1. Molecular Anion Binding and Substrate Photooxidation in Visible Light by 2,7-Diazapyrenium Cations

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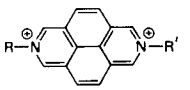
(21.X.86)

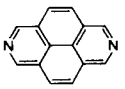
The 2,7-diazapyrenium group (DAP^{2+}) combines the features of pyrene, of methylviologen, and of nucleic-acid intercalators and may thus present a variety of interesting properties. The cations **1** and **2** and the bis-diazapyrenium species **3** have been synthesized and shown to bind molecular anions like aromatic polycarboxylates, giving rise to pronounced shifts of ^{1}H-NMR signals, modifications of UV/VIS absorption spectra, and quenching of fluorescence. The complexes formed probably have a face-to-face structure, and their stability constants are remarkably high, in particular for the bis-diazapyrenium cation **3** which is susceptible to form intercalative chelate complexes such as **9** ($\log K_s \approx 3$ for **1**, up to *ca.* 7 or more for **3a**). Neutral molecules like adenine are also bound, but much less strongly. Visible-light irradiation of Me_2DAP^{2+} (**1**) in presence of various electron donors, such as EDTA, gives the reduced species $Me_2DAP^{+\cdot}$ wich has been characterized by UV/VIS and ESR spectroscopy. The results indicate that Me_2DAP^{2+} (**1**) functions as a *methylviologen analogue, photoactive in visible light.* Thus 2,7-diazapyrenium cations are attractive subunits for incorporation into macropolycyclic structures to give photo- and electroactive receptor molecules.

Introduction. – Molecular units which combine proper geometrical characteristics and specific physico-chemical properties are of much interest for the design of receptor molecules and molecular devices displaying functional features such as electroactivity, photoactivity and chemical reactivity [1]. This is the case namely for porphyrin and α,α'-bipyridine groups which have been incorporated into polytopic coreceptors capable of binding both metal ions and organic substrates [2] [3].

The 2,7-diazapyrenium dications (DAP^{2+}) like **1** are attractive molecular units, since they may be considered to present features resulting from the triple combination of those of pyrene, of methylviologen (= 1,1′-dimethyl-4,4′-bipyridinium; MV^{2+}, **4**), and of nucleic-acid intercalators, which define three classes of compounds very actively studied



1 R = R′ = CH_3
2 R = CH_3, R′ = $C_6H_5CH_2$



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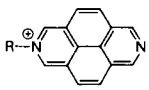
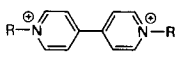
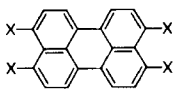


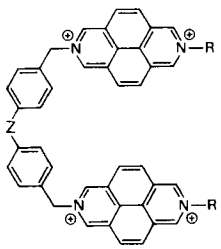
6 R = CH_3



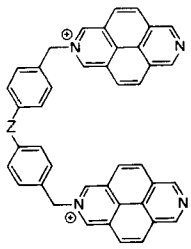
4 R = CH_3



8 X = CO_2



3a R = CH_3, Z = CH_2
3b R = CH_3, Z = O
3c R = CH_3, Z = $(CH_3)_2C$



7a Z = CH_2
7b Z = O
7c Z = $(CH_3)_2C$

[1]) U.A. 422 of the CNRS.

in recent years for their physical, chemical, and biological properties. This led us to explore the variety of properties which these flat and charged species might present: be electroactive, photoactive, and fluorescent, form complexes with electron-rich and anionic substrates, interact with nucleic acids, and even be materials for 'organic metals'. We report here results on the physicochemical, the anionic substrate binding, and the photochemical properties of the 2,7-diazapyrenium dications Me_2DAP^{2+} (**1**) and BzlMe-DAP^{2+} (**2**), and of the dimeric tetracation $[Z(Bzl)_2](DAP)_2^{4+}$ (Z = CH_2, O, $(CH_3)_2C$; **3**). Some studies have been performed with methylviologen (**4**) for comparison purposes. Efficient photocleavage of DNA under irradiation with visible light in presence of **1** and **3a** has been described in [4].

Preparation of the 2,7-Diazapyrenium Compounds 1–3. – Methylation of 2,7-diazapyrene (**5**) with excess MeI gave the *N,N'*-dimethiodide **1** · $2I^-$ [5]. Treatment of **5** with MeI in $CHCl_3$ gave the monomethiodide **6** · I^-, which by benzylation in MeCN with benzyl bromide afforded the *N*-benzyl-*N'*-methyl derivative **2** as a iodide/bromide salt. The dimeric species **3a** was obtained by reacting bis[4-(bromomethyl)phenyl]methane [6] with 2.2 equiv. of 2,7-diazapyrene; the resulting dication **7** (80% yield) was treated with a large excess of MeI to give the salt **3a** · $2Br^-$ · $2I^-$. The reddish-brown methiodides **1** · $2I^-$, **2** · Br^- · I^-, and **3a** · $2Br^-$ · $2I^-$ were converted into the corresponding yellow chlorides **1** · $2Cl^-$, **2** · $2Cl^-$ and **3a** · $4Cl^-$, respectively, either by stirring in H_2O solution with an excess of a AgCl suspension or by passage over an ion-exchange column. Methylation with MeBr was also performed in a few cases. Although most studies were performed with **3a** · $4Cl^-$, the other tetracations of the $[Z(Bzl)_2](DAP)_2^{4+}$ type, **3b** and **3c**, were also prepared, by methods similar to that used for **3a** (see *Exper. Part*).

Binding of Molecular Anions. – *Spectroscopic Observations.* The binding of anionic substrates by the cationic ligands **1**–**3a** was detected and investigated by several spectroscopic methods: ^{1}H-NMR, UV/VIS-absorption, and fluorescence spectroscopy.

Addition of an aromatic polycarboxylate (= substrate) to an aqueous solution of **1**, **2**, or **3a** (pH *ca.* 7.0) gave large upfield shifts of the *^{1}H-NMR resonances* of the substrate anion (up to *ca.* 2 ppm) and smaller shifts for the cationic ligand itself (*ca.* 0.5–1.5 ppm; *Table*). These changes may be attributed to the formation of cation-anion associations, resulting in mutual shielding of the protons of the partners.

