

Ferromagnetic spins interaction in tetraaza- and hexaazacyclophanes

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Tetraaza- and hexaazacyclophanes have been synthesized *via* a one-step palladium catalyzed amination reaction. The chemical oxidation of cyclophanes leads to the formation of radical cations, the presence of which was manifested by the appearance of new bands in UV-Vis-NIR and IR spectra. Spins of radical cations can be magnetically coupled. The nutation pulsed-EPR technique (PEANUT experiment) enables us to determine the multiplicity of the systems for different oxidant/cyclophane ratios. Spins of cyclophanes oxidized to diradical dicationic states interact ferromagnetically to form a pure triplet state.

1. Introduction

The common applications of magnetic materials in modern technology have stimulated the search for new compounds exhibiting magnetic ordering. Very promising materials are organic systems, which can offer the tuning of their properties by an appropriate modification of their molecular chemical structure. An important contribution of Rajca *et al.*¹ and Veciana *et al.*² to the field of magnetic organic compounds should be pointed out. Among different classes of this type of chemical compounds studied to date, alternating oligo- and polyanilines seem especially interesting due to their capability of the formation of relatively stable radical cations created in a multi-step oxidation process. It has been demonstrated that in *p*-phenylenediamine moieties linked to 1,3-benzenediyl or to 1,3,5-benzenetriyl units, after their partial oxidation, high-spin states can be generated.^{3–6} Spins of radical cations can be coupled to form triplet and/or quartet ground states. Similarly, in the case of the simplest linear polyaniline containing alternating *meta-para*-units we have recently found evidence that spins are magnetically coupled and the polymer shows macroscopic ferromagnetic properties.⁷ However, transient nutation experiments performed by pulsed EPR prove that spins generated after the polymer oxidation are mainly uncoupled showing $S = 1/2$ and only a minor part of them can form a triplet state ($S = 1$). The presence of uncoupled spins as dominant paramagnetic species can be caused by a coil-like conformation of the polymer chain as well as by local conformation of amine groups. From this perspective spins ordering can be improved in defined chemical structures, which do not allow the formation of conformational isomers. This concept can be realized by cyclization of linear oligomers, which leads to a more stiff and geometrically better defined

molecular structure. Alternating *meta-para*-cyclic oligoaniline, namely tetraazacyclophane, was synthesized by Ito *et al.*⁸ The oxidation of this compound to diradical dicationic states led to a non-axial triplet state molecule, as predicted above. Tetraazacyclophane was synthesized by Ito in a very poor yield (0.28%), however, a more efficient three-steps preparation method has been reported by Hauck *et al.*⁹ leading to reaction yields of 60–70%.

In this paper we report a facile one-step synthesis of tetraazacyclophane. Additionally we have prepared, for the first time, hexaazacyclophane containing *m-p-p*-substituted benzene rings, in which ferromagnetic and antiferromagnetic spins coupling can be competitive. We have focused on the formation of radical cations, studied by the use of UV-Vis-NIR and IR spectroscopies, in both types of macrocycles. The interactions of spins thus generated have been examined using pulsed EPR spectroscopy for different oxidant/cyclophane ratios. In particular, the effect of the radical cation concentration on the resulting spin state in these compounds has been investigated by the nutation technique (PEANUT experiment).

2. Experimental

Characterization techniques

¹H and ¹³C NMR spectra were recorded on a Varian Mercury (400 and 100 MHz) spectrometer and referenced with respect to TMS and solvents. IR spectra were monitored on a Bio-RAD FTS-165 spectrometer. Solutions of oxidized cyclophanes were put on KBr pellets and solvents were evaporated in a vacuum. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. All synthesized compounds studied were subject to C, H and N elemental combustion analysis.

Pulsed EPR nutation measurements by PEANUT experiment

Nutation pulsed EPR experiments were performed using a Brüker Elexsys 580 EPR spectrometer in pulsed mode at 7 K. The PEANUT experiment (phase-inverted echo amplitude detected nutation) introduced by Stoll *et al.*¹⁰ was used in

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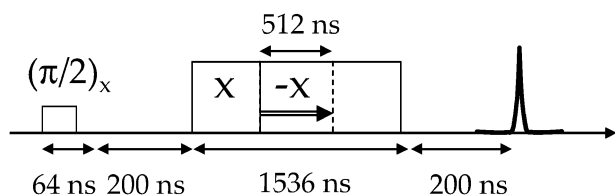
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Scheme 1 Pulses sequence used for the PEANUT experiments.

order to achieve an optimal resolution of nutation frequencies in the recorded spectra.

The PEANUT experiment is described in Scheme 1. In a typical experiment the first pulse used was a selective low power pulse ($B_1 \sim 0.7$ G). This pulse was set up to be a true $\pi/2$ pulse for species having nutation frequencies higher than $S = 1/2$ species in order to better detect eventual signals of $S = 3/2$ or $S = 2$ species. Two steps phase cycling ($+x$, $-x$) was performed on this first pulse. The high turning angle pulses ($B_1 \sim 8$ G) had a constant length of 1536 ns and the x pulse ($-x$ pulse) was incremented (decremented) by 256 steps of 2 ns, respectively. At every step, the spin rotatory echo was integrated using a 76 ns gate centred at its maximum.

