

PHOTOCHEMICAL, PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF A PHOTOISOMERIZABLE CYCLOPHANE AND ITS [2]CATENANES WITH AROMATIC CROWN ETHERS (*) (**)

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Summary – The photochemical, photophysical, and electrochemical behaviour of *t*-1,2-bis(1-benzyl-4-pyridinium)ethylene (*t*-DBBPE²⁺) (used as model compound), a cyclophane made of two *t*-1,2-bis(4-pyridinium)ethylene (BPE) units (**1**⁴⁺), and its catenanes (**1BB**⁴⁺, **1BN**⁴⁺, and **1NN**⁴⁺) with aromatic crown ethers containing two *p*-dimethoxybenzene units (**BB**), one *p*-dimethoxybenzene and one 1,5-dimethoxynaphthalene unit (**BN**), and two 1,5-dimethoxynaphthalene units (**NN**) have been investigated in acetonitrile solution. For both *t*-DBBPE²⁺ and **1**⁴⁺, fluorescence and direct *trans*→*cis* photoisomerization are prevented by the presence of an intramolecular charge-transfer (CT) excited state close to or below the ¹ππ* level, but the triplet-sensitized photoisomerization takes place with high quantum yield. In the **1BB**⁴⁺, **1BN**⁴⁺, and **1NN**⁴⁺ catenanes, also the triplet sensitized photoisomerization is quenched by the presence of lower lying intercomponent CT levels. The intercomponent CT interaction present in the catenanes affects the reduction potentials of the *t*-DBBPE²⁺ units of **1**⁴⁺. Such an interaction, which plays the role of a brake against the free rotation of the two rings of catenanes, is released upon reduction of the **1**⁴⁺ cyclophane.

In the last decade there has been a rapid growth in the knowledge of the photochemical and electrochemical properties of simple molecular species. There is now an emerging need to study the photochemical and electrochemical behaviour of more complex (multicomponent or supramolecular) species in order to extend our knowledge of basic phenomena and find systems that might be useful for practical applications.

Photochemical and electrochemical investigations can give complementary information on the properties of a molecular species since electronic excitation and electron transfer are related processes^{1,2}. Relationships between photochemical and electrochemical properties are particularly important for supramolecular species where charge-transfer interactions are responsible for molecular association. Several catenanes and rotaxanes have been recently investigated by photochemical and electrochemical techniques^{3,4}. Photons and electrons are particularly suitable stimuli to cause structural rearrangements in these types of molecular architectures. The light-driven unthreading of a pseudorotaxane⁵, the electrochemically-driven switching between two transla-

tional isomers of a catenane⁶, an electrochemically switchable molecular shuttle⁷, and the electrochemically-triggered swinging of a [2]catenane⁸ have been reported, and some fast light-induced movements in a molecular shuttle have been claimed to occur⁹. Such simple mechanical molecular machines may play a role in the development of a bottom-up approach to the design and construction of nanometer size devices for information processing and other applications^{1,10-13}.

The construction of catenanes containing photoisomerizable components is a logical step towards an exploratory search for systems capable to perform useful functions. A first attempt in this direction has been made by Vögtle and coworkers¹⁴ by synthesizing catenanes containing azobenzene units. We have concentrated our attention on the *t*-1,2-bis(4-pyridinium)ethylene (BPE) units, which exhibit good electron-accepting properties^{15a,b} and are known to undergo photoinduced *trans*→*cis* isomerization¹⁵.

The compounds investigated and the abbreviations used are shown in figure 1. The bis-*p*-phenylene-34-crown-10 (**BB**), 1,5-naphtho-*p*-phenylene-36-crown-10 (**BN**), and 1,5-dinaphtho-38-crown-10 (**NN**) crown ethers contain the *p*-dimethoxybenzene (*p*-DMB) and/or 1,5-dimethoxynaphthalene (1,5-DMN) electron-donating moieties, whereas the **1**⁴⁺ cyclophane is composed of two *t*-1,2-bis(4-pyridinium)ethylene (BPE) electron-accepting units. *t*-1,2-bis(1-benzyl-4-pyridinium)ethylene (*t*-DBBPE²⁺) is a model for such units.

(*) Dedicated to Professor Fernando Montanari on the occasion of his 70th birthday.

