# Approaches to the Azahelicene System: Synthesis and Spectroscopic Characterization of Some Diazapentahelicenes

by **Tullio Caronna***, **Serena Gabbiadini**, **Andrea Mele**, and **Francesco Recupero**

Dipartimento di Chimica del Politecnico, Via Mancinelli 7, I-20131 Milano

The synthesis and spectroscopic characterization of some diazahelicenes is presented. The synthetic approach varies according to the location of the N-atoms; thus, three different synthetic pathways are used (*Schemes 1–3*). A description of UV/VIS and of fluorescence and phosphorescence emission is also reported. NMR Spectra show the importance of the distorted backbone of these molecules.

**Introduction.** – Helicenes [1] constitute a class of molecules with many intriguing characteristics. The fact that, despite their aromaticity, these molecules cannot be planar for sterical reasons confers them properties such as chirality, self-assembling in the solid state with the building of columnar systems, the ability to behave as organic conductor [2], *etc.* Since the first synthesis in 1955 by *Newman* and *Lednicer* [3], a great deal of work has been carried out on helicenes with a backbone composed of C-atoms only or on helicenes containing selected heteroatoms [4]. In these last years, particular interest was paid, *e.g.*, to thiohelicenes, a class of molecules with alternating thiophene and benzene rings that showed an interesting self-assembling behaviour in the solid state [5]. In the case of separation of the two enantiomers, very high $[\alpha]_{500}^{23}$ values were found [6]. The two enantiomers of the nine-ring thiohelicene showed distinctive circular dichroism spectra [7], and, according to the current theories, it was possible to attribute the absolute configuration of the right-handed helix to the (+)-enantiomer [8].

In a different context, N-containing heterocycles are receiving an increasing interest owing to the fact that their complexes with transition-metal ions show interesting properties in harvesting (VIS) light and reemit it at a wavelength that depends on the used metal ion [9]. Furthermore, when the heteroaromatic compound used for the complexation has more than one N-atom in its skeleton, the formation of a large supramolecular complex is possible, and the properties of this kind of system has been the field of study for many research groups [10].

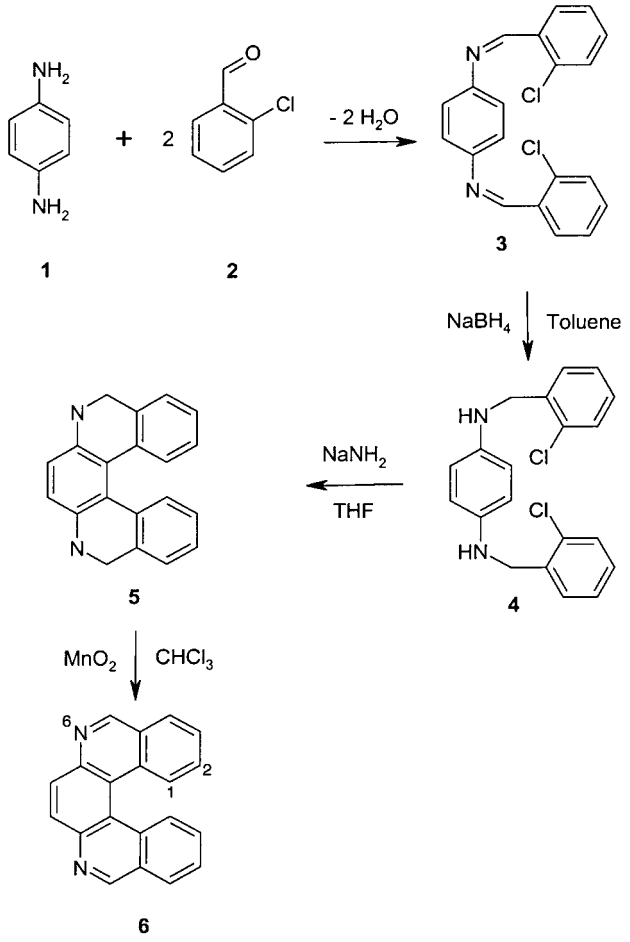
We now report synthetic pathways for the production of diazapentahelicenes. In these molecules, the properties of helicenes are combined with those of N-heterocycles, which eventually will allow the formation of supramolecular complexes between transition-metal ions and this kind of asymmetric ligand. These complexes may constitute the starting point for the study of emitters of circularly polarized light, whose wavelength may be tuned by changing the complexing ion.