The obtained time-domain oscillating signal was treated with second order polynomial baseline correction, sinebell transformation and symmetrical zero-filling (256 zeroes added). Then it was Fourier transformed using a numerical FFT software to yield the corresponding nutation spectrum. Two-dimensional maps (Magnetic Field vs. Nutation spectrum) were obtained by successively performing PEANUT experiments at 200 magnetic field values spaced by steps of one Gauss.

The spin multiplicities of detected species were obtained by comparing the measured nutation frequency (ν_{nut}) to the nutation frequency previously measured for known $S = 1/2$ systems ($\nu_S = 1/2$) and using the following relationship:

$$\nu_{\text{nut}} = \sqrt{S(S+1) - m_S(m_S+1)} \cdot \nu_{S=1/2}$$

This relationship is valid for low magnetic field excitation (i.e. $B_1 \ll D$, D the axial zero field splitting parameter of the considered species).¹¹ In the described experimental conditions $\nu_{S=1/2} \sim 23$ MHz (established by measurements with nitroxide free radicals). Then the preceding relationship predicts $\nu_{S=1} \sim 32$ MHz and $\nu_{S=3/2} \sim 40$ MHz (for $m_S = \pm 1/2 \leftrightarrow \pm 3/2$ transitions).

Reagents

1,4-Phenylenediamine, 1-bromo-4-butylbenzene, 1-bromo-4-*tert*-butylbenzene, 1,3-dibromobenzene, palladium acetate, ($\text{Pd}(\text{OAc})_2$), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, (BINAP), tris-*tert*-butylphosphine, (*t*-Bu₃P), tris(dibenzylideneacetone)-dipalladium(0), $\text{Pd}_2(\text{dba})_3$, sodium *tert*-butoxide, (*t*-BuONa), anhydrous acetonitrile, anhydrous butyronitrile, diphenylamine and 4-butylaniline were purchased from Aldrich. Diphenylamine was purified by liquid chromatography using CH_2Cl_2 /ethyl acetate (20:1). 4-Butylaniline was distilled under reduced pressure. *N*-Bromosuccinimide (NBS) was crystallized from water.

Synthesis

All glassware was oven-dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.

***N,N'*-Bis(4-butylphenyl)-1,4-phenylenediamine (1).** Bis[(4'-butylphenyl-4-aminophenyl)-4''-*tert*-butylphenylamine (2). Diamines **1** and **2** were prepared according to the procedure described in ref. 12.

Tetraazacyclophane, C1. Tris(dibenzylideneacetone)-dipalladium(0), $\text{Pd}_2(\text{dba})_3$ 45.8 mg (0.05 mmol) and tris-*tert*-butylphosphine, (*t*-Bu₃P) 16.2 mg (0.08 mmol) were dissolved in 3 ml of dry toluene and stirred for 30 min. Then 1,3-dibromobenzene (0.236 g, 1 mmol), diamine **1** (0.372 g, 1 mmol), sodium *tert*-butoxide (0.282 g, 3 mmol) and 22 ml of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 12 h under an argon atmosphere. The reaction mixture was then cooled to room temperature and washed with 30 ml of distilled water. The aqueous phase was extracted with three 10 ml portions of diethyl ether. The organic layers were combined and dried over MgSO_4 . Removal of the solvents followed by chromatography on silica gel (CH_2Cl_2 /hexanes/0.5% ν MeOH, 1:4) resulted in a white solid. The resulting solid was recrystallized from CH_2Cl_2 /hexanes to give 0.195 g (0.218 mmol, 43.7% yield) of **C1** as white crystals. ¹H NMR (400 MHz, C_6D_6) δ , 7.29–7.26 (m, 8H), 6.96–6.94 (m, 8H), 6.91 (t, $J = 7.6$ Hz, 2H), 6.86 (s, 8H), 6.78 (dd, $J = 8.0$ Hz, 2.4 Hz, 4H), 6.68 (t, $J = 2.0$ Hz, 2H), 2.42 (t, $J = 8.0$ Hz, 8H), 1.51–1.44 (m, 8H), 1.29–1.20 (m, 8H), 0.84 (t, $J = 7.6$ Hz, 12H). ¹³C NMR (100 MHz, C_6D_6) δ , 149.8, 145.4, 143.3, 137.8, 129.6, 126.2, 125.5, 115.1, 35.4, 34.1, 22.7, 14.1. IR (cm^{-1}) 3026, 2954, 2925, 2854, 1590, 1505, 1489, 1330, 1297, 1275, 1239, 1114, 830, 768, 695. Anal. Calcd. for $\text{C}_{64}\text{H}_{68}\text{N}_4$: C, 86.10; H, 7.62; N, 6.28. Found: C, 85.22; H, 7.52; N, 6.15. $m/z = 892.7$.

