Phosphorescence of Cyclophanes and Cyclophane/Ag^+ Complexes

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Phosphorescence in ethanol at 77 K of the cyclophanes **1–14** has been investigated. It is shown that the phosphorescence characteristics are strongly determined by transannular interaction between the benzene rings. This interaction does not occur in cyclophanes **9** and **14**. Phosphorescence quenching by silver perchlorate of paracyclophanes and benzene derivatives **15–20** is due to the formation of arene/Ag^+ ground state complexes. From the quenching data it is concluded that the complexes of paracyclophanes with Ag^+ ions are more stable than the corresponding complexes of the benzene derivatives by approximately two orders of magnitude. Various factors are discussed regarding this marked difference in complex stability.

Introduction

Cyclophanes are of great current interest [1] because of their unusual geometrical features and correspondingly interesting physical and chemical properties.

Although photoluminescence of [2,2]paracyclophane (**1**) has been studied in detail [2] phosphorescence data of derivatives of **1** and other compounds structurally related to **1** have as yet not been reported in the literature. The present study deals with phosphorescence properties of **1**, the **1**-derivatives **2–8**, the three- and fivefold bridged cyclophanes **10–13** as well as with [2,2,2]paracyclophane (**9**) and [2,2]metacyclophane (**14**) (formulae see Table 2).

For the purpose of comparison phosphorescence characteristics of various methyl benzenes as well as dimethyl o-phthalate (compounds **15–20**, Table 2) that represent the arene units present in the cyclophanes studied were also measured.

Our main interest, however, was focussed on the formation and properties of cyclophane/$AgClO_4$ complexes. Although complexation of arenes (and related electron donor molecules) in their ground states with silver ions is a well-known phenomenon [3], it has not been studied in much detail with cyclophanes. So far [2,2,2]paracyclophane (**9**) is the only member of this class of compounds that has been extensively investigated regarding Ag^+ complexation [4, 5] (vide infra). However, it was recently shown [6] that formation of silver salt complexes of arenes can be studied by phosphorescence spectroscopical methods and conclusions were reached on the stability of the [2,2]paracyclophane (**1**)/$AgClO_4$ ground state complex. While the approach was only briefly presented in [6] and application was restricted to **1** and p-xylene it will be explored in detail in the present communication and applied to the compounds listed in Table 2.

Experimental

Substances

All substances studied are described in the literature and their constitutions unequivocally proven. The purity of the freshly sublimed samples was ascertained by standard instrumental analytical methods. The fluorescence and phosphorescence spectra proved to be independent of the excitation wavelength; the phosphorescence decay curves were monoexponential.

Ethanol was of Merck Uvasol quality and the purity of silver perchlorate >98.5% (Riedel de Haen, No. 31 497).

Measurements

Fluorescence and phosphorescence spectra were measured on an Aminco-Keirs spectrophosphorimeter and a Perkin-Elmer MPF 44 E spectrofluorimeter.

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Fluorescence/phosphorescence quantum yield ratios Φ_p/Φ_f were derived from the quantum corrected total luminescence spectra measured in ethanol at 77 K on the MPF 44E spectrofluorimeter.

Phosphorescence lifetimes (ethanol, 77 K) were determined using the Aminco-Keirs spectrophosphorimeter equipped with an oscillograph Tektronix 5403 for measurements in the msec range.