Me_2DAP^{2+} (**1**) possesses strong absorptions in the VIS domain (λ_{max} (ε): 416 (14300), 390 (8300) nm; see also *Fig. 2* below). *Charge-transfer absorption* appeared, accompanied by a colour change of the solution from yellow to orange, when a donor molecule such as indole acetate was added to an aqueous solution of **1**. The absorption bands also decreased in intensity and broadened towards longer wavelength on addition of an excess of an aromatic anion such as naphthalene-2,6-dicarboxylate. Similar but weaker spectral effects were found for other donor molecules like EDTA, nitrilotriethanol, or ascorbate. Charge-transfer complexation has been observed and studied for methylviologen (**4**) itself (see for instance [7–19]), but the corresponding absorptions are markedly stronger in the VIS for **1** as compared to **4** (with indole acetate, ε = 200 and 20, respectively; aqueous solution, 5 mM of each compound; for **4** see also [15]). In view of the numerous studies which have been devoted to the spectroscopic, photophysical, and photochemical properties of **4** (including its use as redox relay species in photochemical light energy storage cycles, see below), $MeDAP^{2+}$ (**1**) and its derivatives represent excellent candidates for

Table. *Shifts* ([Hz]) *Observed for the* ^{1}*H-NMR Signals* (at 200 MHz) *of Ligand and Substrate on Complexation in Aqueous Solution*

Ligand		Signal[b] [ppm]	Substrate[c]					
			Benzene-1,4-dicarboxylate	Benzene-1,3,5-tricarboxylate	Benzene-1,2,3,5-tetracarboxylate	Naphthalene-2,6-dicarboxylate	**8**	Adenine
BzlMeDAP^{2+} 2 Cl$^-$	(**2**·2 Cl$^-$)	2H–C(α), (9.98, *s*)	52	71	22	148	162	(*ca.* 4)
		2H–C(α'), (9.88, *s*)	54	70	25	158	206	(*ca.* 5)
		CH_2 (6.24)	21	30	12	89	71	(*ca.* 3)
		S	190	295	73	(430)[e]	235/310[f]	
$[CH_2(Bzl)_2](DAP)_2^{4+}$ 4 Cl$^-$	(**3a**·4 Cl$^-$)	2H–C(α) (10.15, *s*)	91	105	52	197		35
		2H–C(α') (10.10, *s*)	86	114	60	170		40
		CH_2 (6.39)	70	73	44	121		34
		S	405	450	110	(450)[e]		

[a]) Displacements of ^{1}H-NMR signals in an aq. soln. of ligand/substrate 1:1 with respect to the signals of the pure ligand and substrate under the same conditions; concentration: 15 mM for Me_2DAP^{2+} and BzlMeDAP^{2+}, 4 mM for $[CH_2(BzC)_2](DAP)_2^{4+}$; at 20°.

[b]) α and α' refer to positions C(1)/C(3) and C(6)/C(8) of the DAP moiety in **2** and **3a**; S: signal(s) of anionic substrate.

[c]) Sodium salts.

[d]) In the case of ligand Me_2DAP^{2+} (**1**), the following signals (and shifts) were observed: 10.08 (181 Hz) and 8.90 ppm (181 Hz) for ligand and 404 Hz for substrate; in the case of MV^{2+} (**4**): 9.06 (99 Hz) and 8.53 ppm (126 Hz) for ligand and 10 Hz for substrate.

[e]) Multiplet signal.

[f]) Shifts for the 2 *AB d* of **8**.

shifting into the visible range processes which occur in the near-UV with **4** itself. These compounds thus represent *visible-light-sensitive analogues of methylviologen.*

The diazapyrenium cations show *strong fluorescence (Fig. 1)*. The intensity of fluorescence does not increase linearly with concentration; for instance, for BzlMeDAP^{2+} 2 Cl$^-$ (**2** · 2 Cl$^-$), the intensity at 2×10^{-5} M is *ca.* half that expected from the intensity at 2×10^{-6} M. Similar self-quenching occurs for instance also with acridine dyes like proflavine [20]. It may be attributed to intermolecular auto-association such as the stacking dimerisation of the acridine-orange cation [21]. Significantly, the emission spectrum of the $[Z(Bzl)_2](DAP)_2^{4+}$ species **3a** at 1.5×10^{-5} M has similar shape as, but is more than an order of magnitude weaker than that of its 'monomeric' analogue BzlMeDAP^{2+} (**2**) at the

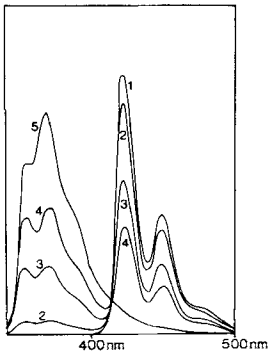


Fig. 1. *Quenching of the fluorescence of the* N*-benzyl-*N*-methyl-2,7-diazapyrenium dication* (**2**) *by the naphthalene-2,6-dicarboxylate dianion. Curve 1:* fluorescence spectrum of **2**·2 Cl$^-$; *Curves 2–5* are obtained on addition of increasing amounts of anionic substrate and correspond to the following dianion/dication ratios: *Curve 2,* 1; *3,* 5; *4,* 10; *5,* 100; the emission below 400 nm is due to the anionic substrate; aq. solns.; concentration of **2**·2 Cl$^-$, 10^{-5} M; excitation wavelength, 336 nm; 20°.

same concentration. This strong intramolecular quenching could indicate that the two DAP^{2+} units of **3a** are preferentially in the *'syn' orientation* (folded conformation) represented in structure **3** in equilibrium with the corresponding *'anti'* form (unfolded conformation). Intramolecular stacking has been shown to occur in bifunctional compounds containing two nucleic bases [22], two caffeine groups [23], or two intercalator-type units (ethidium, acridine) [24]. The crystal structure of a bifunctional intercalator containing two phenanthridinium groups linked by a diphenylmethane bridge was found to display a *'syn'* orientation as shown in **3** [25]. The absence of upfield shifts of the ^{1}H-NMR signals of **3a** compared to **2** *(Table)* may be due to the distance (*ca.* 10 Å) (see also [25]) between the DAP^{2+} subunits in the folded form **3a** and their tilting with respect to each other (as indicated by measurements of nuclear *Overhauser* effects [26]).

