An NMR study on the conformation of naphthalene–viologen linked compounds: effect of flexible spacer length

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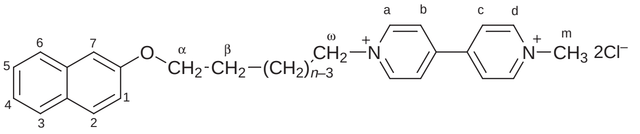
The conformational equilibria of naphthalene–viologen compounds linked with a flexible polymethylene bridge [–$(CH_2)_n$–; $n = 3, 5, 7, 9, 12$] were examined by NMR spectroscopy and molecular modeling. The chemical shift of the donor–acceptor dyad molecules depends on the linkage length and concentration. The equilibrium constants for the intramolecular and the intermolecular complexation were obtained from the chemical shift variation with concentration at high salt concentration. The complexation-induced chemical shifts (CISs) of the intra- and intermolecular complexes are obtained for molecules of $n = 3$ and 5. The molecules with longer linkages ($n = 9$ and 12) show aggregation behavior and the critical coagulation concentrations were obtained as 1.7 and 10 mM, respectively. Comparing the NMR results with molecular modeling calculations indicates that the naphthalene moiety can take various positions and orientations with respect to the bipyridinium moieties depending on the length of the linkage.

Introduction

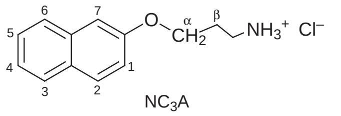
The efficiency of the intramolecular photoinduced electron transfer reactions in electron donor (D)–acceptor (A) systems depends on the interaction between the donor and acceptor groups, which is closely correlated with the distance and the relative orientation. A conventional strategy for controlling these parameters has been linking the donor and the acceptor pair with a rigid spacer such as steroid or phenyl groups.[1,2] D–L–A molecules where the linkage (L) is a flexible spacer such as a polymethylene chain [–$(CH_2)_n$–] are easier to prepare than molecules with a rigid spacer. However, studies on the electron transfer reactions within the molecule usually become complicated due to the distribution of the transfer rates among different conformations of the molecule.[3] To restrict the distance and orientation between the donor and acceptor groups linked by flexible bridges, many studies along this line adopted the cyclophane-type geometry.[4] Baldes and Schneider, for example, showed that polyazacyclophanes have different conformations in the presence and absence of metal cations, which is an example of cation-induced allosterism.[5]

Viologens (1,1′-dialkyl-4,4′-bipyridinium salts) have been studied as electron mediators in solar energy conversion[6] and for reductive transformations of organic compounds.[7] They are also widely incorporated in many supramolecular systems as an electron acceptor from photo-excited or ground-state electron donors.[2,8–12] Aromatic groups such as naphthalene,[8] carbazole,[9] anthracene[10] and phenothiazine[11] have been incorporated into D–$(CH_2)_n$–viologen type molecules as donor groups. These molecules can form intramolecular as well as intermolecular ground-state charge transfer complexes, and the photoinduced electron transfer reactions are greatly facilitated due to the proximity of the electron donor and acceptor. The inhibition of the charge transfer interaction and enhancement of the fluorescence of the aromatic groups upon the complexation with cyclodextrins forming rotaxane-type complexes were also reported for those molecules.[8–11] However, little attention has been paid to the conformation of the intramolecular charge transfer complexes in the ground state.

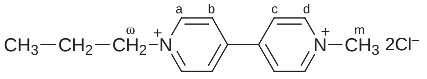
In the course of studies on the linkage length dependence of the intramolecular charge transfer interaction and the photoinduced electron transfer reaction rates in naphthalene–$(CH_2)_n$–viologen molecules,[8] we found strong dependence of the NMR spectra of naphthalene and viologen moieties on the length of linkage. This is in contrast to the observation that the formation constants of the intramolecular charge transfer complexes are relatively insensitive to the length of linkage. These findings motivated us to study the conformational equilibria of the molecules by NMR spectroscopy and molecular modeling. We report here how the most likely conformations and the intermolecular complexation behavior change as the chain length varies for the naphthalene–$(CH_2)_n$–viologen (NC_nV) molecules. Compounds NC_3A and C_3V were used as references for the disconnected molecules.



