267. Syntheses and Cyclization Reactions of Bifunctional 1,2-Bis(styryl)benzenes and Some Aza Analogues

Macrocyclic Aza Compounds. V[1]).

by **Carl-Peter Ehrensperger, Manfred Heberlein** and **Peter Skrabal**

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich, CH-8092 Zürich

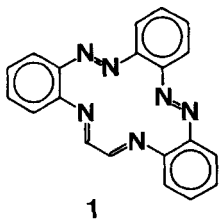
(3.X.78)

Summary

The syntheses of the bis(styryl)benzenes **4** and **5** and of the aza analogue **3** are described. Diamine **3** and dialdehyde **5** were cyclized to the 14-membered macrocycles **19** and **27**, respectively. Diamine **4** and glyoxal give the 28-membered macrocycle **28**. The cyclizations are discussed.

Introduction. – Our interest in macrocyclic aza compounds with annulene perimeters, such as **1**, has already been discussed [2]. The synthetic approach to **1**, namely cyclization of 1,2-bis(2-aminophenylazo)benzene (**2**) with glyoxal, was unsuccessful. We assumed that the low reactivity of the amino groups in **2** – due to the phenylenebisazo group [3] – and its instability were responsible for the failure of the cyclization and the observed rearrangement [1] [2]. To test this hypothesis and to extend our knowledge of such cyclizations we proposed to synthesize the carbon analogues of **2**, namely **3** and **4** which are expected to be more reactive, and the dialdehyde **5** *(Scheme 1)*.

Scheme 1



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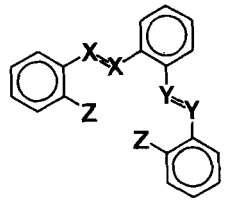
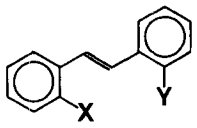


	2	3	4	5
X	N	CH	CH	CH
Y	N	N	CH	CH
Z	NH_2	NH_2	NH_2	CHO

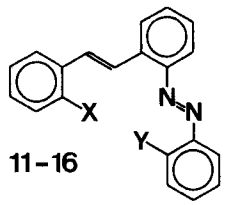
[1]) Part IV: [1].

Syntheses. – *2-Amino-2'-(2-aminophenylazo)stilbene* (**3**). In principle, the diamine **3** can be synthesized by introduction of a phenyleneazo group into a stilbene derivative or introduction of a styrylene group into an azobenzene derivative. The styrylene group, the *Wittig* (or *Wittig-Horner*) reaction and the anil synthesis, are limited by the position of the required substituents. Thus *o*-formyl- and *o*-halogenomethylazobenzenes cyclize to give indazole derivatives [4][2]), and the anil-synthesis is only successful with *p*-substituents [6]. For the former route the amine-nitroso condensation is the method of choice [7]. Therefore diamine **3** was synthesized according to *Scheme 2*, pathway (a). Selective reduction of 2,2'-dinitrostilbene (**6**) [8] with NaHS gave 2-amino-2'-nitrostilbene (**7**) (76%). 2-Acetylamino-2'-aminostilbene (**9**) was obtained *via* acetylation of **7** to **8**, followed by reduction. Condensation of **9** with 2-nitrosoacetanilide yielded 2-acetylamino-2'-(2-acetylaminophenylazo)stilbene (**11**) (58%) which finally on hydrolysis gave **3** (42%) in an overall yield of *ca.* 7% based on 2-nitrobenzyl chloride as starting material for **6**.

Scheme 2

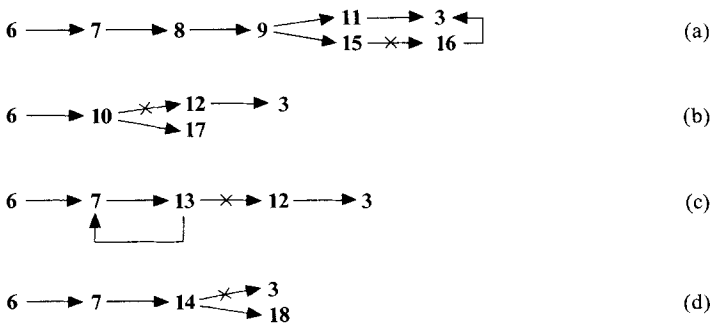


6–10



11–16

	6	7	8	9	10	11	12	13	14	15	16
X	NO_2	NH_2	NHAc	NHAc	NH_2	NHAc	NH_2	NO_2	NO_2	NHAc	NHAc
Y	NO_2	NO_2	NO_2	NH_2	NH_2	NHAc	NHAc	NHAc	NO_2	NO_2	NH_2



As indicated in the pathways b–d of *Scheme 2*, shorter routes to **3** appeared attractive[3]). The shortest route, condensation of diamine **10** [10] with 2-nitrosoacetanilide to give 2-(2-acetylaminophenylazo)-2'-aminostilbene (**12**) and hydrolysis to **3**, failed at the first stage (*Scheme 2*, pathway b). Besides unidentified by-products, *ca.* 40% of 2,2'-bis(acetylamino)azoxybenzene and *ca.* 15% of 2-acetylamino-2'-(2-indolyl)azobenzene (**17**, *Scheme 3*) were obtained. Formation of azoxybenzene

[2]) For this reason, the synthesis of 1,2-bis(2-formylphenylazo)benzene, the formyl analogue of **2**, has not yet been achieved [5].

