309. Aspects of Cyclization Reactions of 2,2'-Diaminoazobenzene and 1,2-Bis(2-aminophenylazo)benzene Macrocyclic Aza Compounds, II[1])

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(4. IX. 76)

Summary. Cyclization of diamine **5** with phthalaldehyde and of diamine **6** with glyoxal results in formation of the macrocyclic amino alcohol **8** and the rearrangement product **16**, respectively. The properties and stability of **8** and the reactions of **6** with other bifunctional molecules are discussed.

1. Introduction. – The stability of azo compounds increases with increasing inductive and mesomeric interactions of the azo group with its substituents [2]. Thus in contrast to azomethane azobenzene is resonance stabilized. An additional stabilization resulting from coordination of one of the nitrogen atoms to a metal ion is found in metal complexes of azobenzene derivatives. They are chemically as well as photochemically more stable than their metal-free counterparts [3]. Incorporation of the azo group into *benzenoid* π-electron systems also leads to an additional stabilization, *e.g.* in pyridazine, cinnoline and benzo[*c*]cinnoline. Benzo[*c*]cinnoline may be regarded as bridged, planar *cis*-azobenzene, however, it can be classified either as a benzenoid 14-π-electron system or a *cis*-azobenzene derivative depending on the criteria applied to determine its nature[2]).

2. Problem. – Bearing this in mind, we asked ourselves to what extent the properties of azobenzene and oligo-azobenzenes are changed on incorporation into *macrocyclic* rings with $(4n + 2)$- and $(4n)$-perimeters. The macrocycles **1** and **2** were chosen as the first representatives[3]) of these types of compounds. They were of interest to us as potential new chromophores and as ligands for metal complexes[4]).

Formally **1** and **2** may be regarded as benzoannelated derivatives of the hypothetical tetraaza[12]annulene **3** and the hexaaza[14]annulene **4**, respectively. These belong to the class of π-equivalent heteroannulenes which is virtually unknown and is of interest to the theoretical

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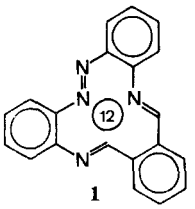
1) Part I: Preliminary Communication, see [1].

2) Among the criteria employed are the nature of the electronic spectrum [4] and a comparison of the pK_a value [5] with those of pyridazine [6] and of azobenzene [7]. See also [3], p. 336.

3) For a related cyclic trisazonaphthalene see Part III: following paper.

4) In recent years metal complexes with planar tri- and tetradentate macrocyclic ligands have been studied extensively. To our knowledge, however, π-equivalent ligands have never been isolated. For references see [8] [9].

chemist[5]). Recent studies have demonstrated that the number of annelated benzenoid π-systems necessary to quench the ring current of the parent annulene is small (1–3) and depends on structural features of the perimeter[6]). In addition to this, in π-equivalent azaannulenes such as **1** and **2** the sp^2-nitrogen atoms are delocalization barriers because of their higher electronegativity compared to carbon. For these reasons **1** and **2** are expected to be atropic macrocycles.



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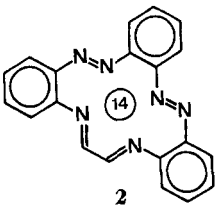

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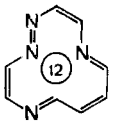

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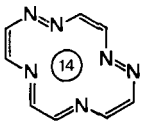

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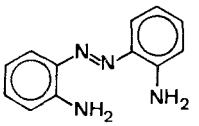
3. Syntheses. – In the syntheses of **1** and **2** we thought it important to introduce the C=N bonds in the last cyclization step because of their instability towards hydrolysis. Thus 2,2′-diaminoazobenzene (**5**) und 1,2-bis(2-aminophenylazo)benzene (**6**) seemed appropriate intermediates for cyclization with phthalaldehyde and glyoxal, respectively.



