156. Synthesis and X-Ray Analysis of
2-(2-2H-benzotriazolyl)-N-(6-quinoxalinyl)aniline, the Rearrangement Product from 1,2-Bis(2-aminophenylazo)benzene and Glyoxal

Macrocyclic Aza Compounds. IV[1])

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Summary

The title compound **2** was synthesized from the intermediates **3** and **4**. It is identical with the rearrangement product of **1** and glyoxal, of which the X-ray structure analysis is described.

1. Introduction. – We have reported on the rearrangement of 1,2-bis(2-amino-phenylazo)benzene (**1**) in the presence of glyoxal to the title compound **2** [2]. The structure of **2** could not be deduced from spectroscopic data and was therefore proved by X-ray structure analysis in combination with an independent synthesis[3]).
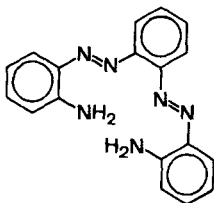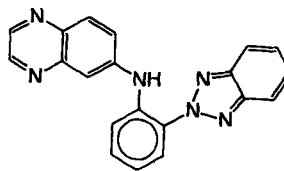
1   2

2. X-Ray Structure Analysis. – Compound **2** crystallizes from methanol in small yellow needles. No specimen with a size larger than $0.05 \times 0.1 \times 0.5$ mm could be obtained, therefore only weak diffraction intensities could be collected.

The crystallographic data are: $C_{20}H_{14}N_6 \cdot 2/3\,CH_3OH$; orthorhombic; $a = 29.326$ (6), $b = 15.925$ (5), $c = 3.899$ (3) Å, $V = 1821$ Å^3; space group: $Pna2_1$ with 4 molecules per unit cell.

The intensity data were collected on a *Siemens*-4-circle diffractometer with Ni-filtered CuKα-radiation ($\lambda = 1.5418$ Å). In a range $4° < \theta < 67°$, 1705 reflections were measured, using the 'five-

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1) Part III: *Skrabal, Steiger & Zollinger* [1].
2) Fellow of the Swiss Federal Ship 1974/75 from the Institute of Organic Chemistry and Technology, Technical University of Warsaw.
3) The independent synthesis was carried out because of the initial uncertainty in some of the N-positions in the X-ray analysis (see [2]).

value'-technique [3], of which 745 were treated as 'unobserved', since their intensities did not exceed twice the statistical error.

Apart from the usual *Lorentz* and polarisation correction no further corrections were made. Absorption effects could be neglected because of the small crystal size and the low value of the linear absorption coefficient ($\mu = 6.94$ cm^{-1}).

The structure was solved by application of the tangent formula [4], using the programs NORMSF, SINGEN and TANGEN of the XRAY-72 computer program system [5]. With a starting set of seven reflections a best R_E-value of 21% [6] was reached for the reflections with $E > 1.30$. An E-map calculated with these phases showed most of the atoms; the missing ones were derived from a subsequent difference synthesis.

Atomic parameters were refined by least-squares analysis with anisotropic temperature factors assigned to the heavy atoms, isotropic ones to the hydrogen atoms. The poor quality of the intensity data led to difficulties concerning the identification of the solvent included in the crystal. The best explanation of a difference synthesis, and the lowest R-value, was obtained with the assumption of 2/3 molecule CH$_3$OH per molecule C$_{20}$H$_{14}$N$_6$, whereas mass spectroscopy indicated 1/3 molecule solvent. Since the resolution of the solvent fragment in the difference electron density map was not quite convincing, the actual amount of solvent present is doubtful.

At convergence, a final R-value of 7.3% was obtained, but in the difference electrondensity map a residual density up to 0.5 e/Å^3 remained near the solvent positions.

