124. On the Use of *N, N'*-Dipyrrolylmethane in Heterocyclic Synthesis. Dipyrrolo[1,2*c*:2',1'*e*]-2*H*-imidazole and its Aromatic Anion

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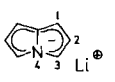
Summary

The pyrrolate ion (**5**) is shown to produce *N, N'*-dipyrrolyl methane (**4**) when reacted with dichloromethane under conditions of weak counter-ion association. 1-Azoniafulvene ion (**13**) is suggested to be the key intermediate in this reaction. *N, N'*-Dipyrrolyl methane (**4**) undergoes intramolecular oxidative coupling when treated with butyllithium and Cu(II)chloride, yielding the novel ring system of dipyrrolo[1,2*c*:2',1'*e*]-2*H*-imidazole (**3**). The latter upon reaction with methyl lithium forms the *Hückel*-aromatic anion **2**. Solutions of the lithium salt are stable for several days. Reaction of the dianion of 2,2'-bipyrrole (**11**) with dichloromethane does not produce **3**, but a pyrrolophane-type dimer (**12**) having its two anticoplanar *N, N'*-bipyrroledityl subunits arranged in a double layer and joined by a methylene group on each side.

Recent publications from our laboratory have discussed the reactions of carboaromatic anions with chlorocarbene [1] [2]. Following our studies of 4-azapentalenyl lithium (**1**) [3] [4], access to new simple heteroaromatic anions was desired. Our interest focused on dipyrrolo-2*H*-imidazolyl lithium (**2**). Surprisingly, this simple analogue of the fluorenyl system as well as its parent compound, dipyrrolo-[1,2*c*:2',1'*e*]-2*H*-imidazole (**3**) or any derivatives thereof, were completely unknown. It is the purpose of this communication to show how the target anion (**2**) and other novel heterocyclic systems can be constructed in a few straightforward steps starting from pyrrole.



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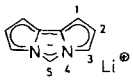

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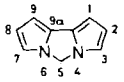

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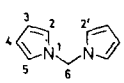

4

The alkylation of alkali salts of pyrrole has been intensively studied and employed in complex syntheses [5]. Control over *N- vs. C*-alkylation can be achieved almost routinely by monitoring the 'freeness' of the pyrrolyl anion [5]. Despite widespread activity in this area a particularly interesting case of *N*-alkylation has not been exploited. The reaction, striking in its simplicity, consists of the formation of *N, N'*-dipyrrolylmethane (**4**) from dichloromethane and 'free' pyrrolyl anion. We took advantage of this reaction to reach our objective.

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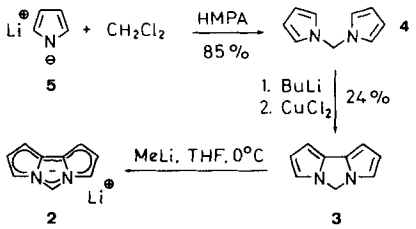
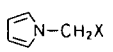
Scheme 1



Results. – The addition of pyrrolyl lithium (**5**) in hexamethyl phosphoric triamide (HMPA) to methylene chloride/HMPA, 1:1 (*v/v*) afforded a single organic product, *N,N'*-dipyrrolyl methane (**4**), in 85% yield. It was fully characterized by its mass spectrometric fragmentation pattern and from the UV., ^{1}H-NMR. and ^{13}C-NMR. spectra. The latter showed only three resonances in agreement with the C_s-symmetry of **4**.

The yield and nature of product in this experiment were independent of the mode of addition. Even when adding **5** slowly to a 50-fold excess of methylene chloride, no *N*-chloromethyl pyrrole (**6**) or *N*-hydroxymethyl pyrrole (**7**) were detected after work-up. As neither of these compounds is expected to be very stable [6], we also quenched the high dilution experiment with sodium methoxide prior to the aqueous work-up. Again, there was no evidence of *N*-methoxymethyl pyrrole (**8**), only **4** was obtained. A sample of **8**, independently prepared from chloromethyl methyl ether and **5**, was found to be stable under the conditions of the preparation of **4**.