Addition of naphthalene-2,6-dicarboxylate or of other molecular anions to an aqueous solution of $BzlMeDAP^{2+}$ (**2**) causes a *strong quenching* of the emission of **2** indicating that complexation takes place *(Fig. 1)*. Charge-transfer quenching of fluorescence by counterions has been observed for dyes like acridinium ions [27].

The fluorescence of the diiodide $\mathbf{1} \cdot 2I^-$ is *ca.* 10% weaker than that of the dichloride $\mathbf{1} \cdot 2Cl^-$ as expected from the greater charge-transfer ability of the former counterion. The emission of anthracene-9,10-dicarboxylate was strongly quenched by addition of even small amounts of $BzlMeDAP^{2+}$ (**2**): 10^{-4}M of the latter reduced the emission of the dianion (10^{-3}M) to less than 10% of its original value. The strong fluorescence of the tetracarboxylate **8** decreased to *ca.* 30% by addition of 2 equiv. of **2**, even at a concentration as low as 10^{-6}M. These results indicate that strong binding occurs between the DAP^{2+} cations and the anionic substrates. The very pronounced effect found in the case of anthracene-9,10-dicarboxylate may be related to the efficient quenching of the excited singlet and triplet states of anthracene derivatives by methylviologen (**4**) [28]. Finally, adenine causes a small decrease of the fluorescence of **3a**.

Binding Constants. The stability of the complexes formed between the cations **1**–**3a** and various aromatic carboxylates has been estimated from the spectroscopic changes (^{1}H-NMR shifts, UV/VIS-absorption bands) described above; for comparison purposes, some measurements have also been performed with methylviologen (**4**) itself. *Job* plots using ^{1}H-NMR and UV/VIS data gave predominantly 1:1 stoichiometry for the complexes between species having the same number of charges; however, complexes of other compositions are also formed, especially between species of different total charge. The coexistence of several such complex species, in different proportions, depending on concentrations, and with different spectral properties, may explain why it was not possible to obtain accurate stability constants by analysis of the spectral changes observed, despite the pronounced effects caused by binding when a DAP^{2+} ligand was titrated with a given molecular anion (see *e.g. Fig. 2*). Attempts to fit the experimental data with formation equilibria of 1:1 and 2:1 complexes yielded quite different binding constants depending on the spectral method and on concentrations. Nevertheless, the effects are so pronounced that a gross estimate of 'overall' stability can be made.

The stability of the 1:1 complexes formed by **2** with benzene-polycarboxylates (COO^--substituted at positions 1,2; 1,3,5, and 1,2,4,5) lie in the range $\log K_s \approx 3.0 \pm 0.4$ (aqueous solution, 20°); binding of the larger naphthalene-2,6-dicarboxylate is somewhat stronger. The complexes formed by **3a** were significantly more stable than those of **2**. In order to gain information about the *relative* binding abilities of **1**, **2**, **3a**, and **4**, some

competition experiments were performed by analysing the shifts of the ^{1}H-NMR signals of the two ligands studied, in 1:1:1 solutions of the two ligands and a given anion. It was found that the complexes of the dimeric species **3a** were at least 10 times more stable than those of the corresponding 'monomeric' unit **2**. On the other hand, the binding of naphthalene-2,6-dicarboxylate by **1** and **2** was similar and was *ca.* one order of magnitude higher than with methylviologen (**4**). Thus, the presence of two diazapyrenium units in **3a** increase markedly the stability of the complexes formed by this chelating ligand compared to **2**, and the greater 'hydrophobicity' of **1** increases substantially its binding ability with respect to **4**.

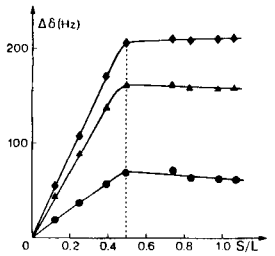


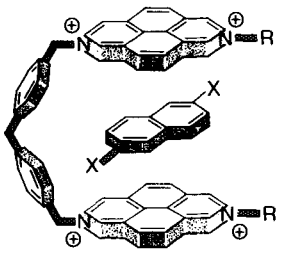
Fig. 2. *^{1}H-NMR study of the formation of a very stable 2:1 molecular complex between dication* **2** *and tetraanion* **8**. Shifts (in Hz at 200 MHz) of the ^{1}H-NMR signals of **2** (= L; top 2 curves, protons at C(α) and C(α') with respect to N; bottom curve, CH_2) on addition of increasing quantities of **8** (= S; sodium salt); concentration of **2**·2 Cl^- 10^{-4} M in D_2O, 20°; see also the *Table*.

The predominant formation of a *2:1 complex* between the dication **2** and the tetracarboxylate **8** is clearly indicated by the ^{1}H-NMR shifts observed as a function of relative concentration of the two species *(Fig. 2)*. Analysis of the ^{1}H-NMR data as well as of VIS-absorption measurements at concentrations of 10^{-4} M and 10^{-5} M, respectively, gave an overall stability constant log $\beta \approx 10$–11 for the $2L + S \rightleftharpoons L_2S$ complexation equilibrium. The very strong emission of **8** allowed to obtain fluorescence-quenching data at 10^{-7} M concentration, giving log $K_1 \approx 6.8$ for the formation of the 1:1 complex LS. Thus, the stability constants for the stepwise formation of the LS and L_2S species may be estimated to be log $K_1 \approx 7$ and log $K_2 \approx 3$–4. Only a lower limit (log K > 8) could be determined for the stability of the complex formed by **8** with $[Z(Bzl)_2](DAP)_2^{4+}$ (**3a**), due to precipitation of the adduct. Strong binding of haematoporphyrin by **2** was also observed.