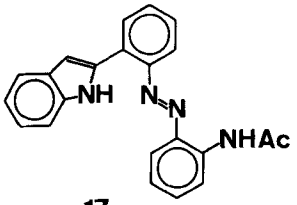
[3]) Details are found in [9].

derivatives is characteristic of nitroso-amine condensations and results from a redox reaction between the amine and the nitroso compound to give a hydroxylamine derivative which condenses with the nitroso compound [5] [11].

For an alternative route *via* **12** to **3** (*Scheme 2*, pathway c) the aminonitrostilbene **7** was condensed with 2-nitrosoacetanilide to give 2-(2-acetylaminophenylazo)-2′-nitrostilbene (**13**) (60%). However, for **13** the selective reduction of the nitro group with NaHS [12] which is normally used in the presence of an azo group failed to give **12**, *ca.* 70% of amine **7** was obtained instead.

Finally, in pathway d of *Scheme 2* another approach to **3** *via* 2-nitro-2′-(2-nitrophenylazo)stilbene (**14**), obtained from **7** and 2-nitrosonitrobenzene, is shown. Reduction of **14**, however, gave mainly the benzotriazole oxide derivative **18** *(Scheme 3)* which is characteristic for reduction of a nitro group in a position *ortho* to an azo group [13][4]). Similarly, the nitro group in **15** – obtained from **9** and 2-nitronitrosobenzene – could not be reduced selectively. Instead of **16**, 2-nitroaniline as well as **9** and **10** were obtained *(Scheme 2*, pathway (a)).

Scheme 3



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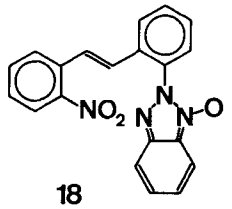

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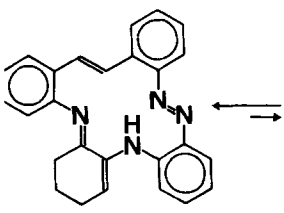
1,2-Bis(2-aminostyryl)benzene (**4**) *and 1,2-bis(2-formylstyryl)benzene* (**5**). Synthesis of **4** is achieved by *Wittig* reaction between 2-aminobenzaldehyde and the ylid from *o*-xylylene-bis(triphenylphosphoniumbromide) with lithium ethylate in ethanol (*ca.* 53%)[5]). *Wittig* reaction of phthalaldehyde with the ylid of *o*-xylylene-bis(triphenylphosphoniumbromide) under high dilution yielded besides polymers (*ca.* 50%) mainly dibenzocyclooctene (29%) and a mixture of *(Z),(E)* isomers of bis-aldehyde **5**. Pure *(E),(E)*-aldehyde was obtained after isomerization of the mixture in naphthalene (*ca.* 3%).

Cyclizations. – *Cyclization of diamine* **3**. Similarly to 1,2-bis(2-aminophenylazo)benzene (**2**) [2], the diamine **3** does not cyclize with glyoxal and derivatives, but decomposes [9]. Therefore 1,2-cyclohexanedione was chosen as an alternative

Scheme 4



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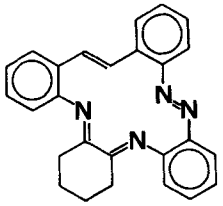

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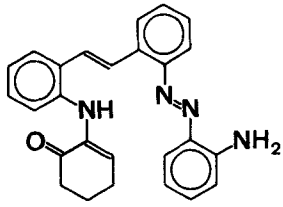

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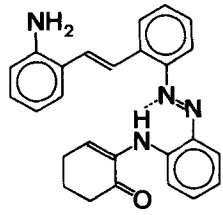

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[4]) However, in an alternative synthesis of diamine **2** the reduction of such nitro groups has been achieved [14].

[5]) The *Wittig* reaction of 2-acetylaminobenzaldehyde gave 1,2-bis(2-acetylaminostyryl)benzene in only *ca.* 15% yield [15].

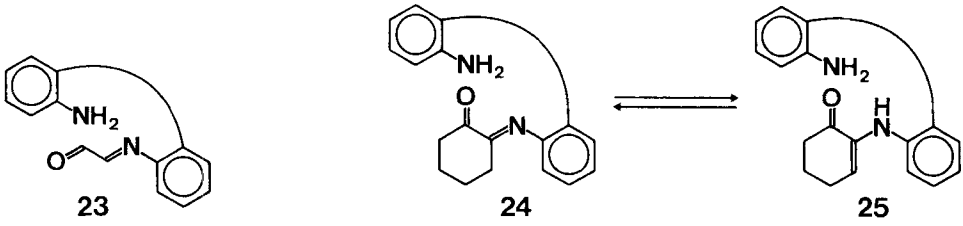
dicarbonyl compound. From its reaction with **3** in benzene with a catalytic amount of piperidine, 18,19,20,22-tetrahydrotetrabenzo[*c,f,i,m*]-1,2,5,8-tetraazacyclotetradecine (**19**) and 2-(2-aminophenylazo)-2′-(2-oxo-6-cyclohexenylamino)stilbene (**21**) were isolated by preparative TLC. (7 and 13% respectively).