Hexaazacyclophane, C2. The same procedure as for preparation of cyclophane **C1** was used. The crude product was chromatographed on silica gel eluting with CH_2Cl_2 /hexanes/1% ν Et₃N, (1:2) and then crystallized in CHCl_3 /hexanes to give 0.234 g (0.175 mmol) of **C2** as a white powder. The reaction yield was 35%. ¹H NMR (400 MHz, C_6D_6) δ , 7.32(t, $J = 2.4$ Hz, 2H), 7.28–7.21 (m, 16H), 6.97 (s, 16H), 6.96–6.95 (m, 8H), 6.87 (t, $J = 8.0$ Hz, 2H), 6.67 (dd, $J = 8.0$ Hz, 2.4 Hz, 4H), 2.42 (t, $J = 7.6$ Hz, 8H), 1.50–1.42 (m, 8H), 1.28 (s, 18H), 1.25–1.20 (m, 8H), 0.84 (t, $J = 7.6$ Hz, 12H). ¹³C NMR (100 MHz, C_6D_6) δ , 149.0, 146.3, 145.3, 142.8, 142.3, 138.3, 129.7, 126.6, 126.1, 124.4, 123.6, 120.5, 115.9, 35.4, 34.4, 34.0, 31.6, 22.7, 14.1. IR (cm^{-1}) 3031, 2957, 2928, 2858, 1592, 1502, 1467, 1316, 1270, 1110, 830, 773, 698. Anal. Calcd. for $\text{C}_{96}\text{H}_{102}\text{N}_6$: C, 86.10; H, 7.62; N, 6.28. Found: C, 86.24; H, 7.74; N, 6.19. $(\text{MH})^+/z = 1339.2$.

Oxidation procedure

The chemical oxidation of cyclophanes was carried out in an argon atmosphere. In a typical procedure 80 μL of 0.01 M solution of cyclophane in CH_2Cl_2 was oxidized with an appropriate amount of 0.04 M oxidant solution in BuCN

and diluted to 200 μl of overall volume. Then 20 μl of oxidized solution was diluted with 0.35 ml of CH_2Cl_2 . These solutions were used directly to UV-Vis-NIR measurements.

The procedure of preparation of EPR samples was similar but anhydrous acetonitrile was used instead of butyronitrile as a solvent for the oxidant. The concentration of cyclophane in EPR samples was typically 0.015 M.

3. Results and discussion

The synthesis of macrocyclic compounds usually requires high-dilution conditions to prevent the formation of high-molecular-weight product. However, we have found that a one-step reaction at medium concentration of 0.04 M of the two diamine derivatives tested at 110 $^\circ\text{C}$ results in the desired cyclic products with acceptable yields.

Thus, in the reaction of *N,N'*-bis(4-butylphenyl)-1,4-phenylenediamine, **1** with 1,3-dibromobenzene we have obtained tetraazacyclophane, **C1** with 43.7% yield. The reaction of bis[(4'-butylphenyl)-4-aminophenyl]-4''-*tert*-butylphenylamine, **2** with 1,3-dibromobenzene gave hexaazacyclophane, **C2** with 35% yield (Scheme 2).

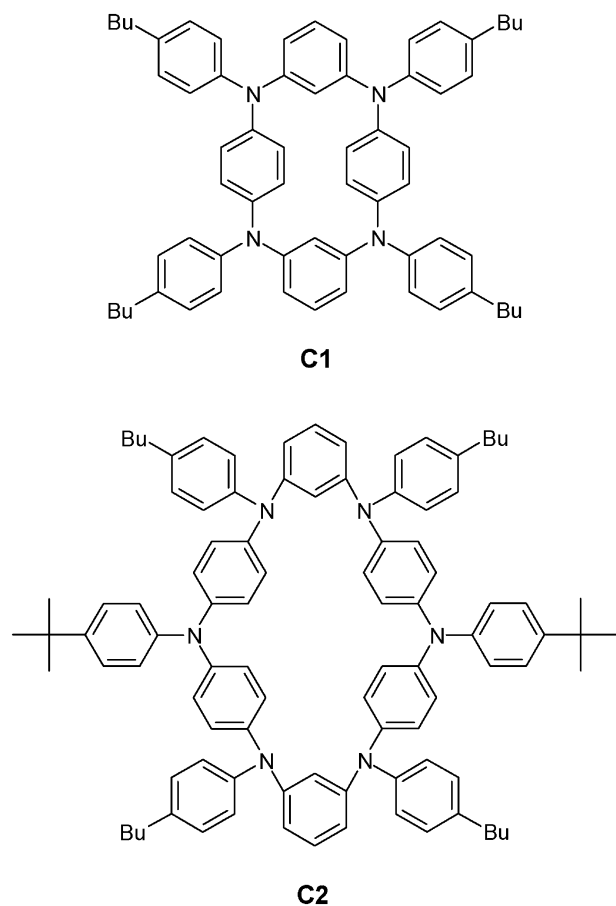
Macrocycles were chemically oxidized with *tris*-(4-bromophenyl)aminium hexachloroantimonate, TBA $\cdot\text{SbCl}_6$, and this process was monitored by UV-Vis-NIR spectroscopy. Neutral

(unoxidized) **C1** UV-Vis-NIR spectrum in CH_2Cl_2 shows one band at 319 nm ($\epsilon = 4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which can be attributed to the $\pi\text{-}\pi^*$ transition in phenylene rings (Fig. 1a).