Of interest is the weak, but non-negligeable complexation of *adenine* by the ligand **3a** detected by fluorescence spectroscopy (log $K_s \approx 2$). It is probable that other *neutral donor* molecules (like aromatic amines and ethers, phenols, indole, *etc.*) would form complexes with acceptor ligands containing the DAP^{2+} unit.

The *marked stability* of the complexes formed by the present molecular cations is in line with the stability-enhancing effects resulting from the combination of polar sites with hydrophobic organic units; such factors also operate in the complexation of organic cations by substituted macrocyclic polyether receptor molecules [29] and by amphiphilic receptors of speleand type [1] [30].

Geometry of the Complexes. Although there is no direct evidence about the structure of the complexes formed, it is likely that they are of the face-to-face type; this would account for the strong shielding observed for the protons of both partners and corresponds to the structure widely found for charge-transfer complexes between flat donor and acceptor molecules [8]. Such stacking occurs for instance in the crystal structure of the complexes formed by $MV^{2+}\cdot 2I^-$ (**4**·$2I^-$) and hydroquinone [31] as well as by pyrene and 2,4,6-trinitroanisole [32]. Since the DAP^{2+} unit combines the features of MV^{2+} and



9 R = CH_3, C = CO_2^-

Fig. 3. *Schematic representation of intercalative, molecular chelating complexation of naphthalene-2,6-dicarboxylate by the folded form of* $[CH_2(Bzl)_2](DAP)_2^{4+}$ (**3a**)

pyrene, one may reasonably expect that its complexes with flat molecular anions have a similar *face-to-face geometry*. The dimeric ligands **3** raise a special problem since the anionic substrate may either lie on a DAP^{2+} subunit independently from the other or be sandwiched between the two DAP^{2+} units in *'syn'* orientation, forming an *intercalative molecular chelate complex*, as schematically represented by **9** *(Fig. 3)*. The latter structure agrees with the larger chemical shifts and the higher stability found for complexes of **3a** compared to the ones of **2** *(Table)*. A similar structure has been proposed for substrate binding by bifunctional ligands containing two caffeine groups [23]. Furthermore, the changes in nuclear *Overhauser* effects occurring for **3a** on binding of naphthalene-2,6-dicarboxylate also agree with a structure such as **9** [26]. However, 2:1 complexes of *'syn'*-**3a** (1 chelated and 1 external substrate) or of *'anti'*-**3a** (2 non-chelated substrates) may also be present. The *'syn'* form shown in **3** should also be favorable for double intercalation with nucleic acids [4]. Strong binding of **1** and **3a** to polynucleotides is indicated by very pronounced fluorescence quenching [33].

Photochemical Properties of the *N,N'*-Dimethyl-2,7-diazapyrenium Dications 1. – Although MV^{2+} (**4**) is known to photooxidize electron donors like EDTA, nitrilotriethanol, and alcohols by irradiation with near-UV light generating the radical cation $MV^{+\cdot}$, the process has low efficiency in the visible even in presence of charge transfer tail absorption [9] [12–14] [16–18] [34–36]. Much higher efficiencies of photoreduction to MV^{2+} are achieved in the visible region when irradiation is performed in presence of photosensitizers (such as acridine dyes [37–40] or $[Ru(bpy)_3]^{2+}$ [41]) which absorb such frequencies. In view of the strong shift to longer wavelength exhibited by Me_2DAP^{2+} (**1**) and by its charge-transfer complexes compared to MV^{2+}, it was hoped that **1** would be able to photooxidize electron donors under visible-light irradiation, in the absence of any photosensitizer, thus becoming an *analogue of* MV^{2+} *photoactive in visible light.*

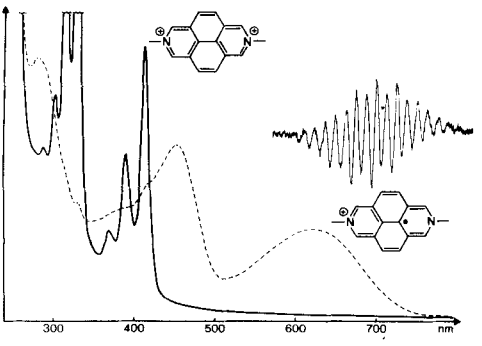


Fig. 4. *Observation of the photoreduction of* Me_2DAP^{2+} (**1**) *by visible light (* > 395 *nm) irradiation in presence of EDTA as electron donor: UV/VIS spectra of* Me_2DAP^{2+} *(——) and of the solution after 5 min irradiation (– – –).* The latter spectrum may be attributed to the reduced species $Me_2DAP^{+\cdot}$. Aqueous solution under Ar at pH 10.0 and 24°; concentrations: Me_2DAP^{2+} 2 Cl^- (**1**·2 Cl^-), 10^{-4} M; EDTA, 0.1 M. The ESR spectrum of the radical cation $Me_2DAP^{+\cdot}$ obtained is shown on top right of the figure.

Indeed, visible-light (395-nm-cut-off filter; 150-W slide projector) irradiation of **1** in degassed aqueous solution adjusted to pH 7.0 in presence of various electron donors (EDTA, nitrilotriethanol, MeOH, i-PrOH, ribose, or glucose) generated a green species which had an UV/VIS spectrum (λ_{max}: 454, 630 nm; *Fig. 4*) similar to that obtained when **1** was reduced electrochemically with < 2 equiv. of electrons (see *Exper. Part*). In most cases, the solution was quickly decolorized by air or O_2, giving back the initial UV/VIS spectrum. However, on longer irradiation or electrochemical reduction, other species were generated; reaction with O_2 of air was much slower and did not lead to complete reversibility. The redox properties of **1** [5] [42] (−0.43 V *vs.* Ag/AgCl in DMF) and the ESR spectrum of $Me_2DAP^{+\cdot}$ [43] have been studied earlier.

