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How light affects 5,10,15-tris(pentafluorophenyl)corrole

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ABSTRACT

5,10,15-Tris(pentafluorophenyl)corrole slowly undergoes oligomerization when left in solution at room temperature, under air and ambient light. This transformation was studied in different solvents (chloroform, dichloromethane, and toluene) and the main resulting products were identified as the 3,3′-corrole dimer **2a** and the 3,3′,17′,3″-corrole trimer **3a**.

The number of publications concerning the chemistry of corroles has increased exponentially during the last decade. The interest for these compounds is due to their potential applications[1] in catalysis,[2] in medicine[3], as energy, and electron transfer systems,[1b,4] as sensors[5] and also due to the discovery of efficient synthetic procedures for the syntheses[6] and functionalization of *meso*- and β-substituted corroles.[7]

It is known that corroles, especially the free-bases, are photosensitive and less stable in solution toward light and air than their porphyrin analogues. The first example describing the photoinstability of corroles was reported for 2,3,17,18-tetraethyl-7,8,12,13-tetramethyl-10-phenylcorrole.[8] When dissolved in dichloromethane and in the presence of air and light, this corrole is slowly transformed into an open-chain biliverdin derivative. This transformation involves the cleavage of the pyrrole–pyrrole bond by dioxygen. In a similar study, a dichloromethane solution of a porphyrin–corrole dyad was stirred under ambient light and the mixture was monitored by UV–vis. The porphyrin–corrole dyad undergoes photocatalyzed ring opening of the corrole moiety to give the corresponding porphyrin–biliverdin species.[9]

Another interesting study was carried out with 10-(4-nitrophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole. It was shown that this compound, in a benzene/methanol solution, is slowly converted, at room temperature and in the presence of air, into a *trans*-AB_2C-porphyrin and a biliverdin-type species.[10]

5,10,15-Tris(pentafluorophenyl)corrole **1a** is by far the most intensively studied corrole[11] and it has been used for essentially all the applications known for corroles.[1,12] Keeping this in mind, the study of the stability of this corrole in solution is of great importance. Corrole **1a**, due to the presence of the electron-withdrawing pentafluorophenyl groups, is more stable than other corroles but it also undergoes ‘decomposition’ when left in solution at ambient light.[13] Since it is a key starting compound in the studies carried out by us[6g,6h] and other groups,[3f,6c,6f] and since the structures of the ‘decomposition’[13a] products of corrole **1a** have not so far been reported, we decided to isolate and to characterize those products. The results of such study are reported here.

The experiments were carried out by stirring solutions of corrole **1a** (10 mg/ml) at room temperature under air and ambient light ($\approx 555\ \mathrm{W\ m^{-2}}$).[14] Chloroform, deuterated chloroform, dichloromethane, and toluene were used as solvents. The reactions were monitored by TLC. After eight days, TLC of all reaction mixtures revealed the formation of a major product with a R_f value lower than that of the starting corrole. The reaction in deuterated chloroform was also monitored by ^1H NMR; the resulting spectra (Fig. 1) show the appearance of a new doublet at δ 9.16 ppm and other new signals between δ 8.76–8.29 ppm.

In order to increase the amount of the new products for structural characterization, corrole solutions were kept under stirring and exposed to ambient light for 30 days. The reaction mixtures were then separated by preparative TLC and the major product was identified as being the corrole dimer **2a** (Scheme 1). The mass spectra of the compounds formed in vestigial amounts in the

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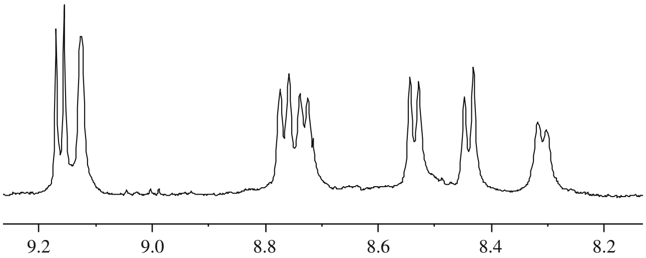


Figure 1. Aromatic region of the ^1H NMR spectrum of dimer **2a**.

halogenated solvents suggest that they are also corrole dimers (*m/z* 1590).

