-systems. The electron transfer rate of *m*-PC*n*V in dimethylsulphoxide (DMSO) decreases monotonously with the methylene chain length and, in the case of *p*-PC*n*V in DMSO, only *p*-PC4V exhibits the intramolecular electron transfer with the rate comparable to that of *m*-PC3V.[5] We have studied the conformation of *p*-PC*n*V in DMSO by ^{1}H NMR. The orientation of the viologen with respect to the porphyrin ring in *p*-PC*n*V was compared with that of *m*-PC*n*V[6] and the difference of the efficiency in the electron transfer process for these compounds was interpreted in terms of the distance between the porphyrin and the bipyridine, based on a proposed relationship, i. e., an exponential dependence of the electron transfer rate on the distance of the donor-acceptor separation.[7]

Experimental

Materials. The viologen-linked porphyrins (*p*-PC*n*V) were synthesized as described previously.[5] Dimethyl-d_6 sulfoxide (DMSO-d_6) was purchased from MSD Isotopes.

NMR Measurements. Solutions of 10 mM *p*-PC*n*V in DMSO-d_6 (1M=1 mol dm^{-3}) were used for ^{1}H NMR measurements. 500 MNz ^{1}H NMR spectra were recorded on a JEOL GSX-500 FT-NMR spectrometer at 27 °C. Typical spectra were recorded with 64 transients, 32 k data points,

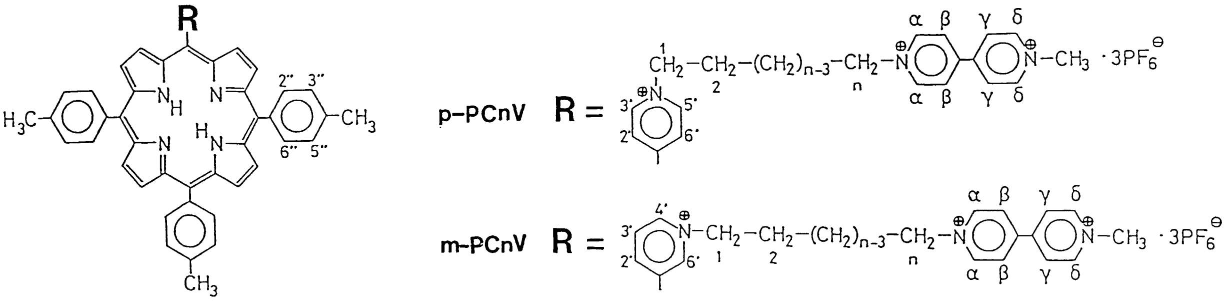

Fig. 1. Molecular structures and numbering systems of viologen-linked porphyrins (*p*-PC*n*V and *m*-PC*n*V).

Table 1. Chemical Shifts[a] on Viologen ^{1}H Resonances of *p*-PC*n*V(n=4—7) in DMSO-d_6

Protons	*p*-PC4V	*p*-PC5V	*p*-PC6V	*p*-PC7V
Methylene Chain				
1-CH_2	5.00(+0.34)	4.95(+0.34)	4.93(+0.34)	4.92(+0.34)
2-CH_2	2.35(+0.34)	2.36(+0.34)	2.30(+0.37)	2.26(+0.33)
3-CH_2	2.35(+0.34)	1.64(+0.28)	1.62(+0.28)	1.58(+0.24)
4-CH_2	4.92(+0.31)	2.24(+0.26)	1.62(+0.25)	1.55(+0.13)
5-CH_2		4.84(+0.17)	2.14(+0.21)	1.51(+0.13)
6-CH_2			4.79(+0.13)	2.08(+0.15)
7-CH_2				4.75(+0.08)
Bipyridyl				
α	9.50(+0.17)	9.47(+0.12)	9.45(+0.11)	9.42(+0.09)
β	8.85(+0.07)	8.84(+0.06)	8.83(+0.06)	8.79(+0.02)
γ	8.79(+0.06)	8.70(−0.04)	8.79(+0.04)	8.72(−0.01)
δ	9.31(+0.03)	9.15(−0.13)	9.28(+0.01)	9.24(−0.03)
N-Me	4.46(+0.02)	4.28(−0.16)	4.44(0.00)	4.41(−0.02)

a) Chemical shifts are given in ppm from TMS. The numbers in the parentheses are the porphyrin ring-current induced shift changes and positive value indicates the downfield shift.

7000 Hz spectral width, and 5.9 μs 90° pulse. Chemical shifts were referenced to the solvent peak (2.5 ppm relative to the signal of tetramethylsilane) and are given in parts per million, ppm.