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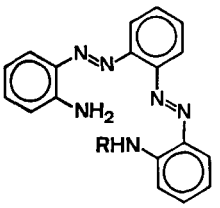
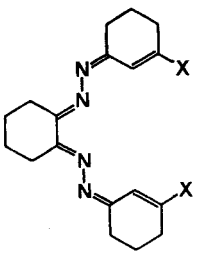


6 (R = H)
7 (R = CH_3CO)

Tribenzo[b,f,j]-*1,4,5,8-tetraaza-cyclododeca-2,4,6,8,10,12-hexaene* (**1**). Since 2,2′-diaminoazobenzene (**5**) is known [12], the synthesis of **1** was a straight forward cyclization of **5** with phthalaldehyde under high dilution.

Tribenzo[c,g,m]-*1,2,5,6,9,12-hexaaza-cyclotetradeca-1,3,5,7,9,11,13-heptaene* (**2**). *o*-Substituted oligo-azobenzenes have been synthesized by the condensation of

5) We have been able to synthesize intermediates such as *i*, but cyclization reactions failed to give any macrocycles in detectable amounts [10].



i (X = *e.g.* OH, OTs, Cl)

6) For recent reviews see [11] and references therein.

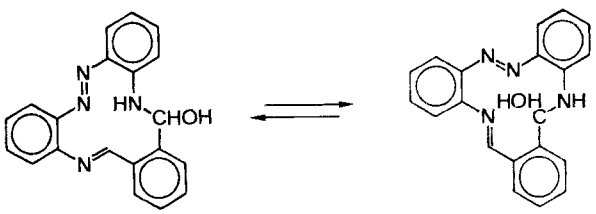
nitrosobenzenes with anilines [13]. Thus diamine **5** was condensed with 2-nitrosoacetanilide to give the bisazobenzene **7** which in turn was hydrolysed to give **6** with an overall yield of *ca.* 10% based on *o*-phenylenediamine as starting material for **5**. Cyclization of **6** with glyoxal was carried out under high dilution.

5 ⟶ **7** ⟶ **6**

4. Results and Discussion. – *The hydroxyamine derivative of* **1**. Condensation of diamine **5** with an equivalent amount of phthalaldehyde resulted in formation of a complex mixture of unstable, orange-red products and polymers. The main component was isolated by preparative TLC. in a yield of 30%. Because of partial decomposition during recrystallization the product was subjected to instrumental analysis directly after chromatography.

An ion at *m/e* 310.124 in the mass spectrum indicated the elementary composition $C_{20}H_{14}N_4$ expected for the macrocycle **1**. IR. and ^{1}H-NMR. spectrum, however, clearly demonstrated that the amino alcohol **8** had been isolated (see Table 1). From structure **8** the instability of the macrocycle can be deduced and also the fact that in the mass spectrum the M^+-H_2O ion is observed instead of the molecular ion. Because of the instability of **8** preparative dehydration attempts failed. Nevertheless, treatment with acid shows **8** to be in an acid-base equilibrium with what we believe to be the immonium ion **9**[7]). This cation is just stable enough for spectrophotometrical evaluation of the pK – analogous to the pK_R^+ of tropylium ions [15] – of the equilibrium. This turns out to be 5.6 in CH_3OH/H_2O 4:1. The reversibility of the equilibrium can be shown by immediate, careful neutralisation. Attempts to deprotonate **9** with various bases (*e.g.* tertiary amines) failed because of decomposition.

From the spectroscopic data available for this equilibrium (including a ^{1}H-NMR. investigation [14]) we can not completely exclude a reversible ring opening. However, since amino alcohol formation is a reversible reaction we believe that **8** is, in the end, ring opened again and reacts to thermodynamically more stable polymers.



