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ANOMALOUSLY STABLE CYCLODEXTRIN COMPLEXES OF PHENOTHIAZINE-VIOLOGEN LINKED COMPOUNDS WITH A LONG SPACER CHAIN [1)]

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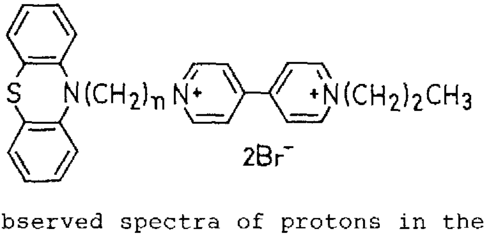
Abstract: Distinct NMR signals due to stable cyclodextrin (CDx) complexes were detected by the use of phenothiazine-viologen linked compounds in combination with either α- or β-CDx. Encasing of the spacer alkyl chains by CDx was suggested to explain the complexing behavior.

Photoinduced electron transfer in donor-acceptor linked compounds has been one of the most popular research subjects in relevance to artificial photosynthesis.[2)] The studies, however, have always been plagued with the flexibilities of the spacer chain between the donor and acceptor moieties. The present authors recently discovered that photochemical behaviors of phenothiazine-viologen linked compounds were remarkably affected by the addition of cyclodextrin (abbreviated to CDx).[3)] Laser excitation of the linked compounds with twelve methylene groups as the spacer afforded phenothiazine-viologen radical pair, when either α- or β-CDx was present in the solution. Fluorescence emission from the phenothiazine moiety was also intensified by the addition of these CDx. These observations were explained on the basis of the conformational change in the spacer on complexation with CDx. Detailed analysis of ^{1}H NMR spectra elucidated novel properties of the CDx complexes as described below.

Proton NMR spectra of the following phenothiazine-viologen linked compounds in D_2O solutions were measured with a 400 MHz spectrometer (JEOL model JNM-GSX400). In order to obtain a reference signal, a sealed glass capillary containing D_2O solution of DSS was placed in the sample tube.



1 (n=12)
2 (n=4)

The observed spectra of protons in the aromatic moieties (viologen and phenothiazine) and methylene groups are shown in Fig. 1.

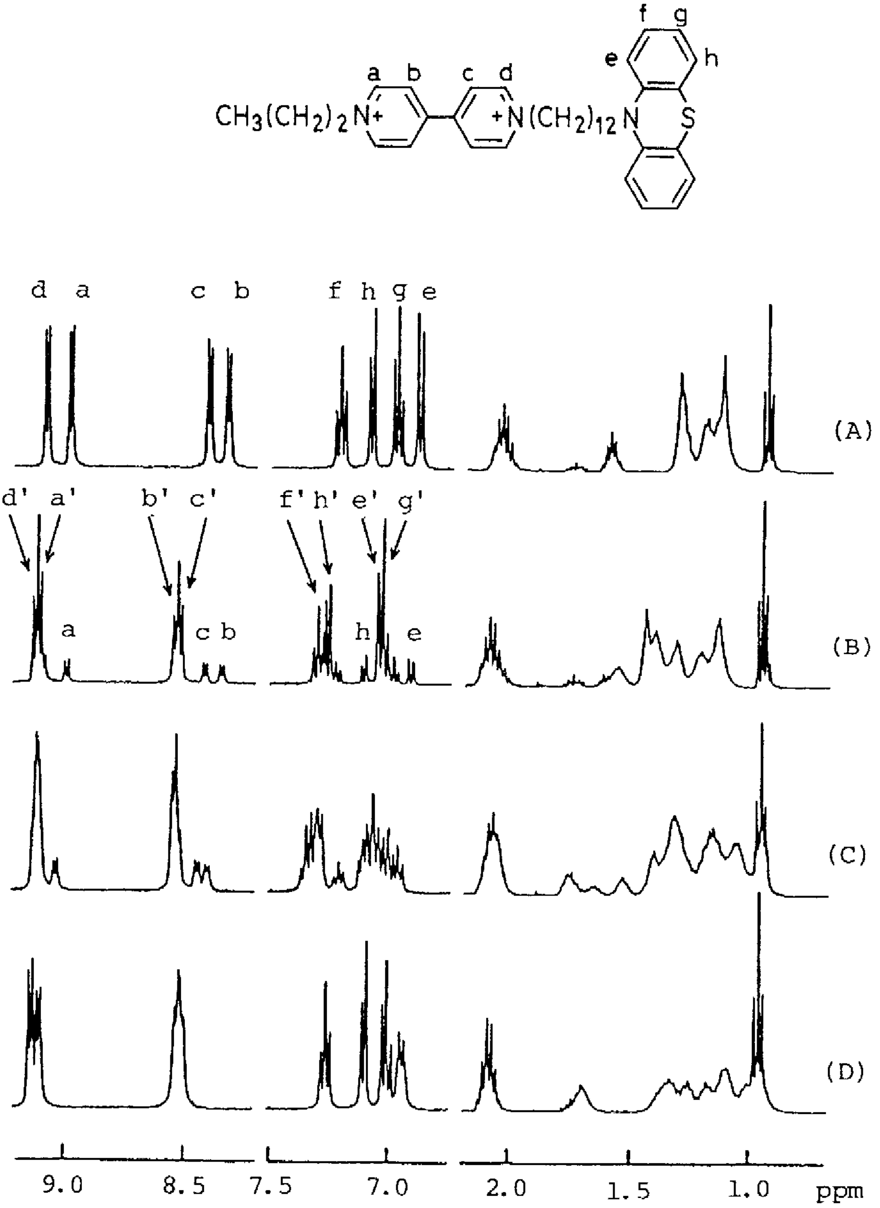


Fig. 1. Change in signal shapes of protons in aromatic- and methylene moieties of 1 (0.4 mM D_2O solution) in the presence of equimolar amounts (0.4 mM) of the following CDx: (B) α-, (C) β-, and (D)γ-CDx. Assignments (a - h) were made as shown in (A) in the absence of CDx, and the corresponding signals in the complexed species were indicated by the same letters with a prime. All measurements were carried out at 30°C.

