83. Caro-Cryptands: Tris-Carotenoid Macrobicyclic Ligands – Synthesis, Crystal Structure, and Dinuclear Copper(I) Complexes

by **Jean-Marie Lehn*** and **Jean-Pierre Vigneron**
Laboratoire de Chimie des Interactions Moléculaires, Collège de France,
11, place Marcelin Berthelot, F-75005 Paris[1])

and **Itka Bkouche-Waksman, Jean Guilhem,** and **Claudine Pascard***
Laboratoire de Cristallochimie, ICSN-CNRS, F-91198 Gif-sur-Yvette

(6.IV.92)

The tris-carotenoid macrobicycles **1** and **2** were obtained in good yields in a one-step macrobicyclisation condensation between the tripode $N(CH_2CH_2NH_2)_3$ and the polyolefinic dialdehydes **5** and **6**. They form dinuclear cryptates by complexation of two Cu^I ions. The crystal structure of the tris-carotenoid compound **2** confirms that it contains three parallel polyolefinic strands. These substances may formally be considered as prototypes of molecular 'cables' formed by three electron-conducting molecular wires.

Among the various strategies for the synthesis of macrobicyclic systems, a particularly direct one is the double-tripode-capping pathway in which two tripodal components are condensed with three α,ω-difunctional chains representing a five-particle-assembly process (see Figure in [1]). It was shown that this could be achieved efficiently in the reaction of the triamine tren ($N(CH_2CH_2NH_2)_3$) with α,ω-dialdehydes leading to the formation of macrobicyclic hexaimines [2] [3]. The latter may bind two metal ions forming dinuclear cryptates [4], *e.g.* with Cu^I, in which the ions are located at the poles of the macrobicyclic structure [2]. The hexaprotonated form of the hexaamino derivatives obtained upon reduction of the six imine functions may yield highly stable and selective anion cryptates by inclusion of molecular dianions, such as dicarboxylates, into the intramolecular cavity [5].

We have now extended this reaction to carotenoid-type polyolefinic dialdehydes and report here the synthesis of the triple-carotenoid macrobicyclic cryptands **1** and **2** and of their dinuclear copper(I) complexes $[2\ Cu \subset \mathbf{1}](PF_6)_2$ (**3**) and $[2\ Cu \subset \mathbf{2}](PF_6)_2$ (**4**).

Tris-Carotenoid Macrobicycles 1 and 2 and Their Dinuclear Cu^I Complexes 3 and 4. – *Syntheses.* The synthesis of the macrobicyclic molecules **1** and **2** is performed in a one-step assembly from their five components. Treatment of 3 equiv. of trienedial **5** with 2 equiv. of tren ($N(CH_2CH_2NH_2)_3$) leads to the assembly of the five components giving in a single step the macrobicyclic hexaimine **1** in *ca.* 50% yield. Similarly, reaction of 3 equiv. of the heptaene crocetin dialdehyde (**6**) with 2 equiv. of tren gives the macrobicycle **2** also in *ca.* 65% yield. Treatment of **1** and **2** with 2 equiv. of $[Cu(MeCN)_4](PF_6)$ affords the dinuclear Cu^I complexes **3** and **4** in *ca.* 50 and 70% yield, respectively.

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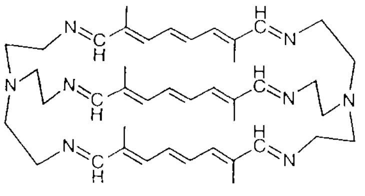
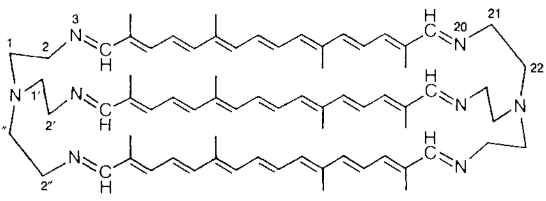
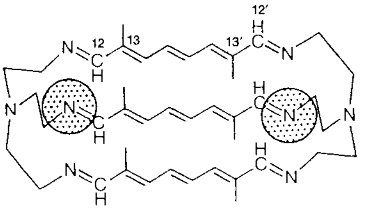
[1]) UPR N° 285 of the CNRS.