The final atomic parameters are listed in *Table 1*[4]). A stereoscopic plot [7] of the molecule is shown in *Fig. 1*, bond lengths and angles with estimated standard devia-
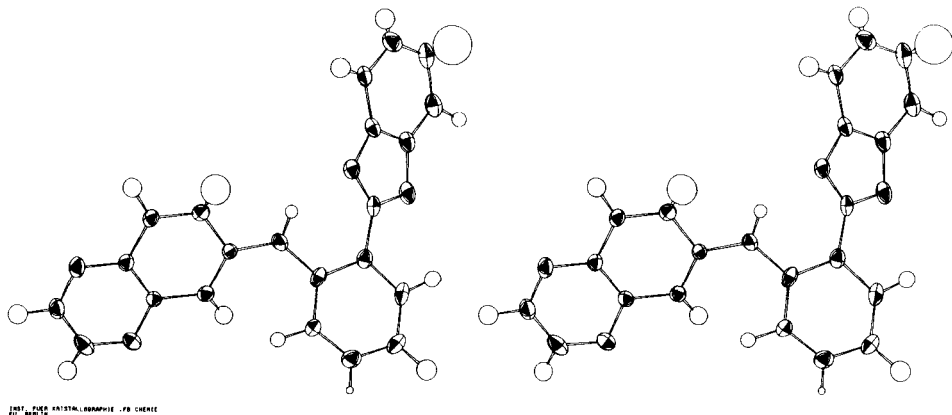

Fig. 1. *Stereoscopic plot of* **2**

tions in *Fig. 2*. The three ring systems quinoxaline (1), benzene (2) and benzotriazole (3) are planar, with mean deviations from least-squares planes as given in *Fig. 2*. The angles between the ring systems are $(1)/(2) = 37.3°$, $(1)/(3) = 42.7°$ and $(2)/(3) = 29.1°$. Nitrogen atoms N(21) and N(33) are linked by an intramolecular hydrogen bond, with $N-N = 2.75$ Å and $H-N = 2.04$ Å. Torsion angles are given in *Table 2*.

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[4])   The list of observed and calculated structure factors can be obtained from one of the authors (*P. L.*).

Table 1. *Atomic parameters of* **2**; e.s.d.'s in parentheses; temperature factors are given by

$$T_{aniso} = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)],$$
$$T_{iso} = \exp[-8\pi^2 U \sin^2\theta/\lambda^2] \quad (U_{ij} \text{ and } U \text{ in } 10^2 \text{ Å}^2)$$

| Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(11)	0.4412 (2)	0.2202 (5)	−0.189 (4)	4.8 (4)	7.3 (5)	5.5 (7)	−0.3 (4)	−0.5 (5)	0.5 (5)
C(12)	0.4746 (3)	0.1672 (8)	−0.266 (−)	4.3 (5)	11.5 (9)	6.7 (9)	−0.4 (6)	−0.3 (6)	−0.1 (9)
C(13)	0.4741 (3)	0.0830 (7)	−0.167 (5)	5.4 (6)	7.3 (7)	8 (1)	1.4 (5)	−0.2 (7)	−1.5 (8)
N(14)	0.4397 (2)	0.0487 (5)	−0.003 (4)	5.4 (5)	6.2 (5)	7.9 (8)	−1.7 (4)	−1.0 (6)	−1.0 (6)
C(15)	0.3662 (3)	0.0685 (5)	0.254 (5)	5.2 (5)	4.4 (5)	6.0 (8)	0.6 (4)	−0.5 (6)	0.2 (6)
C(16)	0.3311 (3)	0.1213 (5)	0.335 (5)	4.3 (5)	4.8 (5)	6.5 (8)	0.1 (4)	−2.3 (6)	−0.4 (6)
C(17)	0.3322 (3)	0.2086 (5)	0.245 (5)	3.5 (4)	4.3 (5)	6.3 (8)	0.4 (4)	−1.5 (6)	−0.1 (6)
C(18)	0.3687 (3)	0.2402 (5)	0.072 (4)	4.9 (5)	3.9 (5)	6.1 (7)	0.3 (4)	−0.2 (6)	0.7 (6)
C(19)	0.4056 (3)	0.1013 (5)	0.073 (4)	4.7 (5)	4.8 (5)	5.9 (8)	0.5 (4)	−1.1 (6)	−0.4 (6)
C(110)	0.4051 (3)	0.1868 (5)	−0.018 (4)	4.1 (5)	5.1 (5)	5.5 (7)	−0.3 (4)	−0.2 (5)	−1.1 (6)
N(21)	0.2947 (2)	0.2558 (5)	0.342 (5)	3.8 (4)	5.4 (4)	8.6 (8)	0.8 (3)	0.1 (6)	0.5 (6)
C(21)	0.2911 (3)	0.3436 (5)	0.394 (6)	7.4 (6)	3.8 (5)	4.2 (7)	1.2 (4)	−0.3 (6)	0.6 (5)
C(22)	0.2476 (3)	0.3821 (5)	0.388 (5)	5.6 (5)	5.5 (5)	5.5 (7)	1.0 (5)	−0.7 (6)	−0.7 (7)
C(23)	0.2452 (4)	0.4680 (6)	0.431 (5)	8.3 (7)	5.2 (6)	7 (1)	2.6 (5)	1.0 (7)	−0.5 (7)
C(24)	0.2826 (4)	0.5162 (6)	0.476 (5)	9.8 (8)	4.1 (5)	10 (1)	0.4 (5)	0.1 (9)	−1.4 (8)
C(25)	0.3236 (4)	0.4786 (6)	0.485 (5)	7.2 (6)	6.9 (7)	6.4 (8)	−0.9 (5)	−0.2 (7)	−1.5 (7)
C(26)	0.3287 (3)	0.3944 (5)	0.445 (5)	5.9 (6)	4.3 (5)	7.1 (9)	−0.0 (4)	0.6 (7)	−0.3 (6)
N(31)	0.1696 (3)	0.3718 (5)	0.202 (4)	5.7 (5)	6.8 (5)	7.5 (9)	2.9 (4)	0.1 (6)	1.5 (6)
N(32)	0.2066 (2)	0.3346 (4)	0.340 (4)	5.7 (4)	5.4 (4)	6.0 (7)	2.1 (4)	0.4 (6)	−0.8 (5)
N(33)	0.2021 (2)	0.2552 (4)	0.453 (4)	5.2 (4)	5.2 (4)	6.2 (6)	1.4 (4)	−0.8 (5)	1.0 (5)
C(34)	0.1337 (3)	0.1641 (7)	0.430 (5)	4.9 (5)	7.0 (7)	8.1 (9)	1.2 (5)	0.8 (7)	−0.9 (8)
C(35)	0.0896 (4)	0.1663 (9)	0.327 (6)	6.3 (7)	10 (1)	7.4 (9)	−1.8 (7)	1.4 (9)	−2.2 (9)
C(36)	0.0683 (4)	0.2371 (8)	0.172 (5)	6.9 (7)	9.8 (8)	6.6 (9)	3.1 (6)	0.3 (7)	−1.2 (8)
C(37)	0.0920 (4)	0.3087 (8)	0.114 (5)	6.2 (6)	8.6 (8)	8 (1)	2.5 (6)	−0.6 (8)	0.5 (8)
C(38)	0.1583 (3)	0.2376 (6)	0.374 (4)	4.4 (5)	6.5 (6)	5 (6)	1.5 (4)	0.6 (6)	1.1 (6)
C(39)	0.1382 (3)	0.3099 (6)	0.226 (5)	5.6 (5)	6.3 (6)	6.6 (8)	1.7 (5)	0.8 (6)	1.0 (7)
H(12)	0.498 (2)	0.187 (4)	−0.40 (2)	5 (2)					
H(13)	0.502 (3)	0.047 (4)	−0.27 (3)	7 (3)					
H(15)	0.364 (3)	0.003 (4)	0.31 (3)	6 (3)					
H(16)	0.305 (3)	0.104 (6)	0.37 (4)	13 (4)					
H(18)	0.365 (2)	0.298 (5)	−0.04 (3)	6 (3)					
H(21)	0.270 (2)	0.233 (4)	0.43 (2)	3 (2)					
H(23)	0.217 (2)	0.488 (4)	0.48 (3)	5 (2)					
H(24)	0.280 (2)	0.573 (5)	0.57 (3)	6 (3)					
H(25)	0.349 (2)	0.504 (3)	0.56 (2)	2 (2)					
H(26)	0.358 (2)	0.367 (4)	0.41 (2)	4 (2)					
H(34)	0.150 (2)	0.117 (5)	0.52 (3)	6 (3)					
H(35)	0.077 (3)	0.136 (5)	0.31 (3)	3 (3)					
H(36)	0.035 (4)	0.262 (4)	−0.01 (2)	19 (6)					
H(37)	0.081 (2)	0.358 (4)	0.07 (2)	3 (2)					
C(01)	0.451 (1)	0.395 (2)	0.54 (1)	12.5 (9)					
O(01)	0.4530 (8)	0.408 (2)	0.81 (1)	19.1 (9)					
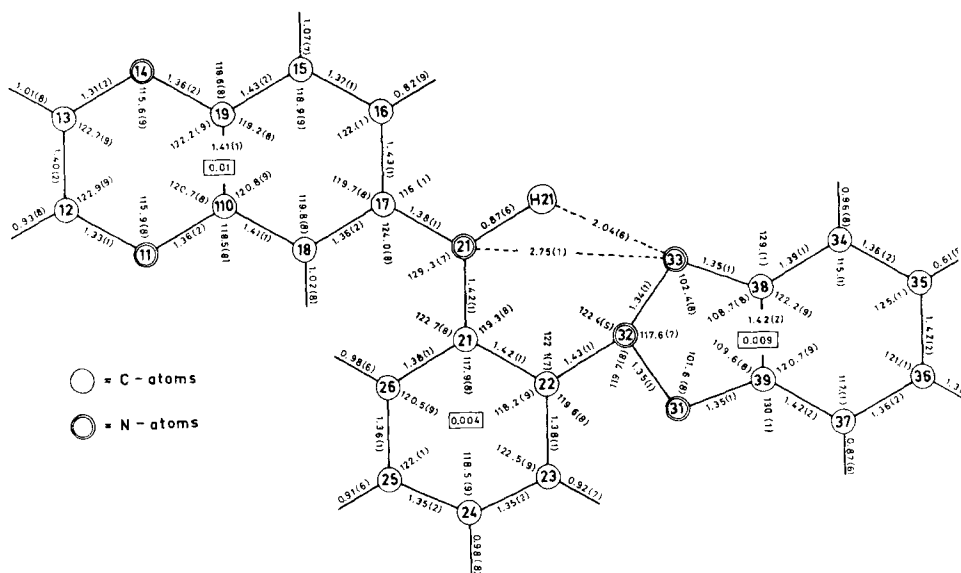
Fig. 2. *Bond lengths and angles of* **2** (e.s.d.'s in parentheses; digits in ring system centers indicate thei mean deviations from least squares planes in Å)

