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Experimental and theoretical studies of the low-lying electronic states of the simplest benzylic amide [2]catenane

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Abstract

The lowest electronically excited states of the simplest benzylic amide [2]catenane (**1**) have been studied by a combination of experimental and theoretical techniques. Experimentally, steady-state and transient absorption spectra, emission spectra, and the optoacoustic response in solution have been recorded for the catenane and a model compound (*N,N'*-dibenzylisophthalic diamide (**2**)), as well as the electron energy loss spectrum of the catenane deposited on the Au(111) surface. The theoretical picture builds on the results of semiempirical quantum chemical calculations and shows that partial delocalisation of the electronic states over the many chromophores of the catenanes can occur. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The preparation and property characterisation of topologically non-trivial chemical objects is currently attracting a considerable amount of interest [1–4]. Catenanes are a class of molecules in which two or more macrocycles are interlocked to form the commencement of a chain. With respect to its topologically trivial counterparts these mechanically interlocked molecules offer an additional degree of freedom in the form of the circumvolution of the macrocycles. It is this degree of freedom which

offers unique perspectives for the design of novel materials with custom-designed properties. In analogy with the properties of the more successful organic materials (e.g., -hexathiophene whose performance in a thin-film transistor rivals that of silicon [5,6]) one may think that for the materials science the properties of interest are likely to be electronic or vibro-electronic. Fundamental and applicative reasons therefore require the study of the vibrational and electronic properties of these molecules in different phases and by different, possibly complementary, techniques.

Here we report the first study of the electronic states of a benzylic amide [2]catenane (**1**, Fig. 1). This catenane is prepared through a serendipitously discovered one-step self-assembly process [7–11], whose high versatility can be used to generate a very large family of molecules. The flexibility of the self-assembly process is accompanied in this class of molecules by the intriguing pseudosymmetry of the prototypical catenane in which eight phenyl groups, eight amide groups, and eight methylene groups form two macrocycles that are tightly threaded one through the other, and in which the chemical interactions between the two rings are only non-bonding or weakly bonding (hydrogen bonding). Apart from the more standard spectroscopic characterisation of the electronic states in solution, electron energy loss

spectroscopy (EELS) has been applied to study the spectroscopic properties of the catenane in the solid state. The spectroscopic properties of the catenane are compared with those of *N,N'*-dibenzylisophthalic diamide (**2**, Fig. 1), which contains the same chromophores as the catenane. Semiempirical calculations are used to simulate and analyse the experimental results.

2. Experimental and computational procedures

2.1. Absorption spectroscopy

The electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer using commercially available spectrograde solvents.

2.2. Steady-state fluorescence spectroscopy

Emission spectra, corrected for the wavelength dependence of the detection system, were recorded on a Spex Fluorolog II emission spectrometer using an RCA-C31034 GaAs photomultiplier as detector. Samples were prepared as a solution in *N,N*-dimethylformamide (DMF) with an absorbance between 0.1 and 0.2 at an excitation wavelength of 285 nm. Deoxygenation did not lead to a noticeable increase in fluorescence intensity.

2.3. Optoacoustic calorimetry

Optoacoustic measurements were performed and analyzed as described previously [12,13]. Samples were prepared as a solution in DMF with an absorbance of ~ 0.07 at the excitation wavelength (308 nm). Reference signals were obtained using 2-hydroxybenzophenone (Aldrich 99%) with the same optical density as the corresponding sample and measured under identical conditions.

2.4. Electron energy loss spectroscopy

The EELS experiments were performed in a two-chamber ultrahigh-vacuum system equipped with a high-resolution spectrometer (ISA-Riber). The base pressure in the analysis and preparation chambers

Fig. 1. Solid state structure of benzylic amide [2]catenane (**1**) as determined by X-ray crystallography and structure of *N,N'*-dibenzylisophthalic diamide (**2**).

was 2×10^{-10} and 5×10^{-10} Torr, respectively. The spectrometer consists of two identical hemispherical electrostatic selectors, one acting as monochromator, the other as analyser. The energy of the incident electron beam can be varied from 0 up to 150 eV. The instrumental resolution is set to 0.03–0.05 eV. The spectrometer has an acceptance angle of 1.5° . All the EELS measurements were carried out in the specular reflection geometry ($\vartheta_i = \vartheta_r = 45^\circ$). An Au (111) single crystal was used as substrate. It was cleaned by sputtering annealing cycles until no contaminants were detected in the high-resolution EEL spectrum and a clear LEED (low-energy electron diffraction) pattern was obtained. The catenane was sublimed at $\sim 190^\circ\text{C}$ from a Knudsen cell with a quartz crucible, previously outgassed up to $\sim 250^\circ\text{C}$. The film was deposited onto the Au(111) held at room temperature, the deposition rate was monitored by a quartz oscillator balance. The spectra were collected on a $\sim 100 \text{ \AA}$ thick film.