Phosphorescence quenching curves were measured according to the following procedure: ethanol solutions containing silver perchlorate and the arene in known concentrations were prepared at room temperature. Arene concentration was $5 \cdot 10^{-4}$ M for the cyclophanes and $1 \cdot 10^{-3}$ M for the benzene derivatives. The solutions were filled in cylindrical phosphorescence cuvettes (inner diameter: 2 mm) and cooled to 77 K within 15 s. The phosphorescence decay curves were measured using the Aminco-Keirs spectrophosphorimeter. The excitation wavelength was 280 nm in all experiments while the emission wavelength was in each case λ_{max} i.e. the wavelength, where the phosphorescence spectrum of the unperturbed arene has its maximum of intensity. During measurement the rotating can phosphoroscope was in operation (rotation speed: approx. 14000 r.p.m., cycle time: approx. 2 ms); light-passage from the source to the sample was then interrupted by fast mechanical shutting of the exit slit of the excitation monochromator and the phosphorescence decay curve plotted. The phosphorescence intensity I_p of the long-lived phosphorescence component (uncomplexed arene) at zero time was obtained from the decay curve using the procedure described by Winefordner [7]. Under otherwise identical experimental conditions but in the absence of silver perchlorate the phosphorescence spectrum of the arene was plotted and the phosphorescence intensity I_p^0 at λ_{max} taken from the spectrum. Plotting $\log(I_p/I_p^0)$ against $\log[\mathrm{AgClO_4}]$ yielded the quenching curves (see Figure 3). It proved not necessary to apply any correction terms to the intensities measured because (i) the period for shutting the exit slit was short compared to the phosphorescence lifetime τ_p of the unperturbed arenes (see Table 2), (ii) τ_p was large compared to the cycle time of the phosphoroscope and (iii) I_p and I_p^0 were measured under identical conditions of excitation.

AgClO$_4$ half-value concentrations $[Q_H]_p$ of phosphorescence quenching i.e. AgClO$_4$ concentration where $I_p = 1/2\, I_p^0$ were obtained from the phosphorescence quenching curves. $[Q_H]_p$ values proved to be reproducible within approx. ± 30%.

I_p^0/I_p *values* at a given AgClO$_4$ concentration (last column in Table 2) were measured in the same way as described above. AgClO$_4$ concentrations used were $1 \cdot 10^{-3}$ M for the cyclophanes and $1 \cdot 10^{-1}$ M for the benzene derivatives. I_p^0/I_p values proved to be reproducible within approx. ± 20%.

The quality of the $[Q_H]_p$ and I_p^0/I_p values obtained is characterized by their reproducibility but can be further tested in two ways: (i) $I_p^0/I_p = 2$ is expected if $[Q_H]_p = 1 \cdot 10^{-3}$ M in the case of the cyclophanes or $1 \cdot 10^{-1}$ M in the case of the benzene derivatives. Experimental figures (Table 2) are between 1.14 and 2.20 (mean value: 1.74), (ii) $[Q_H]_p$ and I_p^0/I_p values must correlate within experimental error. The cyclophanes studied fit the equation

$$I_p^0/I_p = -\,10.78 \log[Q_H]_p - 30.70$$

the correlation coefficient being 0.9786. A uniform correlation for the cyclophanes and the benzene derivatives studied is not possible because I_p^0/I_p values had to be determined at different AgClO$_4$ concentrations for these two series of compounds.

AgClO$_4$ half-value concentrations $[Q_H]_{fl}$ of fluorescence quenching in ethanol at room temperature were obtained from Stern-Volmer plots (intensity measurement).

According to the procedure described in [8] it was tested to what extent inner filter effects due to the absorption of light by silver perchlorate may falsify the luminescence quenching measurements. For all compounds studied E_g (see Eqs. (1) and (2) in [8]) was determined at $\lambda = 280$ nm (i.e. excitation wavelength, vide supra) and a cell pathlength $l = 0.2$ cm (phosphorescence) or $l = 1$ cm (fluorescence) respectively. The concentrations of arenes were $c = 5 \cdot 10^{-4}$ M (cyclophanes) or $c = 1 \cdot 10^{-3}$ M (benzene derivatives). Under otherwise identical conditions E_l (AgClO$_4$) was determined using $1 \cdot 10^{-3}$ M or $1 \cdot 10^{-1}$ M solutions respectively. In all cases $(K_0 - K)\,100/K_0$ (see l.c. [8]) was found to be < 3 (%). Comparison of the quantum corrected phosphorescence excitation spectra of the uncomplexed arenes and the arene/AgClO$_4$ complexes reveals that inner filter effects due to the absorption of light by the complexes is also well below this limit.