6 X = Cl
7 X = OH
8 X = OCH_3

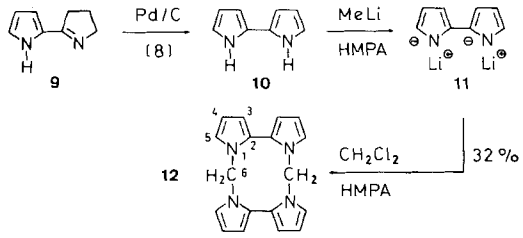
The 2,2'-dilithium salt of *N,N'*-dipyrrolyl methane (**4**) underwent intramolecular oxidative coupling when reacted with Cu(II)chloride[1]), giving dipyrrolo-[1,2*c*:2',1'*e*]-2*H*-imidazole (**3**) in 24% yield *(Scheme 1)*. The linking of two pyrrolyl-subunits was unambiguously established from the bathochromic shift of the UV. spectrum of **3** compared to that of the starting material **4** [λ_{max} (**3**) $_{EtOH}$: 293 nm ($\varepsilon = 16100$) *vs.* λ_{max} (**4**) $_{EtOH}$: 222 nm ($\varepsilon = 7750$)]. ^{1}H-NMR., ^{13}C-NMR. and mass spectra confirmed that ring closure to the novel heterocyclic system (**3**) had been achieved.

Reaction of the colourless compound **3** with methyl lithium in THF at 0°, gave the wine-red lithium salt of the heteroaromatic anion **2** in quantitative yield. Solutions of **2** are stable at room temperature for several days in the absence of air. Hydrolysis of **2** regenerates **3**. The aromatic salt is characterized by its ^{1}H-NMR. and ^{13}C-NMR. spectra *(vide infra)*.

In the successful synthesis of **3** summarized in *Scheme 1*, the strategic step, *i.e.* the introduction of the methylene group joining the pyrrolyl moieties, was performed first and the ring closure to the final product accomplished thereafter.

[1]) For reference to oxidative coupling in heterocyclic chemistry see the reviews [7].

Scheme 2



We have also attempted synthesis of **3** by the inverse sequence, *i.e.* the two pyrrole units were connected first in the 2,2′-position followed by the introduction of the *N*, *N*′-methylene grouping. The remarkable unexpected outcome of this experiment however was the dimerization to **12**.

2,2′-Bipyrrole (**10**) was obtained by a known procedure [8] and converted to the dilithium salt (**11**). The reaction of **11** with dichloromethane in HMPA afforded a single product, which was readily identified as the dimer **12**. Regardless of the mode or rate of addition, no **3** could be detected in these experiments.

The planar formula attributed to **12** in *Scheme 2* is certainly misleading. Spectroscopic data (UV., ^{1}H-NMR., ^{13}C-NMR.) and model considerations suggest that the compound has C_{2h}-symmetry. In particular, the ^{1}H-NMR. spectrum of the methylene protons is that of an *AB* spin-system (of double intensity) with a large shift difference between the geminal hydrogen atoms [$\Delta\delta_{AB}(\text{ppm})_{DMSO} = 0.67$]. Moreover, the UV. spectrum, although similar to that of 2,2′-bipyrrole (**10**), exhibits reduced absorbance [λ_{max} (**10**) $_{benzene}$: 281 nm ($\varepsilon = 17\,300$) *vs.* λ_{max} (**12**) $_{benzene}$: 277 nm ($\varepsilon = 8\,350$)]. We suppose that the molecule has a pyrrolophane-type structure with a slightly twisted anticoplanar array of the bipyrrolyldiyl moieties. This is shown below in two perspective views *(Fig. 1)*[2]).