NC_nV : $n = 3, 5, 7, 9, 12$



NC_3A



C_3V

Experimental

The naphthalene–viologen linked compounds were prepared by coupling 2-hydroxynaphthalene with a 1,ω-dihaloalkane, followed by reaction with 1-methyl-4,4′-bipyridinium iodide and counter ion exchange to chloride.[8,10] NC_3A and C_3V were prepared by standard procedures.[8] NMR measurement was carried out at 25 °C on Bruker DPX-250 or Varian Unity 600 MHz NMR spectrometers in D_2O solutions with TSP (sodium 3-trimethylsilyl[2,2,3,3-$^2H_4$]propionate) as an internal standard. Molecular modeling calculations were carried out using the CVFF force field provided in the Insight II/Discover modeling program package.[13]

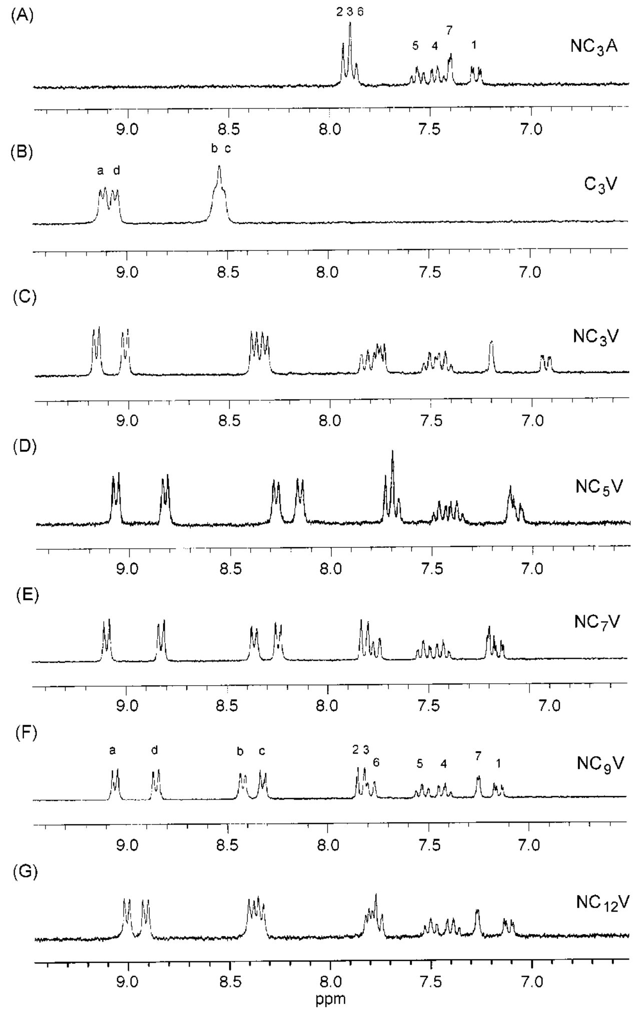


Fig. 1 Linkage length dependence of the ^{1}H NMR spectra of aromatic protons in NC$_n$V: (A) and (B) are spectra of the disconnected molecules. Peak assignments of protons are shown in (A), (B) and (F). All spectra were obtained at 1.0 mM sample concentration in D_2O solution at 25 °C.

Table 1 Chemical shift change ($\Delta\delta$) induced by linkage formation between naphthoxy and viologen moieties[a,b]

Proton	$n = 3$	$n = 5$	$n = 7$	$n = 9$	$n = 12$	δ_{ref}[e]
Naphthol[c]						
1	−0.34	−0.19	−0.12	−0.12	−0.16	7.27
2	−0.17	−0.21	−0.10	−0.08	−0.12	7.91
3	−0.09	−0.24	−0.10	−0.08	−0.11	7.91
4	−0.04	−0.08	−0.04	−0.04	−0.07	7.46
5	−0.06	−0.10	−0.04	−0.03	−0.06	7.56
6	−0.03	−0.09	−0.03	−0.01	−0.03	7.79
7	−0.20	−0.27	−0.20	−0.15	−0.13	4.33
Viologen[d]						
a	+0.04	−0.03	−0.02	−0.06	−0.11	9.12
b	−0.17	−0.26	−0.18	−0.13	−0.16	8.55
c	−0.21	−0.37	−0.29	−0.21	−0.19	8.54
d	−0.04	−0.22	−0.23	−0.21	−0.14	9.06
Alkyl						
α	+0.09	−0.30	−0.29	−0.21	−0.17	4.33
β	+0.48	−0.47	−0.48	−0.46	−0.44	2.25
ω	+0.32	+0.04	+0.02	0.03	−0.07	4.70
m	−0.08	−0.05	−0.11	−0.14	−0.09	4.51

[a] See text for labeling of protons. [b] Obtained with 1.0 mM solutions in D_2O solvent at 25 °C. [c] $\delta_{NC_nV} - \delta_{NC_3A}$. [d] $\delta_{NC_nV} - \delta_{C_3V}$. [e] Chemical shifts in the disconnected molecules, NC$_3$A and C$_3$V.