Results and Discussion

Phosphorescence properties of cyclophanes

In Fig. 1 the phosphorescence spectra (ethanol, 77 K) of [2,2]paracyclophane (**1**), [2,2,2]paracyclophane (**9**) and p-xylene (**15**) are given. Additional phosphorescence data (phosphorescence lifetimes τ_p, phosphorescence/fluorescence quantum yield ratios Φ_p/Φ_f) are listed in Table 1.

While the phosphorescence characteristics (and also the $S_1 - S_0$ transition energies observed in absorption and fluorescence, Table 1) of **9** and **15** are very similar, they are different from the data of **1**. In contrast to the phosphorescence of **9** and **15** the spectrum of **1** is unstructured. Therefore the energy of the 0−0 transition cannot be derived from the spectrum. However, comparison of the spectra shows clearly that the phosphorescence transition energy of **1** is significantly lower than that of **9** and **15**. A similar relation was previously observed for **1** and [4,4]paracyclophane (where the benzene units are connected by C_4 bridges) and attributed to the different inter-ring separation in these compounds (3.093 Å in **1** [9] but ≈ 3.5 Å in [4,4]paracyclophane) [10]. It was shown by quantum mechanical calculations that the energy of the lowest triplet state becomes lower with decreasing inter-ring separation and correspondingly increasing transannular interaction between the benzene units [10]. In **9** the benzene rings cannot reach a sandwich configuration and their centres are separated by approx. 4 Å [5]. Thus transannular interaction in **9** is expected to be low.

The spectral relation observed for [2,2]paracyclophane (**1**) and p-xylene similarly applies to the **1**-homologues **2−6** and the corresponding benzene homologues **16−18** (Table 2). All **1**-homologues studied have unstructured phosphorescence spectra which lie at longer wavelengths than the spectra of the benzene homologues and the phosphorescence lifetimes are shorter than that of the benzenes.

The threefold bridged cyclophanes **11−13** (Table 2) show no measurable phosphorescence. Similarly fluorescence is weak and probably due to impurities. The very efficient radiationless deactivation of the electronically excited states of these molecules is possibly due to considerable changes in the nuclear configuration of the excited states compared to the ground state thus leading to high

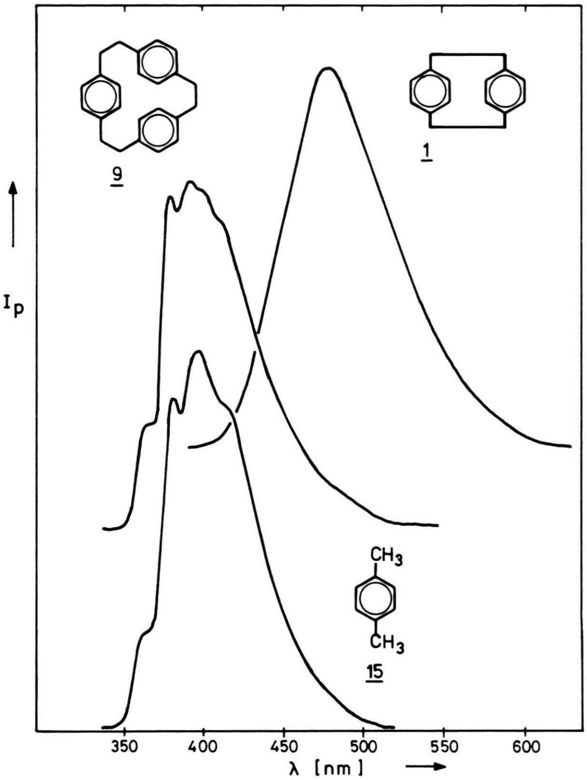


Fig. 1. Phosphorescence spectra (ethanol, 77 K) of [2,2]paracyclophane (**1**), [2,2,2]paracyclophane (**9**) and p-xylene (**15**). The spectra were normalized to the same height of the most intense band.

