64. The Crystal Structure of *trans*-2,2'-Azoquinoxaline

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Dedicated to Prof. Dr. *Silvio Fallab* on the occasion of his 60th birthday

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The structure of the title compound obtained from 2(1*H*)-quinoxalinone oxime by the template effect of Co(II) and Ni(II) ion has been determined by three dimensional X-ray analysis.

Introduction. – Recently, the reaction product of 2(1*H*)-quinoxalinone oxime and $CoCl_2 \cdot 6H_2O$ was reported to be 1,2,4,5-tetrazino[1,6-*a*:4,3-*a'*]diquinoxaline according to elemental analysis, UV/VIS, IR, ^1H-NMR and mass-spectral data [1]. However, when the X-ray structure determination of the above product was carried out, it was found to be a new azo-compound instead of a tetrazine derivative. We now report the results of a complete X-ray analysis of 2,2'-azodiquinoxaline.

Crystal Data, Structure Determination and Refinement. The compound under investigation ($C_{16}H_{10}N_6$, mol. wt. 286.3, $F(000) = 296$), has been synthesized as described before and crystallized from EtOH soln. as deep red monoclinic needles elongated along *a*; $a = 469.6(1)$, $b = 1224.4(2)$, $c = 1205.8(2)$ pm, $\beta = 104.10(1)°$; $U = 672.4(4)\ 10^6\ pm^3$, space group $P2_1/n$ (No. 14 Int. Tables), $D_x = 1.41\ gcm^{-3}$ for $Z = 2$.

Data collection carried out on a four-circle diffractometer (*Enraf Nonius CAD4*, graphite monochromated MoK_α radiation, $\lambda = 71.069$ pm, $\mu = 0.085\ mm^{-1}$, $\vartheta - 2\vartheta$ scan, $T = 293$ K) using a crystal mounted along *a* with

Table 1. *Atomic Coordinates and Thermal Parameters* U_{eq} (in pm^2) *of Non-H-Atoms.* $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Atom	*x*	*y*	*z*	U_{eq}
N(2')	0.0688(3)	0.0411(1)	0.5201(1)	484(5)
N(1)	0.3643(3)	0.1799(1)	0.4870(1)	431(5)
C(2)	0.2237(3)	0.0913(1)	0.4451(1)	389(5)
C(3)	0.2281(3)	0.0480(1)	0.3367(1)	450(6)
N(4)	0.3740(3)	0.0943(1)	0.2702(1)	466(5)
C(5)	0.6850(3)	0.2424(1)	0.2441(1)	474(6)
C(6)	0.8301(4)	0.3353(1)	0.2828(1)	546(6)
C(7)	0.8207(4)	0.3793(2)	0.3890(1)	589(7)
C(8)	0.6675(4)	0.3280(2)	0.4558(1)	529(6)
C(9)	0.5157(3)	0.2309(1)	0.4186(1)	391(5)
C(10)	0.5223(3)	0.1877(1)	0.3108(1)	389(5)

Table 2. *Atomic Coordinates and Thermal Parameters* U_{iso} (in pm^2) *of H-Atoms*. The form of the isotropic thermal parameter: $\exp[-8\pi^2 U_{iso}(\sin\nu/\lambda)^2]$.

Atom	x	y	z	U_{iso}
H(3)	0.125(3)	−0.022(1)	0.312(1)	602(50)
H(5)	0.683(3)	0.212(1)	0.167(1)	519(40)
H(6)	0.933(3)	0.376(1)	0.239(1)	582(50)
H(7)	0.935(3)	0.448(1)	0.414(1)	746(50)
H(8)	0.657(3)	0.355(1)	0.527(1)	520(50)

dimensions 0.1 × 0.1 × 0.3 mm, 1752 symmetry independent reflections, $\sin\vartheta/\lambda \leqslant 6.84$ nm^{-1}. The structure was solved by direct methods (MULTAN 80). Refinement, including non-H-atoms with anisotropic and H-atoms with isotropic thermal parameters, led to $R = 0.038$ for 950 observed reflections ($I \geqslant 2\sigma(I)$). A final difference map revealed no significant residual peaks. The final atomic positional and thermal parameters are given in *Table 1* and *2*.

Molecular Structure. The bond lengths and valence angles with their standard deviations are presented in *Table 3* and *4*. A drawing of the molecule showing the labeling scheme is given in *Fig. 1*.

The molecule has an almost perfectly planar structure: the maximum deviation from least-squares plane through all non-H-atoms is 2 pm (N(1) and N(2')). The two chemically equivalent parts are related by a center of symmetry, requiring the quinoxaline rings to be parallel and the torsional angle C(2)–N(2')–N(2'i)–C(2i) to be exactly 180°. The torsional angle N(1)–C(2)–N(2')–N(2'i) is 178.6(2)°.

The exocyclic bond deviates less than 1° from the sp^2 plane defined by atoms N(1), C(2) and C(3), whereas the opening of the valence angle C(3)–C(2)–N(2') to 123.2° may be produced by the short intramolecular contact distance of 269 pm between C(3) and N(2'i). These facts indicate tight conjugation of the two quinoxaline moieties through the azo linkage. Nevertheless, we cannot observe stretched N=N bond nor shortened N–C(sp^2) distance as reported for *o*-amino-azotoluene by *Kurosaki et al.* [2]; the distances N(2)–N(2'i): 123.1(2) pm, C(2)–N(2'): 143.0(2) pm and the valence angle C(2)–N(2')–N(2'i): 113.6(1) are in rather close agreement with those found by *Brown* [3] [4] in *trans*-azobenzene and *trans*-azotoluene.

Table 3. *Bond Distances* (in pm). Numbers in parentheses are e.s.d. in the least significant digits.