For the macrocycle the ^{1}H-NMR. spectra in CS_2 (and C_6D_6) show only tautomer **19**. It exhibits one hydrogen-bonded proton (NH) at 10.18 ppm (10.80), exchangeable with D_2O, and the olefinic proton of the cyclohexenoneimine moiety appears as a triplet ($^3J_{CH-CH_2} = 5$ Hz) at 6.42 ppm (6.28). The distinction between structures **21** and **22** (including tautomers) for the 1:1 condensation product is based on the comparison of the ^{1}H-chemical shift (in $CDCl_3$) of the NH_2 protons (5.85 ppm) with those of the diamine **3** (3.80 and 5.80), 2,2′-diaminoazobenzene (5.50) [2] and the stilbenes **7** (3.67) and **9** (3.60). Thus the chemical shift of the NH_2 protons is characteristic of the position *ortho* to the azo group in **21**. Furthermore the compound is characterized by a strong IR. band at 1665 cm^{-1} ($CHCl_3$) typical of the cyclohexenone CO group, and medium absorptions at 3475 and 3380 cm^{-1} for NH-deformation vibrations.

A priori one would assume that **21** would be cyclized to **19** under the conditions described. However, it mainly decomposes. This observation throws some light on the cyclization pathway of diamine **3**. Cyclization of **3** does not occur by a simultaneous nucleophilic addition of both amino groups to cyclohexanedione. Therefore, because **21** does not cyclize to a significant extent, the 1:1 condensation product **22** is likely to be an intermediate in the cyclization pathway. Since the amino group *ortho* to the vinyl group is the more reactive one in diamine **3**, **21** is probably formed to a larger extent than **22**. On the other hand **22** – whenever formed – will cyclize more readily than **21**.

In the comparison of glyoxal with cyclohexanedione as cyclization reagents for diamine **3**, a point of interest concerns the accessibility of the trajectory for the nucleophilic addition to the carbonyl group [16] in the intermediates **23** and **24**. Molecular models demonstrate that in both **23** and **24** the amino group can

Scheme 5

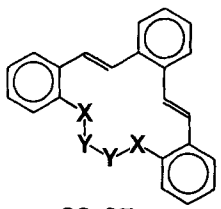


approach the carbonyl group in non-planar conformations. In **24**, however, there is considerable steric hindrance between the cyclohexanedione moiety and the benzene rings. Thus, not only from the point of view of reactivity, but also for steric reasons, cyclization should be favoured with glyoxal. Among numerous reasons to account for the opposite observation, the predominance of the hydrogen bonded conformation **22** in the tautomeric equilibrium **24** ⇄ **25** may be invoked.

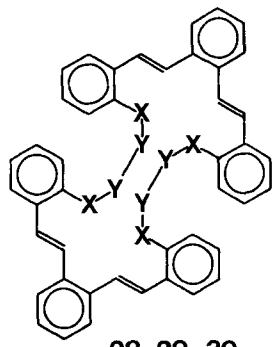
Cyclization of diamine **4**. From the reaction of equimolar amounts of **4** and monomeric glyoxal in toluene with a catalytic amount of acetic acid under high dilution a pale yellow compound was isolated (43%)[6]) which is not **26** (MS.) but a 2:2 condensation product **28**, the configuration of which is not yet known. The IR. spectrum (KBr) indicates by virtue of a strong band at 965 cm^{-1} and no absorption for a (*Z*) out-of-plane deformation vibration that the configuration of all C=C bonds is (*E*). Additional support for **28** stems from reduction to **29** in 46% yield with $LiAlH_4$.

The reaction mixture might contain (MS.) trace amounts of the 14-membered ring **26**, besides **28** and polymers, but the data are equivocal. The following observations suggest that the 28-membered macrocycle is formed by a thermodynamically controlled reaction [15]. Work-up of the reaction mixture immediately after mixing the reactants gave a quantitative yield of polymers. The macrocycle **28** is obtained only after stirring the reaction mixture for 24 h. Addition of *o*-phenylenediamine to the reaction mixture or to isolated **28** under the reaction conditions gives a quantitative yield of quinoxaline.

Scheme 6



26, 27



28, 29, 30

	26	**27**	**28**	**29**	**30**
X–Y	N=CH	CH=N	N=CH	NH–CH_2	CH=N

Cyclization of dialdehyde **5**. Condensation of dialdehyde **5** with *ca.* 10% excess hydrazine hydrate in acetic acid gave 82% of the 14-membered macrocycle **27**[7]). Only traces of the 2:2 reaction product **30** were indicated by mass spectroscopy of the reaction mixture.

Conclusion. – Cyclizations of diamine **3** with 1,2-cyclohexanedione and of **4** with glyoxal demonstrate the enhanced reactivity of **3** and **4** compared to 1,2-bis(2-aminophenylazo)benzene (**2**). Under the same conditions diamine **2** decomposes or rearranges, but can be cyclized with the more reactive oxalyl chloride [2]. Since glyoxal can polymerize or disproportionate, it is a suitable cyclization reagent only for the reactive diamine **4**.

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[6]) By TLC., the total yield of **28** is *ca.* 80%.

[7]) The bonding situation in the 14-membered macrocycle **27** and the properties of several other macrocycles such as **19** and those derived from diamine **2** [2] will be discussed in a forthcoming paper.

The cyclization results with diamine **4** – formation of the 28-membered macrocycle **28** as main product, but only traces of the 14-membered macrocycle **26** – and the opposite situation observed with dialdehyde **5** are likely to be the consequences of the thermodynamically and kinetically controlled reactions of diamine **4** and dialdehyde **5**, respectively. Contrary to azomethine bonds the azine bonds in **27** are stable under the reaction conditions.

We thank Prof. *H. Zollinger* for his continued encouragement.