2.5. Calculations

Molecules with more than 100 atoms still pose a significant challenge for any level of quantum chemical calculations, even more so when the purpose is to investigate properties of electronically excited states. We have therefore employed the semiempirical CNDO/S method [14,15], which we have used before to study large molecular systems [16–19]. In our calculations the self-consistent field (SCF) procedure was followed by configuration interaction (CI) of singly excited configurations in the space of 40 occupied and 32 unoccupied molecular orbitals, which were chosen by considering that the lowest electronic transitions could be either phenyl or carbonyl $\pi\pi^*$ transitions, or $n_O\pi^*$ transitions (vide infra). The calculations were performed on the geometry obtained for **1** from X-ray crystallography [8].

2.6. Compounds

[2](1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane (1',17',14',20'-tetraaza-2',6',15',19'-tetraoxo-3',5',9',12',16',18',22',25'-tetra-benzocyclohexaco-sane)-catenane (**1**) and *N,N'*-dibenzylisophthalic diamide (**2**) have been

synthesised according to previously described procedures (Refs. [7] and [20], respectively).

3. Results and discussion

The steady-state absorption spectra of the catenane and the model compound dissolved in DMF are depicted in Fig. 2. Inspection of this figure shows that the spectrum of the reference compound accounts for the position and the shape of the bands of the lowest electronic transitions of the catenane. The molar absorption coefficient at the maximum of the band (266 nm, 4.7 eV) is $\sim 10000 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the catenane and $\sim 2300 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the reference compound. The absorption at 266 nm can be largely ascribed to the isophthalic amide chromophore, the benzyl groups (typical $\epsilon = 200 \text{ l mol}^{-1} \text{ cm}^{-1}$) making a minor contribution. The 4:1 ratio can be taken to be indicative of the fact that four of these chromophores are present in the catenane. Implicitly, this argues in favor of an additive nature of the electronic transitions. Notice that, in that case, the molar absorption coefficient observed for the catenane does not imply that it is a fully-allowed transition. On the contrary, the transition should then be considered as 'semi-forbidden', and only obtains such a large molar absorption coefficient on account of the presence of four chromophores in the molecule. At lower energies, the absorption spectrum of the reference compounds shows two substantially weaker shoulders at 278 nm (4.5 eV) and 287 nm (4.3 eV)

Fig. 2. Absorption spectrum of the benzylic amide [2]catenane (**1**) (full line) and *N,N'*-dibenzylisophthaldiamide (**2**) (dotted line) in DMF solution. The units on the left refer to **1**, the units on the right to **2**.

with extinction coefficients of 1300 and 800 l mol⁻¹ cm⁻¹, respectively. These shoulders are less distinct in the spectrum of the catenane, which only allows for the assignment of a shoulder at 287 nm ($\epsilon = 2500$ l mol⁻¹ cm⁻¹).

Emission spectra of the two compounds dissolved in DMF obtained after excitation at 285 nm are shown in Fig. 3. The emission quantum yield of both compounds is extremely low, as can be deduced from the peak centered at 310 nm, which derives from Raman scattering of the solvent. The emission of the reference compound starts around 320 nm (3.9 eV), while the emission of the catenane is seen to be displaced to *higher* energies by 0.2 eV with a seemingly slightly smaller width than that of the reference compound (0.9 eV). Although these observations might in first instance seem to go against the intuitive notion that the catenane is a larger system than the model compound, they are in agreement with the absorption spectra: for the reference compound a detectable absorption starts to show up at ~ 318 –320 nm (3.9 eV), while for the catenane this occurs at ~ 300 –302 nm (4.1 eV). The higher excitation energy of the emitting state and the slightly smaller emission width in the catenane can be rationalized when it is realised that the emitting state most probably derives from the isophthaloyl moiety(ies). In the model compound this chromophore is at liberty to adopt a more planar conformation than in the catenane. As a result, excited states, which are not localised on the phenyl ring, are expected to have a higher excitation energy in the catenane than in the reference compound. The slightly broader emission

of the reference system can similarly be ascribed to the flexibility of the side chains that can have different torsional potentials in the ground and in the electronically excited states, a factor that can contribute substantially to an increase of the Stokes shift. Such a degree of freedom is locked in the catenane. It will be interesting to support this notion for the reference compound with higher-resolution spectra when they become available in the future.