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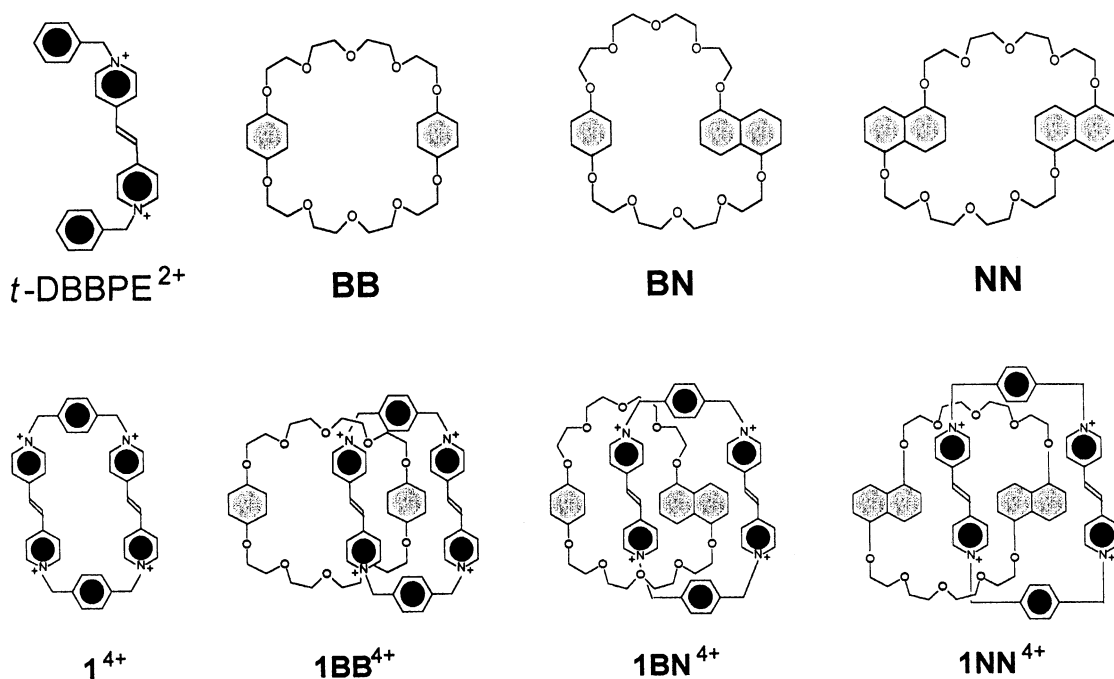


Fig. 1 - Structural formulae of the compounds examined.

EXPERIMENTAL

The synthesis, purification, and characterization of the investigated compounds will be reported elsewhere^{6,16}.

The solvent used was acetonitrile Merck Uvasol for the photophysical and photochemical experiments and Aldrich extra-dry for the electrochemical ones. *p*-Dimethoxybenzene (*p*-DMB), 1,5-dimethoxynaphthalene (1,5-DMN), biacetyl (2,3-butanedione) and tetraethylammonium tetrafluoroborate were Fluka, while benzanthrone (7*H*-benz[*de*]anthracene-9-one) was Baker Reagent grade. All the experiments were carried out at room temperature, and the concentrations of the catenanes and related components were in the range 10^{-5} - 10^{-4} M, unless otherwise noted.

Absorption spectra were recorded with a Perkin Elmer $\lambda 6$ spectrophotometer. Uncorrected emission and corrected excitation spectra were obtained with a Perkin Elmer LS50 spectrofluorimeter. Emission spectra in CH₃CN rigid matrix were recorded at 77 K using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. Luminescence quantum yields (uncertainty $\pm 15\%$) were determined using naphthalene in degassed cyclohexane as a standard ($\Phi=0.23$)¹⁷.

Photochemical experiments were carried out with a medium-pressure Q400 Hanau mercury lamp, whose light was filtered with interference filters ($\lambda=313$ nm for direct photochemistry, $\lambda=365$ nm and 436 nm for benzanthrone and biacetyl photosensitized reactions, respectively). For the photosensitization experiments the solutions were degassed by the «freeze-thaw-pump» method and the light was absorbed only by the photosensitizer (biacetyl 6.0×10^{-2} M; benzanthrone 5.0×10^{-5} - 1.0×10^{-4} M). The incident light intensity was measured using the ferric oxalate actinometer¹⁸. In the direct irradiation experiments the photon intensity was of the order of 10^{-7} Nh ν /min; in the photosensitized experiments the intensity was reduced by means of a grey filter ($T=1\%$). The experimental error on the photochemical quantum yields was $\pm 20\%$.