Corrole dimer **2a** was previously obtained as a minor product (3% yield) in the thermal dimerization of corrole **1a**.[15] It is interesting to note that, under thermal conditions, **1a** leads mainly to a 2,2′,18,18′-corrole dimer (18% yield) and to a 2,3′-corrole dimer (10% yield). These compounds are not observed in the photodimerization of **1a**, being the 3,3′-corrole dimer the main product (28% yield in $CHCl_3$). The regioselectivity observed is probably due to the fact that position C-3 is more electron-rich than C-2.[7c]

The mass spectrum of **2a** shows a molecular peak at *m/z* 1590 $(M)^{\bullet +}$ and the ^1H NMR spectrum (Fig. 1) shows the typical features of this dimer: one doublet at δ 9.16 ppm assigned to the resonances of β-pyrrolic protons H-18,18′ and one singlet at δ 9.12 ppm corresponding to the resonances of the β-pyrrolic protons H-2,2′. From Figure 2 it is evident that the amount of dimer **2a** increases with the time of ambient light exposure.

The yields of dimer **2a** obtained in different solvents, after 30 days of ambient light exposure, are shown in Table 1. The results show that corrole **1a** is much more stable in toluene than in the halogenated solvents. From the toluene solution the starting corrole was recovered in 90% and dimer **2a** was isolated in 10% yield (entry 4). Comparing the stability of corrole **1a** in chloroform and in dichloromethane (entries 1 and 3) it is evident that it is less stable in chloroform.

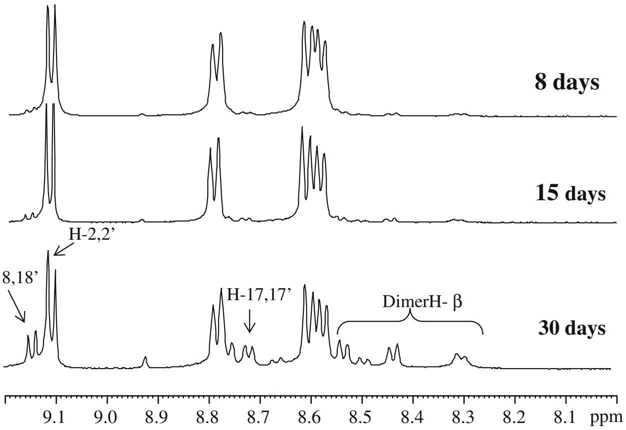


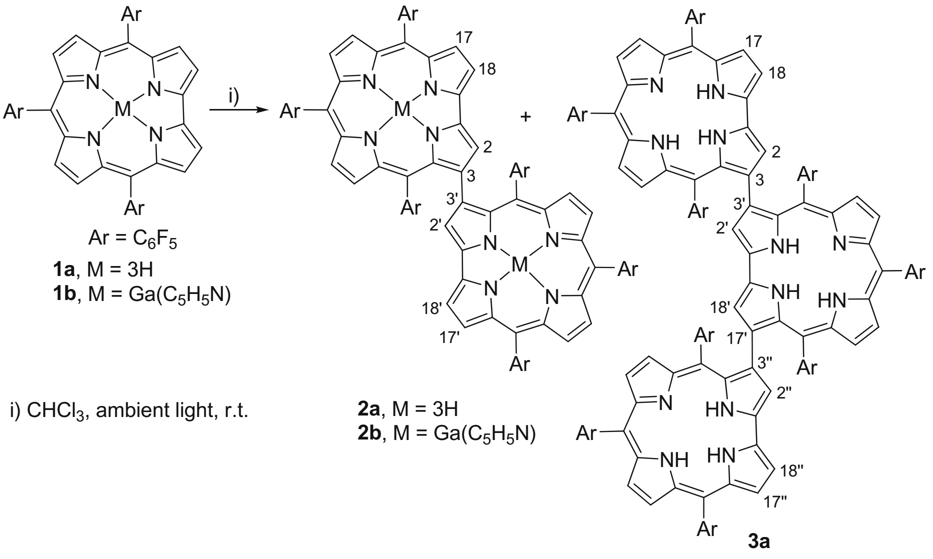
Figure 2. Aromatic region of the ^1H NMR spectra of the $CDCl_3$ solution of corrole **1a** after exposition to ambient light for 8, 15, and 30 days. (Only ca. half of these periods correspond to effective light irradiation).