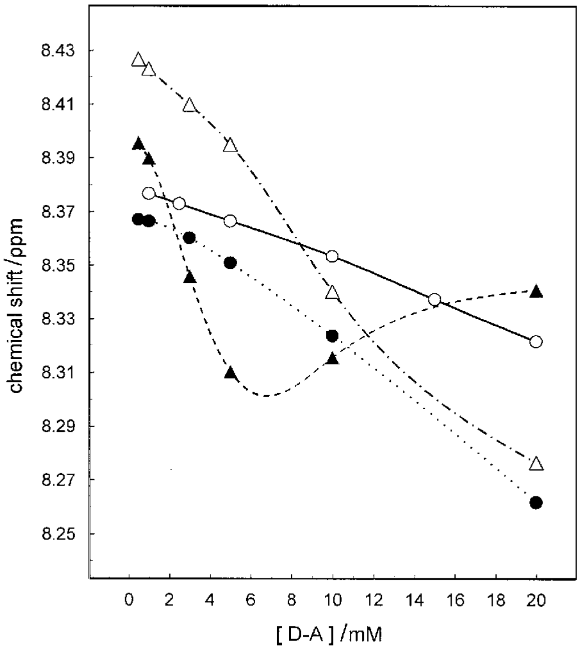


Fig. 2 Concentration dependence of the H$_b$ chemical shift of NC$_n$V in salt free D_2O solution at 25 °C: $n = 3$ (○), $n = 5$ (●), $n = 9$ (△), $n = 12$ (▲).

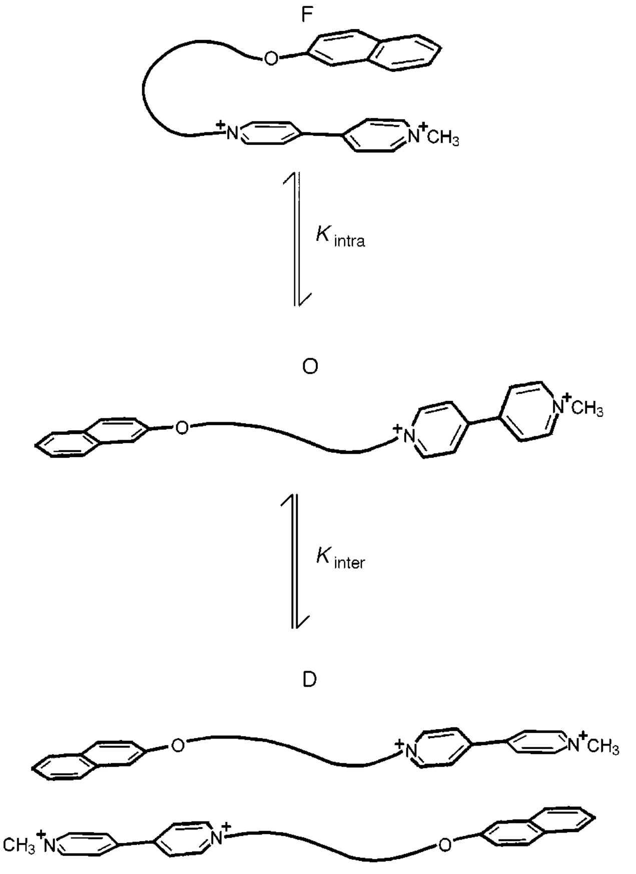
Results and discussion

^{1}H NMR spectra of aromatic moieties in NC$_n$V molecules together with those of NC$_3$A and C$_3$V are shown in Fig. 1. Peaks were clearly assigned with the aid of COSY and NOESY spectra. The spectra show a large variation according to the linkage length. Methyl protons (H$_m$) and methylene protons adjacent to the viologen and naphthoxy groups (H$_\alpha$ and H$_\omega$) are also sensitive to the linkage length. Table 1 summarizes the dependence of proton chemical shifts on the number of methylene groups in the linkage, with respect to those in the disconnected molecules. $\Delta\delta$ is the chemical shift change induced by linking the donor and the acceptor groups with alkyl chains of various length.