The emission spectra shown in Fig. 3 have been obtained on samples with the same absorbance at 285 nm. The observation that the integrated emission intensity is about the same in both compounds is in nice agreement with the conclusion on the nature of the excited states drawn from the absorption spectra. The weakness of the fluorescence of both compounds precluded a reliable measurement of the lifetime of the excited state from which the emission originates. As yet, several explanations can be put forward for the apparent substantial energy gap between absorption and emission, and the weakness of the emission, e.g., large differences between the equilibrium geometries of the ground and excited states. The combination of the results from the optical spectroscopy measurements with the results of EELS demonstrate, however, that it derives from a very low transition dipole moment for the S_0 – S_1 transition. In other words, the lowest-energy transition, which is responsible for the fluorescence, is not observed in absorption.

The extremely low emission quantum yields observed for both compounds indicate the dominance of radiationless decay processes, most probably internal conversion to the ground state. This notion is confirmed by transient absorption spectroscopy and photoacoustic calorimetry. Transient absorption measurements did not show the presence of any transients, which suggests that efficient intersystem crossing to a (long-lived) triplet state is not the cause of the weakness of the fluorescence. To rule out the possibility of transients not absorbing in the visible spectral range, photoacoustic measurements were carried out. The photoacoustic response was the same as that of the hydroxybenzophenone reference solution, indicating that no heat is stored in transient species on a timescale of ~ 100 ns to microseconds.

The solution work has established that the lowest electronic transitions of the catenane have small

Fig. 3. Fluorescence spectrum of the benzylic amide [2]catenane (1) (full line) and *N,N'*-dibenzylisophthaldiamide (2) (dotted line) in DMF solution.

transition dipole moments. It is of interest to probe the behaviour of the electronic states further by studies in the solid phase. This is pursued here by investigating the catenane as a thin film on the Au(111) surface by EELS [21,22]. Fig. 4 presents the EEL spectrum obtained with three different energies of the probing electrons. These spectra provide not only information on the dipole-active but also on the dipole- and spin-forbidden states, since the excitation probability for these forbidden transitions decreases with increasing energy of the probing electron. From the comparison of the spectra, it is interesting to notice that the transitions located at 3.7 and 4.6 eV are only present for low energies of the exciting electron, indicating that they derive from forbidden transitions. Their intensity is due to an exchange-type mechanism. In this resonant-like process, the incom-

ing electron with kinetic energy E_0 is captured in one of the unoccupied states above the vacuum level, the system then makes a transition to a lower electronically excited state and transfers the excess energy back to another electron, which is subsequently detected with a kinetic energy $E_0 - E_T$. The kinetic energy difference between the incoming and the outgoing electron, E_T , is the energy of the electronic state.

Inspection of Fig. 4 confirms the features observed in solution. The EELS band located at 4.6 eV most probably corresponds to the strongest feature observed in absorption at 4.7 eV. The lower-energy band corresponds to the weak or nearly-forbidden band from which the observed emission originates. It appears that the shift from solution to the surface decreases the excitation energy (4.1 eV in emission, 3.7 eV on the gold surface; 4.7 in absorption, 4.6 eV on the surface). We thus see that the hypothesis raised by the optical spectroscopic measurements, i.e., emission originates from a lower-lying state than the ones observed in absorption, is confirmed by the EELS measurements. We can moreover conclude that the lowest electronic states of the catenane are similar in solution and on a surface. Their ‘forbidden’ nature is maintained while their energy is slightly downshifted.

