ORGANIC LETTERS

2008
Vol. 10, No. 18
4013−4016

Efficient Synthesis of Substituted Dihydrotetraazapentacenes

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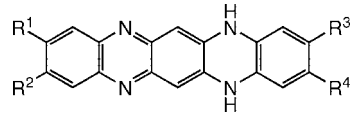
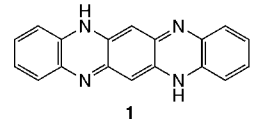
Received July 3, 2008

ABSTRACT



We describe a versatile and very efficient synthesis of previously unknown substituted 5,14-dihydro-5,7,12,14-tetraazapentacenes (DHTAPs). A structural study by NMR spectroscopy showed that the conjugated π-system of the pentacyclic skeleton rearranges depending on the electronic effect of the substituent(s).

Interest in heterocyclic π-systems such as dihydrotetraazapentacene (DHTAP) derivatives of **1** and/or **2** has re-emerged[1−8] owing to the presence of nitrogen atoms which offers a number of opportunities to manipulate and control the electronic properties, the stability, and the supramolecular arrangement in the solid state.[9] The structure of this long known molecule,[10−13] also called fluorindine or 5,12-dihydroquinoxalino(2,3-*b*]phenazine, has been erroneously reported for more than one century as the 5,12-dihydrotetraazapentacene **1**.[4,7,8,14−16] In 1987, its true structure (i.e., 5,14-dihydro form **2**) was determined by NMR[17,18] and revealed that **2** can be viewed as a phenazine ring connected to a benzene ring by two NH which break the delocalization of the π-system in the pentacene skeleton.[19]



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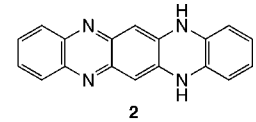


2

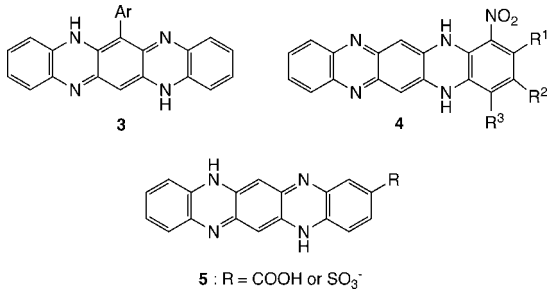
DHTAP derivatives of type **1** and/or **2** have been investigated in a wide range of applications, including (1) electronic plastics such as electrical conductors;[14,20] organic thin-film transistors (OTFTs);[4] organic light emitting diodes (OLEDs)[1,7,8] and photovoltaic cells;[2,21] (2) cosmetics (as hair colorants);[3] (3) heterogeneous catalysts (as catalysts for dehydrogenation reactions);[22] (4) electrochromism (as electroactive materials);[23] (5) complexation (as model com-

(1) Lazarev, P. I. WO2007085810, 2007.
(2) Lazarev, P. I.; Sidorenko, E. N.; Nokel, A. WO2007020442, 2007.
(3) Lagrange, A. FR2864782, 2005.
(4) Ma, Y.; Sun, Y.; Liu, Y.; Gao, J.; Chen, S.; Sun, X.; Qiu, W.; Yu, G.; Cui, G.; Hu, W.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 4894.
(5) Koutentis, P. A. *Arkivoc* **2002**, *vi*, 175.
(6) Lazarev, P. I.; Sidorenko, E. N. WO2007066098, 2007.
(7) Casu, M. B.; Imperia, P.; Schrader, S.; Falk, B. *Surf. Sci.* **2001**, *482−485*, 1205.
(8) Casu, M. B.; Imperia, P.; Schrader, S.; Falk, B.; Jandke, M.; Strohriegl, P. *Synth. Met.* **2001**, *124*, 79.
(9) Winkler, M.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805.
(10) Nietszki, R. *Chem. Ber.* **1895**, *28*, 1357.
(11) Nietzki, R.; Slaboszewicz, J. *Chem. Ber.* **1901**, *34*, 3739.
(12) Fischer, O.; Hepp, E. *Chem. Ber.* **1890**, *23*, 1789.
(13) Fischer, O.; Hepp, E. *Chem. Ber.* **1895**, *28*, 293.
(14) Jenekhe, S. A. *Macromolecules* **1991**, *24*, 1.
(15) Stille, J. K.; Mainen, E. L. *Macromolecules* **1968**, *1*, 36.
(16) (a) Badger, G. M.; Pettit, R. *J. Chem. Soc.* **1951**, *4*, 3211. (b) Beecken, H.; Musso, A. *Chem. Ber.* **1961**, *94*, 601.
(17) Armand, J.; Boulares, L.; Bellec, C.; Pinson, J. *Can. J. Chem.* **1987**, *65*, 1619.
(18) Sawtschenko, L.; Jobst, K.; Neudeck, A.; Dunsch, L. *Electrochim. Acta* **1996**, *41*, 123.
(19) Miao, Q.; Nguyen, T.-Q.; Someya, T.; Blanchet, G. B.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 10284.
(20) Inoue, H.; Noda, K.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 332.
(21) Antinucci, M.; Chevalier, B.; Ferriolo, A. *Solar Energy Mat. Solar Cells* **1995**, *39*, 271.
(22) Manassen, J.; Khalif, S. *J. Am. Chem. Soc.* **1966**, *88*, 1943.
(23) Johannsen, I.; Jorgensen, M. WO9429314, 1994.