Table 1. Photophysical parameters of [2,2]paracyclophane (**1**), [2,2,2]paracyclophane (**9**) and p-xylene (**15**). $\tilde{\nu}_a(0-0)$: 1. absorption band; $\tilde{\nu}_{fl}$(max): spectral centre of gravity of the fluorescence; $\tilde{\nu}_p(0-0)$: phosphorescence (0−0-transition); $\tilde{\nu}_p$(max): spectral centre of gravity of the phosphorescence; τ_p: phosphorescence lifetime; Φ_p/Φ_f: phosphorescence/fluorescence quantum yield ratio. Absorption spectrum in ethanol at room temperature, all other data refer to ethanol solutions at 77 K.

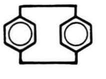
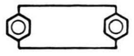
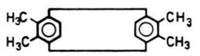
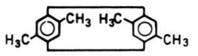
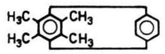
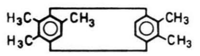
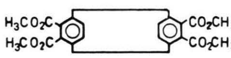
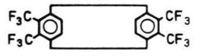
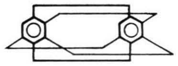
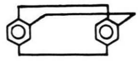
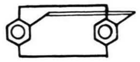
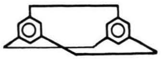
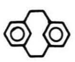
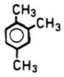
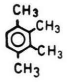
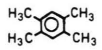
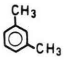
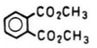
Arene		$\tilde{\nu}_a(0-0)$ [cm^{-1}]	$\tilde{\nu}_{fl}$(max) [cm^{-1}]	$\tilde{\nu}_p(0-0)$ [cm^{-1}]	$\tilde{\nu}_p$(max) [cm^{-1}]	τ_p [sec]	$\frac{\Phi_p}{\Phi_f}$
	1	32 250	28 570	-	20 920	4.5	2.97
	9	36 232	35 088	27 397	25 510	6.5	1.67
	15	36 364	35 842	27 624	25 253	8.8	0.62

Table 2. Photophysical parameters. $\tilde{\nu}_p$: spectral centre of gravity of the phosphorescence (0–0-band in brackets); τ_p: phosphorescence lifetime; $[Q_H]_p$: half-value concentration of phosphorescence quenching by AgClO$_4$; I_p^0: phosphorescence intensity in the absence of AgClO$_4$, I_p: phosphorescence intensity in the presence of AgClO$_4$ (AgClO$_4$ concentration = $1 \cdot 10^{-3}$ M (cyclophanes), $1 \cdot 10^{-1}$ M (benzene derivatives)). All data refer to measurements in ethanol at 77 K.

Arene		$\tilde{\nu}_p$ [cm^{-1}]	τ_p [sec]	$[Q_H]_p$ [mole/l]	I_p^0/I_p
	1	20 920	4.50	$6 \cdot 10^{-4}$	5.12
	2	21 050	2.30	$2 \cdot 10^{-4}$	9.4
	3	20 920	1.75	$1 \cdot 10^{-3}$	1.36
	4	20 965	2.30	$5 \cdot 10^{-4}$	4.04
	5	20 285	0.95	$2.5 \cdot 10^{-4}$	7.90
	6	20 285	1.50	$1 \cdot 10^{-3}$	2.20
	7	20 620	3.20	1	—
	8	19 230	1.0	$1 \cdot 10^{-1}$	—
	9	25 510 (27 397)	6.50	$1 \cdot 10^{-3}$	1.14
	10	22 220	4.60	$\sim 1 \cdot 10^{-3}$	—
	11	no measurable phosphorescence			
	12	no measurable phosphorescence			
	13	no measurable phosphorescence			
	14	no measurable phosphorescence			
	15	25 253 (27 624)	8.80	$1.5 \cdot 10^{-1}$	1.24
	16	24 938 (27 778)	7.50	$2 \cdot 10^{-1}$	—
	17	25 000 (27 778)	7.10	$1 \cdot 10^{-1}$	2.19
	18	24 938 (27 778)	6.80	$2.5 \cdot 10^{-1}$	—
	19	25 381 (27 624)	7.70	$1 \cdot 10^{-1}$	1.83
	20	22 420	0.75	> 2	—