Experimental Part

General. – Equipment for instrumental analysis and materials for chromatography have been described [2]. Chemicals and solvents of highest available purity grade were purchased from *Fluka AG*, Buchs. In some cases coated silica gel was used for plates and columns: silica gel plates (60 F254) or silica gel 60 F254 (0.063–0.200 mm, *Merck AG*, Darmstadt) were treated for 10–15 sec with a saturated (12 h, RT.) methanolic solution of K_2CO_3 and then dried for 12 h at 120°. For preparative TLC., a suspension of 55 g silica gel (60 F254 G) with or without 1 g K_2CO_3 in 135 ml H_2O was shaken for *ca.* 1 min, then put onto 2 plates (20×20 cm). The plates were dried for 12 h at RT. and then for 12 h at 120° (layer thickness *ca.* 2 mm).

2-Amino-2'-(2-aminophenylazo)stilbene (**3**). – *2,2'-Dinitrostilbene* (**6**) was obtained by a modified procedure [8]: 500 mg (2.92 mmol) *o*-nitrobenzyl chloride and 495 mg (8.84 mmol) KOH were dissolved by warming in 2 and 6 ml C_2H_5OH, respectively. The solutions were cooled to RT., when the KOH solution was added dropwise to the *o*-nitrobenzylchloride. After 3 h the crystalline precipitate was collected, washed with 90% C_2H_5OH until the filtrate was colourless and with hot water until a chloride test was negative. Recrystallization from 1-chloro-2,3-epoxypropane gave 161 mg (41%) **6**, m.p. 197.5–198° ([8]: 196°).

2-Amino-2'-nitrostilbene (**7**). To a suspension of 200 mg (0.74 mmol) **6** in 25 ml C_2H_5OH, heated under reflux with stirring, were added 280 mg (3.78 mmol) $NaHS \cdot H_2O$ dissolved in a small amount of H_2O. The yellow suspension turned greenish and then red-brown. Refluxing was continued for a further 10 min and the solution filtered. The residue was washed with $CHCl_3$, and the filtrate was diluted with 200 ml H_2O and extracted with $CHCl_3$ until the organic layer remained colourless. The combined $CHCl_3$ layers were washed with H_2O and dried (Na_2SO_4). After concentration and preparative TLC. (2 plates, $CHCl_3$) the orange (main) band was eluted with $CHCl_3$ to give 137 mg (77%) **7**, m.p. 105–105.5° (from C_2H_5OH). – UV./VIS. (C_6H_6): 293 (10,800), 370 (6650). – IR. ($CHCl_3$): 3470*m*, 3390*m*, 3070*w*, 3010*w*, 2870*w*, 1620*s*, 1570*s*, 1510*m*, 1490*s*, 1455*s*, 1345*s*, 1305*s*, 1265*s*, 1165*m*, 1145*m*, 965*s*, 870*m*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.67 (*s*, 2 H, NH_2); ~6.5–7.9 (*m*, 10 H, ar. H and CH=CH). – MS. (100°): 240 (M^+, 61), 223 (45), 206 (18), 195 (19), 194 (28), 193 (21), 180 (17), 166 (32), 121 (35), 120 (24), 106 (35), 93 (100), 92 (30), 79 (34), 77 (72), 76 (21), 63 (18), 52 (58), 51 (61), 50 (38), 39 (38).

$C_{14}H_{12}N_2O_2$ (240.1) Calc. C 69.97 H 5.04 N 11.67% Found C 69.96 H 5.19 N 11.71%

2-Acetylamino-2'-nitrostilbene (**8**). A solution of 366 mg (1.52 mmol) **7** in 17 ml (180 mmol) acetic anhydride was stirred for 3 h at RT. The reaction mixture was poured onto ice and the precipitate collected, washed with H_2O and dried *in vacuo* to give 382 mg (89%) **8**, m.p. 189.5–190° (from $CHCl_3$). – UV./VIS. (C_6H_6): 350 (shoulder, 3350). – IR. (KBr): 3260*s*, 1645*s*, 1600*w*, 1560*w*, 1510*s*, 1480*w*, 1450*m*, 1370*w*, 1350*m*, 1300*m*, 1260*w*, 960*m*, 750*m*. – MS. (260°): 282 (M^+, 25), 223 (21), 194 (14), 165 (20), 163 (14), 162 (25), 147 (33), 121 (27), 120 (58), 119 (24), 106 (25), 104 (14), 93 (100), 92 (38), 91 (12), 90 (12), 89 (14), 77 (16), 65 (12), 43 (46).

$C_{16}H_{14}N_2O_3$ (282.1) Calc. C 68.06 H 5.00 N 9.93% Found C 67.21 H 5.07 N 9.80%

2-Acetylamino-2'-aminostilbene (**9**). To 200 mg (0.71 mmol) **8** in 60 ml C_2H_5OH under reflux, 6.30 g (85.1 mmol) $NaHS \cdot H_2O$ in a small volume of H_2O were added and the mixture was heated for 60 min under reflux. The resulting suspension was filtered and the residue washed with $CHCl_3$.