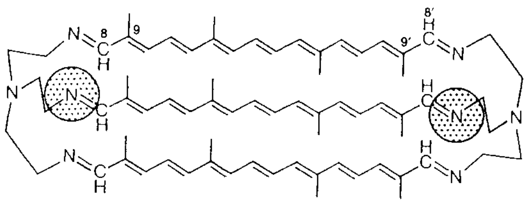
1



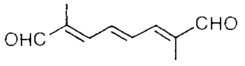
2 (arbitrary numbering)



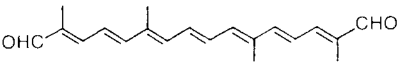
3 (carotenoid numbering)



4 (carotenoid numbering)



5



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The structures of compounds **1**–**4** agree with their microanalytical and spectral properties (see below). They are confirmed by the determination of the crystal structure of macrobicycle **2**. Furthermore, in view of earlier structural data on a related species, the complexes **3** and **4** may be expected to possess a structure of dinuclear cryptate type in which a Cu^I ion is complexed at each end of the macrobicycle and coordinated to the 4 N-sites (see the crystal structure of such a dinuclear complex in [2]).

Properties. The compounds **1** and **2** represent ligands of the macrobicyclic cryptand type on one hand. On the other hand, one may also view them, in particular **2**, as a molecular fiber or 'cable' formed by three polyolefinic strands. Since carotenoid derivatives, such as the caroviologens, were shown earlier to represent an approach to molecular wires [6] [7], systems like **2** may be considered as prototypes for multi-threaded electron-conducting molecular 'cables'. Indeed, in the design of electronic molecular devices [8], multi-component structures of this type may help answering the questions whether a bunch of components provides improved properties and whether redundancy is required for proper operation, for decreasing the risk of failure of the device.

The ^1H-NMR spectra of the free ligands **1** and **2** and of their complexes **3** and **4** show notable differences (*Figs. 1* and *2*). In particular, the CH_2CH_2 unit of the free ligands **1** and **2** presents signals of the *ABCD* type, all four protons being different; this indicates an unsymmetrical structure which is also sufficiently rigid so as not to undergo conformational averaging by a twisting motion around the N,N-bridgehead axis. This agrees with the conformation found in the crystal structure when motionally frozen on the NMR time scale. High-temperature NMR measurements of **1** in $C_2D_2Cl_4$ indeed show coalescence of the four CH_2CH_2 signals at 2.33 and 2.92 ppm and at 3.23 and 3.68 ppm into two broad resonances at *ca.* 2.7 and 3.5 ppm, respectively, with a coalescence temperature of *ca.* 340 K. The corresponding free energy of activation $\Delta G_c^{\neq}$ is calculated to be *ca.* 16 kcal/mol.

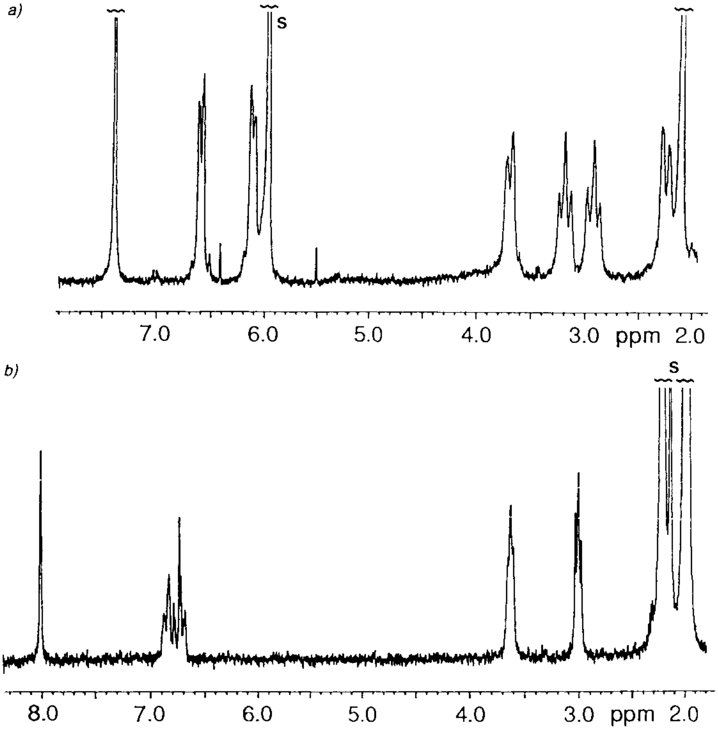

Fig. 1. ^{1}*H-NMR Spectra* (200 MHz) a) *of cryptand* **1** *in* $C_2D_2Cl_4$ *and* b) *of its dinuclear* Cu^I *complex* **3** *in* CD_3CN (s = solvent)

In contrast, the CH_2CH_2 resonances of the corresponding complexes **3** and **4** are of A_2X_2 type, indicating either a highly symmetrical structure or conformational averaging by rapid torsional oscillation around the N,N-bridgehead axis. The olefinic protons display a compression of signals into a narrower ppm range, and the C*H*=N signal undergoes a downfield shift of *ca.* 0.5 ppm on complexation.