**Results.** – The synthesis of diazapentahelicenes proved to be complex because each of the three diazapentahelicenes reported in this paper required a different approach.

Two diazapentahelicenes are reported in the literature: the 1,14-diazapentahelicene that was synthesized to be used as proton sponge because the proton is located between the two facing N-atoms [11], and the 6,9-diazapentahelicene (**6**) prepared as an extension of the synthesis of phenanthridine [12]. Because the 1,14 isomer may accommodate a proton between the N-atoms, we were not interested, at this stage, to repeat its synthesis in view of the subsequent complex formation with larger ions, which would probably not fit in.

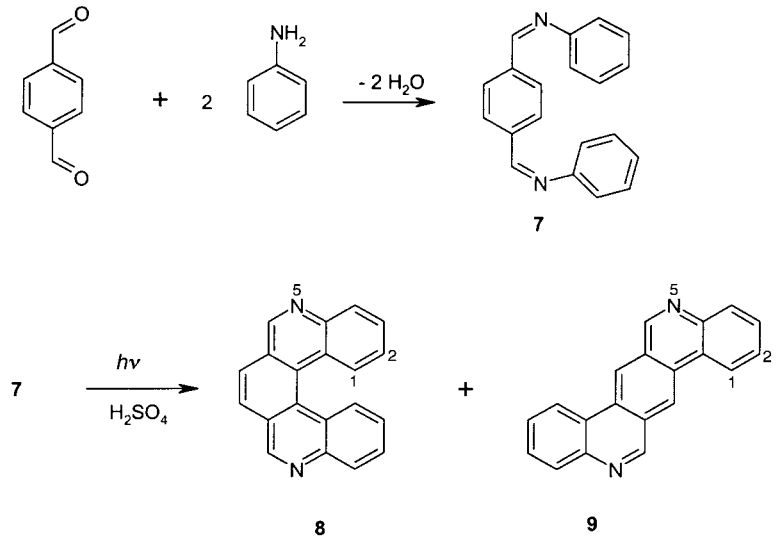
The synthesis of the 6,9-diazapentahelicene (**6**) was modified and simplified by us with respect to the reported conditions [12]. While the general synthetic approach starting from **1** and **2** was the same (see *Scheme 1*), we found that, instead of generating $KNH_2$ by adding potassium to liquid ammonia to promote the ring closure of **4** (obtained from **3**), this could be achieved by the simpler use of $NaNH_2$ in anhydrous tetrahydrofuran.

*Scheme 1*



Simple, but difficult in the workup, was the synthesis (*via* **7**) of the 5,10-diaza[5]helicene (**8**), which also yielded the isomer **9**, as reported in *Scheme 2*. Other attempts involving the use of $BF_3$ in different solvents, as suggested in the literature [13], did not give appreciable results either because of precipitation of the complex formed between the diimino derivative **7** and $BF_3$, which prevented photolysis, or because the photolysis of the soluble complex produced a tar.

*Scheme 2*

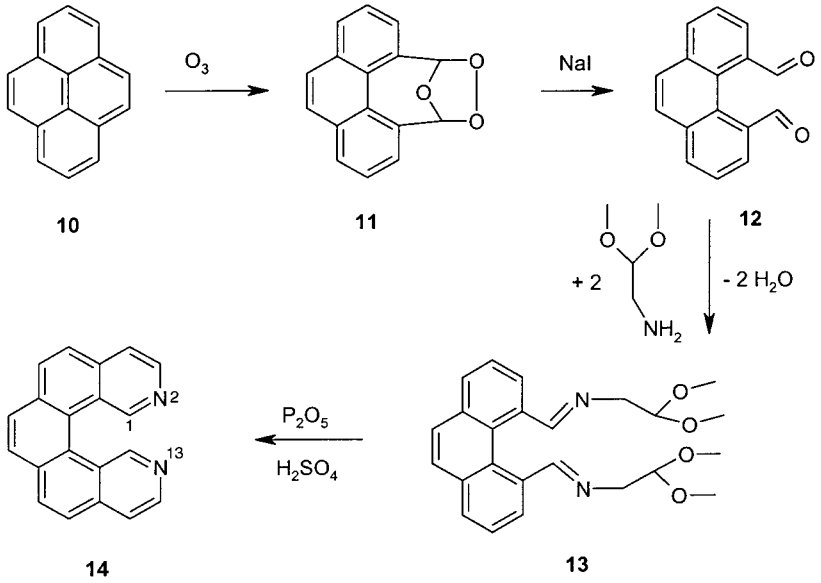



Finally, we found that the easiest approach to the synthesis of 2,13-diazapentahelicene (**14**) was ozonolysis of pyrene (**10**), followed by formation of the dialdehyde **12** from intermediate **11** [14], and subsequent ring closure of **13** (see *Scheme 3*).