The filtrate was diluted with H_2O and extracted with $CHCl_3$ until the organic layer showed only weak fluorescence. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated to give 167 mg (93.2%) crude **9**, m.p. 149.5–150.5° (from $CHCl_3$). – UV./VIS. (C_6H_6): 346 (8320). – IR. ($CHCl_3$): 3430*m*, 3380*m*, 3000*w*, 1680*s*, 1620*m*, 1580*m*, 1495*m*, 1445*m*, 1375*m*, 1300*m*, 975*m*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 2.14 (*s*, 3 H, $COCH_3$); 3.60 (*s*, 2 H, NH_2); ~6.6–8.0 (*m*, 11 H, ar. H and NH). – MS.: 252 (M^+, 55), 234 (16), 223 (18), 219 (37), 210 (24), 209 (100), 208 (24), 196 (15), 195 (61), 194 (99), 165 (18), 118 (28), 117 (30), 93 (26), 89 (17), 83 (16), 55 (15), 45 (50), 44 (15), 43 (30), 41 (22).

2-Acetylamino-2'-(2-acetylaminophenylazo)stilbene (**11**). To a stirred solution of 426 mg (1.69 mmol) **9** in 11 ml CH_3CO_2H were added 426 mg (2.60 mmol) *o*-nitrosoacetanilide [17] at RT. The reaction was followed by TLC. ($CHCl_3/CH_3OH$ 99:1). After complete reaction of **9** the mixture was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with $CHCl_3$. The dried extracts (Na_2SO_4) were concentrated and chromatographed (53×3.5 cm, 200 g SiO_2, $CHCl_3$). Rechromatography of the orange (main) fraction on silica gel plates (PF254, *Merck AG;* $CHCl_3/CH_3OH$ 99:1) yielded 393 mg (58.4%) **11**, m.p. 209–210° (from C_2H_5OH). – UV./VIS. (C_6H_6): 302 (19,300), 394 (7800). – IR. ($CHCl_3$): 3430*m*, 3400*m*, 2930*m*, 2860*w*, 1680*s*, 1590*s*, 1500*s*, 1440*s*, 1370*w*, 1300*s*, 1150*m*, 1000*w*, 970*m*. – ^{1}H-NMR. (D_6-DMSO): 2.07 (*s*, 3 H, $COCH_3$); 2.18 (*s*, 3 H, $COCH_3$); 7.16–8.05 (*m*, 12 H, ar. H and CH=); 8.14 (*d*, $^3J_{CH=CH}$ = 16, 1 H, CH=); 8.27 (*qa*, 1 H, ar. H); 9.69 (*s*, 1 H, NH); 10.08 (*s*, 1 H, NH). – MS.: 398 (M^+, 100), 381 (18), 380 (33), 365 (15), 356 (27), 355 (22), 313 (31), 220 (32), 210 (15), 209 (26), 208 (84), 207 (59), 206 (37), 205 (18), 194 (17), 193 (21), 180 (17), 179 (27), 165 (30), 146 (28), 128 (24), 108 (15), 107 (37), 92 (15), 65 (29), 43 (76).

$C_{24}H_{22}N_4O_2$ (398.2) Calc. C 72.33 H 5.57 N 14.07% Found C 72.02 H 5.61 N 13.88%

Diamine **3**. A solution of 800 mg (2.01 mmol) **11** in 88 ml C_2H_5OH under reflux were mixed with 31.7 g (565 mmol) KOH in 50 ml H_2O. Heating was continued and the course of the reaction was followed by TLC. ($CHCl_3/CH_3OH$ 99:1). After the hydrolysis was complete the solution was poured onto a crushed ice/K_2CO_3 mixture, the red precipitate was collected, washed with H_2O and dried to give 295 mg (46.7%) **3**, m.p. 150–151° (from C_2H_5OH). – UV./VIS. (C_6H_6): 297 (16,000), 350 (shoulder, 12,300), 430 (shoulder, 5800). – IR. ($CHCl_3$): 3470*m*, 3390*m*, 3300*w*, 3060*w*, 2990*w*, 2930*w*, 2860*w*, 1610*s*, 1575*m*, 1485*s*, 1455*m*, 1405*m*, 1320*s*, 1160*s*, 975*m*. – ^{1}H-NMR. ($CDCl_3$): 3.85 (*s*, 2 H, NH_2); 5.84 (*s*, 2 H, NH_2); 6.71–7.94 (*m*, 14 H, ar. H and CH=CH). – MS. (120°): 314 (M^+, 7), 209 (24), 208 (100), 207 (13), 193 (12), 180 (7), 165 (14), 107 (29), 106 (7), 92 (24), 90 (7), 80 (8), 66 (7), 65 (43), 52 (8), 51 (7), 39 (13).

$C_{20}H_{18}N_4$ (314.2) Calc. C 76.38 H 5.77 N 17.83% Found C 76.36 H 5.80 N 17.64%

1,2-Bis(2-aminostyryl)benzene (**4**). – To a suspension of 2.79 g (23.1 mmol) *o*-aminobenzaldehyde and 7.88 g (10.0 mmol) *o*-xylylenebis(triphenylphosphoniumbromide) [18] in 50 ml dry C_2H_5OH under N_2, 170 ml of a 0.2M solution of C_2H_5OLi in dry C_2H_5OH (34.0 mmol) were added. The mixture was stirred for 1 h at RT., filtered from undissolved material and the filtrate diluted with 200 ml H_2O. After stirring for 15 min the crystalline precipitate was collected, washed with 60% C_2H_5OH and dried to give 1.66 g (53.2%) pure **4**, yellow prisms, m.p. 175–176°. – UV./VIS. (C_2H_5OH): 279 (22,500), 349 (17,500). – IR. (KBr): 3450*w*, 3410*m*, 3340*m*, 3200*w*, 3030*m*, 1615*s*, 1580*m*, 1495*s*, 1330*m*, 1310*m*, 1270*s*, 1175*w*, 1050*w*, 970*s*, 755*s*. – ^{1}H-NMR. ($CDCl_3$): 3.78 (*s*, 4 H, 2 NH_2); 6.64–7.62 (*m*, 16 H, ar. H and 2 CH=CH). – MS. (90°): 312 (M^+, 43), 219 (25), 218 (23), 207 (26), 206 (43), 106 (100).