Compared with the peak positions in the disconnected compounds, both the viologen and naphthoxy protons show an upfield shift. If direct transfer of charge through bonds had made a significant contribution, a downfield shift would have been observed for the donor protons.[14] Thus the upfield shifts both in the donor and acceptor groups can be ascribed mainly to the ring current effect. This is further supported by the fact that both the donor and acceptor protons in the carbazole,[9a] anthracene,[10] or phenothiazine–viologen[11a] linked compounds show a downfield shift upon adding cyclodextrins (CDs). Addition of CDs disrupts the interaction between the aromatic donors and viologen acceptor in the linked compounds by forming rotaxane-type CD complexes.[8–11]

The X-ray crystallographic studies showed that the charge transfer complexes formed between the aromatic donor and viologen acceptor have a face-to-face arrangement.[15,16] It is evident that there would be a significant contribution from the cofacial structure even though the flexibility of the bridges allows for considerable fluctuation of conformation and distance. We assume that the open and the folded cofacial structures are the two extremes of conformational change. The donor/acceptor groups are independent in the open structure, but they constitute an intramolecular charge-transfer complex in the folded structure. The exchange between the structures would be fast on the NMR time scale.

Fig. 2 shows the concentration dependence of the H$_b$ proton chemical shifts for various chain lengths. They show a large upfield shift as the concentration is increased, and the trend dramatically depends on the chain length. Considering only the intramolecular conformational equilibrium mentioned above, the chemical shift would not change with concentration since the mole fraction of the open and the folded species does not depend on the concentration. Therefore, we introduce another equilibrium process, intermolecular charge transfer complexation as shown in Scheme 1.



Scheme 1

Trimer and higher aggregates may be formed as well, but their contribution would not be significant at low concentrations. Molecules with short chains ($n = 3$, 7) show rather monotonic dependence of the chemical shift on the concentration, whereas longer molecules ($n = 9$, 12) exhibit more complex behavior. The origins for this behavior are different, and we will treat each case separately.

Molecules with short linkages and the effect of ionic strength

The observed chemical shift is a population-weighted average of the three conformations [eqn. (1)], where F, O and D denote

$$\delta_{obs} = \frac{[F]\delta_F + [O]\delta_O + 2[D]\delta_D}{[D - A]_{tot}} = \frac{K_{intra}[O]\delta_F + [O]\delta_O + 2K_{inter}[O]^2\delta_D}{[D - A]_{tot}} \quad (1)$$

the folded, open, and dimer conformations, respectively. Using the definition for equilibrium constants and mass balance [eqn. (2)], the concentration of the open conformations is given by eqn. (3).

$$K_{intra} = \frac{[F]}{[O]},\ K_{inter} = \frac{[D]}{[O]^2},\ [D - A]_{tot} = [F] + [O] + 2[D] \quad (2)$$

$$[O] = \frac{-K_{intra} - 1 + \sqrt{(1 + K_{intra})^2 + 8K_{inter}[D - A]_{tot}}}{[D - A]_{tot}} \quad (3)$$

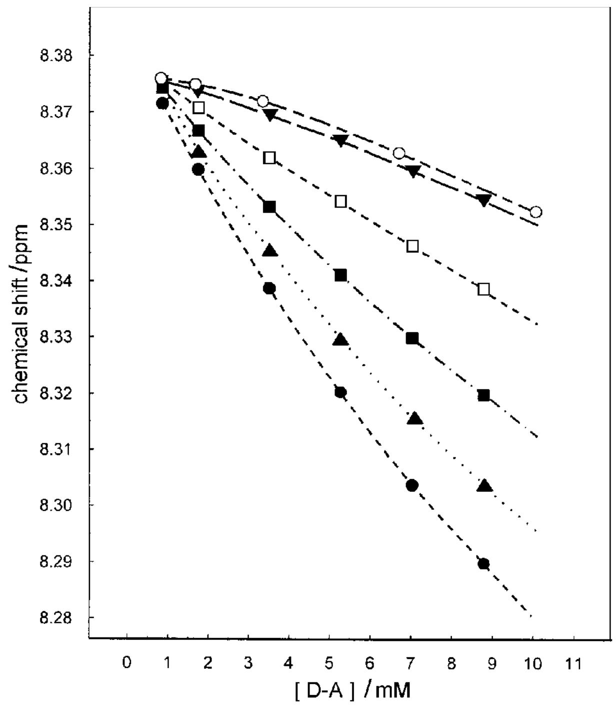


Fig. 3 Concentration dependence of the H_b chemical shift of NC_3V at various [NaCl]: 0 M (○), 0.01 M (▼), 0.05 M (□), 0.1 M (■), 0.2 M (▲), and 0.3 M (●).