The characterization of diazapentahelicenes **6**, **8**, and **14** and of the linear analogue **9** was achieved by NMR spectroscopy according to the following strategy: *i*) protons in the $\alpha$ position with respect to the N-atom were chosen as the starting point for the assignment, due to the typically high value of their chemical shifts [15]; *ii*) the diagnostic pattern of coupling constants within isoquinoline moieties ($J(2,3) = 6$ Hz, $J(4,5) = 8-9$ Hz) allowed us to distinguish protons belonging to carbocyclic and heterocyclic rings; *iii*) the analysis of the spin systems provided information on the positions of the N-atoms (*e.g.*, 1 *ABCD* system and 2 isolated protons for **6**, **8**, and **9**; 2 *AB* systems and 2 isolated protons for **14**); *iv*) further ambiguities in structure assessment were resolved by steady-state nuclear *Overhauser* enhancement (NOE) difference spectra [16].

For the sake of clarity, we report two examples of NOE difference spectra (*Fig. 1*) exploited for the distinction of azahelicene **8** and its linear analogue **9**. It is worth noting that a key role is played by the protons in $\beta$-position with respect to the N-atom, namely H–C(7) of **8** and H–C(14) of **9**, see *Fig. 2*. Indeed, only the geometry of linear **9** is consistent with NOEs experienced by H–C(1) and H–C(13) upon selective saturation of the H–C(14), whilst the selective saturation of the homologue proton (H–C(7)) in **8** can yield only a single NOE on the almost periplanar H–C(6). The full set of NOEs is summarized in *Fig. 2*.

*Scheme 3*




In *Tables 1* and *2*, the UV/VIS, fluorescence and phosphorescence maxima of the synthesized diazapentahelicenes and of the isomeric compound **9** are reported. At first glance, the most striking feature is that no phosphorescence emission from the planar diazadibenzoanthracene **9** was detected, while the diazapentahelicenes **6**, **8**, and **14** showed both the phosphorescence and fluorescence emissions even with very different

Table 1. *UV/VIS Maxima* ($\lambda_{max}$ in nm; EtOH) *of the 6,9-, 5,10-, and 2,13-Diazapentahelicenes* **6**, **8**, *and* **14**, *respectively, and of Diazadibenzoanthracene* **9**

| **6** | **8** | **14** | **9** |
|---|---|---|---|
| 205 | 207 | 204 | 219 |
| 225 | 293 | 226 | 227 |
| 257 | 320 | 266 | 286 |
| 298 | | 307 | 300 |
| 340 | | 320 | 320 |
| 380 | | | 350 |

Table 2. *Fluorescence and Phosphorescence Maxima* ($\lambda_{max}$ in nm; EtOH) *of the 6,9-, 5,10-, and 2,13-Diazapentahelicenes* **6**, **8**, *and* **14**, *and of Diazadibenzoanthracene* **9** *and Ratios of Their Intensities*

| | Fluorescence | Phosphorescence | Fluorescence/phosphorescence[a]) |
|---|---|---|---|
| **6** | 424, 438 | 505, 533 | 0.9, 1.0 |
| **8** | 412, 438 | 490, 530 | 6.6, 7.6 |
| **14** | 443, 472 | 510, 550 | 2.4, 2.4 |
| **9** | 413, 440, 465 | – | – |

[a]) Intensity ratios are reported for the first-cited fluorescence to the first-cited phosphorescence maximum.