10.1021/ol801509v CCC: $40.75
Published on Web 08/26/2008

pounds of polymers);[24] and (6) therapy (as anticataract agents).[25] However, the improvement of the properties is limited by a difficult access to a wide range of substituted DHTAPs.

Different methods of preparation of the parent DHTAP **1** and/or **2** are reported in the literature.[4,14,16,20] The syntheses of a few N- and C-substituted analogues are also described but only for symmetrical systems, which limits the number of different substituents.[4,5,12,13,23,26] To the best of our knowledge, molecules of type **3**−**5** are the only three examples of unsymmetrical substituted DHTAPs.[1,6,23,25,27,28] Substitution of the terminal hydrogen atom in **5** appeared much more attractive[19] since this pattern is less disruptive while maintaining essentially intact the tetraazapentacene skeleton for intermolecular packing in the solid state. Although patented, the syntheses of **5** show strong limitations.[1,6,23,25] In addition, the distribution of the conjugated π-systems (5,12- or 5,14-dihydro form) in **5** is erroneously or not reported (no NMR data available), whereas its determination appears to be a key parameter for a comprehensive study of the observed properties.



3 **4**

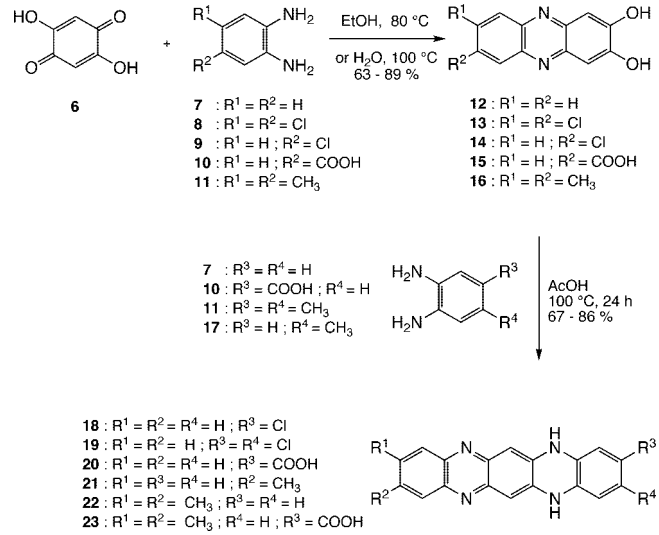
5 : R = COOH or SO_3^-

An alternative route, more versatile, that would give access to new end-functionalized dihydrotetrazapentacenes of type **2** could be useful to enlarge the scope of this class of heterocyclic compounds. Herein, we report a versatile, facile, and very efficient two steps preparation of symmetrical and *unsymmetrical* DHTAPs, for which the substituents in 2,3,9,10-positions can be easily varied. A structural study by NMR spectroscopy showed a possible rearrangement of the conjugated π-system depending on the nature of the substituent(s).

The commercially available 2,5-dihydroxy-*p*-benzoquinone **6** was first reacted smoothly with various substituted *o*-diaminobenzenes **7**−**11** (1.1 equiv) in alcohol (or water) to afford high yields of substituted 2,3-dihydroxyphenazines **12**−**16** (Scheme 1). To the best of our knowledge, only **12** has been reported in the literature[29−31] but never fully characterized (no NMR data available).

The phenazine intermediates **12**−**16** are then reacted with an excess of substituted *o*-diaminobenzenes (10 equiv) in the presence of glacial AcOH for 24 h yielding

Scheme 1. Synthesis of **18**−**23**



6

7 : $R^1 = R^2 = H$
8 : $R^1 = R^2 = Cl$
9 : $R^1 = H$; $R^2 = Cl$
10 : $R^1 = H$; $R^2 = COOH$
11 : $R^1 = R^2 = CH_3$

12 : $R^1 = R^2 = H$
13 : $R^1 = R^2 = Cl$
14 : $R^1 = H$; $R^2 = Cl$
15 : $R^1 = H$; $R^2 = COOH$
16 : $R^1 = R^2 = CH_3$