The dependence of chemical shifts on the total concentration is completely defined by eqns. (1) and (3). Therefore unknown parameters such as δ_F, δ_O, δ_D, K_{intra} and K_{inter} can be obtained from nonlinear least-squares fitting of δ_{obs} as a function of $[D - A]_{tot}$. Though the overall quality of fit was not too bad, the experimental data showed a large deviation from the theoretical prediction, especially at low sample concentrations. The reason for this discrepancy is ascribed to the change in ionic strength. Since the the viologen moiety is positively charged, the ionic strength increases as the concentration increases, which causes both the magnetic susceptibility and the intermolecular interaction to change. To confirm the effect of ionic strength, NaCl was added to a 1 mM solution of NC_3V solution. The chemical shift of the H_d proton in viologen decreased from 9.015 to 9.008 ppm when the salt concentration was varied over 0–0.2 M. The H_1 proton of the naphthoxy group showed a downfield shift of 0.006 ppm over the same salt concentration change. The chemical shifts show a large change at low salt concentration range, and they approach the limiting values at high salt concentrations. This confirms that the ionic strength is an important factor for chemical shift variation in charged molecules.

To avoid the complication caused by the change in ionic strength, an excess amount of salt should be added. Fig. 3 shows the concentration dependence of the H_b proton chemical shift of NC_3V at various concentrations of NaCl. The experimental data at [NaCl] = 0.3 M was used for the nonlinear least-squares fitting procedure, and the result exhibited excellent fitting over the whole concentration range. We also fitted the NMR titration data for other protons. For all protons, δ_O values agree with that of the corresponding protons in the disconnected molecules within ±0.02 ppm. This can be regarded as evidence of the validity of Scheme 1.

The fitting of NMR titration data to eqns. (1) and (3) gives K_{intra} and K_{inter} values. The values obtained from fitting of all protons of NC_3V were averaged and found to be 0.16 ±0.01 for K_{intra} and $14 \pm 2\ M^{-1}$ for K_{inter}. The K_{intra} value is in good agreement with that from absorption spectroscopy.[8] The average K_{inter} value ($14\ M^{-1}$) is about the square of the corresponding value ($3.6\ M^{-1}$) determined for NC_3A and dimethyl viologen.[8] This implies that two pairs of naphthoxy–viologen

Table 2 Calculated intramolecular and intermolecular complexation-induced chemical shifts for NC_3V and NC_5V

	$n = 3$			$n = 5$		
	$\Delta\delta_{intra}$ [a]	$\Delta\delta_{inter}$ [b]	δ_O [c]	$\Delta\delta_{intra}$ [a]	$\Delta\delta_{inter}$ [b]	δ_O [c]
Naphthol						
1	−2.21	−0.87	7.25			
7	−1.20	−0.75	7.38	−1.27	−0.98	7.38
Viologen						
a	+0.23	−0.52	9.13	−0.21	−0.96	9.12
b	−1.08	−0.85	8.54	−1.47	−1.31	8.57
c	−1.45	−0.83	8.52	−1.57	−1.15	8.50
d	−0.35	−0.47	9.06	−0.94	−0.67	9.03
Alkyl						
α	+0.55	−0.34	4.36	−1.55	−0.83	4.33
ω	+2.15	−0.21	4.73	+0.22	−0.61	4.71
m	−0.01	−0.18	4.52	−0.21	−0.34	4.51

[a] $\Delta\delta_{intra} = \delta_F - \delta_O$. [b] $\Delta\delta_{inter} = \delta_D - \delta_O$. [c] Calculated chemical shifts for the open conformation.

interactions are involved for the stabilization of the intermolecular complex, as can be seen in Scheme 1.

The complexation-induced chemical shifts (CIS), $\Delta\delta_{intra} = \delta_F - \delta_O$ and $\Delta\delta_{inter} = \delta_D - \delta_O$, are also obtained from nonlinear least-squares fitting, and they are shown in Table 2. The $\Delta\delta_{intra}$ and $\Delta\delta_{inter}$ values are changes in chemical shifts when all the molecules adopt the folded intramolecular complex or the dimeric intermolecular complex, respectively. The observed chemical shift changes in Table 1 ($\Delta\delta$ values) are about 1/7 of $\Delta\delta_{intra}$ of the corresponding protons. This is to be expected from a K_{intra} value of the 0.16 as the fraction of the intramolecular complex in solution is only 0.14. Interestingly, as can be seen in Table 2, $\Delta\delta_{intra}$ values are considerably different from those of $\Delta\delta_{inter}$. This suggests that the arrangement of the donor/acceptor moieties in the intramolecular complex is quite different from that in the intermolecular complex.