Discussion. – Double nucleophilic substitution on dichloromethane has rarely been encountered [10] and it is remarkable that the *N*, *N*′-dipyrrolyl methane formation (**5** → **4**) in *Scheme 1* occurs at all. From the experiments described above, it was seen that the formation of the second C,N-bond in **4** is very efficient, *i.e.* has a much higher rate than the initial step. It was not possible to halt the reaction at the level of monosubstitution, even under conditions of high dilution. Clearly, two successive S_N2-type reactions (*i.e.* **5** → **6** → **4** in *Scheme 3*) can hardly account for these findings, and a S_N1-type process, proceeding *via* the 1-azoniafulvene ion (**13**) seems more likely for the formation of the second C,N-bond. The ion **13**, a special case of an iminium ion [11] is precisely what we would expect to intercept **5** with the efficiency observed *(Scheme 3)*.

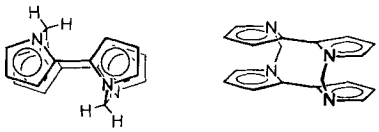
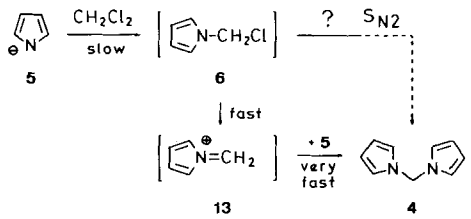


Fig. 1. *Perspective views of compound* **12**

[2]) An X-ray structure determination of **12** is in progress [9].

Scheme 3



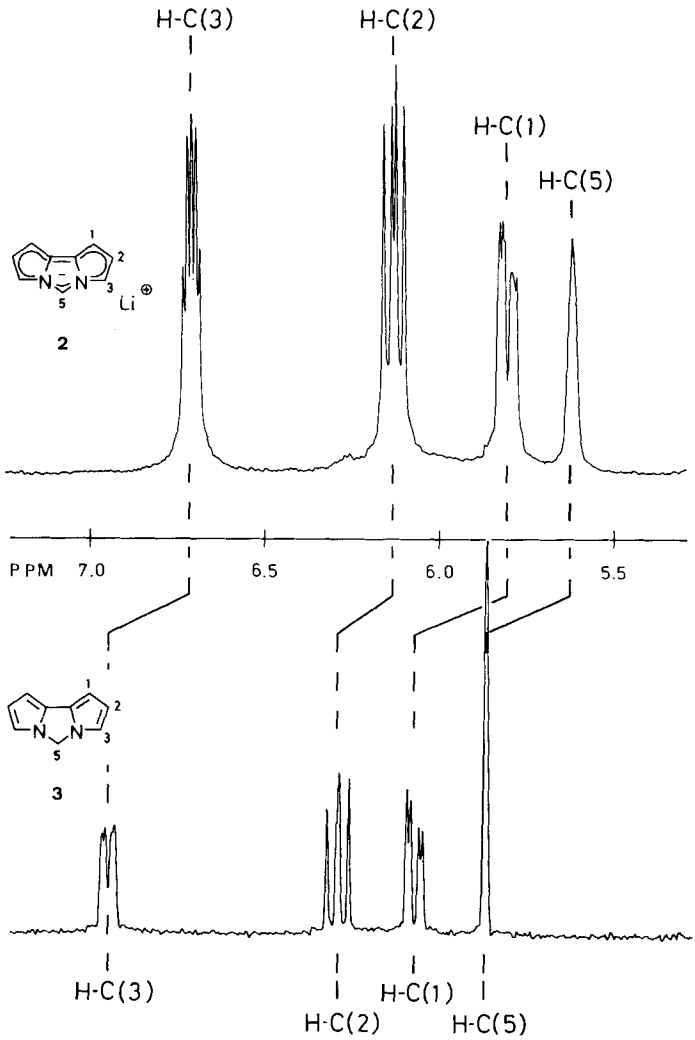
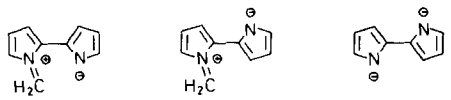


Fig. 2. *^{1}H-NMR. spectra of* **2** *(lithium salt) and* **3** at 100 MHz in d_8-tetrahydrofurane

The 1-azoniafulvene ion (**13**), although to our knowledge unknown in solution chemistry, is readily formed in the gas phase by electron impact on *N*-alkyl pyrroles [12], and is commonly invoked in the interpretation of mass spectra of this class of compounds.