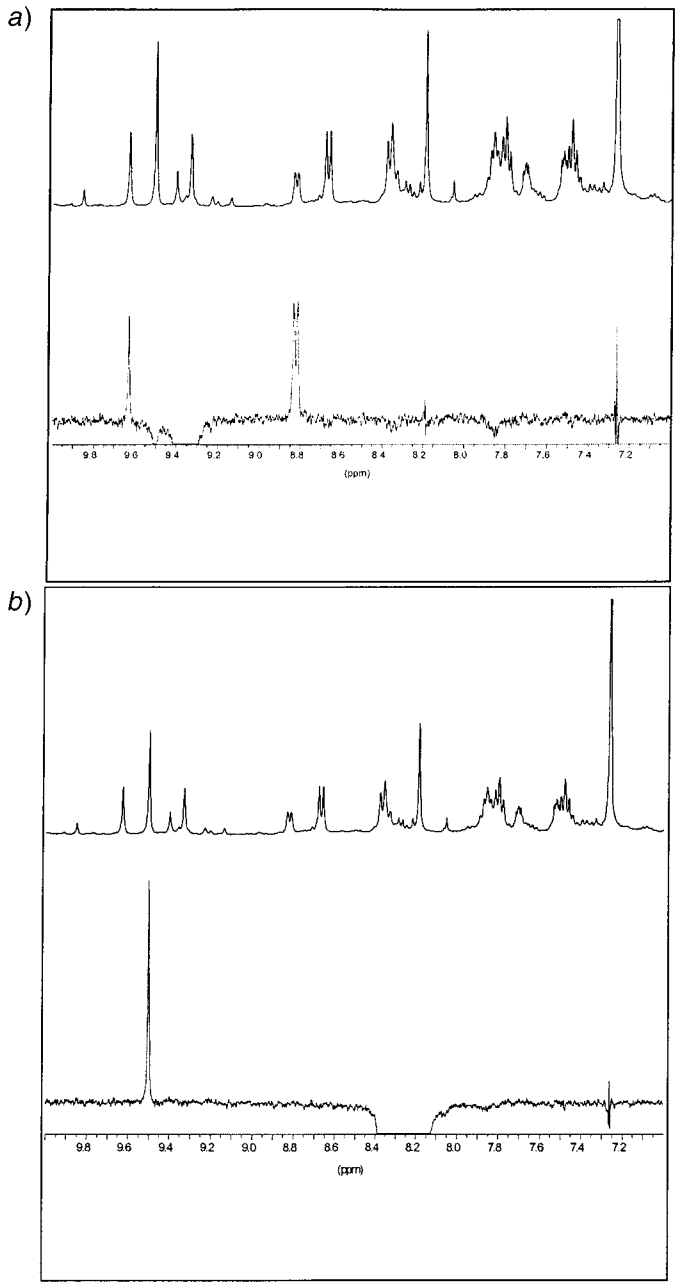



Fig. 1. a) *NOE Difference spectrum* (bottom trace) *obtained after selective saturation of the H–C(14) signal* (9.33 ppm) *of compound* **9** (peak enhancement at 9.63 (H–C(13)) and 8.82 ppm (H–C(1)); top trace: control spectrum (off resonance)). b) *NOE Difference spectrum* (bottom trace) *obtained after selective saturation of the H–C(7) signal* (8.19 ppm) *of compound* **8** (peak enhancement at 9.50 ppm (H–C(6)); top trace: control spectrum (off resonance)).

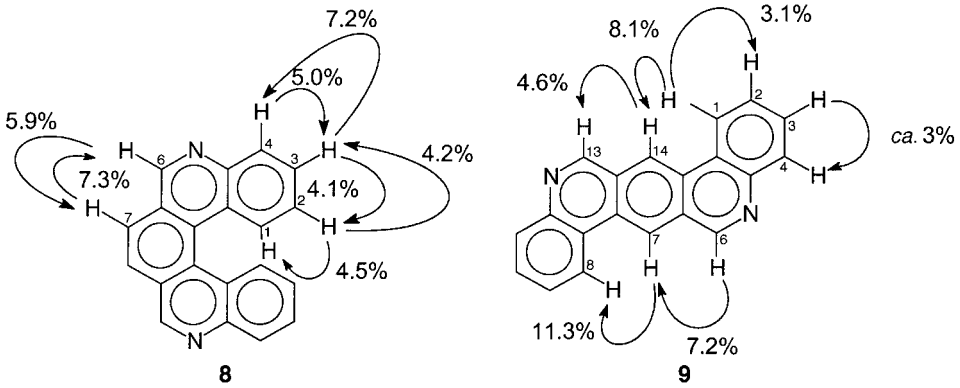



Fig. 2. *Steady-state NOEs [%] of compounds* **8** *and* **9**. The arrows start at the saturated proton and point toward the proton experiencing enhancement due to dipolar coupling.

intensities. The positions of the N-atoms in the diazapentahelicenes obviously influence the possibility of intersystem crossing. This fact is important in the heterocyclic series, and possibly may influence the properties of the metal complexes that we will study in the future.