$C_{22}H_{20}N_2$ (312,2) Calc. C 84.57 H 6.46 N 8.97% Found C 84.90 H 6.70 N 8.84%

1,2-Bis(2-formylstyryl)benzene (**5**). – 3.09 g (23.1 mmol) Phthalaldehyde and 7.88 g (10.0 mmol) *o*-xylylenebis(triphenylphosphoniumbromide) [18] were dissolved in 100 ml dry C_2H_5OH under N_2. Over a period of 4 h with stirring, a solution of C_2H_5OLi (60 ml, 0.4M, 24.0 mmol) in dry C_2H_5OH was gradually added from a *Hershberg* funnel so that after each addition the yellow colour of the ylid disappeared again. The solution was then diluted with 150 ml H_2O, stirred for a few more min and extracted with $CHCl_3$. The extracts were evaporated and the residue dissolved in toluene. After evaporation of *ca.* 50% of the solvent, crystalline triphenylphosphine oxide was filtered off, the filtrate was evaporated and the residue chromatographed [300 g SiO_2, ether/petroleum ether (60–90°)

1:1]. The first few fractions gave 590 mg (28.9%) dibenzocyclooctene (m.p., IR. and MS.) [19]. The following greenish-yellow fluorescent fractions gave 1.03 g of an oily mixture which was rechromatographed [600 g SiO_2, $CHCl_3$/petroleum ether (60–90°)/ether 4:5:1] into 5 components of which the 2 with the smallest Rf values on TLC. ($CHCl_3$) gave 260 mg (7.7%) of a crude dialdehyde mixture. This was isomerized over a period of 5 h at 210° in naphthalene and rechromatographed [300 g SiO_2, $CHCl_3$/petroleum ether (60–90°)/ether 4:5:1] to give 115 mg (3.4%) pure (*E*),(*E*)-dialdehyde **5**, m.p. 114–116°. – UV./VIS. (DMF): 257 (31,000), 293 (shoulder, 18,000), 340 (16,000). – IR. (KBr): 3070*w*, 3030*w*, 2940*w*, 2860*w*, 2750*w*, 1695*s*, 1600*m*, 1580*m*, 1480*m*, 1290*w*, 1190*w*, 965*m*, 870*w*, 760*s*, 660*w*. – ^{1}H-NMR. ($CDCl_3$): 7.20–8.00 (*m*, 16 H, ar. H and 2 CH=CH); 10.26 (*s*, 2 H, 2 CHO). – MS. (91°): 338 (M^+, 8), 320 (100), 303 (61), 291 (66), 219 (56), 202 (27), 191 (36), 178 (28), 165 (23), 118 (20), 77 (21).

$C_{24}H_{18}O_2$ (338.1) Calc. C 85.17 H 5.37 O 9.46% Found C 85.15 H 5.43 O 9.51%

2,2′-Diaminostilbene (10) was obtained from **6** [10] (75%), m.p. 174–174.5° ([8]: 176°).

2-(2-Acetylaminophenylazo)-2′-nitrostilbene (13). – A solution of 47 mg (0.20 mmol) **7** and 44 mg (0.27 mmol) *o*-nitrosoacetanilide [17] in 1.1 ml $CHCl_3$ and 0.15 ml CH_3CO_2H was heated under reflux for 6 h. After dilution with $CHCl_3$ the solution was extracted with aqueous $NaHCO_3$ and H_2O and dried (Na_2SO_4). After evaporation of the solvent the residue was chromatographed on one plate (60 F254 G, C_6H_6). The orange (main) band was eluted with $CHCl_3$ to give 36 mg (46.6%) **13**, m.p. 176–177° (from C_2H_5OH). – IR. ($CHCl_3$): 3400*w*, 2940*w*, 1690*s*, 1595*s*, 1510*m*, 1485*w*, 1445*w*, 1350*m*, 1315*m*, 1305*m*, 1160*w*, 970*w*. – ^{1}H-NMR. ($CDCl_3$): 2.18 (*s*, 3 H, $COCH_3$); 7.07–8.00 (*m*, 12 H, ar. H and CH=); 8.05 (*d*, $^3J_{CH=CH}$ = 16, 1 H, CH=); 8.65 (*qa*, 1 H, ar. H); 9.66 (*s*, 1 H, NH). – MS. (310°): 386 (M^+, 9), 369 (22), 327 (73), 281 (23), 238 (32), 236 (37), 225 (28), 220 (35), 210 (78), 209 (40), 208 (61), 207 (29), 181 (31), 180 (23), 179 (35), 178 (23), 165 (39), 134 (39), 120 (44), 108 (29), 107 (65), 93 (41), 92 (43), 77 (43), 65 (80), 63 (23), 43 (100), 39 (26).