In comparison, the free ligand and the dinuclear Cu^I cryptate of an analogous macrobicyclic structure possessing a diphenylmethane group as central unit, display *both* only two resonances for the CH_2CH_2 fragment [2b], as is the case here only for the complexes **3** and **4**. This points to the special conformation features of the free macrobicycles **1** and **2**.

The complexes **3** (deep-orange) and **4** (deep reddish-brown) display a deeper colour than the corresponding free ligands **1** (yellow) and **2** (orange). The UV/VIS spectra (*Figs. 3* and *4*) present a strong absorption and a shoulder for the free ligands (**1** (λ_{max} [nm] (ε)): 318 (235000); **2**: 415 (190000)). The complexes **3** and **4** display a small shift to longer wavelength and a broadened strong absorption band with a tail into the visible (**3**: 326 (120000); **4**: 430 (310000)). As expected, the compounds **1** and **3** with the shorter polyene system absorb at *ca.* 100-nm shorter wavelength than **2** and **4** with the extended polyene unit. Fluorescence measurements of the ligands or their complexes do not reveal any particular feature.

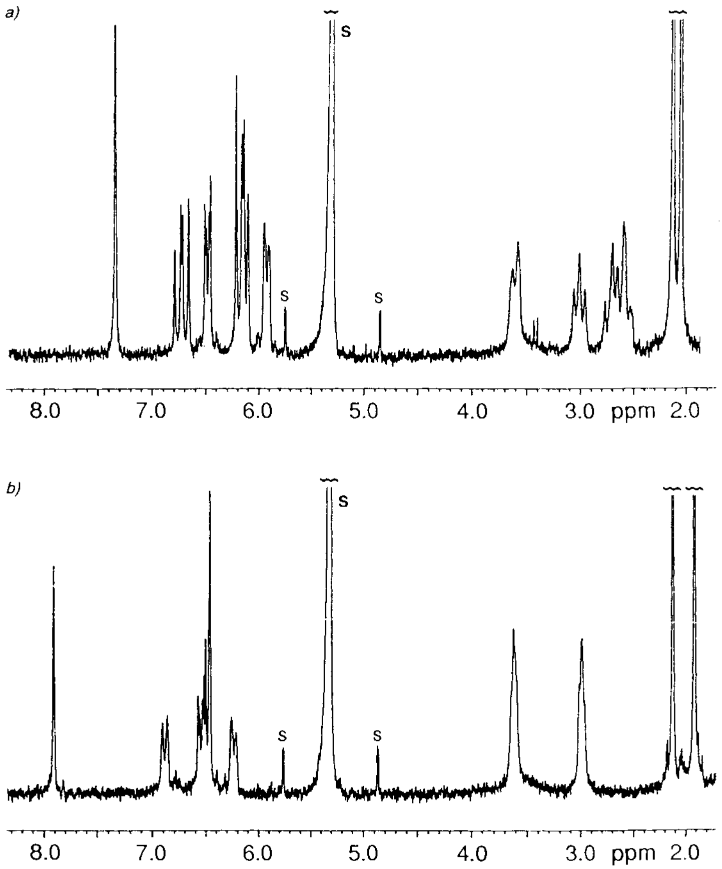

Fig. 2. *^{1}H-NMR Spectra* (200 MHz) a) *of cryptand* **2** *and* b) *of its dinuclear Cu^I complex* **4** *in CD_2Cl_2* (s = solvent)