7 : $R^3 = R^4 = H$
10 : $R^3 = COOH$; $R^4 = H$
11 : $R^3 = R^4 = CH_3$
17 : $R^3 = H$; $R^4 = CH_3$

18 : $R^1 = R^2 = R^4 = H$; $R^3 = Cl$
19 : $R^1 = R^2 = H$; $R^3 = R^4 = Cl$
20 : $R^1 = R^2 = R^4 = H$; $R^3 = COOH$
21 : $R^1 = R^3 = R^4 = H$; $R^2 = CH_3$
22 : $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$
23 : $R^1 = R^2 = CH_3$; $R^4 = H$; $R^3 = COOH$

substituted DHTAP derivatives **18**−**23** (scheme 1). DHTAPs bearing chloride atoms (**18** and **19**) or methyl groups (**21** and **22**) could only be characterized at room temperature in the solid state owing to their insolubility, in contrast to compounds **20** and **23** which are slighly soluble in DMSO. This lack of solubility might be explained by different arrangements in the solid state depending on the nature of the substituents. The solid-state NMR spectra of the unsoluble compounds at room temperature (**18**, **19**, **21**, and **22**) were recorded and compared to that of the parent DHTAP **2**. The fine structure of the ^{13}C CPMAS signals observed for **2**, **19**, **21**, and **22** is consistent with a well-organized network of the molecules in the solid state (Figures S24 and S26−S28, Supporting Information). In contrast, **18** shows broad signals in agreement with an amorphous arrangement in the solid state (Figure S25, Supporting Information). The assignment of the signals for each compound could be determined by comparison with the parent system **2** and by CPPI experiments which show only quaternary carbon atoms and CH_3 groups (CH carbons are quasi not visible) (Figures S24−S28, Supporting Information).

The NMR studies in solution were run in DMSO-d_6 at room temperature for **20** and **23** and at 50 °C for **22**. The protons 1−4 and 8−11 of the parent DHTAP **2** form an AA′ BB′ pattern centered at δ = 6.50 and 7.50 ppm, respectively (Figure 1a).[17] The ^1H NMR spectrum of **22** shows the same pattern centered at 6.50 ppm for the protons 1−4 and a singlet at 7.43 ppm for the protons 8 and 11 (Figure 1b). This result is consistent with the presence of the σ-donor methyl groups on the phenazine moiety (positions 9 and 10), as expected for **22** which was obtained as product from condensation between **16** and **7**. In contrast, the ^1H NMR spectrum of **20** shows an AA′ BB′ pattern centered at 7.60 ppm (Figure 1c) which is in agreement with the presence of the electron-withdrawing group COOH in position 2, whereas we could

(24) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419.
(25) Naito, C. GB988331, 1962.
(26) Witt, O. N. *Chem. Ber.* **1887**, *20*, 1538.
(27) Hassan, M. A.; Fandy, R. F.; El-Amine, T. M. *J. Heterocycl. Chem.* **2001**, *38*, 179.
(28) Goswami, N. K.; Gupta, R. R. *Indian J. Chem.* **1982**, *21B*, 365.

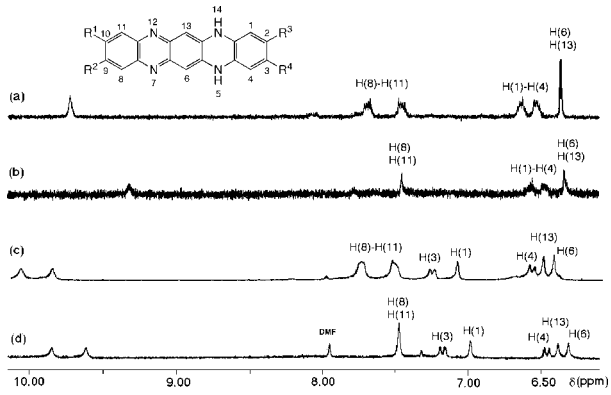


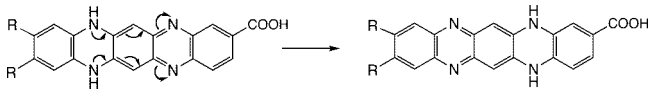
Figure 1. ^{1}H NMR spectra in DMSO-d_6 of: (a) **2**, (b) **22**, (c) **20**, and (d) **23**. The range 0−6.00 ppm is omitted for clarity.

expect its location in position 9. Indeed, molecule **20** results from the condensation of **15** with **7** so that the presence of the COOH substituent could be envisaged on the phenazine ring instead of the benzene ring of the DHTAP.