8a **8b**

Table 1. *IR.* (*KBr*)[a]) *and* ^{1}*H-NMR.* (*CDCl*$_3$)[b]) *data of* **8**

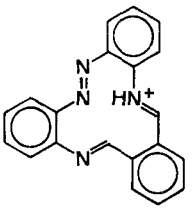
δ_{CHOH}	$\delta_{OH,\ NH}$	$\nu_{NH,\ OH}$
4.90	5.75, 6.10	3300, 3390, 3470

a) In cm^{-1}.
b) In ppm, relative to internal TMS.

7) The ion **9** represents only one possible mesomeric structure for one conformer. The position of the absorption band at 468 nm indicates that a tautomeric equilibrium with an azonium ion can be neglected [14].

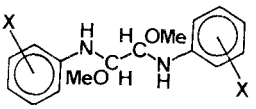
Table 2. *UV./VIS. data (C_6H_6) of* **5** *and* **8**

	λ_{max} (ε)
5	316 (10.370), 329 (sh, 7650), 420 (sh, 8850), 448 (10.050), 468 (10.120)
8	316 (9650), 432 (6370), 470 (sh, 4920)



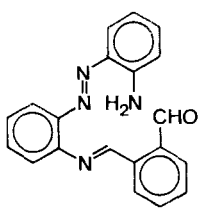
9 + $2H_2O \rightleftarrows$ **8a** + H_3O^+

Amino alcohols are known to be unstable intermediates [16]. It has been demonstrated, however, that electron attracting substituents in the aniline moiety [17], metal complex formation [18] and electron attracting aza nitrogen atoms in heterocyclic π-electron systems [19] in conjunction with mesomeric stabilizations can lead to stabilization of amino alcohols or amino ethers which may even be isolated. We have found that the reactions of *o*- and *p*-nitroaniline and 2-aminoazobenzene with glyoxal in methanol produce isolable amino ethers **10** [20]. We therefore conclude that the phenyleneazo group, acting as an electron acceptor, could be responsible for the thermodynamic stabilisation of amino alcohol **8**.

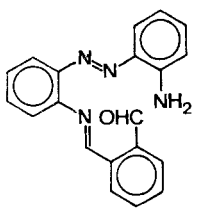


10 (X = *o*-NO_2, *p*-NO_2, *o*-N=N–Ph)

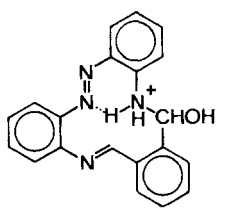
The situation can be looked at from another point of view: A careful inspection of molecular models of the likely intermediates **11** in the cyclization and the protonated amino alcohols **12** derived from them indicates that the cyclization proceeds predominantly *via* conformer **11a** to **12a**. In conformation **11a** the amino group can approach the carbonyl group most easily along the minimum energy path suggested by X-ray analysis of various models for the nucleophilic addition to the carbonyl group as well as by computation [21]. The resulting protonated amino alcohol **12a** will preferentially deprotonate, because of hydrogen bonding[8]), to an amino alcohol which, as indicated in Fig. 1 A, has in contrast to one of the amino alcohols resulting from de-



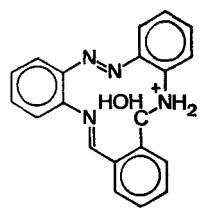
11a



11b



12a



12b

[8]) For a comparison of the transfer of hydrogen bonded and non hydrogen bonded protons see [22].

protonation of **12b** (Fig. 1 B) no lone pair oriented antiperiplanar to the C—OH bond. Since the three orbital orientations can not interconvert by rotation about the C—N bond because of fixation in the macrocycle, the amino alcohol **8** might also be a result of a kinetically unfavoured dehydration[9]). The instability of **8** and **9**, however, precludes clarification of this question.