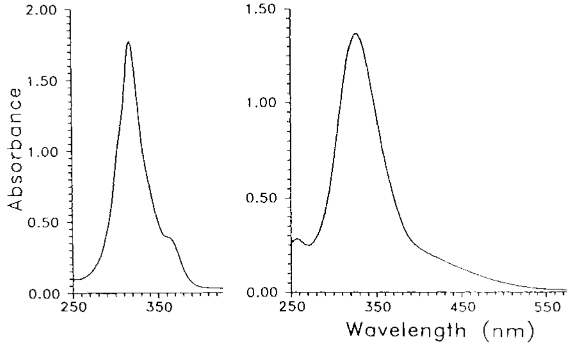

Fig. 3. *UV/VIS Spectra of cryptand* **1** (left) *and of its dinuclear Cu^I complex* **3** (right) *in MeOH/CH_2Cl_2 1:1*

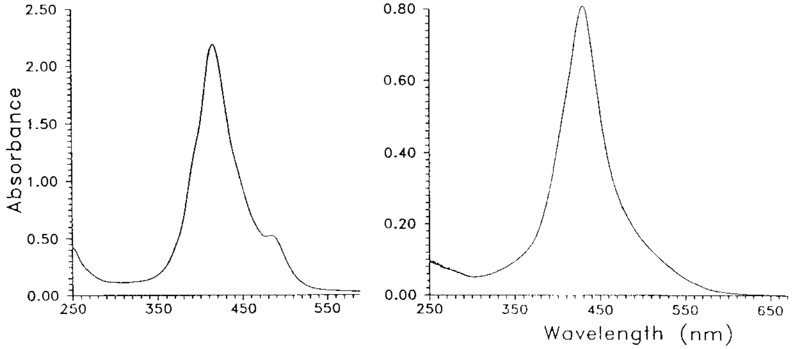

Fig. 4. *UV/VIS Spectra of cryptand* **2** (left) *and of its dinuclear Cu^I complex* **4** (right) *in MeOH/CH$_2$Cl$_2$ 1:1*

Electrochemical measurements in MeCN solution do not give reversible cyclic voltammetry oxidation or reduction waves. Reduction potentials of – 0.93 V (irr.) and – 0.31 V (ads.) *vs.* SCE are obtained for cryptate **4** with a glassy carbon electrode.

Crystal Structure of Cryptand **2**. The cryptand **2** is crystallized from CH$_2$Cl$_2$, and its crystal structure is determined. Two views are shown in *Fig. 5*. The results confirm the macrobicyclic nature of **2** and give indications about the shape of the molecule, the conformation of the strands, and the distance between the strands.

The molecule is elongated, with the two bridgehead N-atoms N and N′ at a 24-Å distance. The N–N′ axis is a crystallographic ternary symmetry axis. Three pseudo-binary axes, perpendicular to it, pass through each central C=C bond. *Table 1* shows that the bond lengths and valency angles are very regular and agree with the reported values.

Table 1. *Bond Lengths* [Å] *and Bond Angles* [°] *for the Macrobicyclic Molecule* **2**a)

Bond lengths					
C(5)–C(6)	1.35	C(6)–C(7)	1.42	C(9)–C(9.1)	1.50
C(7)–C(8)	1.36	C(8)–C(9)	1.45	C(14)–C(14.1)	1.49
C(9)–C(10)	1.33	C(10)–C(11)	1.42	C(18)–C(18.1)	1.50
C(11)–C(12)	1.36	C(12)–C(13)	1.42	N(3)–C(4)	1.27
C(13)–C(14)	1.37	C(14)–C(15)	1.45	N(20)–C(19)	1.26
C(15)–C(16)	1.32	C(16)–C(17)	1.45	C(2)–N(3)	1.47
C(17)–C(18)	1.35	C(18)–C(19)	1.46	N(20)–C(21)	1.45
C(4)–C(5)	1.46	C(5)–C(5.1)	1.50		
Angles					
N(3)–C(4)–C(5)	123	C(14)–C(15)–C(16)	128	C(8)–C(9)–C(9.1)	122
C(5)–C(6)–C(7)	126	C(15)–C(16)–C(17)	126	C(9.1)–C(9)–C(10)	117
C(6)–C(7)–C(8)	123	C(16)–C(17)–C(18)	126	C(13)–C(14)–C(15)	121
C(7)–C(8)–C(9)	127	C(18)–C(19)–C(20)	122	C(13)–C(14)–C(14.1)	122
C(9)–C(10)–C(11)	128	C(4)–C(5)–C(6)	119	C(14.1)–C(14)–C(15)	117
C(10)–C(11)–C(12)	125	C(4)–C(5)–C(5.1)	123	C(17)–C(18)–C(19)	118
C(11)–C(12)–C(13)	124	C(5.1)–C(5)–C(6)	119	C(17)–C(18)–C(18.1)	125
C(12)–C(13)–C(14)	127	C(8)–C(9)–C(10)	121	C(18.1)–C(18)–C(19)	117

a) Arbitrary numbering of the atoms along each strand of **2**: NC(1)C(2)N(3)C(4)C(5)(Me(5.1))···C(18)(Me(18.1))C(19)N(20)C(21)C(22)N′; atoms of the second and third strand are primed and doubly primed, resp.