We also fitted the NMR titration data of protons in NC_5V. The obtained CIS values are also listed in Table 2. The K_{intra} and K_{inter} values are found to be 0.25 ± 0.01 and 11 ± 0.15 M^{-1}, respectively. Again, the K_{intra} value is in excellent agreement with the value of 0.23 obtained from absorption spectrometry.[8] Other points are essentially the same as those given above for NC_3V.

Molecules with long linkages and aggregation behavior

The variation in chemical shift with concentration change is more complex for molecules with long linkages ($n = 9$, 12). Whereas it has a sigmoidal shape in NC_9V, the variation in chemical shift for $NC_{12}V$ shows the opposite trend below and above *ca.* 6 mM. We attribute the latter behavior to the aggregation of the amphiphilic molecules due to hydrophobic interactions, which may compete with the intermolecular charge transfer interaction between the naphthoxy and viologen moieties. Amphiphilic molecules with long hydrophobic tails tend to form a micelle-like structure beyond a critical concentration in aqueous solution. The viologen group is hydrophilic, whereas the alkyl chain and the naphthalene group are considered to be hydrophobic.

When the exchange process between the monomeric species and the aggregated species is fast on NMR time scale, eqn. (1) can be replaced by eqn. (4), where N is the average number of

$$\delta_{obs} = (C_{mon}\delta_{mon} + NC_{agg}\delta_{agg})\, C_{tot}^{-1} \qquad (4)$$

monomers in the aggregated species and δ_{mon} is the population-weighted average chemical shift of the monomeric species. The

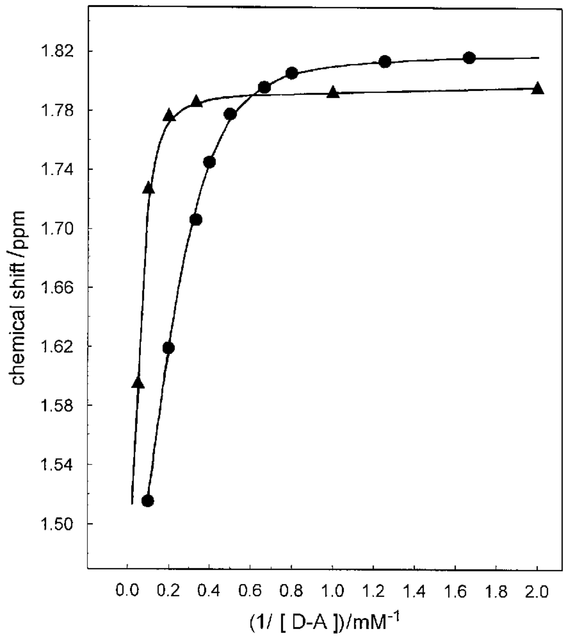


Fig. 4 Dependence of the H_β chemical shift of NC_9V (▲) and $NC_{12}V$ (●) on the reciprocal concentrations of the molecules.

C's are the concentrations of each species. Aggregation usually requires a concentration beyond a certain critical point (CCC; critical coagulation concentration) as is manifested in micelle formation: the concentration is referred to as the CMC (critical micelle concentration) if the coagulated structure is a micelle. In this Scheme, the observed chemical shift below the CCC should be similar to that of the monomer [the first term in eqn. (4)] whereas it becomes dominated by the aggregated species above the CCC [the second term in eqn. (4)]. Therefore a plot of δ_{obs} *versus* C_{tot}^{-1} would show an abrupt change near the CCC.

The chemical shifts of the H_β protons are particularly sensitive to the concentration. They vary more than 0.1 ppm upfield within the 1.0–20 mM concentration range for the NC_9V and $NC_{12}V$ molecules, whereas the corresponding change is only −0.036 and −0.003 ppm for the NC_3V and NC_5V molecules, respectively. The large upfield shifts indicate the change towards a more hydrophobic environment. This supports our conclusion that the aggregation behavior of the molecules with shorter linkages is different to that of molecules having longer linkages.