On the addition of either α- or β-CDx, distinct signals due to complexed species (a' - h') were clearly observed at lower fields with respect to those of free species. The signal intensities of the complexed species increased with the CDx concentration. In the case of **1** and α-CDx, the equilibrium constant for the 1:1 complex formation as evaluated by the integrated signal intensities was 4 x 10^4 M^{-1}. In the case of γ-CDx, the viologen and phenothiazine proton signals changed in their shapes and shifted to lower fields with respect to those of free species, but no separate signals were observed. The low fields shifts increased with the concentration of γ-CDx as shown in Fig. 2. All of these observations clearly indicate the formation of relatively stable, long living complexes in the case of α- and β-CDx.4) On the other hand, rapid exchange between the complex and free species should be responsible to the progressive shifts induced by γ-CDx.

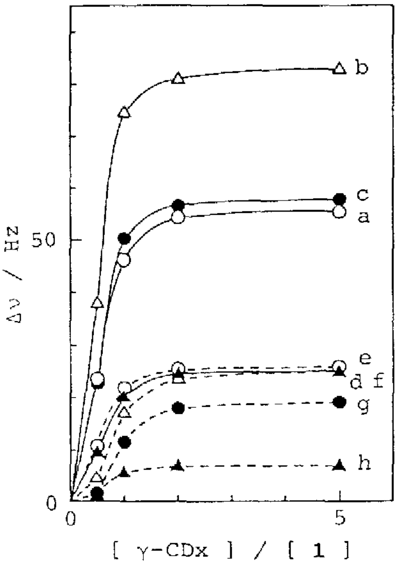


Fig. 2. Effects of γ-CDx concentration on the induced low field shifts of proton signals of **1** (0.4 mM); viologen (———) and phenothiazine moieties (- - - - -).

Assignments of the proton signals were carried out by the aid of NOE and 2D measurements as indicated in Figs. 1 and 2. The induced shifts due to the complex formation with α-CDx are summarized in Table 1.

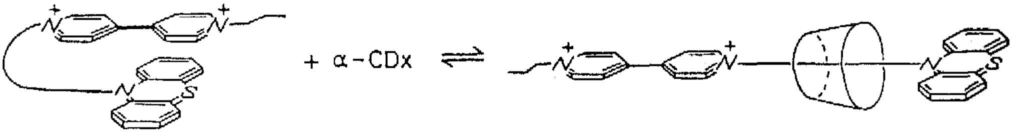
Table 1. The induced shifts (Δν, Hz) due to complex formation between **1** and α-CDx in D_2O solution (0.4 mM each).

Proton Position	a	b	c	d	e	f	g	h
Δν	49	82	45	16	61	33	22	69

$$\Delta\nu = \nu_{\text{with } \alpha\text{-CDx}} - \nu_{\text{without } \alpha\text{-CDx}}$$

The values are reasonably explained if one assumes that the viologen moieties are located on top of the central part of the phenothiazine moieties in the free species and also that the complex formation enforces open, flat structure with extended spacer chain in the cavity of CDx as in the following scheme.

Scheme



The induced shift may be explained due to decrease in the ring current effects on going from the face to face orientation of the free species to the open, flat structure of the complex. The contribution of charge-transfer interaction may not be disregarded either. In agreement with this suggestion, a weak and broad charge-transfer absorption band (λ_{max} at 550 nm) was observed with the free species but it completely disappeared on the addition of CDx. The difference in the three CDx must be ascribed to the cavity size. Space filling models of α-CDx indicate that the viologen unit may be squeezed through the cavity and the encased methylene chain should assume an extended conformation. In the case of γ-CDx, on the other hand, the pore size is large enough for the free escape from the methylene chains. The ^{1}H NMR signals of the methylene chains in Fig. 1, varied in reasonable agreement with the suggested reaction scheme.

In the case of 2 with four methylene groups in the spacer, the ^{1}H NMR signals simply shifted on the addition of either one of the three CDx. Thus, it is clear that relatively small cavity size and long spacer chains are required to stabilize the novel CDx complex discovered here.

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REFERENCES

1) Contribution No. 899 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.
2) J. A. Schmidt, A. R. McIntosh, A. C. Weedon, J. R. Bolton, J. S. Connolly, J. K. Hurley, and M. R. Wasielewski, J. Am. Chem. Soc., 110, 1733 (1988).
3) H. Yonemura, H. Nakamura, and T. Matsuo, Chem. Phys. Lett., 155, 157 (1989).
4) Willner and his associates reported β-CDx complexes of octyl- and benzyl viologen, but no NMR spectroscopic evidences were provided in the paper: I. Willner, E. Adar, Z. Goren, and B. Steinberger, New J. Chem., 11, 769 (1987).

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