The same value was obtained by Hauck *et al.*⁹ for tetraazacyclophane containing *p*-tolyl groups. Upon oxidation new bands characteristic of radical cations appear. In the spectra of **C1** oxidized to mono- and dicationic states (as calculated from the oxidant to **C1** molar ratios, Ox/C1 = 1 and 2) three new bands appear which are located at 435, *ca.* 900 and 1140 nm. The long wavelength band (1140 nm) can originate from an intervalence (IV) excitation associated with an electron transfer from the neutral phenylamine center to the phenylamine radical cation center. This type of transition has previously observed for phenylenediamine derivatives^{13,14} as well as in the case of ladder macromolecular systems.¹⁵ The absorption band at *ca.* 900 nm originates from the presence of localized excitation of the triarylamine radical cations.

More diabatic electron distribution¹⁶ can be caused by the non-planar structure of tetraazacyclophane.^{8,9} The presence of two NIR bands unequivocally indicates that localized and delocalized polarons co-exist in these oxidation states and have been detected for other oligomers and polymers containing phenylenediamine moiety.^{13,14,17}

Further oxidation of **C1** to tri- and tetracationic forms (the oxidation with 3 and 4 equivalents of Ox, respectively)



Scheme 2 Chemical structures of tetraazacyclophane **C1** and hexaazacyclophane **C2**.

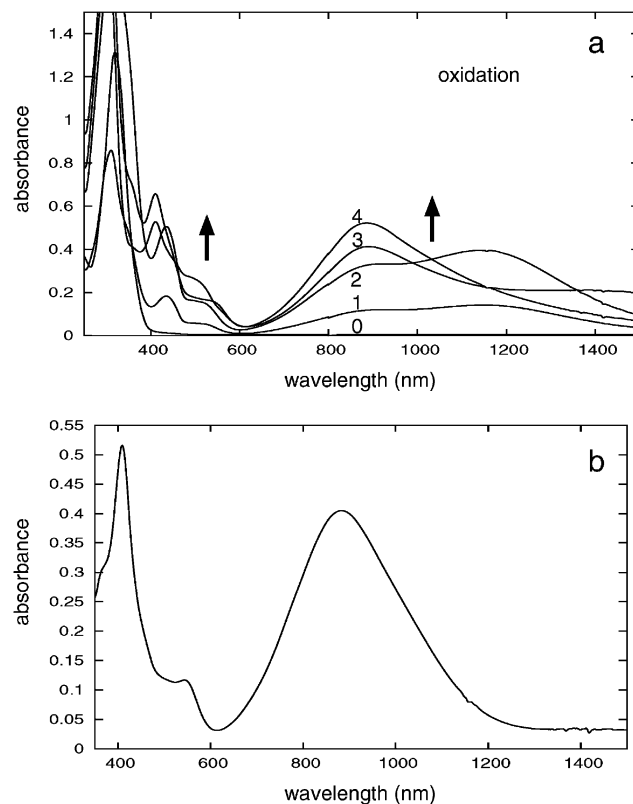


Fig. 1 The UV-Vis-NIR spectra of tetraazacyclophane **C1** oxidized with TBA $\cdot\text{SbCl}_6$ in $\text{CH}_2\text{Cl}_2/\text{BuCN}$ solution (the concentration of cyclophane, $c = 2.7 \times 10^{-4} \text{ M}$) (a): (0) Ox/C1 = 0, (1) Ox/C1 = 1, (2) Ox/C1 = 2, (3) Ox/C1 = 3, (4) Ox/C1 = 4; (b) difference spectrum obtained by subtraction of spectrum "1" from "3".

leads to the disappearance of the above-mentioned low-energy absorption. The tricationic form corresponds to the presence of one radical cation on the first *p*-phenylenediamine moiety and two radical cations or spinless dications on the second one. If we assume that the absorption of the monocationic state of one *p*-phenylenediamine segment is not influenced by the charge density of the second segment (which is separated by 1,3-benzenediyl), the subtraction of the spectra "3" (corresponding to the tricationic form) and "1" (corresponding to the monocationic form) should show the band characteristic of the dicationic state (Fig. 1b). This difference spectrum shows a band centered at 886 nm similar to that registered for the tetracationic state (spectrum "4").