Table 1
Yields of the products obtained after exposing corrole **1a**, in different solvents, at ambient light for 30 days

Entry	Solvent	Corrole **1a**	Dimer **2a**	Trimer **3a**
1	$CHCl_3$	35%	28%	4%
2	$CHCl_3$[a]	47%	18%	1%
3	CH_2Cl_2	50%	15%	1%
4	$C_6H_5CH_3$	90%	10%	—

[a] Irradiated for 15 days with a 500 W lamp (white light).

From the reactions carried out in the halogenated solvents we were also able to isolate one minor product for which, based on its spectroscopic data, we could assign the trimeric structure **3a**.[16] The MALDI mass spectrum of this product shows a molecular ion peak at *m/z* 2385 corresponding to $(M+H)^+$. Its ^1H NMR spectrum shows one doublet at δ 9.20 ppm corresponding to two β-pyrrolic protons and one singlet at δ 9.13 ppm corresponding to four β-pyrrolic protons. These signals are similar to the ones observed for protons H-18,18′ and H-2,2′, respectively, of compound **2a**. In the HSQC spectrum (based on ^{13}C inverse detection) we observed correlations between the signals at δ 9.20 and 9.13 ppm and the carbon signal at δ 118.0 ppm, which is typical for the resonances of corrole carbons C-2,18. These data can only be explained if the three corrole units are linked by the same type of carbon atoms. In this way, the doublet at δ 9.20 ppm is assigned to the res-



Scheme 1.

onances of protons H-18,18″ and the singlet at δ 9.13 ppm to the resonances of H-2′,18′ and H-2,2″ and the large signal at δ 118.0 ppm corresponds to the resonances of C-2,18, C-2′,18′, and C-2″,18″. To the best of our knowledge, this is the first example of a corrole trimer where the three corrole units are directly linked through their β-pyrrolic positions.

It is worth referring that a minor blue product (<1% yield) was also isolated from the chloroform solutions of **1a**. More studies are being carried out in order to fully elucidate the structure of this compound.

The stability of corrole **1a** in $CHCl_3$ was also evaluated under artificial light (480 W.m^{-2}, white light) (entry 2). After 15 days of irradiation (ca. 8 h/day) more than half of the starting corrole was consumed and dimer **2a** was isolated in 18% yield.

We also studied the photostability of the gallium(III) complex **1b**, which is considered to be the prototype metallocorrole,[17] in chloroform. This experiment allowed to compare the photostability of the free-base 5,10,15-tris(pentafluorophenyl)corrole and its gallium(III) complex. In this case, and under air and ambient light (≈555 W.m^{-2}) conditions, we isolated a major product (54% yield) which was identified, by mass and ^{1}H NMR spectra, as the 3,3′-corrole dimer **2b**.[18,19] Other 3,3′-metallocorrole dimers have already been described.[20]

The ^{1}H NMR spectrum of **2b** shows spectroscopic features similar to the ones of compound **2a**: one doublet at δ 9.30 ppm, assigned to the resonances of protons H-18,18′, and two very close singlets at δ 9.212 and δ 9.206 ppm corresponding to the resonances of protons H-2 and H-2′. This very small difference in the resonances of H-2 and H-2′ is probably due to a less symmetric conformation of this dimer induced by the presence of the two pyridine molecules coordinated to the gallium ion. Other signals are observed between δ 8.94 and 8.67 ppm.

In order to clarify the role of light in this reaction, a dark control experiment in chloroform was performed. It was carried out, under the same conditions described above, but in the absence of light. In this case, after 8 days, TLC showed that the only compound present was corrole **1a**. This control experiment was extended for 8 more days, but the TLC continued to reveal that only corrole **1a** was present. In this way we believe that the mechanism of the oligomerization of corrole **1a** involves radical reactions where light has a preponderant role.

2. Conclusions

During the last decade corroles became candidates for a wide variety of applications. As they are not very stable in solution, their photostability is an important parameter and must be defined. In this study, we demonstrate for the first time that under air and light, 5,10,15-tris(pentafluorophenyl)corrole in solution, slowly evolves to the 3,3′-corrole dimer **2a** and the 3,3′,17′,3″-corrole trimer **3a** (main products). This is clearly different from what was observed in the photostability studies of other free-base corroles which give mainly biliverdin-type compounds. Since 5,10,15-tris(pentafluorophenyl)corrole (or its derivatives) is the most studied corrole, we believe that the present study is an important contribution to clarify how corrole **1a** is affected by ambient light.