An analogous planar azoniafulven intermediate (**14**) resulting from the reaction of **11** with dichloromethane may, for stereoelectronic reasons [13], explain why dimerization occurred instead of the formation of **3**. However, the conformation of the dimer *(Fig. 1)*, with anticoplanar arrangement of the adjacent dipyrrolediyl units brings a simpler explanation to mind. The starting dianion (**11**), due to lone pair and charge repulsion, may well be present in solution in its anticoplanar form **11′**, and maintain this conformation throughout the entire process **11** → **12**. The intramolecular ring closure to **3**, regardless of its mechanism, cannot then occur from **11′** or the corresponding **14′**, simply for geometric reasons[3]).

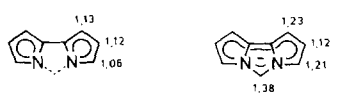


14 **14′** **11′**

The experimental evidence taught that the oxidative intramolecular coupling has to be the last step in the construction of **3**. For the latter reaction there is ample intermolecular precedent (see *e.g.* [7] and [15]). It is not surprising that base treatment of this novel hetero ring system produces a stable anion **2** having its 14 π-electrons delocalized over three five-membered rings condensed in series.

The ^{1}H-NMR. spectra correlated in *Figure 2* nicely demonstrate how charge delocalization occurs when going from **3** to **2**. It is immediately seen that all proton resonances, including that of H–C(5), appear at higher field in the spectrum of the lithium salt **2**. The gross features of these changes can be rationalized in terms of the approach of *Schaefer & Schneider* [16] at the ordinary *Hückel*-MO (HMO) level [17][4]). The upfield shift of the ^{1}H-resonances of H–C(1), H–C(2) and H–C(3) reflect essentially the changes in π-electron density at the corresponding carbon centres. Qualitative HMO predicts that these changes are more important for

Scheme 4. *HMO charge orders for the C-atoms of compound* **3** *and its anion* **2**[5]).



3 **2**

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[3]) We found that 2,2′-bipyrrole has a zero dipolar moment in benzene. Thus already this precursor seems to prefer the anticoplanar conformation in solution (*cf.* [14]).

[4]) These qualitative arguments neglect the effects of differential ring current and counter ion association.

[5]) Perturbation operators for heteroatoms were taken from [17b].

H–C(1) and H–C(3) than for H–C(2), as shown by the charge orders reproduced in *Scheme 4*. The fact that also H–C(5) of **2** is shielded relative to H–C(5) of **3** indicates that rehybridization and ring current effects are overbalanced by the negative charge. Again, HMO assigns a fairly large charge order to that anionic centre.

Clearly, the system **2/3** is an interesting heterocyclic analogue to fluorene and its anion, and some of its chemistry can be predicted on this basis. We shall report shortly on the less readily anticipated reactions of **2** with chlorocarbene.

For valuable advice the authors are indebted to Mrs. *J. Rupp* and Dr. *G. Bernardinelli*. Technical assistance by Mrs. *F. Kloeti* (MS.), Miss *G. Fariello* (syntheses) and Mr. *J.P. Saulnier* (NMR.) is gratefully acknowledged. Financial support was provided by the *Swiss National Science Foundation* (grant No 2.172-0.78).