To gain more information about the photoproduct, a solution of **1** and EDTA (as electron donor) was irradiated and its UV/VIS spectrum measured after successive intervals of time. The generation of increasing amounts of the green substance showed isosbestic points at five wavelengths between 340 and 430 nm, indicating that a single species was formed (*Fig. 4;* see also *Exper. Part*). The ESR spectrum of the photogenerated product gave a signal ($g = 2.0022$, $a(N(2),N(7)) \approx 4.48$ G, $a(CH_3N(2),CH_3N(7)) \approx 4.38$ G) in agreement with that reported for the $Me_2DAP^{+\cdot}$ radical cation in MeOH ($a(N(2),N(7)) = 4.70$ G, $a(CH_3N(2),CH_3N(7)) = 4.39$ G) [43], although the resonance lines were broader and the hyperfine coupling with the aromatic protons (1.83 and 0.40 G) [43] was not resolved *(Fig. 4)*. The spin concentration of the ESR solution indicated that *ca.* 6.5% of Me_2DAP^{2+} was reduced to $Me_2DAP^{+\cdot}$ under the conditions used. From these results, an approximate absorption coefficient $\varepsilon \approx 15000$ could be estimated for the absorption band at *ca.* 620 nm of the radical cation.

Taken together, the above results show that Me_2DAP^{2+} (**1**) undergoes photoreduction initially to the radical cation $Me_2DAP^{+\cdot}$. Further reduction to unidentified species occurs on longer irradiation, in line also with the lack of electrochemical reversibility found in aqueous solution [42].

When **1** was replaced by MV^{2+} (**4**) in the same experiments, no reduction to the blue $MV^{+\cdot}$ radical cation was observed. However, UV irradiation of MV^{2+} in the presence of electron donors is known to yield $MV^{+\cdot}$ *via* photooxidation of the donor by the strongly oxidant excited state of MV^{2+} [9] [12–14] [16–18] [34–36]. It is thus clear that **1** is indeed capable to photooxidize efficiently various electron donors under visible-light irradiation. More quantitative studies are required for establishing the reactivity towards different donor molecules, the qualitative sequence of increasing donor efficiency found here being: glucose, ribose, nitrilotriethanol, EDTA as well as MeOH < i-PrOH (see *Exper. Part*).

The mechanism and products of the photooxidation are expected to be similar to those found when MV^{2+} was used. Photooxidation of tertiary amines $R_2N{-}CH_2R$ begins with electron transfer from the N lone pair and produces a secondary amine and an aldehyde *via* hydrolysis of an intermediate immonium ion [10]. Photooxidation of i-PrOH produces acetone [10]. By analogy with MV^{2+}, the overall processes for Me_2DAP^{2+} may be represented by *Eqns. 1* and *2*.

$$2\,Me_2DAP^{2+} + R_2N{-}CH_2R' + H_2O \xrightarrow{h\nu} 2\,Me_2DAP^{+\cdot} + R_2NH + R'CHO + 2\,H^+ \quad (1)$$

$$2\,Me_2DAP^{2+} + R_2CHOH \xrightarrow{h\nu} 2\,Me_2DAP^{+\cdot} + R_2CO + 2\,H^+ \quad (2)$$

Since protons are generated, reduction followed by protonation is more likely in case *2* than in case *1* where the medium is buffered by the donor. Indeed, whereas photoreduction was reversible by reaction with O_2 when using nitrilotriethanol or EDTA as donor, it was only partially reversed when MeOH or i-PrOH and especially glucose or ribose were employed. Ribose photooxidation could play an important role in the DNA photocleavage reactions which the DAP^{2+} cations have been found to perform [4].

Photochemical hydrogen generation by H_2O photoreduction in visible light may be achieved with systems employing a photosensitizer PS ($[Ru(bpy)_3]^{2+}$, acridine dye) and a relay compound R (MV^{2+}, $[Rh(bpy)_3]^{3+}$ *etc.*) [38–41] [44]. In view of the photochemical properties described above, Me_2DAP^{2+} (**1**) could play the combined role of PS and R since it is photoreduced in visible light whereas MV^{2+} is not. It would be of interest to check if Me_2DAP^{2+} is more stable or not than MV^{2+} in H_2-generation experiments, since the latter is known to lose progressively its efficiency due to irreversible reduction [45] in the course of reaction. On the other hand, the radical cation $Me_2DAP^{+\cdot}$ may well not be reducing enough to generate H_2 in a pH range where it might be stable and electrochemically sufficiently reversible.

Conclusions. – The results described above indicate that the DAP^{2+} cation is an attractive molecular subunit for the design of artificial receptor molecules [1] [46] capable of binding anionic or neutral molecular substrates, in particular flat molecules *via* a stacking type of interaction as present also in intercalation processes. It represents a way of incorporating charges into a hydrophobic molecular framework, thus taking advantage of the synergistic binding properties which result from the simultaneous operation of electrostatic and hydrophobic effects. Combination of polar functional sub-units with hydrophobic shaping components forms the basis for the design of amphiphilic receptor molecules of the *speleand* type [1] [30][2]).

In addition to substrate binding, the DAP^{2+} group confers electroactivity and photoactivity and may thus endow molecular receptors with properties of interest for the development of sensitive probes for anion binding, of reagents for nucleic acids [4] [33], proteins, saccharides or lipid membranes (for instance with R=CH_3 and R′ = $CH_3(CH_2)_n$ in **1**), of detection devices for various anionic or neutral molecular substrates. Furthermore, DAP^{2+} derivatives may also be of interest as components for studies on 'organic metals', since both methylviologen [48] and pyrene [49] derivatives have been used to this end.

Incorporation of DAP^{2+} groups into macropolycyclic structures[3]) should yield receptor molecules of *cyclointercaland* type, endowed with novel complexation selectivities *via* intercalative binding of substrate into the intramolecular cavity, as well as photochemical and electrochemical reactivity towards bound substrates.

We thank *J. J. André* for recording the ESR spectra and *E. Anklam* for help in the electrochemical experiments as well as *ICI Pharma* and *ORIS-Industrie (A.J.B.)* and the *Collège de France (J.J.)* for financial support.

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[2]) One may note that an approach to synthetic vaccines involves the design of amphiphilic peptides combining a polar, functional side (epitope) with a hydrophobic, structural side [47].

[3]) A macrocycle containing two viologen units has been reported recently [50].