$C_{22}H_{18}N_4O_3$ (386.2) Calc. C 68.36 H 4.70 N 14.51% Found C 67.96 H 4.64 N 14.44%

2-Nitro-2′-(2-nitrophenylazo)stilbene (14). – A solution of 200 mg (0.83 mmol) **7** and 126 mg (0.83 mmol) *o*-nitronitrosobenzene [20] in 5.4 ml CH_3CO_2H was stirred at 40° for 3 h. The mixture was cooled to 10° and the precipitated **14** was collected and washed with H_2O. From the filtrate after dilution with H_2O additional **14** could be extracted with $CHCl_3$ to give a total yield of 288 mg (92.7%), m.p. 139.5° (from C_6H_6). – IR. ($CHCl_3$): 2980*w*, 1585*m*, 1555*m*, 1500*s*, 1460*m*, 1335*s*, 1295*w*, 1275*w*, 1145*w*, 955*m*. – MS. (80°): 374 (M^+, 5), 357 (60), 310 (45), 281 (59), 223 (42), 222 (100), 207 (41), 195 (42), 194 (41), 178 (33), 167 (39), 166 (42), 165 (81), 152 (41), 151 (32), 93 (36), 92 (46), 91 (61), 89 (30), 77 (67), 76 (34), 73 (52), 71 (30), 69 (33), 65 (41), 63 (36), 57 (69), 55 (54), 51 (43), 44 (38), 42 (39), 41 (74), 39 (57).

$C_{20}H_{14}N_4O_4$ (374.1) Calc. C 64.15 H 3.77 N 14.98% Found C 64.18 H 3.96 N 14.91%

2-Acetylamino-2′-(2-nitrophenylazo)stilbene (15). – A solution of 100 mg (0.40 mmol) **9** and 100 mg (0.66 mmol) *o*-nitronitrosobenzene [20] in 5 ml $CHCl_3$ and 5 ml CH_3CO_2H was stirred for 6 h at RT., diluted with $CHCl_3$, extracted with aqueous $NaHCO_3$ and H_2O and dried (Na_2SO_4). After evaporation the residue was chromatographed on 2 plates (60 F254 G, $CHCl_3$/CH_3OH 99:1) and the orange (main) band was eluted with $CHCl_3$ to give 80 mg (52.2%) of **15**, m.p. 179–180° (from CH_3OH). – IR. ($CHCl_3$): 3430*m*, 3380*w*, 3070*w*, 3000*w*, 1680*s*, 1590*m*, 1580*m*, 1500*s*, 1480*s*, 1445*s*, 1370*s*, 1350*s*, 1300*s*, 1155*m*, 970*m*. – ^{1}H-NMR. (60 MHz, D_6-DMSO): 2.12 (*s*, 3 H, $COCH_3$); 7.25–8.33 (*m*, 14 H, ar. H and CH=CH); 9.78 (*s*, 1 H, NH). – MS. (120°): 386 (M^+, 50), 311 (30), 310 (20), 309 (19), 208 (32), 207 (100), 206 (42), 205 (21), 165 (17), 77 (15), 43 (71).

18,19,20,22-Tetrahydrotetrabenzo[*c,f,i,m*]-1,2,5,8-tetraazacyclotetradecine (19) and 2-(2-aminophenylazo)-2′-(2-oxo-6-cyclohexenylamino)stilbene (21). – A solution of 100 mg (0.32 mmol) diamine **3** in 4.8 ml warm C_6H_6 was cooled to 40° and 50 µl piperidine and 535 mg (4.77 mmol) 1,2-cyclohexanedione were added. The mixture was stirred at 40° and the reaction followed by TLC. (coated plates, $CHCl_3$). After complete reaction of **3** (*ca.* 30 h) the solution was decanted from undissolved cyclohexanedione which was extracted with benzene. The combined C_6H_6 layers were evaporated and

the residue chromatographed on 2 plates (coated silica gel 60 F254 G, $CHCl_3$). The cyclotetradecine **19** (red, uppermost band) and the stilbene **21** (orange, second band from top) were eluted with C_6H_6 and **19** recrystallized from C_6H_6. Compound **21** was rechromatographed on 1 plate (coated silica gel 60 F254 G, $CHCl_3$), but could not be crystallized.

19: yield 9 mg (7.2%), m.p. 232.5–233.5°. – UV./VIS. (C_6H_6): 325 (shoulder, 13,900), 460 (3300). – IR. (KBr): 3040*w*, 2920*w*, 1600*s*, 1560*s*, 1510*s*, 1470*m*, 1445*m*, 1380*m*, 1340*m*, 1320*s*, 1235*m*, 1210*m*, 1155*m*, 1145*m*, 1105*m*, 965*m*, 765*m*, 745*s*. – ^{1}H-NMR. (CS_2): 1.87 (*qa*, 2 H, alicycl. H); 2.35–2.64 (*m*, 4 H, alicycl. H); 6.42 (*t*, $^3J = 5$, 1 H, olef. H); 6.59–7.97 (*m*, 13 H, ar. H and CH=); 8.22 (*d*, $^3J = 17$, 1 H, CH=); 10.18 (*s*, 1 H, NH). – MS. (103°): 390 (M^+, 100), 389 (31), 362 (11), 361 (12), 297 (12), 296 (12), 272 (13), 271 (15), 246 (11), 208 (14), 195 (12), 183 (23), 182 (16), 181 (11), 180 (10).