Results and Discussion

^{1}H NMR spectra of *p*-PC*n*V have been unambiguously assigned from the combined analyses of the connectivities in ^{1}H–^{1}H chemical shift correlated and nuclear Overhauser effect correlated spectroscopies. Chemical shifts for the viologen proton resonances of *p*-PC*n*V are given in Table 1. Pyridyl 2′, 6′ and 3′, 5′ protons resonate at 9.09 and 9.52 ppm, respectively, and the shifts of the other proton resonances are essentially identical with those of the corresponding resonances of *m*-PC*n*V previously reported. These shifts are essentially independent of the sample concentration (1—50 mM), indicating the absence of significant intermolecular interaction. The porphyrin ring current induced shifts for the viologen proton resonances of *p*-PC*n*V were calculated using the data obtained for appropriate model compounds as previously described.[6] The ring current shifts (δ_{RC}) of the viologen proton resonances are summarized in Fig. 2 and their plots are individually compared with those of *m*-PC*n*V in Fig. 3. The δ_{RC} value of the 1-CH$_2$ proton resonance for *p*-PC*n*V is +0.34 ppm and decreases to ca. 0 almost monotonously for protons further away, along chemical bonds, from the porphyrin ring. Similarity in their δ_{RC} plots (Fig. 2) indicates that the orientation of the viologen with respect to the porphyrin is not significantly different among the *p*-PC*n*V. These results suggest that the methylene chain of *p*-PC*n*V is in energetically stable all-*trans* extended conformation as found for *m*-PC*n*V. Anomalously large negative δ_{RC} detected for the δ and N-Me protons of *p*-PC5V may not be explained in terms of its conformational features.

Assuming the extended all-*trans* conformation for the methylene chain, the closest edge-to-edge distances between the two π-systems ($R_{\pi\pi}$) in *p*-PC*n*V with n=4, 5, and 6 are 1.03, 1.13, and 1.27 nm, respectively, and are compared with $R_{\pi\pi}$ of 0.85, 0.92, and 1.09 nm for *m*-PC*n*V with the corresponding *n* value, respectively. Therefore, the fact that *p*-PC*n*V (n>4) does not exhibit the intramolecular electron transfer leads to conclusions that the electron transfer in DMSO occurs

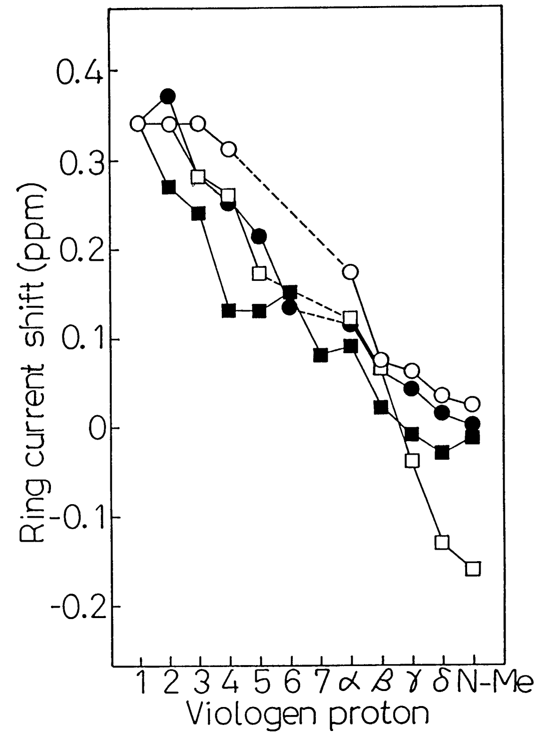

Fig. 2. Plots of the ring current induced chemical shift against viologen protons of *p*-PC*n*V in DMSO-d_6. *p*-PC4V(○), *p*-PC5V (□), *p*-PC6V (●), *p*-PC7V (■).