The complexity of the lowest electronically excited states of the [2]catenane does not allow us to push the present qualitative analysis any further. Additional information can be obtained from the quantum-chemical calculations, whose results are given in Table 1. The first excited state is calculated to be at 4.17 eV, which should be compared with a solution-phase excitation energy of ~ 4.1 eV. This state is actually the first of a set of 16 electronic states that are spread over ~ 0.6 eV and are all characterised by very weak transition dipole moments from the ground state, although we notice that some of the states with excitation energies ~ 4.7 eV have a larger oscillator strength than the ones with lower excitation energies. These results are in agreement with the solution spectra and the electron energy loss measurements. Analysis of the wavefunctions of this cluster of electronic states shows that they are best described as a combination of $n_o\pi^*$ and L_b phenylic states (B_{2u} in the local D_{6h} symmetry). In particular, the two stronger transitions ($S_9 \rightarrow$

Fig. 4. Electron energy loss spectrum of the benzylic amide [2]catenane (**1**) on a gold (111) surface. The feature observed for an electron kinetic energy of 100 eV at 2.5 eV derives from a gold plasmon, and is not associated with **1**.

Table 1
Summary of CNDO/S results for benzylic amide [2]catenane (**1**)
for the first 60 electronic states

<i>n</i>	Singlet ΔE	f_0	Triplet ΔE
1	4.167	0.005	2.9055
2	4.169	0.005	2.9098
3	4.397	0.003	3.0495
4	4.402	0.002	3.0547
5	4.415	0.005	3.0822
6	4.417	0.005	3.0829
7	4.493	0.006	3.0858
8	4.545	0.005	3.0976
9	4.663	0.016	3.7925
10	4.663	0.007	3.7940
11	4.686	0.005	3.8291
12	4.694	0.008	3.8311
13	4.715	0.011	3.8835
14	4.719	0.007	3.8914
15	4.727	0.002	3.9051
16	4.730	0.002	3.9080
17	5.502	0.020	3.9170
18	5.507	0.015	3.9207
19	5.578	0.041	3.9245
20	5.599	0.059	3.9261
21	5.607	0.123	3.9441
22	5.609	0.265	3.9467
23	5.672	0.009	3.9505
24	5.679	0.106	3.9553
25	5.697	0.027	4.1795
26	5.705	0.032	4.1818
27	5.756	0.152	4.4017
28	5.778	0.157	4.4066
29	5.835	0.118	4.4210
30	5.847	0.019	4.4231
31	5.855	0.006	4.4977
32	5.858	0.001	4.5461
33	5.887	0.032	4.7209
34	5.891	0.012	4.7235
35	5.987	0.025	4.7400
36	6.001	0.015	4.7488
37	6.030	0.007	4.7499
38	6.061	0.009	4.7765
39	6.077	0.050	4.7934
40	6.096	0.030	4.7958
41	6.098	0.059	4.8989
42	6.110	0.098	4.9036
43	6.139	0.005	4.9529
44	6.188	0.003	4.9556
45	6.215	0.824	5.2427
46	6.218	0.207	5.2454
47	6.265	0.040	5.4498
48	6.266	0.102	5.4548
49	6.274	0.035	5.5304
50	6.288	0.293	5.5361
51	6.293	0.313	5.6912

Table 1 (continued)

<i>n</i>	Singlet ΔE	f_0	Triplet ΔE
52	6.310	0.244	5.6983
53	6.314	0.186	5.7301
54	6.343	0.131	5.7753
55	6.347	0.008	5.8433
56	6.349	0.009	5.8498
57	6.360	0.021	5.8551
58	6.367	0.016	5.8578
59	6.389	0.029	5.8703
60	6.405	0.104	5.8732

S_0 – S_n transition energies (eV), and corresponding oscillator strengths, f_0 ; T_1 – T_n transition energies (eV). Description of the nature of the states is in the text and partly in Fig. 5.

S_0 and $S_{13} \rightarrow S_0$ at 4.66 and 4.72 eV, respectively) can be associated with L_b states of the *p*-xylyl fragments. At higher excitation energies the calculations find a cluster of charge-transfer states of the benzaldehyde type, which have, in agreement with the experimental results, larger, though not particularly strong, oscillator strengths. Finally, the intense transition observed in the EEL spectrum at 6.2 eV, which corresponds to the β transition of benzene (to the E_{1u} states in the local D_{6h} symmetry), is predicted correctly by the calculations.

The excitation energies of the lowest triplet states are given in Table 1 as well. In agreement with the results obtained for the singlet states, the calculations show that the lowest triplets are a set of eight levels whose wavefunction corresponds to 3L_a benzenic states ($^3B_{1u}$ in the local D_{6h} symmetry).