It should be stressed, however, that the chemical oxidation of the macrocycles does not correspond to equilibrium conditions and a co-existence of the species at different oxidation levels should be expected which can originate from local inhomogeneities of the solution and possible disproportionation reactions. As a result of these processes the following species may appear:

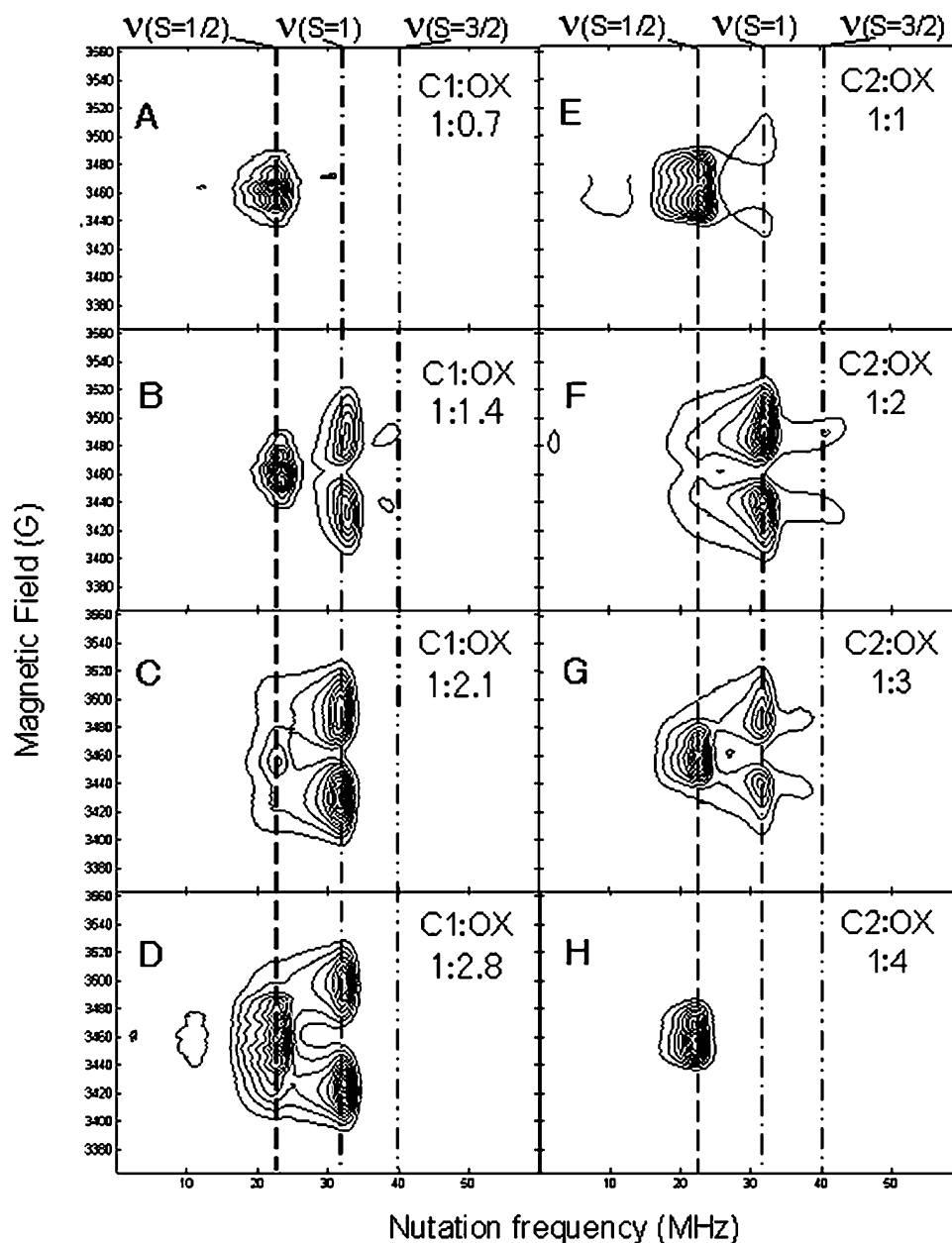
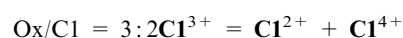
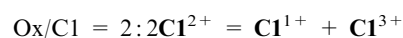
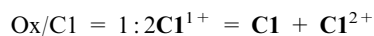


Fig. 2 Pulsed EPR nutation spectra of C1 and C2 oxidized by increasing amounts of oxidant. Each spectrum is normalized to its own maximum intensity. Contour plots were plotted with lines connecting points having 10, 20, ..., 90 and 99% of the maximum intensity. The nutation frequencies expected for $S = 1/2$, $S = 1$ and $S = 3/2$ (see Experimental section) are indicated by dotted lines.

Among different oxidation forms the diradical dicationic state is especially interesting because in this case spins can be magnetically coupled to form the triplet state $S = 1$. This state can be detected using EPR spectroscopy.

Pulsed EPR nutation spectra of **C1** samples prepared from the same stock solution after addition of increasing amount of the oxidant are shown in Fig. 2 in the frames A, B, C and D, respectively. The following evolution of the spectra can be observed: (i) in spectrum A ($Ox/C1 = 0.7$), the contour plot is centered around 23 MHz and 3465 G, which corresponds to $S = 1/2$ species, consistent with the production of the monoradical monocation. (ii) In spectra B and C this signal decreases to the benefit of two signals centered around 32 MHz nutation frequency and around 3430 G and 3490 G magnetic field values, which is attributed to a $S = 1$ species and is consistent with the formation of the diradical dication of **C1**. (iii) In spectrum D, a new signal centered around 23 MHz and 3465 G appears at the expense of signals from $S = 1$ species, which is consistent with the formation of a radical trication having $S = 1/2$ as spin multiplicity.