Fig. 4 compares the dependence of the chemical shifts of the H_β protons of NC_9V and $NC_{12}V$, plotting δ_{obs} *versus* C_{tot}^{-1} according to eqn. (4). The abrupt changes in the slope of the plots are found at 1.7 and 10 mM for $NC_{12}V$ and NC_9V, respectively, which can be regarded as the CCC for the respective molecule. The plot for the H_β protons of NC_3V (not shown) does not have any abrupt slope change. The slope becomes progressively greater as $1/C_{tot}$ decreases, reflecting facilitation of the intermolecular dimerization at high concentrations as discussed in the preceding section. The variation in the chemical shift of H_b protons of $NC_{12}V$ also shows an abrupt slope change near 1.7 mM, in agreement with the results for the H_β proton. This is expected as the aggregation changes the molecular environment of the viologen moiety too.

The water molecules at the interface of a hydrocarbon phase and a water phase are highly structured. Formation of an aggregated species increases the entropy since the amount of structured water molecules decreases. This is the thermodynamic origin of hydrophobic interactions.[17] The free energy change when amphiphilic molecules are brought from the water phase to a micellar phase ($\mu_{mic} - \mu_{HC}$) is −3.2 kJ mol^{-1} per CH_2 group,[17] which corresponds to a decrease in the CMC of 10 times when the alkyl chain length increases by two carbon

Table 3 Energy values (kcal mol^{-1}) for NC$_n$V molecules in the open and the two folded conformations obtained from molecular modeling.

n	Open	A	B	$E_A - E_{open}$	$E_A - E_B$
3	307.6	288.6	291.2	−19.0	−2.6
5	308.4	288.4	296.8	−20.0	−8.4
7	309.8	289.6	298.8	−20.2	−9.2
9	310.6	292.7	295.2	−17.9	−2.5
12	312.7	298.2	301.1	−14.5	−2.9

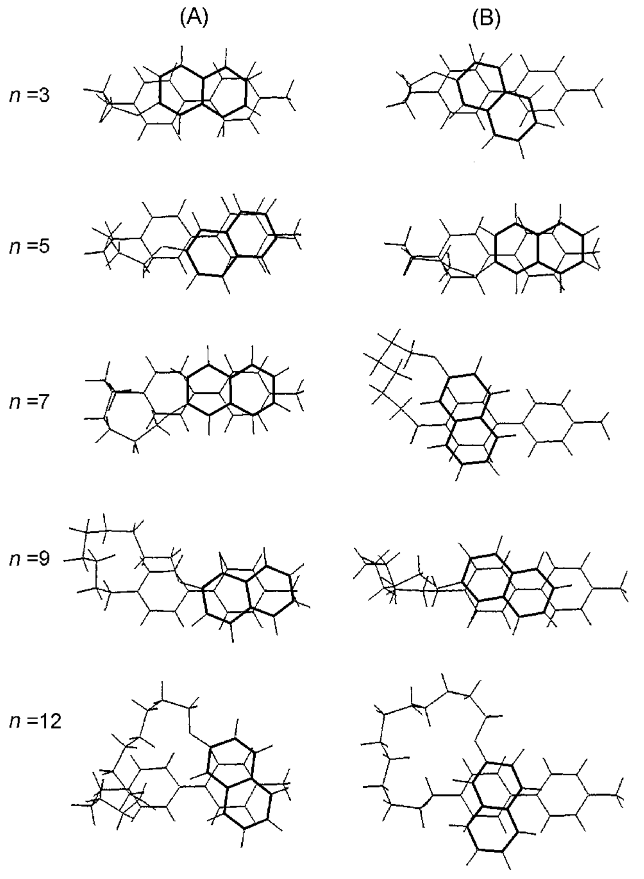


Fig. 5 Two energy-minimized structures in the folded conformations of NC$_n$V: (A) conformations with the lowest energies, (B) conformations of local minimum with the next lowest energies.

atoms.[18] For NC$_n$V molecules, the CCC decreased by 6 times whereas the expected ratio is 30 since the chain length decreases by three carbon atoms from $n = 12$ to 9. This discrepancy is probably due to the naphthalene group. Unlike normal amphiphilic molecules with long hydrocarbon tails, NC$_n$V may form loosely packed aggregates due to the presence of the bulky naphthalene group, and much of the hydrophobic parts of the molecules would still be exposed to water even in the aggregated structure. Therefore the free energy change is expected to be smaller than that in typical amphiphiles with a straight chain, and chain length has a less profound effect on the critical concentration. A similar result was obtained by Okano *et al.*, who studied amphiphiles with phenyl derivatives as head groups.[19]