Experimental Part

General remarks. – UV. spectra (λ_{max} [nm](ε)): *Beckmann* Acta-III spectrometer. – IR. spectra ($\tilde{\nu}$[cm^{-1}]): *Perkin-Elmer* IR-257 spectrometer. – ^{1}H-NMR. spectra (δ[ppm] relative to internal TMS. Multiplicity: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *qi* = quintet, *m* = multiplet, br. = broad, *J*[Hz] = apparent coupling constant): *Varian* XL-100 spectrometer operating at 100.1 MHz (pulsed mode). – ^{13}C-NMR. spectra (δ[ppm] relative to internal TMS, multiplicity for off-resonance decoupling: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet): *Varian* XL-100 spectrometer operating at 25.2 MHz (pulsed mode); dipolar moment [Debye]: WTW-Dipolmeter DMO1 (Weilheim/Germany), Mass spectra (MS.) (*m/z*, base peak in italics, metastable peaks with asterisk): *Varian* MAT-SMA spectrometer.

Further abbreviations: RT. = room temperature; i.V. = *in vacuo*.

Dipyrrolo[1,2c:2',1'e]-2H-imidazolyl lithium (**2**). A solution of 50 mg (0.35 mmol) of **3** in 0.5 ml d_8-THF is injected through a gastight septum at 0° into 0.5 ml of a 2M solution of methyl lithium in d_8-THF and kept under argon. After slow warm-up (2 h) to RT. the NMR. spectra of the wine-red solution are recorded.

^{1}H-NMR. (d_8-THF) (*cf. Fig. 2*), δ[ppm]: 5.65 (narrow *m*, 1 H, H–C(5)); 5.80 (*d*, br., 2 H, $^3J_{H-C(1),H-C(2)} = {}^3J_{H-C(8),H-C(9)} = 3.5$, H–C(1) and H–C(9)); 6.14 (*d*×*d*, 2 H, $^3J_{H-C(2),H-C(1)} = {}^3J_{H-C(8),H-C(9)} = 3.5$ and $^3J_{H-C(2),H-C(3)} = {}^3J_{H-C(7),H-C(8)} = 2.5$, H–C(2) and H–C(8)); 6.71 (*d*×*t*, 2 H, $^3J_{H-C(2),H-C(3)} = {}^3J_{H-C(7),H-C(8)} = 2.5$, $^4J_{H-C(1),H-C(3)} = {}^4J_{H-C(7),H-C(9)} \approx {}^4J_{H-C(3),H-C(5)} = {}^4J_{H-C(5),H-C(7)} = 1.25$, H–C(3) and H–C(7)).

^{13}C-NMR. (d_8-THF) δ[ppm]: 83.39 (*d*, C(5)), 89.65 (*d*), 108.8 (*d*), 109.2 (*d*) (tentative assignment: C(1)/C(9), C(3)/C(7) and C(2)/C(8) respectively), 129.7 (*s*, C(9a) and C(9b)).

Dipyrrolo[1,2c:2',1'e]-2H-imidazole (**3**). The solution of 1.46 g (10 mmol) *N,N'*-dipyrrolylmethane (**4**) in 15 ml benzene is stirred at RT. under argon protection for 24 h with 11 ml of a 2M solution of butyllithium in hexane in the presence of 200 mg of tetramethyl ethylenediamine (TMEDA). The resulting mixture is added dropwise under argon protection to a stirred emulsion of 3.0 g (20 mmol) of anhydrous $CuCl_2$ in 5 ml benzene. After 2 h the mixture is hydrolyzed with 2N HCl and filtered. The filtrate is exhaustively extracted with ether and water. The combined ether extracts are dried over $MgSO_4$, treated with charcoal and concentrated i.V. The crude product is purified by column chromatography (silicagel *Merck*, type 60, hexane/ether 4:1). After chromatography 346 mg (24% yield) **3** are obtained as colourless crystals, which can be recrystallized from small amounts of ether. M.p. 104–105°.