rates of both $S_1 - S_0$ internal conversion and $T_1 - S_0$ intersystem crossing [11].

Different from **11**–**13** the fivefold bridged cyclophane **10** (Table 2) shows broad unstructured phosphorescence the spectral centre of gravity surprisingly lying at somewhat shorter wavelengths (450 nm) than that of [2,2]paracyclophane (**1**) (478 nm) (compare also the pentamethyl derivative **6**, Table 2) though inter-ring separation in **10** (2.97 Å [12]) is smaller than in **1** (3.093 Å [9]) and correspondingly transannular interaction between the benzene units is expected to be stronger in **10**.

In contrast to m-xylene (**19**) and [2,2]paracyclophane (**1**) no phosphorescence was observed with [2,2]metacyclophane (**14**) (Table 2). The $S_1 - S_0$ transition of **14** observed in absorption ($\approx$ 36 760 cm^{-1}) and fluorescence (34 246 cm^{-1}) lies very close to that of m-xylene (in absorption: 36 764 cm^{-1}, in fluorescence: 34 246 cm^{-1}). Thus transannular interaction can be excluded in **14** which is the anti-isomer.

Phosphorescence quenching by AgClO$_4$

Phosphorescence quenching (in ethanol at 77 K) of arenes (and other π-electronic donor molecules) by AgClO$_4$ (and other silver salts) is due to the formation of arene/Ag$^+$ ground state complexes of the charge-transfer type [6, 13, 14]. As a result of the heavy-atom (Ag$^+$) induced increase of intersystem crossing these complexes do no fluoresce. Moreover, the complexes do not longer emit the phosphorescence of the unperturbed donors but their inherent phosphorescences; compared to that of the donors these are less structured, lie at longer wavelengths, and particularly have much shorter lifetimes (in the ms range). As an example the phosphorescence spectra of p-xylene (ethanol, 77 K) in the absence of $AgClO_4$ (curve c) and in the presence of 1 M $AgClO_4$ (curves a and b) are given in Figure 2. Curve a has been measured using a phosphoroscope speed of ≈ 14000 r.p.m. (corresponding to a cycle time of the phosphoroscope of ≈ 2 ms); the spectrum observed results from the superposition of the shortlived phosphorescence of the complex and the long-lived phosphorescence of the uncomplexed portion (approx. < 7%) of p-xylene. Curve b has been measured using a much lower phosphoroscope speed (≈ 200 r.p.m.; cycle time of the phosphoroscope: ≈ 150 ms); while the short-lived phosphorescence of the complex is now eliminated the long-lived phosphorescence of the uncomplexed p-xylene is observed which is identical with the phosphorescence of p-xylene in the absence of $AgClO_4$ (curve c) within experimental error.

At silver ion concentrations high enough to complex all arene molecules present in the solution the phosphorescence decay curves are monoexponential with the phosphorescence time-constant of the respective arene/Ag$^+$ complex [6, 14]. At lower silver ion concentrations the decay curves are biexponential exhibiting the time constants of the phosphorescence of the unperturbed donor and the complex. Thus the behaviour of silver ions is in marked contrast to that of other heavy-atom spin-orbit coupling perturbers [14, 15].