## Experimental Part

1. *General.* All the solvents were distilled and dried before use. Pyrene, benzene-1,4-diamine, 2-chlorobenzaldehyde, terephthalaldehyde (= benzene-1,4-diacarboxaldehyde), aniline, and aminoacetaldehyde dimethyl acetal are commercial products and were used without further purification. Irradiations were carried out in a *Rayonet RPR-100* photochemical reactor equipped with 16 lamps irradiating at 254 nm. Absorbance spectra: *Hewlett-Packard Vectra-8453* spectrophotometer. Emission spectra: *Jasco FP-770* equipped with a phosphorimeter. NMR Spectra: *Bruker ARX-400* or *Bruker Avance-500* spectrometer, at 400 and 500 MHz, resp.; $CDCl_3$ solns.; $\delta$ in ppm rel. to $SiMe_4$ (= 0 ppm), $J$ in Hz. Mass spectra: *Finnigan MAT TSQ-70*, electron ionization.

2. *6,9-Diazapentahelicene* (= *Dibenzo[*a,k*][4,7]phenanthroline*; **6**). Synthesis essentially according to [12], except for the use of $NaNH_2$ (see below).

N,N′-*Bis(2-chlorobenzylidene)benzene-1,4-diamine* (**3**). A soln. of benzene-1,4-dimine (30 mmol; **1**) and 2-chlorobenzaldehyde (60 mmol; **2**) in toluene (50 ml) was refluxed for 4 h in a *Dean-Stark* apparatus; after this time, no more $H_2O$ was eliminated. Evaporation and crystallization from EtOH gave **3**. M.p. 143° ([17]: 145°).

N,N′-*Bis(2-chlorobenzyl)benzene-1,4-diamine* (**4**). To a soln. of **3** (30 mmol) in anh. toluene (60 ml), $NaBH_4$ (30 mmol) was added portionwise at r.t. under mechanical stirring. The resulting soln. was refluxed for 3 h. After cooling, the soln. was concentrated, treated with $H_2O$, and extracted with $Et_2O$. The combined org. soln. was dried ($Na_2SO_4$) and evaporated. The resulting **4** was used without further purification.

*6,9-Diazapentahelicene* (**6**). A suspension of 50% $NaNH_2$ in toluene (1.2 g) was flushed with $N_2$ and washed with anh. hexane until the toluene was removed. Anh. THF (10 ml) was added, the suspension cooled to 0°, and a soln. of **4** (7.1 mmol) in anh. THF (15 ml) added. The solution was slowly brought first to r.t. and subsequently warmed to boiling for 1 h. After cooling, a $NH_4Cl$ soln. was added, the mixture concentrated under vacuum and extracted with $Et_2O$, and the extract dried and evaporated: 0.5 g of **5**.

A soln. of the crude **5** (0.5 g) in $CHCl_3$ (20 ml) was treated with $MnO_2$ (5 g). The suspension was stirred at r.t. for 15 h, the solid filtered off, the filtrate evaporated, and the residue chromatographed (silica gel, AcOEt/$Et_3N$ 50:1): 20 mg (4%) of **6**. M.p. 154–155° ([12]: 155–156°). $^1$H-NMR: 9.44 (*s*, 2 H); 8.53 (*d*, $J$ = 8.6, 2 H); 8.30 (*s*, 2 H); 8,14 (*dd*, $J$ = 8.1, 1,5, 2 H); 7.69 (*ddd*, $J$ = 8.1, 6.8, 1.5, 2 H); 7.57 (*ddd*, $J$ = 8.6, 6.8, 1.5, 2 H). MS: 280 ($M^+$).

3. *5,10-Diazapentahelicene* (=*1,6-Diazadibenzo[*c,g*]phenanthroline*; **8**). N,N′-*(1,4-Phenylenedimethylidene)bis[benzenamine]* (**7**). A soln. of terephthalaldehyde (15 mmol; **5**) and aniline (30 mmol; **6**) in EtOH (50 ml) was refluxed for 12 h. The solvent was evaporated and the product crystallized from EtOH: 74% of **7**. M.p. 159–160° ([18]: 157–159°).