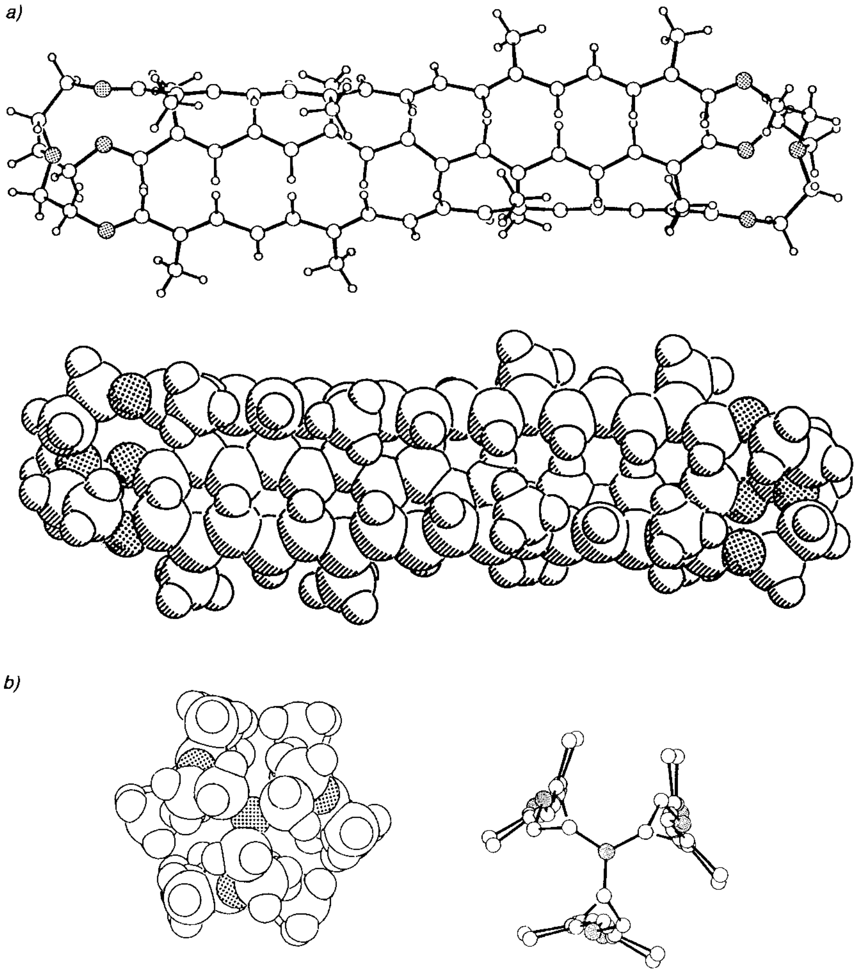

Fig. 5. *Two representations of the crystal structure of cryptand* **2**, a) *side-views and* b) *views along the N,N-bridgehead axis.* Both ball-and-stick and compact representations are shown.

The polyenes are in the (all-*E*)-configuration, and the conformation about the single bonds is s-*trans*. Similar structural features were found in *β*-carotene and in canthaxanthin [9].

Each strand is twisted around every C–C bond, with deviations from the *trans*-conformation in the same direction, that result in a total rotation of 65° of the chain; thus, the Me groups point at *ca.* 140° from each other (see projection in *Fig. 5* and *Table 2*). The small rotation angles per C–C bond and the progressive twist along the strands allow the conjugation to be retained in the three bridges of **2**, which may, therefore, be indeed considered as a three-wire molecular cable.