This set of pulsed EPR nutation spectra gives the following information that cannot be drawn from conventional continuous wave EPR studies. (1) It shows that the different oxidation states appear successively. (2) The spectrum C suggests that the diradical dication $S = 1$ state predominates in the sample. This conclusion is supported by a pulsed EPR spin-echo experiment performed with the same sample (data not shown): the integration of these spectra indicates that the numbers of spins in samples A, B, C and D are of the same order of magnitude, which rules out the hypothesis of a predominant $S = 0$ spin state in sample C. (3) The studied series establishes clearly the $S = 1/2$ spin multiplicity of the radical trication (at least at 7 K) since only very weak signals corresponding to $S = 3/2$ species were observed (see spectrum B signals close to 40 MHz nutation frequency). This supports the model of a trication state consisting of a monoradical cation on one phenylenediamine moiety and a diamagnetic dicationic state on the second phenylenediamine moiety drawn from UV-visible absorption spectra.

The UV-Vis-NIR spectrum of neutral (unoxidized) **C2** in CH_2Cl_2 also shows one band at 336 nm ($\epsilon = 9.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 3a). The spectra of **C2** oxidized chemically can be divided into three types. The first type corresponds to the oxidation of **C2** to mono- and dicationic states.

The spectra show three new bands located at 440, ca. 795 and 1420 nm. The origin of these bands is similar to those observed for **C1**. Thus, the long wavelength band can correspond to the intervalence charge-transfer (IV-CT) between states in which the positive charge is centered at different triarylamine sites. However, a bathochromic shift of this absorption, as compared to that registered for **C1**, indicates a more pronounced delocalization of polarons in **C2** consistent with the chemical constitution of the *p*-amino-phenylenediamine conjugated segment. Similar types of spectra were observed by Hirao *et al.*¹⁷ for star-shaped nonaamine and for aryl triamine, which can be considered as a model compound for hexaazacyclophane. We can also notice that the intensity of 795 nm absorption is ca. 20 times lower than that of 1420 nm, which leads to the conclusion that radical cations are