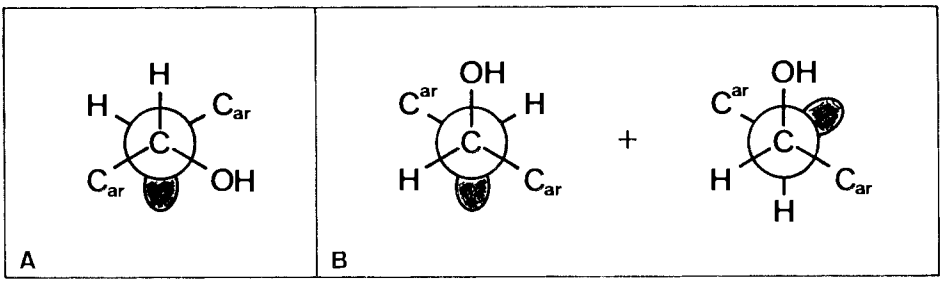
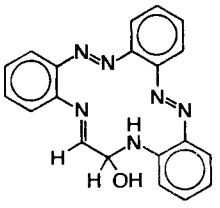


Fig. 1. *Orbital orientation in amino alcohols derived from* **12a** (A) *and* **12b** (B). Only one of each of the two possible diastereomers is shown.

Molecular models also indicate that the two non-planar conformers **8a** and **8b** should be in equilibrium. A dynamic ^{1}H-NMR. study showed a coalescence temperature of $-12 \pm 5°$ and a chemical shift difference, $\Delta\nu$, for the amino alcohol (H–C)-protons of 9 Hz. From these data, a free enthalpy of activation $\Delta G^{\ddagger}_{12°} = 56.0 \pm 1.3$ kJ mol^{-1} (13.4 $\pm$ 0.3 kcal mol^{-1}) for the conformational isomerisation can be estimated [14].

Rearrangement instead of cyclization of diamine **6**. In the reaction of diamine **6** with aqueous glyoxal the main product was isolated by preparative TLC. in 59% yield. On the basis of spectroscopic data the amino alcohol structure **13** had been proposed [1]. Differences[10]) between the ^{1}H-NMR. data of the characteristic structural element in **13** and the same element in 6-membered rings **14**[11]) as well as the stability of the compound towards hydrolysis and reduction – unreasonable for the suggested structure **13** – made it necessary to prove the structure unequivocally by an X-ray analysis.



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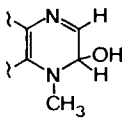

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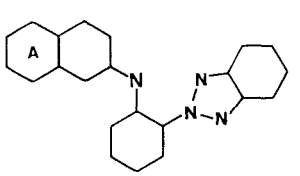
[9]) The concept of orbital orientation control of the cleavage of tetrahedral intermediates has so far been discussed for intermediates with two lone pairs oriented to the C—X bond. This of course is only qualitatively different to the approach presented here. For a recent review see [23].

[10]) These differences together with the electronic spectrum prompted our speculation concerning a delocalized macrocyclic perimeter in **13** [1].

[11]) For an example see [24].

A first refinement[12]) of the structure analysis clearly demonstrated that instead of macrocycle **13** the cyclization reaction had led to an unexpected rearrangement product **15**. For four of the six N-atoms, which were known to be present from mass spectroscopy [1], the positions indicated in **15** are the most likely. Since the structure has to account for the quartet-like *AB*-part in the ^{1}H-NMR. spectrum (Table 3) and, further, it is very probable that the three benzene rings of diamine **6** are still present, the remaining two N-atoms must be in ring A. Of the possible diaza-naphthalenes only quinoxaline derivatives exhibit typical quartet-like *AB*-spectra at low field[13]). Therefore the most likely structure of the rearrangement product is the 6-aminoquinoxaline derivative **16**. This was proved by a final refinement of the X-ray analysis to an R-factor of 7.3% as well as by an independent synthesis [25].



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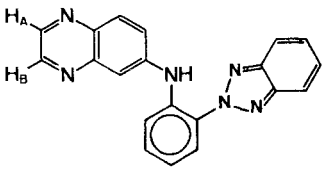

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Table 3. *^{1}H-NMR. and ^{13}C-NMR. data*[a]) *of* **16** (*$CDCl_3$*)

δ_{H_A}	δ_{H_B}	δ_{NH}	J_{AB}	δ_{C_A}	δ_{C_B}
8.62[b])	8.70[b])	9.76	2	141.5[c])	144.4[c])

[a]) Shifts in ppm, internal TMS = O, J in Hz.
[b]) and [c]) Assignment interchangeable.