UV. (EtOH): 293 (16100). – IR. (KBr): 2930, 1520, 1300 and 1080. – ^{1}H-NMR. ($DCCl_3$): 5.61 (*s*, 2 H, 2 H–C(5)); 6.05 (*d*×*d*, 2 H, $^3J_{H-C(1),H-C(2)} = {}^3J_{H-C(8),H-C(9)} = 3.5$, $^4J_{H-C(1),H-C(3)} = {}^4J_{H-C(7),H-C(9)} = 1.0$, H–C(1), H–C(9)); 6.25 (*d*×*d*, 2 H, $^3J_{H-C(1),H-C(2)} = {}^3J_{H-C(8),H-C(9)} = 3.5$,

$^3J_{H-C(2),H-C(3)} = {}^3J_{H-C(7),H-C(8)} = 3.0$, H–C(2), H–C(8)); 6.74 ($d \times d$, 2 H, $^3J_{H-C(2),H-C(3)} = {}^3J_{H-C(7),H-C(8)} = 3.0$, $^4J_{H-C(1),H-C(3)} = {}^4J_{H-C(7),H-C(9)} = 1.0$, H–C(3), H–C(7)). *Cf.* ^{1}H-NMR. in d_8-THF, *Figure 2*. – ^{13}C-NMR. ($DCCl_3$): 61.60 (*t*, C(5)), 96.6 (*d*), 113.0 (*d*) and 114.4 (*d*), tentative assignment: C(1)/C(9), C(3)/C(7) and C(2)/C(8) respectively, 130.0 (*s*, C(9a),C(9b)). – MS. ($C_9H_8N_2$; 144): *144* (M^+), 143, 129, 117, 116, 104, 90, 89.

N,N'-dipyrrolyl-methane (**4**). After dropwise addition of a 1.6M ethereal solution of methyl lithium (35 ml, 55 mmol) under N_2 to a stirred solution of 3.35 g (50 mmol) of pyrrole in 30 ml ether, 30 ml HMPA are added and the ether removed by distillation. The resulting solution of lithium pyrrolate (**5**) in HMPA is added slowly at 25° to a stirred mixture of 16 ml (250 mmol) CH_2Cl_2 and 16 ml HMPA. After 20 h (RT.) the reaction mixture is added to a two-phase extracting mixture of 200 ml ether/saturated aqueous Na_2CO_3-solution 1:1. The ethereal phase is washed twice (aqueous Na_2CO_3-solution) and dried ($MgSO_4$). After removal of ether and crystallization from CCl_4, 3.1 g (85% yield) **4** are obtained. Isolation and purification can alternatively be achieved by column chromatography on silicagel (benzene/ethyl acetate, 2:1). Colourless needles, m.p. 105° (from CCl_4).

UV. (EtOH): 222 (7750). – IR. (cm^{-1}) (KBr): 2950, 1520, 1290. – ^{1}H-NMR. ($DCCl_3$): 5.80 (*s*, 2 H, 2 H–C(6)), 6.17 (*t*, 4 H, *AA'*-part of a *AA'BB'*-system, H–C(3,3'), H–C(4,4')); 6.72 (*t*, 4 H, *BB'*-part of a *AA'BB'*-system, H–C(2,2'), H–C(5,5')). – ^{13}C-NMR. ($DCCl_3$): 61.80 (*t*, C(6)), 109.6 (*d*, C(3,3',4,4')), 120.0 (*d*, C(2,2',5,5')). – MS. ($C_9H_{10}N_2$; 146): 146 (M^+), 117, 105, *80*, 53, 41, 39, 27; m*: 75.5, 35.1.

N-*Methoxymethyl-pyrrole* (**8**). A solution of 50 mmol **5** in HMPA, prepared as described in the preceding synthesis of **4**, is added dropwise to a solution of 4.86 g (60 mmol) chloromethyl methyl ether in 15 ml HMPA at 0°. After 20 h (RT.) the reaction mixture is added to a two-phase extracting mixture of 200 ml ether/saturated aqueous Na_2CO_3-solution 1:1. The ethereal phase is washed twice (aqueous Na_2CO_3-solution) and dried ($MgSO_4$). After removal of ether i.V., the crude product is distilled i.HV. Yield 3.0 g (54%), colourless liquid, b.p. ~60°/0.1 Torr.