Electrochemical measurements were carried out in argon-purged solution with a Princeton Applied Research 273 multi-purpose instrument interfaced to a personal computer. A glassy carbon electrode (0.08 cm², Amel) was used as the working electrode. The counter electrode was a Pt wire and the reference electrode was an SCE (saturated calomel electrode) separated with a fine glass frit. The concentration of the compounds examined was 5.0×10^{-4} M; 0.05 M tetraethylammonium tetra-

fluoroborate was added as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates of 20, 50, 200 and 500 mV s⁻¹. All the reduction processes were fully reversible. The criteria for reversibility were the separation between cathodic and anodic peaks, the close-to-unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing sweep rate. The experimental error on the potential values was estimated to be ± 20 mV.

RESULTS AND DISCUSSION

ELECTROCHEMISTRY

The electrochemical data concerning the reduction of the model compound *t*-DBBPE²⁺, the cyclophane 1⁴⁺ and the three catenanes 1BB⁴⁺, 1BN⁴⁺ and 1NN⁴⁺ are collected in table 1 and schematically shown in figure 2.

The electrochemical behaviour of the model compound *t*-DBBPE²⁺ is characterized by two reversible one-electron waves corresponding to the first and second reduction of the BPE unit.

The 1⁴⁺ cyclophane, containing two BPE units, again shows two reversible reduction waves, but they are bielectronic and slightly shifted to more positive potentials. The involvement of two electrons in each reduction step means that the two BPE units are reduced at the same potential and therefore do not interact with each other.

As far as the three catenanes are concerned, they behave in a similar way: in all cases the voltammograms show a sequence of two reversible one-electron waves and one two-electron wave.

The different reduction behaviour of 1⁴⁺ and its catenanes can be accounted for by considering the charge-transfer interaction between the electron-

TABLE 1 - HALF-WAVE REDUCTION POTENTIALS (V, vs SCE) OBTAINED IN ARGON-PURGED CH₃CN SOLUTION AT ROOM TEMPERATURE

Compound	E_1	E_2	E_3	E_4
DBBPE ²⁺	-0.44	-0.64	—	—
1⁴⁺	-0.42 ^a	-0.62 ^a	—	—
1BB⁴⁺	-0.43	-0.53	-0.65 ^a	—
1BN⁴⁺	-0.44	-0.57	-0.73 ^a	—
1NN⁴⁺	-0.45	-0.59	-0.75 ^a	—

(^a) Two-electron process.

accepting BPE units of **1⁴⁺** and the electron-donating units of the aromatic crown ethers. When **1⁴⁺** is interlocked with the crown ethers (figure 1), the two BPE units *i*) are more difficult to reduce as a consequence of the charge-transfer interaction and *ii*) are no longer equivalent since the «alongside» BPE unit interacts with only one donor moiety whereas the «inside» one interacts with two donor moieties. Therefore, in the catenanes the first bielectronic wave of the free cyclophane splits in two mono-electronic waves, shifted to more negative potentials. The first wave corresponds to the mono-electronic reduction of the «alongside» BPE and the second one to the mono-electronic reduction of the «inside» BPE.

The third wave in the voltammograms of the catenanes involves two electrons and must therefore correspond to the simultaneous second reduction of the two BPE units. This shows that in the catenanes the monoreduced BPE units are still involved in the charge-transfer interaction (as

indicated by the negative shift with respect to the second bielectronic wave of **1⁴⁺**), but occupy equivalent positions. This is presumably the result of a fast rotation of the two rings.

A detailed comparison between the behaviour of the three catenanes draws attention to another interesting feature. The trend of the reduction waves of the **1BB⁴⁺**, **1BN⁴⁺** and **1NN⁴⁺** shows that the BPE units become more difficult to reduce as the electron donor ability increases ($E_{\text{ox}} = +1.17$ V for the 1,5-DMN unit¹⁹ and +1.31 V for the *p*-DMB one³ vs SCE). Furthermore, a comparison between the potentials of the first and second wave shows that the effect of the electron-donating units is more pronounced for the latter. This is due to the fact that the «inside» BPE moiety is topologically forced to experience the nature of the donor units more than the «alongside» BPE unit. These observations are a further indication that the electrochemical behaviour of the catenanes is basically governed by the charge-transfer interaction between electron-donating and electron-accepting components.