The strands are in close contact with each other as can be seen from the interstrand distances between atoms (*Table 2*) and from the compact representation in *Fig. 5*. The

Table 2. *Selected Nonbonded Atomic Distances* [Å] *between the Three Strands and Torsion Angles* [°] *for the Macrobicyclic Molecule* **2**[a])

Nonbonded distances					
N(bridgehead)–N(3)	3.08	C(10)–C(10′)	3.88	C(7)–C(7′)	4.5
N′(bridgehead)–N(3)	3.13	C(15)–C(15′)	4.09	C(11)–C(11′)	4.07
N(3)–N(3′)	4.43	C(17)–C(17′)	4.08	C(13)–C(13′)	4.00
N(20)–N(20′)	4.58	*H*C(4)–C(4′)	3.01	C(19)–C(19′)	4.09
C(5)–C(5′)	4.43	*H*C(9)–*H*C(10)	2.52	*H*C(4)–C(5′)	2.92
Torsion angles					
N–C(1)–C(2)–N(3)	-80.2	(0.6)	N′–C(22)–C(21)–N(20)	-80.5	(0.8)
C(1)–C(2)–N(3)–C(4)	120.8	(0.8)	C(22)–C(21)–N(20)–C(19)	121.5	(1.0)
C(2)–N(3)–C(4)–C(5)	178.4	(0.9)	C(21)–N(20)–C(19)–C(18)	179.8	(1.1)
N(3)–C(4)–C(5)–C(5.1)	10.8	(0.7)	N(20)–C(19)–C(18)–C(18.1)	2.1	(0.7)
N(3)–C(4)–C(5)–C(6)	-168.9	(0.9)	N(20)–C(19)–C(18)–C(17)	-176.5	(1.1)
C(4)–C(5)–C(6)–C(7)	179.1	(0.9)	C(19)–C(18)–C(17)–C(16)	178.4	(1.0)
C(5)–C(6)–C(7)–C(8)	-177.7	(1.0)	C(18)–C(17)–C(16)–C(15)	-178.1	(1.1)
C(6)–C(7)–C(8)–C(9)	180.0	(1.0)	C(17)–C(16)–C(15)–C(14)	-177.9	(1.1)
C(7)–C(8)–C(9)–C(9.1)	4.2	(0.7)	C(16)–C(15)–C(14)–C(14.1)	3.0	(0.8)
C(7)–C(8)–C(9)–C(10)	-177.0	(1.0)	C(16)–C(15)–C(14)–C(13)	-177.7	(1.1)
C(8)–C(9)–C(10)–C(11)	-174.5	(1.0)	C(15)–C(14)–C(13)–C(12)	-174.4	(1.1)
C(9)–C(10)–C(11)–C(12)	-166.4	(1.1)	C(14)–C(13)–C(12)–C(11)	-169.4	(1.1)
C(10)–C(11)–C(12)–C(13)	-176.3	(1.1)	C(13)–C(12)–C(11)–C(10)	-176.3	(1.1)

[a]) For numbering, see *Table 1, Footnote a.*

geometry around each bridgehead N-atom implies that the strands are more apart at each end of the molecule than in the center. The lone pair of the imino N-atoms are pointing outward. The bridgehead N-atoms are directed into the cavity, the macrobicycle being in the '*endo-endo*'-form (*Fig. 5*).

The CH_2Cl_2 molecule lies on the ternary axis, between two molecules of **2**, and rotates between six positions at 60° from each other.

Conclusion. – The amine-aldehyde condensation gives efficient access to a range of molecular structures resulting from the assembly of several components bearing two or more functional groups. The macrobicyclic polyolefinic substances obtained here represent potential components of molecular devices of the molecular wire type, displaying the structural features of a triple-threaded molecular 'cable'. Their ability to bind Cu^I ions in the (amino,triimino) N_4-cups located at each end of the macrobicycle leads to dinuclear complexes that represent a three-wire molecular cable polarized at each end by the bound cation. Such features are reminiscent to some extent of the binding of retinal to opsin in rhodopsin *via* similar *Schiff*-base formation and of the polarization of the condensation product by protonation of the imino N-atom. Further exploration of the physicochemical properties of these and related multiple-strand polyolefinic structures may provide data of interest for delineating the requirements of designing molecular devices, in particular with respect to the interaction between several identical components and to the question of the redundancy that may be desirable for minimizing device failure.

Experimental Part

General. All commercially available chemicals employed were reagent grade and used without further purification. UV/VIS: *Cary 13* spectrometer. NMR Spectra: *Bruker AC-200* or *Bruker AM 400*; chemical shifts in ppm rel. to TMS (= 0 ppm); coupling constants J in Hz. MS: FAB spectra measured at the Laboratoire de Spectrométrie de Masse (*A. Van Dorsellaer*), Université Louis Pasteur, Strasbourg, and at the Laboratoire de Chimie Organique Structurale (*J.-C. Tabet*), Université Pierre et Marie Curie, Paris. The microanalyses were performed at the Service Central de Microanalyse du CNRS, Lyon.