The condensation between **12** and **10** also affords **20** and confirms an erroneous structure for **5** (R = COOH) described in the literature (i.e., a quinoid form).[1,6]

Similarly, we could expect for **23** the presence of the COOH substituent on the phenazine ring and the two methyl groups in positions 2 and 3 since **23** was isolated from condensation between **11** and **15**. However, the NMR spectrum of **23** shows a broad singlet at 7.47 ppm (H(8) and H(11)) and signals for H(1), H(3), H(4), H(6), and H(13) similar to those of **20** (Figure 1c and 1d). As a result, the two methyl groups and the COOH moiety are located in positions 9, 10, and 2, respectively. This structural study clearly demonstrated an unprecedented prototropic rearrangement of the conjugated π-system for **20** and **23** (scheme 2). The nature of the intermediate(s) involved in this double-

Scheme 2. Prototropic Rearrangement in **20** (R = H) and **23** (R = CH_3)



proton transfer should depend on the mechanism of the tautomerization.[32]

In terms of electrochemical properties, the DHTAPs exhibit one poorly reversible oxidative step and multireductive steps which indicate chemical evolution of the

Table 1. Oxidation Potential of DHTAPs

compd	E_{pa} (V) vs Fc/Fc^+
2	−0.03
18	−0.03
19	−0.01
20	+0.01
21	−0.05
22	−0.14
23	−0.02

oxidized and reduced species (EC and ECE mechanisms).[18] Compared to the parent system **2**, molecules **19** and **20** are more difficult to oxidize (Table 1) owing to the presence of electron-withdrawing groups (Cl and COOH). A stronger influence was observed in the case of **20** due to a mesomeric effect. Curiously, the presence of only one Cl atom (molecule **18**) does not affect the oxidation potential compared to **2** (−0.03 V vs Fc/Fc^+ in both cases). As expected, molecules **21** and **22**, bearing electron-donating groups (CH_3), are easier to oxidize and show a cumulative effect by comparison with **2** (−0.05 and −0.14 vs −0.03 V, respectively). In **23**, the antagonist effect between two methyl groups (+I donor) and a COOH moiety (−I and −M acceptor) turns slighly in favor of COOH which accounts for a possible tuning of the redox properties depending on the substituents.

The DHTAPs **18**-**23** show absorption bands between 420 and 650 nm similar to those observed for the parent system **2**,[4] although the chlorinated DHTAPs **18** and **19** displayed a different absorption profile compared to their analogues (Figure 2).

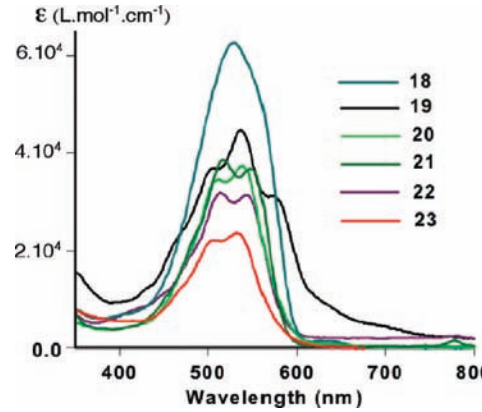


Figure 2. UV−vis absorption of compounds **18**−**23** in DMAA.

It is noteworthy that these observations are consistent with a nonzwitterionic structure for **20** and **23** since a charged form should lead to spectral changes (bathochromic effect) due to a higher degree of π-electron delocalization.[14]

In summary, we have disclosed a versatile, facile and very efficient synthesis of new substituted DHTAPs **18**−**23** for which

(29) Yosioka, I.; Otomasu, H. *Pharm. Bull.* **1954**, *2*, 53.
(30) Römer, A.; Budzikiewicz, H.; Korth, H.; Pulverer, G. *Tetrahedron Lett.* **1979**, *6*, 509.
(31) Pozzo, J.-L.; Clavier, G. M.; Desvergne, J.-P. *J. Mater. Chem.* **1998**, *8*, 2575.
(32) Rumpel, H.; Limbach, H.-H. *J. Am. Chem. Soc.* **1989**, *111*, 5429.

the conjugated π-system in the pentacyclic core can rearrange depending on the electronic effect of the substituent(s). The access to the distribution of the π-system is a key parameter that should be useful for improving the properties of such compounds. The substitution pattern (i.e., positions 2, 3, 9, and 10) appears very attractive[19] since it should favor intermolecular interactions in the solid state for electronic plastic applications. In addition, the introduction of new functionalities on the pentacyclic skeleton will open new perspectives in different areas of chemistry.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique, the Ministère de la Recherche et de l'Enseignement Supérieur, and the Provence Alpes Côte d'Azur Region (PhD grant of C.S.). We also thank Prof. F. Fages and Dr. V. Khodorkovsky (CINaM, Aix-Marseille University) for fruitful discussions, and Dr. F. Ziarelli (Sepectropole, Aix-Marseille University) for solid NMR studies.

Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL801509V