Finally, one can note a particularly large shift of the third wave in the case of the **1BN⁴⁺** and **1NN⁴⁺** catenanes (figure 2). This observation seems to point to some kind of specific interaction, whose nature is at present unclear, between the monoreduced BPE units and the 1,5-DMN donor group.

As expected, also the oxidation potentials of the donor units are affected by the charge-transfer interaction. The oxidation processes, however, are difficult to rationalize because they are irreversible or not fully reversible.

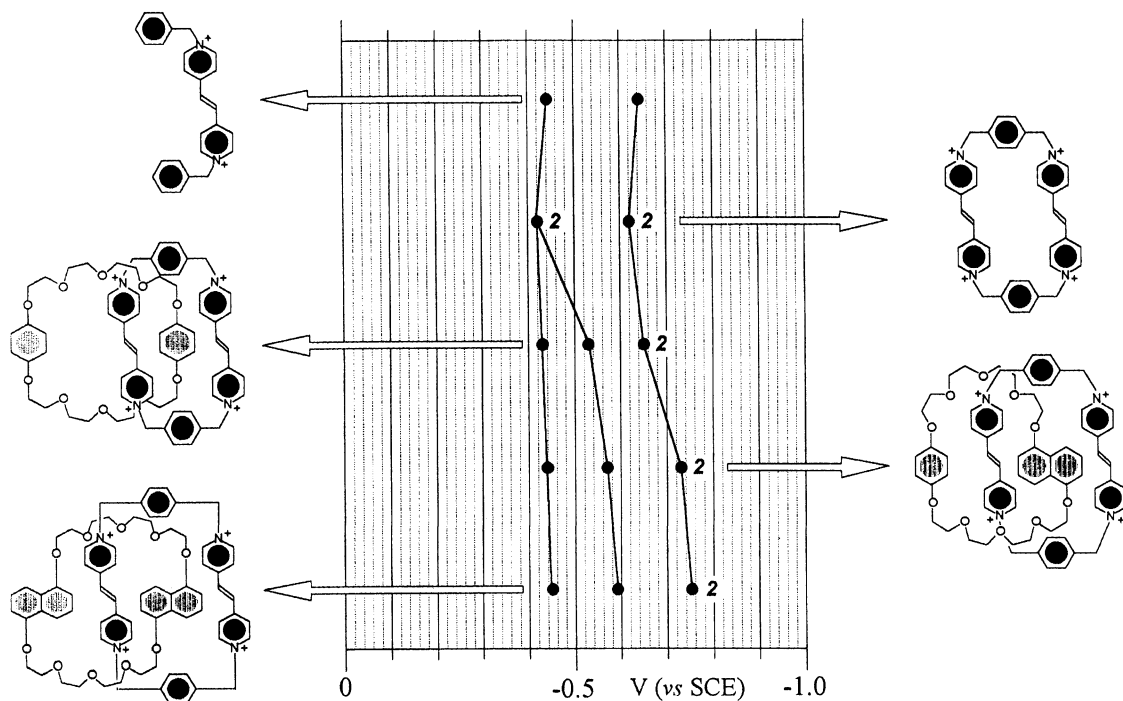


Fig. 2 - Correlations between the half-wave reduction potentials of the *t*-DBBPE²⁺ model compound, the **1⁴⁺** cyclophane and the respective catenanes. Two-electron reduction processes are labelled with the number 2.

ABSORPTION AND EMISSION SPECTRA

The data concerning absorption and emission spectra are collected in table 2.

The absorption spectra of the crown ethers **BB**, **BN** and **NN** are those expected for their chromophoric units. The fluorescence spectra of **BB** and **NN** are identical to those of the respective *p*-DMB and 1,5-DMN model compounds, except for a lower (about 30%) intensity. The luminescence spectrum of **BN** shows only the band of the 1,5-DMN unit, regardless of the excitation wavelength. The excitation spectrum shows that energy transfer from the *p*-DMB to the 1,5-DMN unit is practically 100% efficient. The luminescence quantum yield is equal to that of the 1,5-DMN model compound.