N,N″,N⁗:N′,N‴,N^V-*Bis[2,2′,2″-nitrilotris(ethyl)]tris(all-*trans*-12,12′-diapo-ψ,ψ-carotene-12,12′-diimine)* (**1**). A soln. of $N(CH_2CH_2NH_2)_3$ (438 mg, 3 mmol) in MeCN (150 ml) was added dropwise, under N_2, to a well stirred soln. of all-*trans*-12,12′-diapo-ψ,ψ-carotene-12,12′-dial (**5**; 744 mg, 4.5 mmol) in MeCN (60 ml). After stirring at r.t. for 24 h, the deposited solid was filtered off and dried: 712 mg. This crude product was dissolved in CH_2Cl_2/MeOH 4:1 (*v*/*v*) and the small quantity of insoluble material removed by filtration on silica gel. The filtrate was concentrated and cooled in the refrigerator and the deposited solid filtered off (590 mg) and dissolved again in a minimum volume of CH_2Cl_2/MeOH 4:1. Diffusion of Et_2O gave crystals which were collected and dried: 537 mg (53%). ^{1}H-NMR ($C_2D_2Cl_4$): 2.12 (*s*, 6 CH_3); *ABCD* of CH_2CH_2 at 2.27 (*dd*, J = 11, 3.5, 6 H); 2.94 (*t*, J = 11, 6 H); 3.21 (*t*, J = 11, 6 H); 3.71 (*dd*, J = 11, 3.5, 6 H); 6.14 (*d*, J = 8, 6 H, H–C(14), H–C(14′)); 6.62 (*dd*, J = 8, 3, 6 H, H–C(15), H–C(15′)); 7.42 (*s*, 6 H, H–C(12), H–C(12′)). FAB-MS (pos.): 677 (MH^+). Anal. calc. for $C_{42}H_{60}N_8 \cdot 2\,CH_3OH$ (740): C 71.29, H 9.25, N 15.12; found: C 71.62, H 9.02, N 15.78.

*μ-{*N,N″,N⁗:N′,N‴,N^V*-Bis[2,2′,2″-nitrilotris(ethyl)]tris(all-*trans*-12,12′-diapo-ψ,ψ-carotene-12,12′-diimine)}dicopper(I) Bis(hexafluorophosphate)* ($\mathbf{3} \cdot (PF_6)_2$). A soln. of $[Cu(MeCN)_4](PF_6)$ (130 mg, 0.4 mmol) in CH_2Cl_2 (10 ml) was added to a soln. of **1** (135 mg, 0.2 mmol) in CH_2Cl_2/MeOH 2:1 (30 ml). A strong red colour appeared immediately. The addition of a large volume of Et_2O gave a solid: 187 mg. This crude compound was dissolved in a minimum volume of CH_2Cl_2/MeOH 1:1 and the insoluble material removed by filtration. Diffusion of Et_2O in the filtrate gave a red powder: 155 mg (71%). ^{1}H-NMR (CD_3CN): 2.15 (*s*, 6 CH_3); 3.01 (*t*, J = 5.5, 6 CH_2); 3.64 (*t*, J = 5.5, 5 CH_2); 6.75 (*m*, 12 CH); 8.03 (*s*, 6 CH=N). FAB-MS (pos.): 803 ($[\mathbf{1} \cdot 2\,Cu]^+$). Anal. calc. for $C_{42}H_{60}O_8 \cdot 2\,CuPF_6 \cdot 2\,H_2O$ (1129.53): C 44.62, H 5.71, N 9.91; found: C 44.37, H 5.41, N 9.89.