Table 2. *Torsion angles of* **2** *in degrees*

C(16)–C(17)–N(21)–C(21)	157.2	C(17)–N(21)–C(21)–C(22)	160.4
C(18)–C(17)–N(21)–C(21)	– 23.5	C(17)–N(21)–C(21)–C(26)	– 18.1

Table 3. *Short Intermolecular and Intramolecular Contacts*

Atoms	Contact Distance (Å)	Symmetry Operation for Second Atom	Atoms	Contact Distance (Å)	Symmetry Operation for Second Atom
O(01)–C(01)	2.85 (5)	x, y, 1 + z	N(14)–H(13)	2.47 (8)	1 – x, – y, z + 1/2
H(26)–H(18)	2.4 (1)	x, y, 1 + z	C(13)–H(13)	2.68 (9)	1 – x, – y, z + 1/2
O(01)–N(11)	3.01 (3)	x, y, 1 + z	H(13)–H(13)	2.5 (1)	1 – x, – y, z + 1/2
N(21)–N(33)	2.75 (1)	x, y, z	C(12)–H(36)	2.3 (1)	1/2 + x, 1/2 – y, z
H(21)–N(33)	2.04 (6)	x, y, z	H(12)–H(36)	2.0 (2)	1/2 + x, 1/2 – y, z