*5,10-Diazapentahelicene* (**8**). A soln. of **7** (1.2 mmol) in conc. $H_2SO_4$ soln. (400 ml) was filled into 8 quartz tubes and irradiated at 254 nm for 48 h. After the irradiation time, the acidic soln. was added dropwise into an ice-cold 50% (*w*/*w*) aq. NaOH soln. The resulting soln. was extracted with $CH_2Cl_2$, the org. soln. dried ($Na_2SO_4$) and evaporated, and the residue (0.134 g) chromatographed (silica gel, AcOEt/hexane/$Et_3N$ 100:50:1, then AcOEt/$Et_3N$ 50:1). The fraction containing **8** and **9** was further separated by prep. TLC (AcOEt/$Et_3N$ 50:1).

*Data of* **8**: Yield 2%. M.p. 147–149°. $^1$H-NMR: 9.50 (*s*, 2 H); 8.67 (*d*, *J* = 8.5, 2 H); 8.36 (*m*, 2 H); 8.19 (*s*, 2 H); 7.80 (*dd*, *J* = 7.7, 7.7, 2 H); 7.48 (*dd*, *J* = 7.7, 7.7, 2 H). MS: 280 ($M^+$). Anal calc. for $C_{20}H_{12}N_2$: C 85.69, H 4.31, N 9.99; found C 85.68, H 4.33, N 9.97.

*Data of 5,12-Diazadibenzo[*a,h*]anthracene* (=*Quino[4,3-*j*]phenanthridine*; **9**): Yield 6%. M.p. 319–320° ([19]: 320–321.5°). $^1$H-NMR: 9.63 (*s*, 2 H); 9.33 (*s*, 2 H); 8.82 (*m*, 2 H); 8.36 (*m*, 2 H); 7.86 (*m*, 4 H). MS: 280 ($M^+$).

4. *2,13-Diazapentahelicene* (=*9,12-Diazadibenzo[*c,g*]phenanthrene*; **14**). *Pyrene Monoozonide* (=*4,7-Dihydro-4,7-epoxyphenanthro[4,5-*def*][1,2]dioxocin*; **11**). A soln. of pyrene (3.6 g, 17.8 mmol; **10**) in $CH_2Cl_2$ (400 ml) was cooled to −70° and the stoichiometric amount of ozone was bubbled through. The soln. was flushed with $N_2$ to eliminate the unreacted ozone and then evaporated. The residue was chromatographed (silica gel, hexane/$CH_2Cl_2$ 3:2): 2.14 g (48%) of **11** that was used immediately for the next step.

*Phenanthrene-4,5-dicarboxaldehyde* (**12**). A soln. of **11** (2 g, 8 mmol) and NaI (4 g, 27 mmol) in AcOH (90 ml) was stirred at r.t. for 4 h. Then, sat. $Na_2S_2O_3$ soln. was added to reduce the formed $I_2$, and the mixture was extracted with $CH_2Cl_2$. The org. layer was washed with $NaHCO_3$ soln., dried ($Na_2SO_4$), and concentrated, the precipitate (4-hydroxyphenanthro[4,5-*cde*]oxepin-6(4*H*)-one) filtered off, and the filtrate chromatographed (silica gel, $CH_2Cl_2$): 0.5 g (25%) of **12**. M.p. 169–171° ([14]: 169–171°). $^1$H-NMR 10.13 (*s*, 2 H); 7.91–8.32 (*m*, 8 H). MS: 234 ($M^+$).

N,N′-(*Phenanthrene-4,5-diyl)bis[2,2-dimethoxyethan-1-amine]* (**13**). A soln. of **12** (0.5 g, 2.14 mmol) and aminoacetaldehyde dimethyl acetal (0.51 g, 4.28 mmol) in toluene (20 ml) was refluxed for 12 h in a *Dean-Stark* apparatus; after this time, no more $H_2O$ was eliminated. The solvent was evaporated: **13**, which was used for the next step without further purification.