Molecular conformations from molecular modeling calculations

Monomeric species determine the NMR spectra when the concentration is sufficiently below the CCC even for molecules with long alkyl linkages. A sample concentration of 1 mM is far below the CCC for all chain lengths. Thus, the chemical shift change caused by linking the donor and acceptor groups in Table 1 is essentially due to the intramolecular interaction in the folded conformation. To correlate the NMR results with the molecular conformations, we conducted molecular modeling calculations using the CVFF force field provided in the InsightII/Discover modeling program package.[13] Fig. 5 shows the energy-minimized structures (A) and the structures of local minima (B) which give the next lowest energy. The energies of the open and the folded (A and B) conformations are compared in Table 3. For all cases, the folded conformations are energetically more favorable than the open ones, presumably due to π–π interaction.[20]

In agreement with the X-ray crystallographic studies on the viologen and aromatic donor complexes, the energy-minimized structures show cofacial arrangements between the pyridinium and the naphthalene rings. However, the relative position of the aromatic rings depends on the chain length. The naphthol group sits in the middle of the viologen moiety in NC$_3$V, whereas it is on top of the outer pyridinium ring in NC$_5$V. For molecules with longer linkages, it appears that interaction of the naphthalene moiety with the outer pyridinium ring is favored, but interaction with the inner pyridinium ring is also allowed at the expense of a small amount of conformational energy.

Data from NMR chemical shifts (in Table 1) show excellent agreement with the suggested structures from the molecular modeling. The protons (H$_\alpha$) adjacent to the ether oxygen atom where the naphthalene ring is attached show a progressive upfield shift as the naphthol group moves from the inner part to the outer part of the viologen moiety, *i.e.* +0.09, −0.17, −0.21, −0.29, −0.30 ppm for $n = 3, 12, 9, 7, 5$, respectively. H$_c$ protons, showing the most prominent shift among the viologen protons, exhibit exactly the same trend. The naphthol ring protons show a similar trend. The protons superimposed on the inner part of the viologen ring (H$_1$, H$_2$, H$_3$, H$_7$) show larger shifts than those on the outer part (H$_4$, H$_5$, H$_6$). H$_1$ and H$_7$ next to the linkage site show a particularly large shift.

The $\Delta\delta_{intra}$ values in Table 2 also agree well with the modeling calculations. The energy-minimized structure for NC$_5$V predicts a large change in $\Delta\delta_{intra}$ for H$_m$ and H$_\alpha$ protons, whereas H$_\omega$ proton is expected to experience a large change in the NC$_3$V case. The change for the viologen protons ($\Delta\delta_{intra}$ for H$_a$ and H$_d$ protons) leads to the same conclusion. It is interesting to note that $\Delta\delta_{intra}$ values are much more sensitive to position than $\Delta\delta_{inter}$. This seems to reflect the fact that the energy barrier between the molecular conformations in the intramolecular complex is larger than that in the intermolecular complex.

The variation of $\Delta\delta$ is much greater in molecules with shorter chains than in those with longer linkage chains. For molecules with shorter linkages ($n = 3$ and 5), the two structures with lowest energies differ only in the relative orientation of the bipyridinium and naphthalene moieties, while the relative position of the two rings is almost the same. This seems to result in a large difference in $\Delta\delta$ values depending on the position of the protons in the molecules. However, for molecules with longer linkages ($n = 9$ and 12), the naphthalene moiety takes a position on the top of different pyridinium rings in the two conformations of lowest energy. Since the energy difference between the two structures is relatively small, the two structures are more or less averaged in the observed NMR spectra, and the $\Delta\delta$ values do not vary much according to the proton position. NC$_7$V also takes the two extreme conformations, but the energy difference is much greater than those in NC$_9$V and NC$_{12}$V, giving a larger difference in $\Delta\delta$ depending on the position.

Conclusions

The NMR studies of naphthalene–viologen compounds linked with flexible polymethylene chains of various length show surprisingly rich dynamic and structural features. The molecules form intramolecular as well as intermolecular charge transfer complexes. Also the molecules with long bridges aggregate to give micelle-like structures. Even though the structure is highly dynamic due to the flexibility of the linkage chain, we could deduce possible molecular structures for various chain lengths from NMR data and molecular modeling calculations. The relative positions of the pyridinium and naphthalene rings and their orientations depend on the length of the linkages.

Acknowledgements

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