The crystal packing is shown in *Figs. 3 a* and *b*. The short *c* axis of 3.90 Å leads to close intermolecular contacts (*Tab. 3*) in the *z*-direction. The distance H(26) – H(18) is 2.4 Å and that between the solvent molecules, O(01) – C(01), which are orientated nearly parallel to *c*, is 2.85 Å. Because of uncertainty in the positional parameters of the solvent molecules no further comment on this result can be made[5]). Two other

[5])   As a referee has pointed out, the 2/3 occupancy of the solvent sites would be in accord with the following distribution of solvent molecules: head-to-head orientation of two methanol molecules ($CH_3OH \cdots HOCH_3$) in two consecutive unit cells and empty sites in every third unit cell (3*c* superlattice). On the one hand, the observed difference between the electron densities assigned to the CH_3 and to the OH group, respectively, is not significant – in accord with the above model. On the other hand, no reflections corresponding to a 3*c* superlattice have been observed. This may be due to the small size of the available crystals or to the absence of correlation between parallel stacks of solvent molecules in different unit cells (*Fig. 3a*).
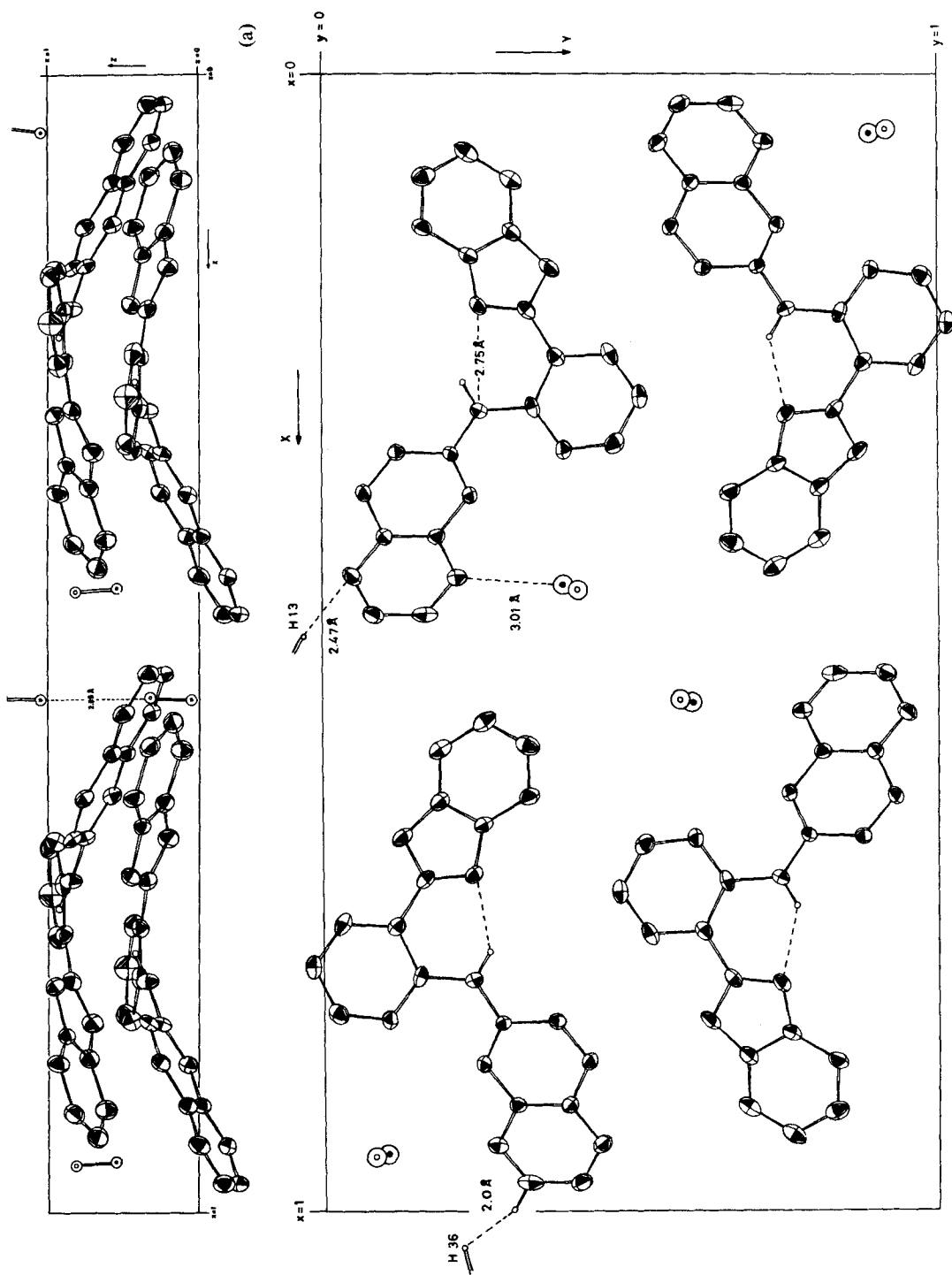
Fig. 3. *Projection of the unit cell of* **2** *onto the (x–z)-plane (a) and the (x–y)-plane (b)*