TABLE 2 - ABSORPTION AND EMISSION PROPERTIES IN AIR-EQUILIBRATED CH₃CN SOLUTION AT ROOM TEMPERATURE

Compound	Absorption		Emission	
	λ_{\max} (nm)	ϵ_{\max} ($M^{-1}cm^{-1}$)	λ_{\max} (nm)	Φ_{em}
BB	290	5200	320	0.11
BN	295	11500	330	0.38
NN	295	17600	330	0.26
<i>t</i> -DBBPE ²⁺	324	42000	372	6×10^{-4}
1⁴⁺	316	48000	376	4×10^{-4}
1BB⁴⁺	319	49000	—	—
	440	1100	—	—
1BN⁴⁺	316	55700	—	—
	470	920	—	—
1NN⁴⁺	307	49000	—	—
	490	1100	—	—

The absorption spectrum of *t*-DBBPE²⁺ (figure 3) is practically identical to that of the analogous *t*-1,2-bis(1-methyl-4-pyridinium)ethylene (*t*-DMBPE²⁺) compound which contains methyl instead of benzyl substituents in the 1-pyridinium positions. *t*-DBBPE²⁺ (figure 3) and *t*-DMBPE²⁺^{15a-c} exhibit the characteristic fluorescence band of the *t*-bis(pyridinium)ethylene unit²⁰. However, the fluorescence quantum yield of *t*-DBBPE²⁺ is very low (~6% of that of *t*-DMBPE²⁺, for which $\Phi=0.01$ ^{15a,b} has been reported). This observation can be attributed to the presence in *t*-DBBPE²⁺ of a charge-transfer excited state [hereafter indicated by CT(*intra*) for a reason that will be explained later

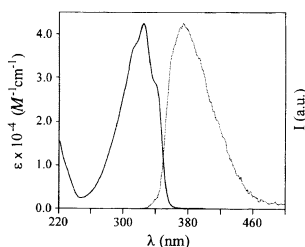


Fig. 3 - Absorption (—) and emission (.....) spectra of *t*-DBBPE²⁺ in air-equilibrated CH₃CN solution at room temperature.

on] at comparable or even lower energy than the fluorescent ¹ $\pi\pi^*$ level ($E^{00} \sim 3.6$ e V, from the first feature of the fluorescence spectrum at 77 K). The presence of a charge-transfer excited state at relatively low energy is expected since the bis(pyridinium)ethylene moiety is an electron acceptor ($E_{1/2}$ *t*-DMBPE^{2+/+} = -0.53 V vs SCE)^{15c} and the benzyl moiety is a weak electron donor ($E_{1/2}$ C₆H₅CH₃^{0/+} = 1.98 V vs SCE)²¹. This CT(*intra*) excited state cannot be seen in absorption presumably because the charge-transfer transition exhibits a very weak molar extinction coefficient compared to that exhibited by the ¹($\pi \rightarrow \pi^*$) transition ($\epsilon_{\max} = 4.2 \times 10^4 M^{-1}cm^{-1}$). We will see later that the presence of a CT(*intra*) excited state below the ¹ $\pi\pi^*$ level is also needed to explain the photochemical results.

The absorption spectrum of **1⁴⁺** is slightly different in shape and much weaker than that expected for two *t*-DBBPE²⁺ units. A fluorescence band identical both in shape and intensity to that exhibited by *t*-DBBPE²⁺ is observed.

The absorption spectra of the catenanes are different from the summation of the spectra of the respective components (table 2). As shown for **1NN⁴⁺** in figure 4, the UV bands of the two macrocyclic components are reduced in intensity with noticeable changes in the band structure. Furthermore, a tail in the 350-400 nm region and a new, broad, relatively weak band in the visible region are observed. Such spectral changes indicate an electronic interaction of the two macrocyclic components in the catenane structure. The new band in the visible region can be assigned³ to charge-transfer transitions from the electron-donor units of the crown ether to the electron-acceptor units of the tetracationic cyclophane. This assignment is consistent with the observed blue shift (figure 4,

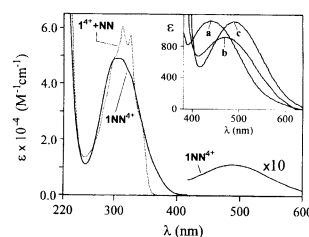


Fig. 4 - Comparison of the absorption spectrum of the **1NN⁴⁺** catenane (—) with the sum of the spectra of the separated components (.....) (CH₃CN solution). The inset shows the CT(*inter*) absorption band of (a) **1BB⁴⁺**, (b) **1BN⁴⁺** and (c) **1NN⁴⁺** in CH₃CN solution.