Alternative cyclizations of diamine **6**. Comparison of diamine **6** with the phenylazostilbene **17** and the distyrylbenzene **18** indicates that one of the limitations for cyclization of **6** is the low reactivity – due to the phenyleneazo group – of its amino groups. **6** does not react with freshly neutralized[14]) aqueous glyoxal or glyoxal in anhydrous solvents nor with 1,2-cyclohexadione under mild conditions but either rearranges or decomposes under vigorous conditions in the presence of a catalyst such as H^+. However, the diamines **17** and **18** can be cyclized with 1,2-cyclohexadione and **18** can also be cyclized with glyoxal [27] [28].

On the other hand, the macrocycles **19**[15]) [29] and **20** [27] can be obtained in small yields (6% and 18%, respectively) from the reactions of **6** with 1,2-dibromoethane and with oxalyl chloride.

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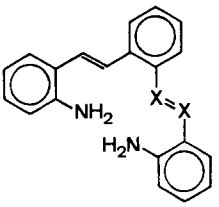
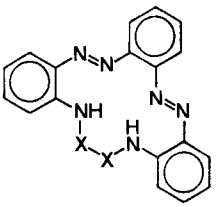
12) R-Factor of 11.6% from *ca.* 1000 significant intensities (total number = 1700); the small proportion of significant intensities is due to the small size of the crystal [25].
13) For examples see [26].
14) Aqueous solutions of glyoxal (*Fluka AG*) had pH 5–6.
15) Attempts to oxidize **19** to **2** have so far been unsuccessful.



17 (X = N)
18 (X = CH)

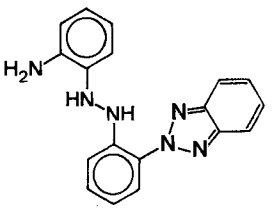


19 (X = CH_2)
20 (X = CO)

In recent years the template synthesis [8] has been shown to be a valuable alternative to the synthesis of macrocyclic ligands and the subsequent metallation [9]. In the template reaction of diamine **6** with glyoxal as well as with 1,2-dibromoethane in the presence of Ni^{II}-, Co^{II}- and Cu^{II}-salts a fast and quantitative complex formation of the diamine is observed. The complexes of **6**, however, do not cyclize under mild conditions, and decompose under vigorous conditions. In our opinion this is due to even lower reactivity of the amino functions in the complexes *vs.* the free diamine.

Conclusions and open questions. The results presented demonstrate the instability of the macrocycles **8** and **9** derived from diamine **5** and that cyclization reactions of diamine **6**, which has a low reactivity, are rendered difficult by its instability. Therefore the present synthetic approach suggests that the macrocycles **1** and **2** have no potential as new chromophores or metal complex ligands.

On the other hand the interesting observations of amino alcohol stabilization in macrocycle **8** and rearrangement of **6** deserve further investigation. To decide whether the amino alcohol is a thermodynamically stabilized intermediate and/or dehydration is a kinetically unfavoured reaction controlled by orbital orientation requires a study of the appropriate models. One possible route for the formation of the rearrangement product **16** is an inter- and/or intramolecular disproportionation of diamine **6** to the benzotriazole derivative **21**[16]), which than rearranges to semidine **22** which in turn cyclizes with glyoxal to **16**.



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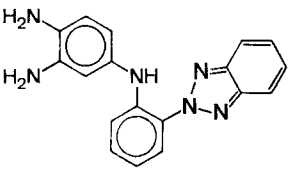

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This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*, project No. 4430.2. We thank Prof. *H. Zollinger* for his continued encouragement of this work and *P. S.* thanks Prof. *P. Rys* for many stimulating discussions.