short intermolecular contacts are noteworthy: $N(14) - H(13) = 2.47$ Å and $H(12) - H(36) = 2.0$ Å. The latter is significantly below the $H - H$ *van der Waals* distance of 2.4 Å; H(36) was very difficult to locate in difference *Fourier* syntheses, and refinement of its parameters resulted in an unusually long C, H-bond length of 1.3 Å and a large isotropic $U = 0.19$ Å^2.

3. Synthesis. – Structure **2** suggested a possible synthesis from two sub-units, a quinoxaline and a 2-phenyl-2*H*-benzotriazole derivative. 6-Halogenoquinoxalines [8] and 2-(2-aminophenyl)-2*H*-benzotriazole (**4**) [9] are known. Therefore 6-chloro-quinoxaline (**3**) was synthesized *via* reduction [10] of 4-chloro-2-nitroaniline, which was commercially available, and condensation of the resulting 4-chloro-1,2-phenyl-enediamine with sodium glyoxal bisulfite [8]. Reaction of **3** with the benzotriazole **4** in the presence of potassium carbonate and copper powder yielded **2** which was identical in all respects with the rearrangement product [2].

3   4

Experimental Part

General. 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.

6-Chloroquinoxaline (**3**). 4-Chloro-2-nitroaniline (*Fluka AG*) was reduced to 4-chloro-1,2-phenylenediamine [10], which in turn gave **3** according to [8].

2-(2-Aminophenyl)-2H-benzotriazole (**4**) was obtained according to [9].

2-(2-2H-benzotriazolyl)-N-(6-quinoxalinyl)aniline (**2**). 220 mg (1.05 mmol) **4** and 160 mg (0.97 mmol) **3** were refluxed in the presence of 200 mg K$_2$CO$_3$ and 100 mg Cu-powder in 4 ml nitrobenzene for 12 h. After cooling, the reaction mixture was diluted with 20 ml CHCl$_3$ and filtered. The filtrate was subjected to column chromatography [40 × 4 cm, eluent: CHCl$_3$]. The yellow, main fraction was rechromatographed on 4 thick layer plates (CHCl$_3$). The uppermost yellow band gave after elution with CHCl$_3$ and recrystallization from CH$_3$OH 10 mg (3%) of **2**. For analytical and spectroscopic data see [2] [11].

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