Since the phosphorescence lifetimes of the complexes are shorter by 2 to 3 orders of magnitude than that of the unperturbed arenes the intensity (at zero time) of the phosphorescence of the unperturbed arenes in the presence of Ag$^+$ ions can be easily derived from the decay curves using a technique that is well-known in time-resolved phosphorescence spectroscopy [7] (see als "Experimental"). Thus by determining the intensity of phosphorescence of the unperturbed arene molecules at various Ag$^+$ concentrations the half-value concentration $[\varrho_H]_P$ of phosphorescence quenching by $AgClO_4$, i.e. the $AgClO_4$ concentration at which the intensity of the arene phosphorescence is half the intensity observed in the absence of quencher can be estimated. Inner filter effects that would falsify the quenching data were small with the experimental conditions used (see "Experimental").

Typical quenching curves are shown in Figure 3. At $AgClO_4$ concentrations far below the concentration of the donor the decrease in phosphorescence

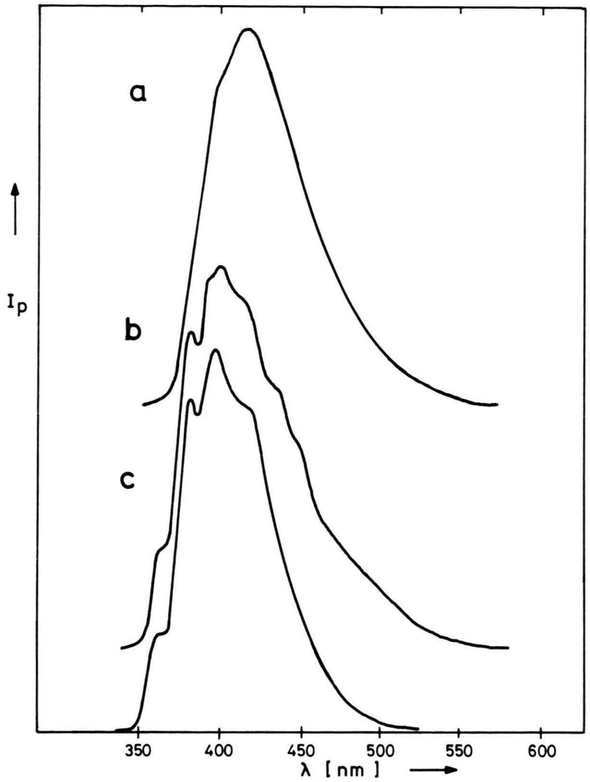


Fig. 2. Time-resolved phosphorescence spectra (ethanol, 77 K). Curve a: spectrum of the p-xylene/$AgClO_4$ complex plus uncomplexed p-xylene (cycle time of the phosphoroscope ≈ 2 ms); curve b: spectrum of the uncomplexed p-xylene in the presence of the complex (cycle time of the phosphoroscope ≈ 150 ms); curve c: spectrum of p-xylene in the absence of $AgClO_4$. The spectra were normalized to the same height of the most intense band.

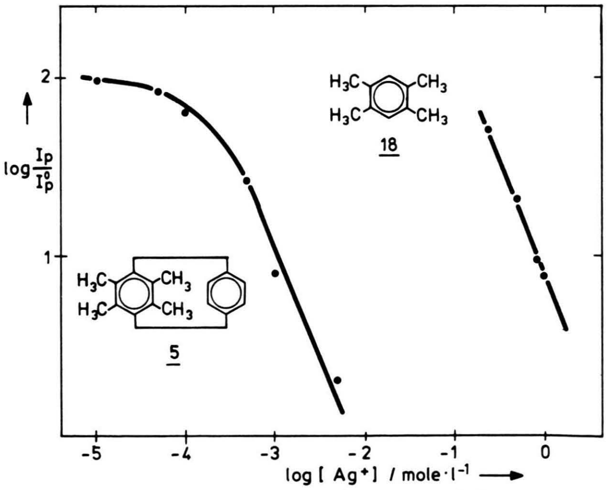
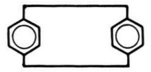
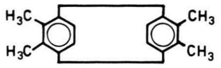
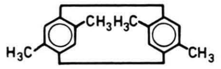
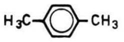
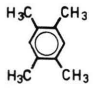


Fig. 3. Phosphorescence quenching curves (ethanol, 77 K, quencher: $AgClO_4$) (for details see text).