inset) when *p*-DMB (which is more difficult to oxidize) replaces one or two 1,5-DMN as a donor in the macrocyclic crown ether. It should be noticed that the CT bands of the catenanes in the visible region, hereafter indicated by CT(*inter*) to avoid confusion with the previously discussed CT(*intra*) exhibited by *t*-DBBPE²⁺ and **1⁴⁺**, receive contributions from a number of electronic transitions. More specifically, in the symmetrical **1BB⁴⁺** and

1NN^{4+} catenanes three CT(*inter*) transitions can be expected (*i.e.*, from external donor to internal acceptor, from internal donor to external acceptor, and from internal donor to internal acceptor). On the same basis, six different CT(*inter*) transitions can be expected for the asymmetrical 1BN^{4+} catenane, since it can assume two different translational conformers (*i.e.*, with each donor unit of the asymmetric macrocycle in the «inside» or «alongside» positions). The contribution of transitions of different energy explains why the CT(*inter*) bands are very broad (figure 4).

None of the catenanes shows the fluorescent bands characteristic of their chromophoric units. Clearly, the low energy CT(*inter*) levels offer a fast radiationless decay route to the fluorescent levels of the components, as schematized for 1NN^{4+} in figure 5.

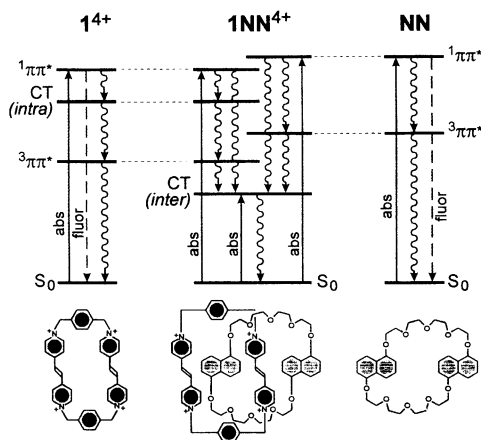
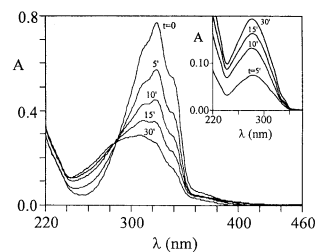


Fig. 5 - Schematic energy-level diagrams for 1NN^{4+} and its components.

PHOTOCHEMICAL BEHAVIOUR

The photochemical behaviour of the $t\text{-DMBPE}^{2+}$, which is analogous to $t\text{-DBBPE}^{2+}$ since it contains methyl instead of benzyl substituents in the 1-pyridinium positions, was studied by Whitten, Tokumaru, and coworkers¹⁵. In acetonitrile solution, a *trans*→*cis* photoisomerization was observed upon both direct excitation in the $1\pi\pi^*$ band^{15b} and triplet sensitization with biacetyl^{15a,d}. $t\text{-DBBPE}^{2+}$ undergoes a reaction in CH_3CN solution when irradiated in the $1\pi\pi^*$ band with 313 nm light. A decrease in the intensity of the $1\pi\pi^*$ absorption band and two isosbestic points (at 275 and 355 nm) are observed. From FABMS and ^1H NMR spectroscopic analyses we have found that the photoproduct is a cyclobutene derivative¹⁶, excluding the presence of the *cis* isomer in the reaction mixture. In an attempt to obtain a photoinduced *trans*→*cis* isomerization of $t\text{-DBBPE}^{2+}$, we have then performed photosensitization experiments by using biacetyl as a triplet sensitizer. The biacetyl phosphorescence was quenched with rate constant $1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; the spectral variations (figure 6) were different from those obtained upon