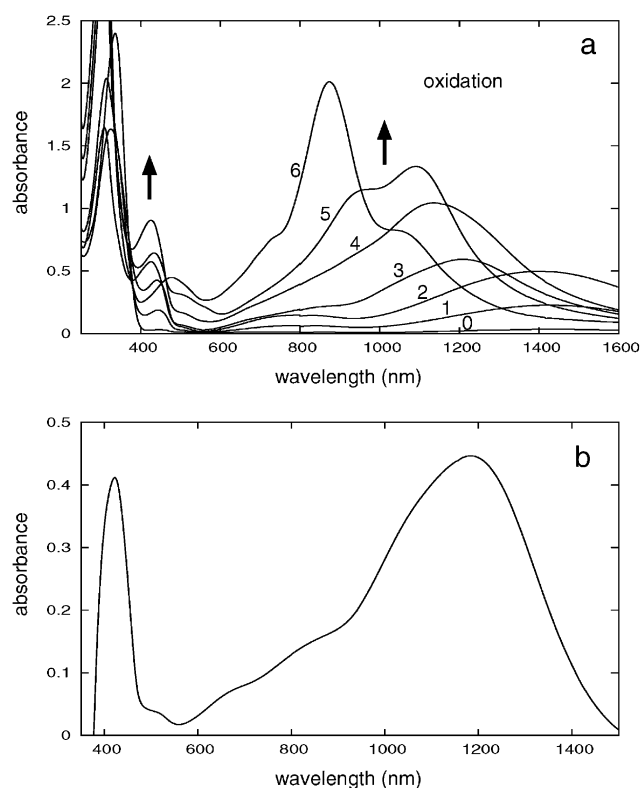


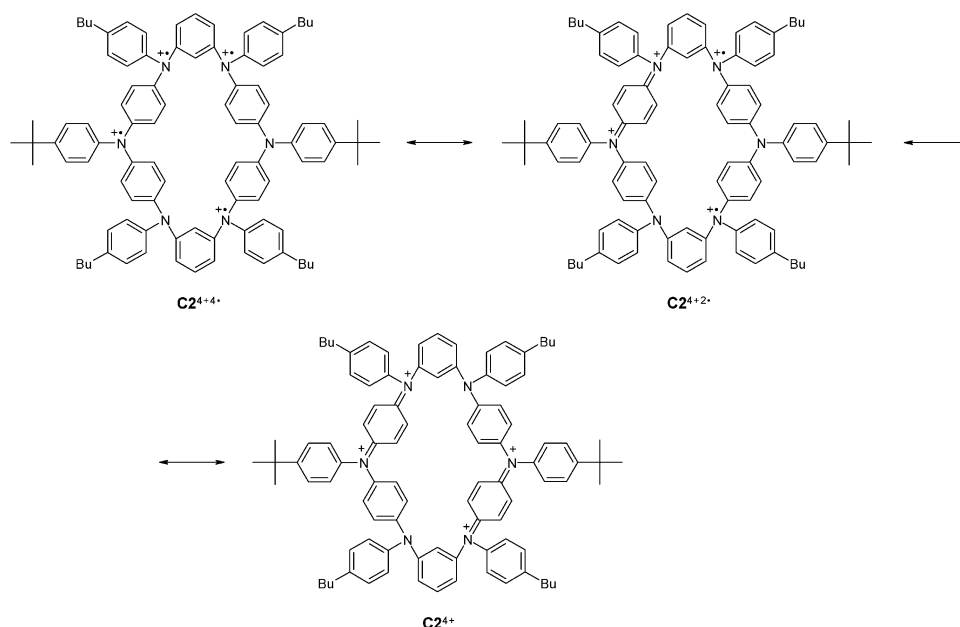
Fig. 3 The UV-Vis-NIR spectra of hexaazacyclophane **C2** oxidized with $TBA \cdot SbCl_6$ in $CH_2Cl_2/BuCN$ solution (the concentration of cyclophane, $c = 2.5 \times 10^{-4} \text{ M}$) (a): (0) $Ox/C2 = 0$, (1) $Ox/C2 = 1$, (2) $Ox/C2 = 2$, (3) $Ox/C2 = 3$, (4) $Ox/C2 = 4$, (5) $Ox/C2 = 5$, (6) $Ox/C2 = 6$; (b) difference spectrum obtained by subtraction of spectrum “1” from “3”.

predominantly preserved in the delocalized polarons form. The second stage of oxidation corresponds to the formation of tri- and tetracationic states. The spectra are dominated by one broad band in the NIR region. In these oxidation levels it is not possible to predict solely on the basis of UV-Vis-NIR measurements whether the introduced charge is stored in the form of spinless bipolarons (dications) or diradical dications. Especially, the oxidation of **C2** with 4 equivalents of oxidant can lead to $C2^{4+4\bullet}$ and/or $C2^{4+2\bullet}$ and/or $C2^{4+}$ (Scheme 3).

The difference spectrum (Fig. 3b) obtained by the subtraction of spectrum “1” (corresponding to monocationic state) from that of “3” (corresponding to tricationic form) shows one peak at 1180 nm with a shoulder at ca. 900 nm similar to that observed for spectrum “4”. Thus, we can suppose that most of the charge is stored in the dicationic form. Further oxidation with 5 equivalents of oxidant causes a hypsochromic displacement of the NIR band to 1090 nm with a shoulder centered at 950 nm. This shoulder becomes the dominant band located at 874 nm in the spectrum of **C2** oxidized with 6 equivalents of oxidant.

Pulsed EPR nutation spectra of oxidized **C2** samples with 1, 2, 3 and 4 equivalents of oxidant are shown in frames E, F, G and H of Fig. 2. This behaviour is qualitatively similar to the oxidation induced evolution of the spectra of **C1**.

In spectrum E, corresponding to the addition of one equivalent of oxidant to **C2**, one can notice that most of the



Scheme 3 Structures of hexaazacyclophane oxidized to tetracationic state.

signal is centered around 23 MHz nutation frequency and between 3450 and 3480 G magnetic field values, corresponding to a $S = 1/2$ species consistent with the monoradical monocation of **C2**. In spectrum F, most of the signal is found around 32 MHz nutation frequency and 3440 and 3485 G magnetic field values. This spectrum corresponds to an almost pure $S = 1$ state, which is consistent with the formation of the diradical dication of **C2**. In spectrum G, corresponding to the addition of 3 equivalents of oxidant, the main signal is that of $S = 1/2$ species observed at 23 MHz nutation frequency, $S = 1$ (at 32 MHz) signals are relatively weak and $S = 3/2$ (at 40 MHz) signals are in the minority.

This spectrum shows clearly that monoradical trications ($S = 1/2$) are the dominant spin-charge configurations as in **C1** of a similar oxidation level. In this case we can consider the formation of a spinless dication on one *p*-amino-phenylenediamine conjugated segment and a radical cation on the second segment. However, the disproportionation reaction: $2\mathbf{C2}^{3+} = \mathbf{C2}^{2+} + \mathbf{C2}^{4+}$ can also take place. The presence of relatively weak signals of $S = 1$ can be attributed to the presence of diradical dicationic state. The appearance of $S = 3/2$ signals would be caused by the stacking of two cyclophanes: the first one being in the monocation radical state and the second one in the diradical dicationic state. This hypothesis is under investigation.