Acknowledgments

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14. *Experimental procedure:* Solutions of corrole **1a** (20 mg, 2.51×10^{-5} mol) in different solvents (2 ml) were stirred at room temperature and were exposed to two different light sources under stirring for 30 days. The experiments with ambient light were carried out near the laboratory glass window. Samples were exposed to ambient light on sunny summer days, with an averaged light fluence rate of 555 W m^{-2} (measured with a Laser Power/Energy Meter Coherent model FieldMaxII-TOP coupled to a power detector head PowerSens Model PS19Q). In the experiments with artificial light, a 500 W halogen white light projector (500 W halogen lamp) with a fluence rate of 480 W m^{-2} also measured with a Laser Power/Energy Meter Coherent model FieldMaxII-TOP was used. The progress of the reaction was monitored by TLC or ^{1}H NMR spectroscopy. The resulting compounds were separated by preparative TLC using a 2:1 mixture of chloroform/light petroleum as the eluent.

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16. *Spectroscopic data for compound* **3a***:* ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.20 (d, 2H, J = 4.3 Hz, H-18,18″), 9.13 (s, 4H, H-2′,18′ and H-2,2″), 8.78–8.77 (m, 4H, H-β), 8.61–8.36 (m, 10H, H-β). ^{13}C NMR (from HSQC $CDCl_3$, 75 MHz): δ 129.0 (C-β), 126.9 (C-β), 126.8 C-β), 118.0 (C-2,18, C-2′,18′ and C-2″,18″). UV–vis ($CHCl_3$) λ_{max} (logε) 414 (5.53), 579 (4.92), 618 (4.88) nm. HRMS (ESI) *m*/*z* calcd for $C_{111}H_{31}N_{12}F_{45}$ $[M+2H]^{2+}$ 1193.1033, found 1193.1007; calcd for $C_{111}H_{32}N_{12}F_{45}$ $[M+3H]^{3+}$ 795.7379, found 795.7373.
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18. *Experimental procedure:* A solution of gallium(III)(pyridine) complex of 5,10,15-tris(pentafluorophenyl)corrole (22 mg, 0.023 mmol) in chloroform (2 ml) was stirred at room temperature and exposed to ambient light for 30 days. The progress of the reaction was monitored by TLC. The two resulting compounds were isolated and purified by preparative TLC using a 150:50:1 mixture of ethyl acetate/light petroleum/pyridine as the eluent.
19. *Spectroscopic data for compound* **2b***:* ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.30 (d, 2H, J = 4.0 Hz, H-18,18″), 9.212 and 9.206 (2s, 2H, H-2 and H-2′), 8.94–8.92 (m, 4H, H-β), 8.84 (d, 2H, J = 4.6 Hz, H-β), 8.70–8.67 (m, 4H, H-β). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.6 (C-18,18′), 119.8 (C-2,2′), 124,0 (C-β), 125.3 (C-β), 127.2 (C-17), 127.4 (C-β), 137.0, 140.7, 141.3, 143.2, 143.38. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −159.28 (dd, 2F, J_1 = 30.0 Hz, J_2 = 8.5 Hz, F_{ortho}), −161.31 to −161.76 (m, 10F, F_{ortho}), −177.42 (t, 2F, J = 21.2 Hz, F_{para}), −177.73 (t, 2F, J = 21.2 Hz, F_{para}), −179.66 (t, 2F, J = 21.2 Hz, F_{para}), −185.88 to −186.49 (m, 8F, F_{meta}), −187.59 to −187.75 (m, 2F, F_{meta}), −189.19 to −189.29 (m, 2F, F_{meta}). UV–vis ($CHCl_3$) λ_{max} (log ε) 425 (5.08), 582 (4.16), 616 (4.42) nm. HRMS (ESI) *m*/*z* calcd for $C_{74}H_{15}F_{30}Ga_2N_8$ $[M+H-2py]^{+}$ 1722.9471, found 1722.9446.
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