Experimental Part

1. *General.* All commercial compounds were reagent grade and used without further purification. For the preparation of 2,7-diazapyrene (**5**) [5] 1,4,5,8-naphthalenetetracarboxylic dianhydride was obtained from *Aldrich Chem. Co.*, as were diphenylmethane, diphenyl ether and diphenylpropane. Solvents were distilled prior to use from an appropriate drying agent. The solubility in H_2O of diazapyrenium salts containing I^- anion was low (*ca.* 2 mM) and anion exchange was required. AgCl used for anion exchange was freshly prepared from aq. solns. of $AgNO_3$ and NaCl or 1N HCl; the precipitate was then washed well with H_2O. Usually, 4 equiv. of $AgNO_3$ were used for 1 equiv. of halogen atom to be replaced (*i.e.* 8 mmol of $AgNO_3$ for 1 mmol of **2** or 0.5 mmol of **3**). The exchange was carried out in the absence of light because of the photosensitivity of the Ag compound. *Caution:* Diazapyrenium salts are not stable in basic solution or in organic solvents and in presence of light. M.p.: *Thomas Hoover* capillary melting point apparatus, uncorrected. UV/VIS: λ_{max} (ε) in nm ^{1}H-NMR: *Bruker WP200;* chemical shifts in ppm relative to TMS (= tetramethylsilane) or TMPS (= 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt; aqueous solutions). ESR spectra: *Bruker-ER-420*-X-band spectrometer. Microanalyses were performed by the 'Service Central de Microanalyse du CNRS'.

2. *2,7-Dimethyl-2,7-diazapyrenium Dichloride* (**1**·2 Cl^-). The 2,7-dimethyl-2,7-diazapyrenium diiodide (**1**·2I^-) [5] was obtained by heating 2,7-diazapyrene (**5**) and excess MeI in MeCN at reflux for 4 h. The crude material (purple solid) was recrystallised from boiling H_2O. Anion exchange was effected by stirring an aq. soln. of **1**·2I^- with a suspension of freshly prepared AgCl for 12 h at r.t. (see also *Method A* for the preparation of **3a**·4 Cl^-, below). The product **1**·2 Cl^- was precipitated as a pale yellow solid by addition of acetone to the aq. soln. ^{1}H-NMR (D_2O): identical to that of **1**·2I^-.

The *triflate* **1**·2 $CF_3SO_3^-$ was obtained by treating **5** with 2.5 equiv. $CF_3SO_3CH_3$ in DMF at reflux for 30 min, evaporating almost to dryness and pouring into Et_2O; the precipitate was filtered, washed with Et_2O, and dried; the product is soluble in H_2O, MeOH, MeCN.

3. *2-Methyl-2,7-diazapyrenium Iodide* (**6**·I^-). MeI (3 ml, 48 mmol) was added to a soln. of **5** [5] (1.0 g, 4.9 mmol) in $CHCl_3$ (20 ml). The mixture was stirred at r.t. for 24 h. The precipitated yellow solid was filtered, washed with $CHCl_3$, and dried *in vacuo*, giving **6**·I^- (1.61 g, 96%). This product was washed with 5 ml of a slightly alkaline soln. (pH *ca.* 8, NH_4OH; *caution*, **6**·I^- is not stable in strongly basic soln.). It was then recrystallized from boiling MeOH giving yellow crystals of **6**·I^-. ^{1}H-NMR (D_2O CF_3COOD, pH *ca.* 1): 5.00 (*s*, CH_3); 8.85, 8.93 (2*d*, J = 9.2, H–C(4), H–C(5), H–C(9), H–C(10)); 10.03, 10.05 (2*s*, H–C(1), H–C(3), H–C(6), H–C(8)). Anal. calc. for $C_{15}H_{11}IN_2 \cdot 0.25\ H_2O$ (350.66): C 51.37 H 3.31 N 7.99; found: C 51.31, H 3.19, N 8.05.

4. *Bis[4-(bromomethyl)phenyl]methane.* From diphenylmethane according to [6]. It was also obtained by the method used for the synthesis of 2.2-bis[4-(bromomethyl)phenyl]propane (see below). The crude material was purified by recrystallisation from toluene; yield 40%, m.p. 151–153° ([6]: 151.5–153.5°).

5. *Bis[4-(bromomethyl)phenyl] Ether.* From diphenyl ether according to [48]; m.p. 93.5–95° ([51]: 94–96°).

6. *2,2-Bis[4-(bromomethyl)phenyl]propane.* A mixture of 2,2-diphenylpropane (6.3 g, 32 mmol), paraformaldehyde (5.0 g), 85% aq. H_3PO_4 soln. (13 ml), and 33% HBr soln. in AcOH (25 ml) was stirred at 110° for 6 h. A further aliquot (25 ml) of HBr/AcOH was added dropwise during this period. The hot mixture was poured into H_2O (300 ml) and left overnight. The crude product (white solid) was filtered, washed with H_2O, dried *in vacuo*, dissolved in CH_2Cl_2, and purified by column chromatography (silica gel, CH_2Cl_2). The solvent was evaporated and the product dried *in vacuo* (11.84 g, 97%). A sample for microanalysis was recrystallised from hexane, m.p. 116.5–117.5°. ^{1}H-NMR ($CDCl_3$): 1.67 (*s*, 2 CH_3); 4.48 (*s*, 2 CH_2); 7.19, 7.31 (2*d*, J = 8.8, 8 arom. H). Anal. calc. for $C_{17}H_{18}Br_2$ (382.13): C 53.43, H 4.75; found: C 53.69, H 4.71.