$C_{26}H_{22}N_4$ (390.2) Calc. C 79.96 H 5.68 N 14.36% Found C 79.89 H 5.70 N 14.15%

21: yield 17 mg (13.0%). – UV./VIS. (C_6H_6): 305 (16,200), 325 (shoulder, 14,450), 428 (shoulder, 5500). – IR. ($CHCl_3$): 3475*m*, 3380*m*, 2940*m*, 2840*w*, 1665*s*, 1630*m*, 1610*s*, 1595*m*, 1570*m*, 1480*m*, 1450*m*, 1410*w*, 1340*m*, 1300*m*, 1160*m*, 1130*m*, 975*m*. – ^{1}H-NMR. (CS_2): 2.01 (*qa*, 2 H, alicycl. H); 2.30–2.56 (*m*, 4 H, alicycl. H); 5.85 (*s*, 2 H, NH_2); 5.91 (*t*, $^3J = 5$, 1 H, olef. H); 6.22 (*s*, 1 H, NH); 6.59–7.78 (*m*, 13 H, ar. H and CH=); 7.83 (*d*, $^3J = 17$, 1 H, CH=). – MS. (100°): 408 (M^+, 5), 210 (81), 209 (97), 208 (92), 205 (57), 184 (54), 119 (100), 102 (54), 97 (68), 93 (54), 85 (54), 83 (92).

Tribenzo[*c,g,k*]-1,2-diazacyclotetradecine (27). – To a solution of 50 mg (0.15 mmol) **5** in 3 ml acetic acid 0.4 ml of a freshly prepared 0.41M solution of hydrazine hydrate (0.17 mmol) in acetic acid were added. After a few min a precipitate was observed. The mixture was stirred at RT. for 12 h. The precipitate was collected, washed with H_2O and recrystallized from dimethylformamide (DMF) to give 41 mg (82%) of **27**, m.p. 280°. – UV./VIS. (DMF): 284 (38,500), 350 (shoulder, 20,000). – IR. (KBr): 3070*m*, 3030*m*, 1620*s*, 1490*m*, 960*s*, 760*s*. – ^{1}H-NMR. ($CDCl_3$): 7.00–7.85 (*m*, 16 H, ar. H and 2 CH=CH); 8.92 (*s*, 2 H, 2 CH=N). – MS. (145°): 334 (M^+, 36), 318 (100), 304 (30), 289 (14), 230 (16), 217 (52), 205 (15), 130 (95), 117 (25), 103 (26), 76 (49), 51 (28).

$C_{24}H_{18}N_2$ (334.2) Calc. C 86.19 H 5.43 N 8.38% Found C 85.24 H 5.77 N 8.26%

Hexabenzo[*b,f,j,p,t,x*]-1,4,15,18-tetraazacyclooctacosine (28). – In 500 ml toluene and 1 ml acetic acid were added simultaneously within 5 min under vigorous stirring, a solution of 936 mg (3.0 mmol) **4** in 250 ml toluene and a solution of 250 ml of 13.2 mmolar glyoxal in toluene (3.3 mmol). The reaction mixture was stirred for 24 h at RT., then filtered and the filtrate evaporated. The oily residue was dissolved in 20 ml THF and stirred for 24 h. A crystalline precipitate was collected, washed with THF and ether, and dried to give 433 mg (43%) **28**, m.p. 281–282° (from DMF). – UV./VIS. (dioxane): 287 (80,500), 377 (shoulder, 35,500). – IR. (KBr): 3060*m*, 3020*m*, 2950*w*, 2870*w*, 1605*s*, 1590*w*, 1480*s*, 1450*m*, 1300*w*, 1205*w*, 1170*w*, 1100*w*, 965*s*, 940*w*, 755*s*. – ^{1}H-NMR. (dioxane-D_8): 6.63–6.74 (*m*, 3 H); 7.11–7.64 (*m*, 28 H): 7.80–7.91 (*m*, 3 H); 8.18 (*s*, 2 H, CH=N). – MS. (145°): 668 (M^+, 61), 345 (20), 333 (52), 319 (26), 230 (50), 217 (100), 204 (20), 130 (56), 117 (48), 106 (31), 73 (22).

$C_{48}H_{36}N_4$ (668.3) Cal. C 86.19 H 5.43 N 8.38% Found C 85.99 H 5.65 N 8.02%

5,6,7,8,25,26,27,28-Octahydrohexabenzo[*b,f,j,p,t,x*]-1,4,15,18-tetraazacyclooctacosine (29). – A suspension of 400 mg (0.60 mmol) **28** and 1.00 g (26.4 mmol) $LiAlH_4$ in 60 ml dry THF were boiled under reflux for 18 h. The reaction mixture was cooled to RT., 5 ml C_2H_5OH were added dropwise, followed by 50 ml ether and 50 ml aqueous KOH (10%). After intensive stirring of the mixture for 30 min, the organic layer was separated and extracted with H_2O. The volume decrease of the organic layer was compensated by addition of ether. During extraction greenish yellow **29** crystallized in the ether layer and was separated by filtration (185 mg, 45.6%), m.p. 250° (from DMF). – IR. (KBr): 3380*s*, 3000*w*, 2930*w*, 2860*w*, 1590*m*, 1570*m*, 1500*s*, 1450*m*, 1330*m*, 1260*m*, 1170*w*, 1140*w*, 970*s*, 750*s*. – ^{1}H-NMR. (D_7-DMF): 3.54 (*s*, 8 H, 4 CH_2); 5.52 (*s*, 4 H, 4 NH); 6.50–7.55 (*m*, 32 H, ar. H and 4 CH=CH). – MS. (125°): 676 (M^+, 30), 351 (15), 339 (32), 326 (15), 232 (27), 218 (50), 130 (28), 118 (100), 106 (46), 91 (30).

$C_{48}H_{44}N_4$ (676.4) Calc. C 85.16 H 6.56 N 8.28% Found C 85.00 H 6.56 N 8.16%

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