Table 3. Half-value concentration $[Q_H]_{fl}$ of fluorescence quenching (ethanol, room temperature) and $[Q_H]_p$ of phosphorescence quenching by $AgClO_4$ (ethanol, 77 K).

Arene		$[Q_H]_{fl}$ [mole/l]	$[Q_H]_p$ [mole/l]	$\frac{[Q_H]_{fl}}{[Q_H]_p}$
	1	$7.3 \cdot 10^{-3}$	$6 \cdot 10^{-4}$	12
	3	$2 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	20
	4	$3.3 \cdot 10^{-2}$	$5 \cdot 10^{-4}$	66
	9	$5.3 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	5
	15	$2.5 \cdot 10^{-2}$	$1.5 \cdot 10^{-1}$	0.17
	18	$\sim 1 \cdot 10^{-2}$	$2.5 \cdot 10^{-1}$	0.4

intensity with increasing $AgClO_4$ concentration is to small to be observable with the method used. Donor concentrations used were $5 \cdot 10^{-4}$ M for the cyclophanes and $1 \cdot 10^{-3}$ M for the benzene derivatives.

In contrast to phosphorescence quenching in rigid media at 77 K fluorescence quenching of arenes in fluid solution at room temperature by $AgClO_4$ was shown to occur in a dynamic process [16]. Formation of a short-lived complex of the electronically excited arene molecule with the silver ion resulting in strong enhancement of intersystem crossing within the complex was assumed. Taking further into account that the arene/Ag$^+$ ground state complexes likewise do not fluoresce (vide supra) conclusions regarding the ground-state complexation can be derived from the ratio $[Q_H]_{fl}/[Q_H]_p$ where $[Q_H]_{fl}$ is the half-value concentration of fluorescence quenchching in fluid solution at room temperature. If $[Q_H]_{fl}/[Q_H]_p \gg 1$ then (i) ground-state complexation is small in fluid solution at room temperature and (ii) increases with decreasing temperature. On the other hand, if $[Q_H]_{fl}/[Q_H]_p < 1$ no definite conclusions are possible regarding the temperature dependence of the complexation equilibrium. Experimental results are given in Table 3. From these it is concluded that Ag$^+$ complexation of the [2,2]paracyclophanes in the ground state is temperature dependent.

Although the complexation equilibrium is temperature-dependent and the solutions studied were prepared at room temperature but analyzed at 77 K and, moreover, the cooling rates may somewhat vary, the experimental results obtained proved to be reasonable reproducible. Obviously, equilibration at any temperature is fast compared to the cooling rate applied to the samples (15 s for the temperature range 293–77 K). Results obtained with the recently studied system triphenylene/$AgClO_4$ in ethanol support this view [14].

The composition, i.e. the molar donor: $AgClO_4$ ratio of the complexes present in ethanol solution at 77 K is not known. However, [2,2,2]paracyclophane (**9**) was found to yield a 1:1 complex at room temperature [4]. At the $AgClO_4$ half-value concentration $[Q_H]_p$ of phosphorescence quenching the concentration of the uncomplexed donor is assumed to be half the total concentration $[D_{tot}]$ of the donor, i.e. $2.5 \cdot 10^{-4}$ M for the cyclophanes and $5 \cdot 10^{-4}$ M for the benzene derivatives respectively. Thus, if $[Q_H]_p > 1/2[D_{tot}]$ no conclusions can be derived regarding the molar donor: $AgClO_4$ ratio of the complexes formed. On the other hand, if $[Q_H]_p < 1/2[D_{tot}]$ is found then formation of complexes $(n \cdot D \ldots AgClO_4)$ $(n \geqq 2)$ may be assumed. It is possibly not fortuitous that the latter case applies only to the highly unsymmetrical cyclophanes **2** and **5** (Table 2).