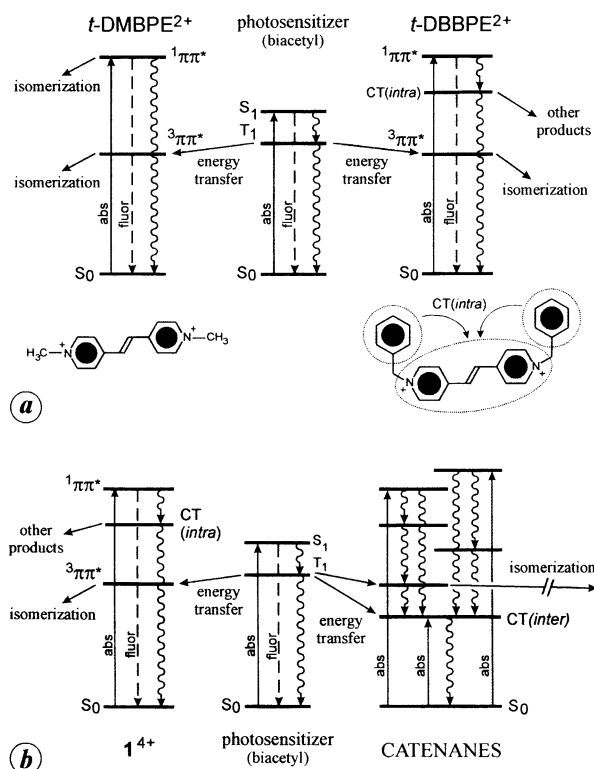


Fig. 7 - Schematic energy-level diagrams illustrating the photophysical and photochemical processes taking place (a) in the t -DMBPE $^{2+}$ and t -DBBPE $^{2+}$ compounds and (b) in 1^{4+} and relative catenanes.

sed and only the $3\pi\pi^*$ excited state is populated (figure 7a). Under such conditions, t -DBBPE $^{2+}$ undergoes photoisomerization as does t -DMBPE $^{2+}$.

Direct light excitation of the catenanes does not cause any appreciable photoreaction. No photoreaction can be observed even when the biacetyl and benzanthrone triplet sensitizers are used. This behaviour can be accounted for on the basis of the diagram shown in figure 7b. In the catenanes low-lying CT(*inter*) levels are present besides the levels of the two macrocyclic components. As shown by the position of the CT(*inter*) absorption bands (figure 4), the CT(*inter*) levels lie certainly below the $1\pi\pi^*$ and CT(*intra*) levels, and therefore they are expected to quench the processes which would originate from such excited states. This explains the lack of any fluorescence and direct photoreaction when these catenanes are excited in their UV bands. Judging from the extension to the red of the tail of the CT(*inter*) absorption bands, the lowest CT(*inter*) level can be as low as 15,000–16,000 cm^{-1} , *i.e.* lower than the T_1 level of the photosensitizer (biacetyl: 19,250 cm^{-1} ; benzanthrone: 16,450 cm^{-1})²² and even than the $3\pi\pi^*$ level of t -DBBPE $^{2+}$ [$E_T(3\pi\pi^*) \approx 17500 \text{ cm}^{-1}$ for t -1,2-bis(4-pyridyl)ethylene^{15d} and for its conjugate acid²³]. Therefore, the potentially reactive $3\pi\pi^*$ level of the isomerizable moiety can be quenched by the presence of the CT(*inter*) state or not populated at all.

CONCLUSION

The [2]catenanes investigated in this paper (figure 1) are composed of a cyclophane and a crown ether component which contain electron-acceptor and electron-donor units, respectively. The results obtained show that the photochemical, photophysical and electrochemical behaviour of the cyclophane and crown ether components is very similar to that of the respective individual moieties, whereas different properties appear when a cyclophane and a crown ether are interlocked in a catenane structure. This is clearly due to the presence of charge-transfer interactions which (i) introduce new, low-lying excited states and (ii) perturb the electron-donor/acceptor properties of the various components. The consequence of the former effect is a drastic, qualitative change in the photochemical and photophysical properties since the reactive and/or luminescent levels of the components are quenched by the lower-lying CT levels. This is the reason why the luminescence of the crown ethers and the luminescence and the direct and sensitized photoreactions of the cyclophanes are not observed in the catenanes (figures 5 and 7). On the electrochemical side, the charge-transfer interaction affects the redox potentials of the components and thereby it causes the removal of degeneracy and other changes in the pattern of the electrochemical processes (figure 2).

It should also be noted that the intercomponent charge-transfer interaction plays the role of a brake as far as the rotation of the two rings is concerned, since it stabilizes the geometrical arrangement which allows the strongest interaction. Reduction of the electron-acceptor components (or oxidation of the electron-donor ones) amounts to release the charge-transfer brake thereby leaving the two rings free to rotate. This principle has already been exploited on similar compounds to construct light-driven⁵ and electrochemically driven⁷ mechanical molecular machines.

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