*2,13-Diazapentahelicene* (**14**). To crude **13** (0.9 g, 2.14 mmol) cooled in an ice bath, conc. $H_2SO_4$ soln. (10 ml) was added dropwise, followed by the addition of $P_2O_5$ (1.7 g) under stirring. The temp. was slowly brought to 160° within 25 min. The resulting mixture was cooled in an ice bath, and a cold 50% (*w*/*w*) aq. NaOH soln. was added dropwise until basicity was reached. The resulting soln. was extracted with $CH_2Cl_2$, the org. layer washed with $H_2O$, dried ($Na_2SO_4$), and evaporated, and the residue (0.080 g) chromatographed (silica gel, AcOEt/$Et_3N$ 50:1): 0.015 g (2.5%) of **14**. M.p.110–112°. $^1$H-NMR: 9.93 (*s*, 2 H); 8.61 (*d*, *J* = 5.8, 2 H); 8.09 (*d*, *J* = 8.6, 2 H); 7.97 (*s*, 2 H); 7.92 (*d*, *J* = 8.6, 2 H); 7.77 (*d*, *J* = 5.8, 2 H). MS: 280 ($M^+$). Anal. calc. for $C_{20}H_{12}N_2$: C 85.69, H 4.31, N 9.99; found C 85.53, H 4.32, N 10.01.

## REFERENCES


[1] R. H. Martin, *Angew. Chem., Int. Ed.* **1974**, *13*, 649.

[2] A. J. Lovinger, C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 264 ; C. Nuckolls, T. J. Katz, T. Verbiest, S. Van Elshocht, H.-G. Kuball, S. Kiesewalter, A. J. Lovinger, A. Persoons, *J. Am. Chem. Soc.* **1998**, *120*, 8656.

[3] M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765.

[4] H. Nakagawa, A. Obata, K. Yamada, H. Kawazura, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1899.

[5] Y. Dai, T. J. Katz, *J. Org. Chem.* **1997**, *62*, 1274; C. Nuckolls, T. J. Katz, L. Castellanos, *J. Am. Chem. Soc.* **1996**, *118*, 1274.

[6] H. Nakagawa, S. Ogashiwa, H. Tanaka, K. Yamada, H. Kawazura, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1903.

[7] T. Caronna, R. Sinisi, M. Catellani, S. Luzzati, S. Abbate, C. Longhi, *Synth. Met.,* in press.

[8] M. B. Groen, H. Wynberg, *J. Am. Chem. Soc.* **1971**, *93*, 2968; D. A. Lightner, D. T. Hefelfinger, T. W. Powers, G. W. Frank, K. N. Trueblood, *J. Am. Chem. Soc.* **1972**, *94*, 3492.

[9] J.-C. Rodriguez-Ubis, B. Alpha, D. Plancherel, J.-M Lehn, *Helv. Chim. Acta* **1984**, *67*, 2264 ; J.-M Lehn, J.-B. Regneouf de Vains, *Tetrahedron Lett.* **1989**, *30*, 2209.

[10] J.-M Lehn, *Pure Appl. Chem.* **1978**, *50*, 871; B. Alpha, V. Balzani, J.-M Lehn, S. Perathoner, N. Sabbatini, *Angew. Chem., Int. Ed.* **1987**, *26*, 1266.
[11] H. A. Staab, M. A. Zirnstein, C. Krieger, *Angew. Chem., Int. Ed.* **1989**, *28*, 86.
[12] S. V. Kessar, Y. P. Gupta, P. Singh, V. Jain, P. S. Pahwa, *J. Chem. Soc. Pak*. **1979**, *1*, 129.
[13] C. M. Thompson, S. Docter, *Tetrahedron Lett.* **1988**, *29*, 5213.
[14] B. L. van Duuren, G. Witz, S. C. Agarwal, *J. Org. Chem.* **1974**, *39*, 1032.
[15] L. M. Jackman, S. Sternell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon Press, New York, 1969.
[16] D. Neuhaus, M. Williamson, 'The Nuclear Overhauser Effect in Structural and Conformational Analysis', VCH Publishers, New York, 1989.
[17] N. M. Rotmistrov, G. V. Kulik, O. S. Nevkipila, V. O. Kovtun, *Mikrobiol. Zh*. (Kiev, 1934–1977) **1967**, *29*, 150; Chem. Abstr. **1967**, *67*, 63976.
[18] N. J. Coville, E. W. Neuse, *J. Org. Chem*. **1977**, *42*; 3485.
[19] L. H. Klemm, W. O. Johnson, A. Weissert, *J. Heterocycl. Chem.* **1971**, *8*, 763.

*Received May 26, 2001*