Stability of cyclophane/$AgClO_4$ ground-state complexes

$[Q_H]_p$ values (Table 2) can be regarded as a relative measure of the stability (i.e. equilibrium constant) of the arene/$AgClO_4$ ground-state complexes at 77 K. With increasing complex stability $[Q_H]_p$ decreases.

A further relative measure of the complex stabilities is the ratio I_p^0/I_p where I_p is the phosphorescence intensity of the unperturbed arene determined at a given $AgClO_4$ concentration which was $1 \cdot 10^{-3}$ M for the cyclophanes and $1 \cdot 10^{-1}$ M for the benzene homologues and I_p^0 is the phosphorescence intensity of the respective arene in the absence of quencher (measured under otherwise identical experimental conditions). I_p^0/I_p values (Table 2) increase with increasing complex stability and are correlated with the $[Q_H]_p$ values (see "Experimental").

Comparison of the $[Q_H]_p$ values leads to the conclusion that the ground state complexes of the paracyclophanes with $AgClO_4$ are more stable than the complexes of the benzene homologues by approx. two orders of magnitude. While this applies to solutions in ethanol at 77 K the same result has previously been obtained for [2,2,2]paracyclophane (**9**) using silver trifluoromethane sulfonate (triflate) as the complexing agent in deuterated methanol at room temperature [4]. However, the puzzle remains why both [2,2]paracyclophanes and [2,2,2]paracyclophane exhibit unusually strong complexation ability against silver ions although these two types of compounds have not much in common regarding their geometrical features and electronic properties (vide supra).

A common feature of both compounds is the cavity formed by the benzene rings. However, as x-ray crystallographic analysis of the [2,2,2]paracyclophane/$AgClO_4$ complex has revealed, the Ag^+ ion (although lying on the three-fold pseudoaxis around which the benzene rings are oriented) is slightly off the cavity formed by the benzene rings [5]. Thus, the previous idea [4, 6] that the higher stability of cyclophane/Ag^+ complexes compared to open chain analogous is due to "cavitation" seems to be rather unlikely.

The complex of [2,2]paracyclophane with tetracyano ethylene (TCNE) was found to be much more stable than the TCNE complex of p-xylene; this was explained with the higher π basicity of the cyclophane due to transannular delocalisation of charge [17]. The observation that the $[Q_H]_p$ values of cyclophanes **7** and **8**, i.e. compounds with electron-withdrawing groups are higher by 2–3 orders of magnitude than that of methylated paracyclophanes (Table 2) indicates that π basicity plays also a role in Ag^+ complexes (see also **20** in Table 2). However, it has to be noted that charge-transfer interaction in organic EDA complexes is different from the bonding in related complexes with silver salts where both charge-transfer from the highest occupied π-MO of the organic molecule to the vacant 5s AO of Ag^+ and back-donation from the filled 4d AO of Ag^+ to the lowest unoccupied π-MO of the organic molecule have to be assumed [18].

The interplay of steric and electronic features is thought to be an important factor for the stability of cyclophane/Ag^+ complexes. It cannot be excluded that the comparatively large stability of the [2,2]- and [2,2,2]paracyclophane/Ag^+ complexes may have quite different causes. However, taking into account that the p-xylene/$AgClO_4$ complex is a 2:1 complex ($(C_8H_{10})_2AgClO_4$) [19] i.e. 1 product molecule is formed from 3 educt molecules during complexation, while the [2,2,2]paracyclophane/Ag^+ complex and possibly also the [2,2]paracyclophane/Ag^+ complex are 1:1 complexes, formation entropy could be relatively less negative in the case of the cyclophane complexes. Clearly, more experimental results are necessary to achieve a well-founded explanation for the unusual high stability of cyclophane/Ag^+ complexes.

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