^{1}H-NMR. ($DCCl_3$): 3.15 (*s*, 3 H, OCH_3); 5.00 (*s*, 2 H, NCH_2O); 6.05 (*t*, *AA'*-part of a *AA'BB'*-system, 2 H, H–C(3,4)); 6.60 (*t*, *BB'*-part of a *AA'BB'*-system, H–C(2,5)). – MS. (C_6H_9NO; 111): 111 (M^+), 81, 80, 67, 53; m* 59.1.

2,2'-Bipyrrole (**10**) (*Cf.* [8] and [18]). A slow current of N_2 is passed by means of an inlet terminating in a fritted glass sinter through a mixture of 500 mg (3.75 mmol) 2,2'-(1'-pyrrolinyl)-pyrrole (**9**) [8] and 250 mg of 5% Pd/C in 10 ml *p*-isopropylmethyl benzene (cymene). The reaction vessel is kept for 2 h at 180°. The reaction mixture is cooled and chromatographed on aluminum oxide (*Fluka*, type 5016-A, activity IV, column 40 × 1.5 cm, benzene). Recrystallization of the crude product from benzene/hexane 3:1 yields 302 mg (61% yield) **10**. By final elution of the Al_2O_3 column with ethanol, 15% of the starting material (**9**) can be recovered. The spectral parameters of **10** are in full agreement with the reported data: UV. [8]; ^{1}H-NMR. [8] [19]; ^{13}C-NMR. [20]; MS. [19].

Dimer (**12**) ([1.1]-*(N,N'',N',N''')*-2,2'-Bipyrrolophane). The dianion (**11**) is prepared by reacting 132 mg (1 mmol) **10** in 3 ml ether under argon with 2.5 ml of a 1.6M ethereal solution of methyl lithium. After dilution of the reaction mixture with 3 ml of HMPA, the double salt (**11**) is added dropwise to 1 ml (1 mmol) dichloromethane in 3 ml HMPA. The mixture is stirred for 20 h at 35°, and then added to a two-phase extracting mixture of 50 ml ether and 50 ml saturated aqueous Na_2CO_3-solution. The aqueous layer is re-extracted with benzene. The combined organic phases are dried ($MgSO_4$) and concentrated i.V. (no **3** could be detected by ^{1}H-NMR. in the crude product at that stage). Column chromatography (aluminum oxide, *Fluka*, type 5016-A, activity IV, benzene) gives 46 mg (32%) of colourless crystalline dimer **12**, m.p. 275–277°.

UV. (benzene): 277 (8350). – ^{1}H-NMR. (d_6-DMSO): 5.48 (*A*-part of a *AB*-system, $^2J_{AB} = 14.5$, 2 H, methylene); 6.15 (*B*-part of a *AB*-system, $^2J_{AB} = 14.5$, 2 H, methylene); 6.20 ($\sim d \times d$, $^3J_{H-C(3),H-C(4)} = 3.5$, $^4J_{H-C(3),H-C(5)} = 1.7$, 4 H, H–C(3,3'',3''')); 6.36 ($d \times d$, $^3J_{H-C(3),H-C(4)} = 3.5$, $^3J_{H-C(4),H-C(5)} = 3.0$, 4 H, H–C(4,4',4'',4''')); 7.72 ($d \times d$, $^3J_{H-C(4),H-C(5)} = 3.0$, $^4J_{H-C(3),H-C(5)} = 1.7$, H–C(5,5',5'',5''')). – ^{13}C-NMR. (d_6-DMSO): 55.85 (*t*, C(6)), 109.3 (*d*, C(3) or C(4)), 113.3 (*d*, C(4) or C(3)), 122.5 (*s*, C(2)), 123.2 (*d*, C(5)). – MS. ($C_{18}H_{16}N_4$; 288): 288 (M^+), *157*, 145, 132.

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