N,N″,N⁗:N′,N‴,N^V-*Bis[2,2′,2″-nitrilotris(ethyl)]tris(all-* trans*-8,8′-diapo-ψ,ψ-carotene-8,8′-diimine)* (**2**). A soln. of $N(CH_2CH_2NH_2)_3$ (292 mg, 2 mmol) in $CHCl_3$ (100 ml) was added dropwise, under N_2, to a well stirred soln. of crocetin dialdehyde (**6**; 888 mg, 3 mmol) in $CHCl_3$ (200 ml). After stirring at r.t. for 4 days, the deposited solid was filtered off: 472 mg. Concentration of the filtrate gave a second crop: 463 mg. The two crops (935 mg) were dissolved in CH_2Cl_2/MeOH 1:1, and Et_2O diffusion gave crystals which were collected and dried: 696 mg (65%). ^{1}H-NMR (CD_2Cl_2): 2.07 (*s*, 6 CH_3); 2.15 (*s*, 6 CH_3); *ABCD* of CH_2CH_2 at 2.55–2.78 (*m*, 12 H), 3.03 (*t*, J = 10.5, 6 H), 3.62 (*d*, J = 4.5, 6 H); polyene moiety at 5.95 (*d*, J = 9, 6 H), 6.14 (*q*, 12 H), 6.48 (*q*, 6 H), 6.74 (*q*, 6 H); 7.37 (*s*, 6 CH=N). FAB-MS (pos.): 1073.6 (MH^+). Anal. calc. for $C_{72}H_{96}N_8 \cdot CH_2Cl_2$ (1157.69): C 75.66, H 8.53, N 9.67; found: C 75.61, H 8.51, N 9.55.

*μ-{*N,N″,N‴:N′,N‴,N^V*-Bis[2,2′,2″-nitrilotris(ethyl)]tris(all-* trans*-8,8′-diapo-ψ,ψ-carotene-8,8′-diimine)}dicopper(I) Bis(hexafluorophosphate)* ($\mathbf{4} \cdot (PF_6)_2$). A soln. of $[Cu(MeCN)_4]$ (PF_6) (65 mg, 0.2 mmol) in CH_2Cl_2 (10 ml) was added to a soln. of **2** (110 mg, 0.1 mmol) in CH_2Cl_2/MeOH 1:1 (20 ml). A strong red colour appeared immediately. The addition of a large volume of Et_2O gave a solid: 125 mg. This crude compound was dissolved in a minimum volume of CH_2Cl_2/MeOH 1:1 and the insoluble material removed by filtration. Diffusion of Et_2O in the filtrate gave a red powder which was filtered and dried: 75 mg (50%). ^{1}H-NMR (CD_2Cl_2): 1.92 (*s*, 6 CH_3); 2.12 (*s*, 6 CH_3); 2.99 (br. *t*, 6 CH_2); 3.62 (br. *t*, 6 CH_2); polyene moiety at 6.22 (*m*, 6 H); 6.51 (*m*, 18 H); 6.88 (br. *d*, 6 H); 7.91 (*s*, 6 CH=N). FAB-MS (pos.): 1200 ($[\mathbf{2} \cdot 2\,Cu]^+$), 1347 ($[\mathbf{2} \cdot 2\,Cu \cdot PF_6]^+$). Anal. calc. for $C_{72}H_{96}N_8 \cdot 2\,CuPF_6$ (1489.79): C 57.99, H 6.49, N 7.52; found: C 57.45, H 6.45, N 7.34.

Crystal-Structure Determination of **2**. $C_{72}H_{96}N_8 \cdot CH_2Cl_2$. Mol. wt. 1157. Trigonal $R3$; $a = 13.351$ (4), $c = 34.765$ (11) Å, $\gamma = 120°$, $V = 5366.9$ Å^3. *Enraf-Nonius-CAD-4* diffractometer, graphite-monochromated Cu$K\alpha$ radiation (1.5418 Å). T 293 K, $\mu = 5.1$ mm^{-1}. For refining parameters, 25 reflections, *Lorentz*-polarisation correction, no absorption correction; 3552 measured reflections up to $\theta = 67°$ with $-15 < h < 15$, $0 < k < 15$, $0 < l < 41$; 3348 independent reflections, 1526 considered as observed with $I > 3\sigma(I)$. Three standard reflections, measured every 2 h show no intensity variation.

The structure is solved by direct methods using SHELXS86 [10]. All H-atoms are in computed positions. One molecule of CH_2Cl_2 is localized on the ternary axis between two molecules. The solvent is disordered between two positions. Anisotropic refinement is achieved by full-matrix least squares on F using SHELX76 [11], isotropic for solvent and H-atoms. For the latter, the temperature factor is taken 20% higher than that of the carrier atom; weight $w = [\sigma^2(F) + 0.02\,F^2]^{-1}$; $R = 6.9\%$ (with 1526 reflexions), $R_w = 7.5\%$; $S = 1.04$; $(\Delta\rho) = \pm 0.3\ e \cdot Å^{-3}$.

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