The spectrum H greatly helps to clarify the discussion of the spin state of the tetracation of **C2**. In this spectrum the only recorded signal has the nutation frequency of 23 MHz which is typical of the $S = 1/2$ spin state in our experimental conditions. However this signal is weak: absolute maximum intensity of spectrum H is eight times lower than that of spectrum E, recorded in exactly the same conditions (data not shown, intensities of spectra shown in Fig. 2 are normalized). These observations lead to two possible

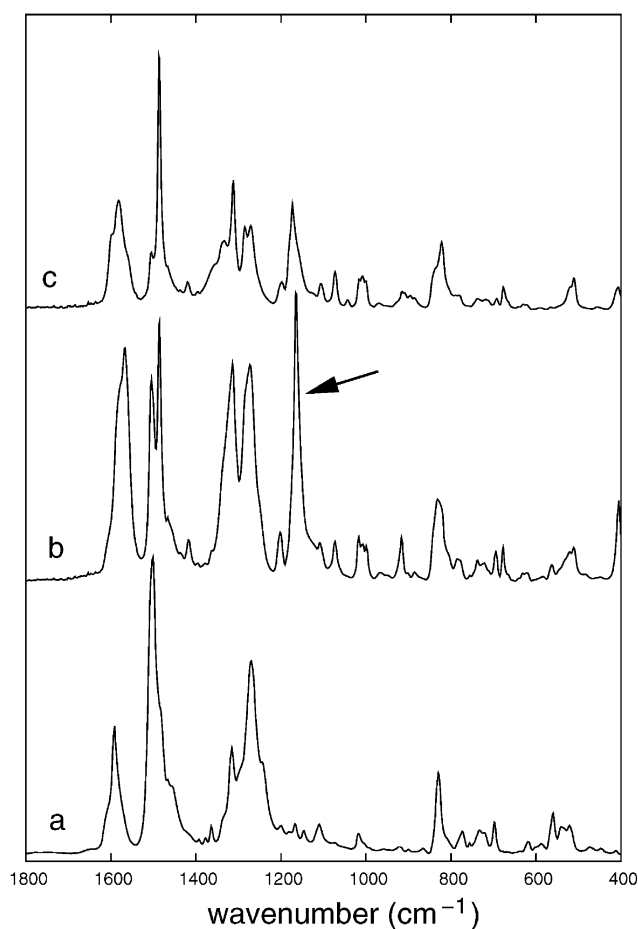


Fig. 4 The IR spectra of hexaazacyclophane **C2**: (a) neutral form, (b) oxidized to diradical dicationic state, (c) oxidized to tetracationic state.

conclusions: (i) the relatively weak $S = 1/2$ signal observed in spectrum H is due to residual monoradical trications and tetracations are only in the diamagnetic state $\mathbf{C2}^{4+}$ (see Scheme 3), or (ii) tetracations are mainly in the diamagnetic state $\mathbf{C2}^{4+}$ but a few of them are in the $S = 1/2$ state $\mathbf{C2}^{4+\bullet}$ (see Scheme 3). In both cases it can be concluded that most of the tetracations are in the diamagnetic state $\mathbf{C2}^{4+}$.

The presence of distinctly different oxidation states is also manifested in the IR spectra of TBA·SbCl₆ treated samples. The IR spectra of **C2** recorded before and after oxidation are presented in Fig. 4. The oxidation of this compound to diradical dicationic state induces several changes due to lowering of the molecule symmetry. The band at 1592 cm⁻¹ attributed to the C=C stretchings of the phenylene ring¹⁴ of neutral **C2** is shifted to 1567 cm⁻¹ and increases in intensity, whereas the band at 1502 cm⁻¹ decreases in intensity after the oxidation. The band at 1486 cm⁻¹ (C=C stretch of phenyl ring + C–N stretch¹⁴) and the band at 1315 cm⁻¹ (C–H bending¹⁸ + C–N–C stretch¹⁴) significantly increase in intensity. Moreover, a strong new band appears at 1164 cm⁻¹ which can be diagnostic for a polaronic state, similar to that observed for oxidized poly(*m-p*-anilines).¹⁹ In the case of **C1** oxidized to diradical dicationic state this mode is placed at 1175 cm⁻¹.

In the spectrum of **C2** oxidized to the tetracationic state the band attributed to the polaronic form decreases in intensity and shifts to 1173 cm⁻¹. A decrease in intensity is also observed for the 1567 cm⁻¹ band together with its shift to 1582 cm⁻¹. This last band overlaps with a band centered at 1595 cm⁻¹ which can be attributed to the C=C stretchings in the quinoid ring.¹⁸ The observed oxidation induced changes seem to suggest that the concentration of the radical cations decreases and they co-exist with an increasing number of a spinless dicationic state. The IR results strongly corroborate the UV-Vis-NIR and EPR findings.

Conclusions

Chemical oxidation of cyclic oligoanilines, namely azacyclophanes, leads to the formation of radical cations in the intermediate oxidation states. In the case of tetraazacyclophane **C1** oxidized to mono- and dicationic states partly localized and delocalized radical cations were detected whereas in the case of hexaazacyclophane **C2** mostly delocalized radical cations were found. The degree of localization of radical cations increases with the increase of the oxidation level. Moreover, the pulsed-EPR measurements produced evidence that multiplicity of the systems depends on the spins' concentration. Spins of both cyclophanes oxidized to a diradical dicationic form can interact ferromagnetically and create an almost pure triplet state, which was not detected to date for other types of oligoanilines. This evidence of the

ferromagnetic character of the coupling is very promising for the future preparation of magnetic polymers containing cyclophane moieties.

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