7. *2-Benzyl-7-methyl-2,7-diazapyrenium Dichloride* (**2**·2 Cl^-). A mixture of **6**·I^- (1 g, 2.9 mmol), benzyl bromide (3 ml, 25 mmol, filtered on a small column of neutral Al_2O_3), and MeCN (150 ml) was heated at reflux for 12 h. A yellow product was filtered, washed with $CHCl_3$, and dried *in vacuo* (oil pump; 1.15 g, 77%). This iodidebromide salt was stirred in the dark for *ca.* 12 h with H_2O (100 ml) and freshly prepared AgCl. The solid was then filtered off and washed with hot H_2O. The filtrate was concentrated *in vacuo* (5 ml) and diluted with acetone (90 ml) when a yellow precipitate was formed; this mixture was allowed to stand overnight and the solid **2**·2 Cl^- was filtered and dried *in vacuo* (0.81 g, 73%). ^{1}H-NMR (D_2O): 4.81 (*s*, CH_3); 6.24 (*s*, $C_6H_5CH_2$); 7.4, 7.5 (2 *m*, $C_6H_5CH_2$); 8.67, 8.68 (2*d*, J = 9.5, H–C(4), H–C(5), H–C(9), H–C(10)); 9.88, 9.98 (2*s*, H–C(1), H–C(3), H–C(6), H–C(8)). Anal. calc. for $C_{22}H_{18}Cl_2N_2$ (381.29): C 69.29, H 4.72, N 7.35; found: C 69.07, H 4.89, N 7.38.

8. *2,2'-(Methylenedibenzyl)bis(2,7-diazapyrenium) Dibromide* (**7a**·2 Br^-). A mixture of **5** (0.2 g, 0.98 mmol) and bis[4-(bromomethyl)phenyl]methane (0.157 g, 0.44 mmol) was stirred and heated under reflux in MeCN (15 ml) for 4 h. A yellow precipitate formed which was filtered, washed with $CHCl_3$, and dried *in vacuo* (0.28 g, 85%). The product **7a**·2 Br^- was recrystallised from hot H_2O. ^{1}H-NMR (D_2O CF_3COOD, pH *ca.* 1): 3.98 (*s*,

CH_2); 6.29 (*s*, 2 CH_2); 7.31, 7.51 (2*d*, *J* = 7.61, 2 C_6H_4); 8.76, 8.92 (2*d*, *J* = 9.37, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.00, 10.09 (2*s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). Anal. calc. for $C_{43}H_{30}Br_2N_4 \cdot 3H_2O$ (816.56): C 63.24, H 4.44, N 6.86; found: C 63.17, H 4.25, N 6.65.

9. *2,2'-(Oxydibenzyl)bis(2,7-diazapyrenium) Dibromide* (**7b**·2 Br^-). As for **7a**·2 Br^- from **5** and bis[4-(bromomethyl)phenyl] ether (75% yield). ^{1}H-NMR (D_2O CF_3COOD, pH *ca.* 1): 6.34 (*s*, 2 CH_2); 6.91, 7.56 (2*d*, *J* = 8.50, 2 C_6H_4); 8.81, 8.91 (2*d*, *J* = 9.40, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.04, 10.12 (2*s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). This compound was used for the next step as obtained.

10. *2,2'-[(Dimethylmethylene)dibenzyl]bis(2,7-diazapyrenium) Dibromide* (**7c**·2 Br^-). As for **7a**·2 Br^-, from **5** and 2,2-bis[4-(bromomethyl)phenyl]propane (90% yield). ^{1}H-NMR (D_2O CF_3COOD, pH *ca.* 1); 1.60 (*s*, 2 Me); 6.33 (*s*, 2 CH_2); 7.33, 7.54 (2*d*, *J* = 8.31, 2 C_6H_4); 8.80, 8.92 (2*d*, *J* = 9.3, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.03, 10.13 (2 *s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). This compound was used for the next step as obtained.

11. *2,2'-(Methylenedibenzyl)bis(7-methyl-2,7-diazapyrenium) Tetrachloride* (**3a**·4 Cl^-). A suspension of **7a**·2 Br^- (0.3 g, 0.39 mmol) in MeCN (50 ml) and MeI (0.5 ml, 8 mmol) was stirred and heated under reflux for 4 h. The red-brown **3a**·2 Br^-·2 I^- was filtered, washed with $CHCl_3$, and dried *in vacuo* (0.37 g, 90%).

Anion Exchange. Method A: A suspension of **3a**·2 Br^-·2 I^- and freshly prepared AgCl in H_2O was stirred at 80–90° for 2 h. The solid was filtered off and washed with hot H_2O. The filtrate was evaporated to give crude **3a**·4 Cl^- (yellow solid, very soluble in H_2O) which was redissolved in a small amount of H_2O, precipitated with acetone, filtered, and dried *in vacuo* at r.t. Since the impurities which may be present are less soluble than **3a**·4 Cl^-, they may be removed if necessary by partial precipitation with acetone from the aq. soln. and filtration, followed by addition of more acetone to precipitate **3a**·4 Cl^- itself. These purifications have to be performed rapidly and in absence of light in order to avoid formation of impurities.

Method B: An *Amberlite C6-50(H)* column was washed with H_2O, 20% HCl soln. and H_2O. A soln. of **3a**·2 Br^-·2 I^- in warm H_2O (*ca.* 500 ml of H_2O for 0.1 g of salt) was placed on the column, which was then washed with H_2O; the product was eluted with conc. HCl (37%). The acid was evaporated and the crude product purified as in *Method A. Caution:* The diazapyrenium cation binds strongly to *Amberlite*, and hence the column should be as short as possible (*ca.* 1- to 2-cm-high, 3-cm-diameter column for 0.1 g of **3a**·2 Br^-·2 I^-). ^{1}H-NMR (D_2O): 4.13 (*s*, CH_2); 5.20 (*s*, 2 CH_3); 6.39 (*s*, 2 CH_2); 7.65, 7.80 (2*d*, *J* = 7.92, 2 C_6H_4); 8.90, 8.96 (2*d*, *J* = 9.44, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.09, 10.15 (2*s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). UV/VIS (H_2O): 417 (23000). Anal. calc. for $C_{45}H_{36}Cl_4N_4 \cdot 9H_2O$ (936.74): C 57.70, H 5.81, N 5.98; found: C 57.80, H 5.54, N 5.86.

Purification by HPLC. **3a**·4 Cl^- obtained by anion exchange may be further purified, if needed, by HPLC on a reverse phase C_{18} column, using a linear solvent gradient from $MeOH/H_2O$ 1:3 to 1:20 with flow rate of 1.5 ml/min over 4 min; concentration of **3a**·4 Cl^- 2.5 mg in 100 µl.