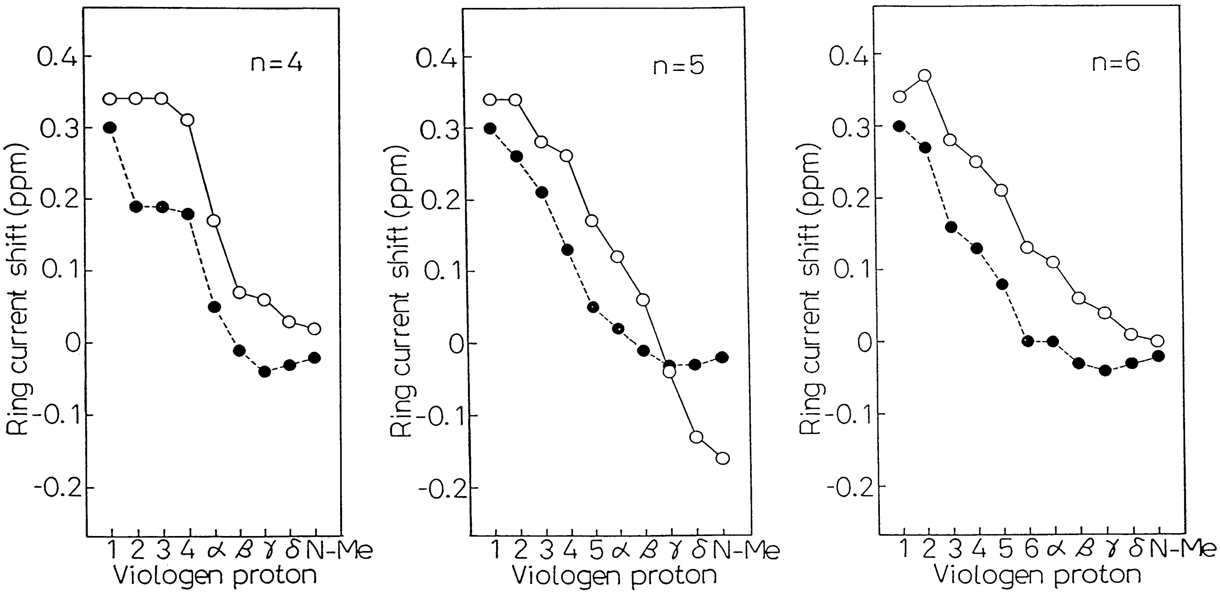

Fig. 3. Plot of the ring current induced chemical shift against viologen proton resonance of *p*-PC*n*V (○) in DMSO-d_6. Similar data for *m*-PC*n*V (●)[6] are also shown for comparison.

when $R_{\pi\pi} <$ ca. 1.1 nm and that the electron is not transfered through the methylene chain. $R_{\pi\pi}$ of 1.1 nm is greater than the theoretical estimate, 0.8 nm, for electron transfer by a short-range tunneling mechanism.[8] Furthermore, $R_{\pi\pi}$ should be considered as a semiquantitative parameter for interpreting the intramolecular electron transfer rate in terms of the molecular structure of these viologen-linked porphyrins, because it does not account for the fact that *m*-PC3V and *p*-PC4V exhibit similar rates.[5] Considering both the conformational flexibility of the methylene chain in solution and the time scale, ns, of the process, $R_{\pi\pi}$ calculated for a molecular structure infered from NMR data may not simply correlate to the electron transfer rate. A conformational change around one of the C–C bonds in themethylene chain, for example, *trans*→*gauche*, alters $R_{\pi\pi}$ as much as ca. 10 and ca. 15% for *p*- and *m*-PC*n*V, respectively.

References

1) S. Aono, N. Kaji, and I. Okura, *J. Chem. Soc., Chem. Commun.*, **1986**, 170.

2) N. Kaji, S. Aono, and I. Okura, *J. Mol. Catal.*, **36**, 201 (1986).

3) I. Okura, N. Kaji, S. Aono, and T. Nishisaka, *Bull. Chem. Soc. Jpn.*, **60**, 1243 (1987).

4) S. Noda, H. Hosono, I. Okura, Y. Yamamoto, and Y. Inoue, *J. Chem. Soc., Faraday Trans. 1*, **86**, 811 (1990).

5) S. Noda, H. Hosono, I. Okura, Y. Yamamoto, and Y. Ionue, *J. Photochem. Photobiol. A: Chem.*, **53**, 423 (1990).

6) Y. Yamamoto, S. Noda, N. Nanai, I. Okura, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **62**, 2152 (1989).

7) D. Gust, T. A. Moore, P. A. Liddell, G. A. Nemeth, L. R. Makings, A. L. Moore, D. Barrett, P. J. Pessiki, R. V. Bensasson, M. Rougee, C. Chachaty, F. C. De Schryver, M. Van der Auweraer, A. R. Holzwarth, and J. S. Connolly, *J. Am. Chem. Soc.*, **110**, 2670 (1988).

8) J. D. Hopfield, *Proc. Nat. Acad. Sci.*, **71**, 3640 (1974).