N(2')–N(2'i)	123.1(2)	N(4)–C(10)	136.6(2)	C(9)–C(10)	141.1(2)
N(2')–C(2)	143.0(1)	C(5)–C(6)	135.0(2)	C(3)–H(3)	99.2(13)
N(1)–C(2)	130.6(2)	C(5)–C(10)	140.6(2)	C(5)–H(5)	100.1(12)
N(1)–C(9)	136.4(1)	C(6)–C(7)	140.0(2)	C(6)–H(6)	94.3(13)
C(2)–C(3)	141.5(2)	C(7)–C(8)	135.8(2)	C(7)–H(7)	100.4(13)
C(3)–N(4)	130.5(2)	C(8)–C(9)	140.2(2)	C(8)–H(8)	93.5(12)

Table 4. *Bond Angles* (in Degrees). Numbers in parentheses are e.s.d. in the least significant digits.

N(2'i)–N(2')–C(2)	113.6(2)	C(3)–N(4)–C(10)	116.2(1)	N(1)–C(9)–C(10)	121.1(1)
C(2)–N(1)–C(9)	115.8(1)	C(6)–C(5)–C(10)	120.2(2)	C(8)–C(9)–C(10)	119.3(1)
N(2')–C(2)–N(1)	113.5(1)	C(5)–C(6)–C(7)	121.0(2)	N(4)–C(10–C(5)	119.6(1)
N(2')–C(2)–C(3)	123.2(1)	C(6)–C(7)–C(8)	120.3(2)	N(4)–C(10)–C(9)	121.4(1)
N(1)–C(2)–C(3)	123.3(1)	C(7)–C(8)–C(9)	120.3(2)	C(5)–C(10)–C(9)	119.0(1)
C(2)–C(3)–N(4)	122.2(1)	N(1)–C(9)–C(8)	119.6(1)		

i) x' = −x; y' = −y; z' = 1 − z

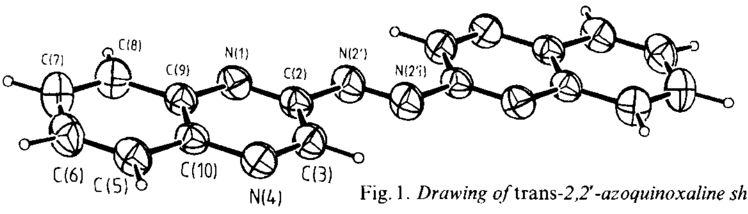

Fig. 1. *Drawing of* trans-*2,2'-azoquinoxaline showing the labeling scheme*

Comparison with azoquinoxaline dioxide [5], 2,7-diazanaphthalene [6], 1,5- and 2,6-diazanaphthalene [7] shows that all bond distances and angles in the quinoxaline system do not deviate from expected values. Approximate C_{2v} symmetry is found for all bond distances in this part. Only the angles N(1)–C(2)–C(3) and C(6)–C(7)–C(8) deviate about 1° from their symmetry equivalents. As presumed, the smallest bond angles (116°) are found at the N-atoms. Characteristic are also the short C–N partial double bonds N(1)–C(2) and N(4)–C(3) with 130.5(1) pm.

Crystal Latice. The molecules are stacked along the short *a*-axis which forms an angle of 43.3° with the molecular plane, leading to an interplanar distance of 342 pm between two molecules within the stack. Neighbouring molecules are also parallel shifted by 322 pm with the result that the central N=N bond is dumped above the middle of the pyrazine rings of two adjacent molecules. The two non-translation equivalent stacks are related by twofold screw axis, to form a typical 'herring-bone' pattern which is shown in *Fig. 2* in a projection along the *c*-axis.

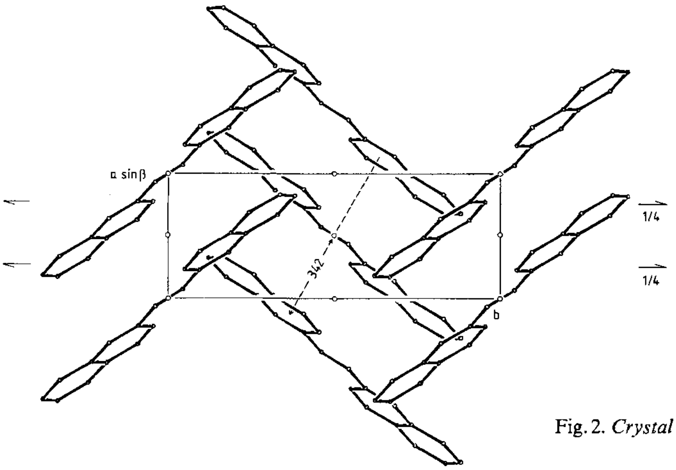

Fig. 2. *Crystal latice of* trans-*2,2'-azoquinoxaline*

Discussion. – The spectral data of the reaction product of 2(1*H*)-quinoxalinone oxime and $CoCl_2 \cdot 6H_2O$ given in the previous paper is consistent with the 2,2'-azoquinoxaline structure [1]. The elemental composition is the same as for 1,2,4,5-tetrazino[1,6-*a*, 4,3-*a*']diquinoxaline. In the IR spectra, the weak stretching vibrations of the azo group cannot be identified. The number and type of protons are the same in both compounds. The relatively intense m/z 258 ($M^+ - N_2$, 56%), 231 (5%), 156 (21%), 129 (100%), 102 (71%) fragment-ion peaks can also be expected from fragmentation of both structures. Consequently, X-ray single-crystal analysis is *the* method which determines the compound unequivocally as *trans*-2,2'-azoquinoxaline.

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