Optical spectroscopy has shown that from an electronic energy point of view the catenane is rather similar to its basic chromophore, the isophtaloyl fragment, but has not enabled us to draw any conclusions as to what extent the excitation is delocalised in the excited states of the catenane. This aspect of the nature of the electronic states of the catenane is further elucidated by considering the charge flow upon excitation. Fig. 5a–d depicts the calculated charge flow upon electronic excitation from the ground state to S_1 , S_2 , S_3 , and S_4 . Inspection shows that the charge flow is neither completely localised on a fragment, nor completely delocalised: it usually involves two or three phenyl rings. The observed presence of delocalised states can be important in

Fig. 5. Charge flow upon electronic excitation for selected low-energy transitions of benzylic amide [2]catenane (**1**). The arrow pointing up means that the electron density is increased, the arrow pointing down means that the electron density is decreased: (a) S_1 , (b) S_2 , (c) S_3 , (d) S_4 .

practical applications based on the non-linear optical properties, NLO, of the catenane. In a sum-over-states approach the response is given by the ratio of a product of electronic transition dipole moments between electronically excited states divided by an energy denominator. Electronic transitions between perfectly localised states of different chromophores would amount to charge-transfer transitions, which usually have zero or very low transition dipole moments [23] and thus reduce the NLO response considerably. Our calculations indicate that for the catenane the electronic states are (partly) delocalised and consequently imply that catenanes might make much

more promising materials for non-linear optical applications than their basic chromophores. Work to investigate the non-linear optical properties of benzylic amide catenanes is now in progress.

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References

- [1] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.
- [2] D.B. Amabilino, J.F. Stoddart, *Chem. Rev.* 95 (1995) 2725.
- [3] H.W. Gibson, M.C. Bheda, P.T. Engen, *Prog. Polym. Sci.* 19 (1994) 843.
- [4] J.-P. Sauvage, *Acc. Chem. Res.* 23 (1990) 319.
- [5] A. Dodabalapur, L. Torsi, H.E. Katz, *Science* 268 (1995) 270.
- [6] A. Dodabalapur, H.E. Katz, L. Torsi, R.C. Haddon, *Science* 268 (1995) 1560.
- [7] A.G. Johnston, D.A. Leigh, R.J. Pritchard, M.D. Deegan, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1209.
- [8] A.G. Johnston, D.A. Leigh, L. Nezhat, J.P. Smart, M.D. Deegan, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1212.
- [9] A.G. Johnston, D.A. Leigh, A. Murphy, J.P. Smart, M.D. Deegan, *J. Am. Chem. Soc.* 118 (1996) 10662.
- [10] D.A. Leigh, K. Moody, J.P. Smart, K.J. Watson, A.M.Z. Slawin, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 306.
- [11] D.A. Leigh, A. Murphy, J.P. Smart, A.M.Z. Slawin, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 728.
- [12] S.E. Braslavsky, G.E. Heibel, *Chem. Rev.* 92 (1992) 1381.
- [13] K. Heihoff, S.E. Braslavsky, K. Schaffner, *Biochemistry* 26 (1987) 1422.
- [14] J. Del Bene, H.H. Jaffè, *J. Chem. Phys.* 48 (1968) 1807.
- [15] K. Nishimoto, N. Mataga, *Z. Phys. Chem.* 13 (1957) 140.
- [16] G. Poggi, G. Orlandi, F. Zerbetto, *Chem. Phys. Lett.* 224 (1994) 113.
- [17] M. Fanti, G. Orlandi, F. Zerbetto, *J. Am. Chem. Soc.* 117 (1995) 6101.
- [18] M. Benz, M. Fanti, P.W. Fowler, D. Fuchs, M.M. Kappes, C. Lehner, R.H. Michel, G. Orlandi, F. Zerbetto, *J. Phys. Chem.* 100 (1996) 13399.
- [19] M. Fanti, G. Orlandi, G. Poggi, F. Zerbetto, *Chem. Phys.* 223 (1997) 159.
- [20] J. Blum, A. Fischer, E. Greener, *Tetrahedron* 29 (1973) 1073.
- [21] G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, P. Lambin, A.A. Lucas, *Phys. Rev. Lett.* 67 (1991) 2171.
- [22] A.A. Lucas, G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, P. Lambin, W. Krätschmer, *Phys. Rev. B* 45 (1992) 13694.
- [23] J. Michl, E.W. Thulstrup, *Spectroscopy with Polarized Light*, VCH, Weinheim, 1986.