[16]) Examples are known for the cyclization of *o*-aminosubstituted azobenzenes to benzotriazole derivatives. See [13], p. 425 ff.

Experimental Part

General. – Melting points are uncorrected. IR. spectra (KBr) were run on a *Beckman* IR-33 (intensities: *s* = strong, *m* = medium, *w* = weak), ^{1}H- and ^{13}C-NMR. spectra ($CDCl_3$) at 90 and 22.63 MHz (*Bruker* WH-90); chemical shifts are given in ppm (internal TMS = 0), coupling constants in Hz (*s* = singlet, *d* = doublet, *q* = quadruplet, *m* = multiplet). Mass spectra were run on a *Hitachi Perkin Elmer* RMU-6 (Organ.-chem. Laboratorium ETH) and electronic spectra on a *Unicam* SP. 800. Silica gel plates were used for thin and thick layer chromatography (F 254, PF 254), and for column chromatography silica gel (0.05–0.2 mm) from *Merck AG*, Darmstadt, was used.

2,2'-Diaminoazobenzene (5). – The crude product obtained according to [12] from 20 g (0.185 mol) *o*-phenylenediamine was subjected to column chromatography (450 g silica gel, eluent chloroform) and afterwards recristallized from chloroform to give 6.0 g **5** (30.6%, lit. [12] 45.3%), m.p. 136° (lit. [12] 133–134°). – ^{1}H-NMR.: 5.50 (*s*, 4H, NH_2); ~6.7–7.0 (*m*, 4H, arom. H); ~7.1–7.5 (*m*, 2H, arom.H); 7.78 (*q*, 2H, arom.H). – MS. (80°): 212 (M^+, 34), 196 (11), 183 (31), 120 (14), 93 (13), 92 (100), 65 (85), 52 (11). – UV./VIS.: see Table 2. – IR.: 3480*m*, 3380*m*, 3080*w*, 1610*s*, 1580*w*, 1490*s*, 1465*m*, 1340*m*, 1320*m*, 1270*m*, 1150*m*.

1,2-Bis(2-aminophenylazo)benzene (6). – *1-(2-Aminophenylazo)-2-(2-acetylaminophenylazo)benzene* (**7**). 0.743 g (3.50 mmol) **5** and 0.575 g (3.50 mmol) *o*-nitrosoacetanilide [30] were dissolved in 20 ml $CHCl_3$ and 1.8 ml CH_3CO_2H and heated for 23 h under reflux. Then the solution was extracted 3 times with 20 ml H_2O and dried over Na_2SO_4. Evaporation of the $CHCl_3$ layer, chromatography of the residue (8 plates PF 254, $CHCl_3$/petroleum ether (80–110°) 1:1), rechromatography of the orange main component (3rd band from top) on 4 plates yielded 0.584 g **7** which were recristallized from CH_3OH (0.524 g, 41.8%), m.p. 164–165°. – ^{1}H-NMR.: 1.95 (*s*, 3H, $COCH_3$); 6.18 (*s*, 2H, NH_2); ~6.4–7.8 (*m*, 11H, arom.H); 8.56 (*q*, 1H, arom.H); 9.92 (*s*, 1H, NH). – MS. (200°): 358 (M^+, 10), 253 (22), 211 (41), 210 (27), 107 (28), 106 (100), 92 (44), 65 (45), 43 (32).

$C_{20}H_{18}N_6O$ (358.2) Calc. C 67.02 H 5.06 N 23.45% Found C 66.89 H 5.17 N 23.63%

Diamine **6**. 0.100 g (0.28 mmol) of **7** were dissolved in 10 ml C_2H_5OH. After addition of 0.900 g KOH in 7 ml C_2H_5OH and 3 ml H_2O the mixture was heated for 1 h under reflux, then poured onto 100 g ice and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4 and evaporated. The residue was recristallized from *n*-pentane to give 76 mg (86%) **6**, m.p. 96–97°. – ^{1}H-NMR.: 6.30 (*s*, 4H, NH_2); ~6.5–8.2 (*m*, 12H, arom.H). – MS. (150°): 316 (M^+, 17), 314 (16), 211 (33), 210 (23), 120 (26), 106 (70), 92 (100), 79 (18), 65 (66). – UV./VIS.: see [1].