12. *2,2'-(Methylenedibenzyl)bis(7-methyl-2,7-diazapyrenium) Tetrabromide* (**3a**·4 Br^-). To a suspension of **7a**·2 Br^- (0.2 g, 0.24 mmol) in MeCN (30 ml), MeBr (3 ml, 55 mmol) was added. The mixture was stirred and heated for 72 h at *ca.* 50° in a closed thick-walled glass bottle; the yellow product **3a**·4 Br^- was filtered, washed with $CHCl_3$, dried, and recrystallised from hot H_2O (0.153 g; 67%). Since **3a**·4 Br^- is soluble in H_2O, anion exchange was not required. ^{1}H-NMR (D_2O): 4.20 (*s*, CH_2); 5.10 (*s*, 2 CH_3); 6.45 (*s*, 2 CH_2); 7.55, 7.69 (2*d*, *J* = 8.06, 2 C_6H_4); 8.90, 8.96 (2*d*, *J* = 7.90, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.15, 10.20 (2*s*, H–C(1,1'), H–C(3,3'), H–C6,6'), H–C(8,8')). Anal. calc. for $C_{45}H_{36}Br_4N_4$ (952.39): C 56.75, H 3.81, N 5.88; found: C 56.61, H 3.95, N 5.76.

13. *2,2'-(Oxydibenzyl)bis(7-methyl-2,7-diazapyrenium) Tetrachloride* (**3b**·4 Cl^-). From **7b**·2 Br^- and MeI like **3a**·4 Cl^- (97% yield). AgCl was used for anion exchange. The product is hygroscopic. ^{1}H-NMR (D_2O): 5.08 (*s*, 2 CH_3); 6.49 (*s*, 2 CH_2); 7.32, 7.79 (2*d*, *J* = 8.53, 2 C_6H_4); 8.95 (*s*, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.15, 10.24 (2*s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). Anal. calc. for $C_{44}H_{33}Cl_4N_4O \cdot 4H_2O$ (848.63): C 62.27, H 4.99, N 6.60; found: C 62.51, H 4.98, N 6.31.

14. *2,2'-[(Dimethylmethylene)dibenzyl]bis(7-methyl-2,7-diazapyrenium) Tetrachloride* (**3c**·4 Cl^-). From **7c**·2 Br^- and MeI like **3a**·4 Cl^- (75% yield). AgCl was used for anion exchange. ^{1}H-NMR (D_2O): 1.81 (*s*, Me_2C); 5.09 (*s*, 2 MeN); 6.48 (*s*, 2 CH_2); 7.59, 7.70 (2*d*, *J* = 8.09, 2 C_6H_4); 8.96 (*s*, H–C(4,4'), H–C(5,5'), H–C(9,9'), H–C(10,10')); 10.17, 10.23 (2*s*, H–C(1,1'), H–C(3,3'), H–C(6,6'), H–C(8,8')). Anal. calc. for $C_{47}H_{40}Cl_4N_4 \cdot 3H_2O$ (856.69): C 65.89, H 5.41, N 6.54; found: C 65.61, H 5.39, N 6.38.

15. *Electrochemical-Reduction Experiments.* They were run with a *PRT-100-1X-Tacussel* potentiostat, a *IG5-LN Tacussel* current integrator and a three-electrode cell with a Hg layer as working electrode. An aq. soln. of the supporting electrolyte Et_4NCl (0.1M, 25 ml) was preelectrolysed at –0.75 V for *ca.* 5 min to give a stable base

line. Then, **1**·2 Cl^- (3.16 mg) in 1 ml of electrolyte soln. was injected with a gas-tight syringe into the cell, and electrolysis was resumed at −0.75 V. After consumption of 1 C, a sample (2.5 ml) was taken from the green soln. using a degassed syringe and transferred into a degassed spectroscopy cell; its UV/VIS was similar to that shown in *Fig. 4* for the photochemically produced species. The procedure was repeated after consumption of 2, 3, and 4 C. UV/VIS: after 1 C: 450 (1400), 615 (800); after 2 C: 451 (1800), 620 (1000); after 3 C: 440 (3300), 580 (1800); after 4 C: 440 (3800), 580 (2100). The absorption coefficients were calculated assuming complete formation of a single species; since this may not be the case, the values given are only indicative.

16. *Photochemical Experiments.* Photoreduction of **1**·2 Cl^- in presence of an electron donor was carried out by irradiating the sample (300 µl of volume, 0.1-cm path length, quartz cell fitted with septum cap) using visible light (395 nm, *Schott*, cut-off filter; slide projector equipped with *Osram 150W Xenophot* bulb). The sample (degassed by N_2 bubbling for 30 min) was placed 8 cm from the projector lens (focused onto the sample) and irradiated for 5 min at 24 ± 2°. UV/VIS spectra were taken of the initial, degassed soln. and of the final irradiated soln. The samples were aq. solns. of **1**·2 Cl^- (5 mM) and donor adjusted to pH 7.0 with HCl. UV/VIS (donor, concentration; absorbance in 1-cm cell): glucose, 0.5M, 440 (0.6), 600 (0.4); ribose, 0.5M, 426 (3.0), 605 (1.8); nitrilotriethanol, 0.5M, 468 (5.8), 605 (1.8); EDTA, 0.15M, 460 (19.6), 630 (8.6); MeOH, 50% *v/v*, 458 (4.1), 620 (2.2); i-PrOH, 50% *v/v*, 455 (17.0), 625 (8.2). *Tris* buffer (0.5M) did not yield a reduced species under the same conditions. The reversibility of irradiated solns. was tested by bubbling O_2 through the soln. for 30 s and remeasuring the spectrum. Also, when the same experiments were performed with methylviologen (**4**·2 Cl^-) instead of **1**·2 Cl^-, no reduced species was detected. Isosbestic points (at 340, 384, 399, 404, and 422 nm) were obtained by taking successive spectra of a degassed sample of 0.1M EDTA and 1.75×10^{-4}M **1**·2 Cl^- at pH 10.0 or pH 7.0 after 1,2,3,5, and 10 min of irradiation; only one of these spectra is represented in *Fig. 4*. At pH 4.0, the isosbestic behaviour was lost, indicating that a more complex process was occurring.

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