$C_{18}H_{16}N_6$ (316.2) Calc. C 68.31 H 5.10 N 26.58% Found C 68.35 H 5.03 N 26.62%

Aminoalcohol *8*[17]). – 0.150 g (0.71 mmol) **5** were dissolved in 10 ml hot C_2H_5OH and mixed with 95 mg (0.71 mmol) phthalaldehyde (*Fluka AG*) in 100 ml hot H_2O[18]). After *ca.* 15 min. the precipitate was collected and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, concentrated and chromatographed (1 plate PF 254, C_6H_6/$CHCl_3$/ethyl acetate 15:5:1). The main band (6th from top) was eluted with $CHCl_3$. Recristallization ($CHCl_3$/petroleum ether (80–110°) 2:3) of the residue (70 mg, 30%) was accompanied by partial decomposition. Spectroscopic data were obtained without recristallization; m.p. (after three recristallizations) 179–182°. – ^{1}H-NMR.: 4.90 (*s*, 1H, C*H*OH); 5.75 and 6.10 (*s*, 2H, NH, OH); ~6.3–7.8 (*m*, 13H, arom.H and CH=N). – MS. (195°): 310 (M^+-18, 31), 309 (21), 308 (24), 221 (22), 212 (52), 205 (15), 120 (10), 109 (10), 108 (100), 92 (53), 80 (24), 65 (18). – IR.: 3470*m*, 3390*m*, 3300*m*, 3070*m*, 2870*w*, 1645*s*, 1620*s*, 1590*s*, 1490*s*, 1475*m*, 1455*m*, 1400*s*, 1320*m*, 1230*m*, 1210*m*, 1160*s*, 1140*s*. – UV./VIS.: see Table 2.

2-(2-2*H*-benzotriazolyl)-*N*-(6-quinoxalinyl)aniline (*16*)[17]). – 18 ml (110 mmol) aqueous glyoxal (30%, *Fluka AG*) were added gradually to a stirred, ice-cold solution of 90 mg (0.28 mmol) **6** in 12 ml CH_3OH. The mixture was stirred for 23 h, diluted with H_2O and extracted with $CHCl_3$.

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[17]) The same result is obtained under high dilution (*ca.* 10^{-4} mol l^{-1} starting materials).

[18]) Reactions in absolute C_2H_5OH and CH_3OH give identical product mixtures [14].

The organic layer was dried over Na_2SO_4, concentrated and chromatographed (1 plate PF 254, $CHCl_3$/petroleum ether 1:1). The yellow, main band was eluted with $CHCl_3$ to give 56 mg **16** (59%), m.p. (from cyclohexane) 110–111°. For X-ray analysis **16** was recristallized from CH_3OH which gives the best results, but CH_3OH is enclosed in the cristals; m.p. 65°. – ^1H- and ^{13}C-NMR.: see [1] and Table 3. – MS. (150°): 338 (M^+, 100), 233 (14), 220 (14), 219 (14). – UV./VIS.: see [1]. – IR.: 3305*w*, 3040*w*, 1602*s*, 1537*s*, 1505*s*, 1490*s*, 1470*m*, 1445*m*, 1360*m*, 1330*s*, 1285*m*, 1225*m*, 1132*m*, 1030*m*, 962*m*, 945*m*, 860*w*, 825*m*, 740*s*.

$C_{20}H_{14}N_6$ (338.2) Calc. C 70.99 H 4.17 N 24.84% Found C 70.91 H 4.45 N 24.47%

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