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Structure Elucidation of Tetrazolo[5,1-*c*]benzo-*as*-triazine. An Interesting Ternary Equilibrium of Tetrazole–Azide Systems

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The title equilibrium has been studied by UV, MS, and NMR. The originally proposed angular structure tetrazolo[5,1-*c*]benzo-*as*-triazine (**3**) is the major component both in solution and in the solid state. By means of ^{13}C NMR spectroscopy, an interesting ternary equilibrium was detected in Me_2SO which involves **3** as the main component (64%), in addition to **2** (25%) and **4** present in smaller amounts (10%).

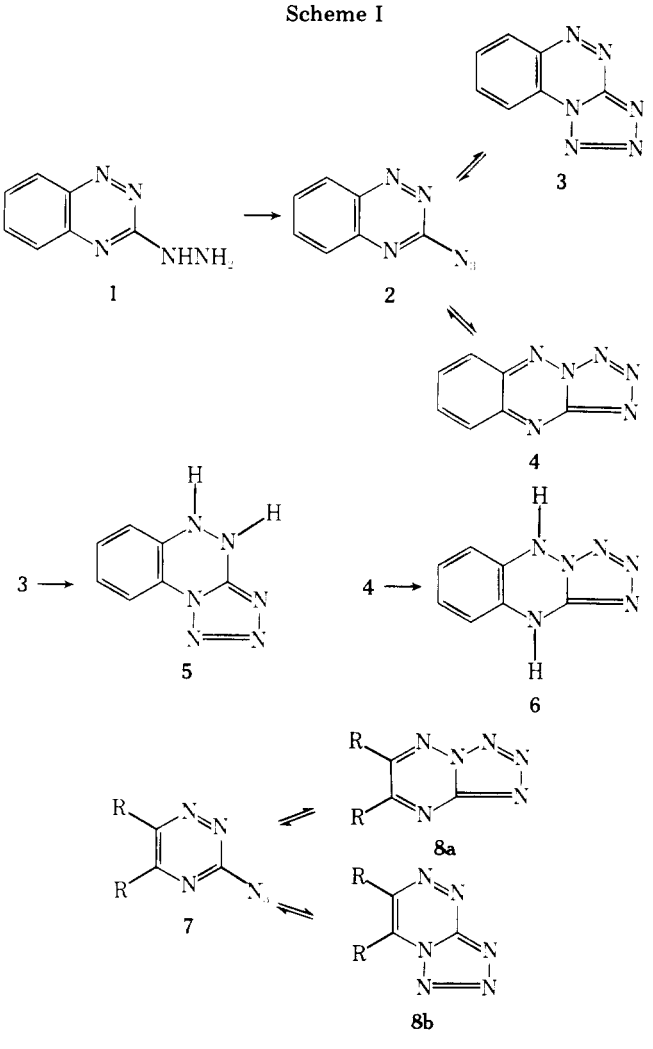
We have recently reported[1] that 3-hydrazinobenzo-*as*-triazine (**1**) can be converted by nitrous acid to tetrazolo[5,1-*c*]benzo-*as*-triazine (**3**) through the intermediate formation of 3-azidobenzo-*as*-triazine (**2**) (Scheme I). The tetrazole compound **3** proved to be stable in crystalline form, and its infrared spectrum recorded in potassium bromide showed no azide band. In solution, however, both azidobenzo-*as*-triazine (**2**) and tetrazolo[5,1-*c*]benzo-*as*-triazine (**3**) could be detected. Theoretically, another direction of ring closure toward the N-2 atom may be assumed in which case the linearly arranged tetrazolo[1,5-*b*]benzo-*as*-triazine (**4**) would form. This alternative was excluded since cyclization of **2** to **4** would involve the destruction of the benzenoid ring of the benzo-*as*-triazine moiety. In the case of the angular structure proposed by us, however, the aromatic sextet of the benzene ring of benzo-*as*-triazine is retained.

Several examples are known from the literature[2] where, in similar cases, the more benzenoid derivative is formed mainly or exclusively.

Shortly after our publication, Paudler et al.[3] found that the single-ring 3-azido-*as*-triazine derivatives **7** give rise to tetrazolo[1,5-*b*]-*as*-triazine compounds **8a** by a ring closure toward the N-2 atom. In no case was any cyclization toward the N-4 atom observed which would have resulted in tetrazolo[5,1-*c*]-*as*-triazine (**8b**), analogous to our case. On the basis of this observation, the above authors concluded that the structure of tetrazolobenzo-*as*-triazine (**3**), proposed by us, may not be correct and suggested reinvestigation of the problem.

Our original proposal for the structure of the tetrazole compound **3** was well supported by a simple UV study. The UV spectrum of the tetrazole compound in question was compared with that of the two possible tetrazoloisoquinolines: the angular tetrazolo[5,1-*a*]isoquinoline (**9**),[4] which occurs in solution only in the tetrazole form, and the linear tetrazolo[1,5-*b*]isoquinoline (**10**),[5] which is, in ethanol and dimethyl sulfoxide solutions, in equilibrium with the azide isomer

Scheme I



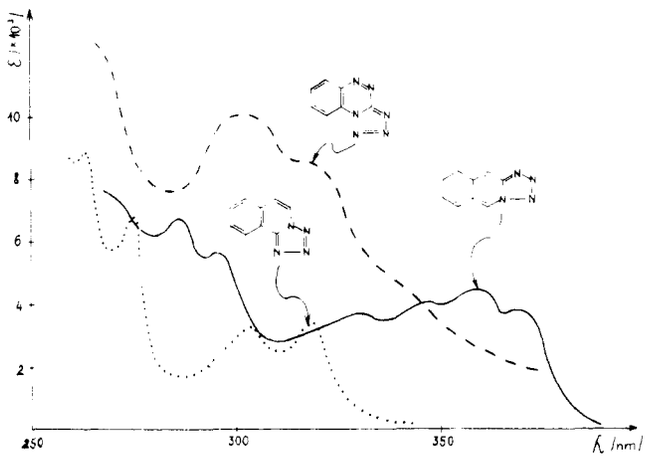
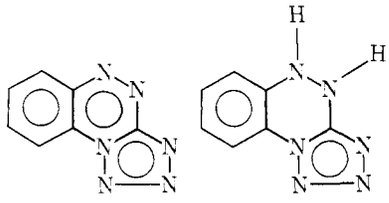


Figure 1. Comparison of UV spectra of tetrazolo[5,1-*a*]isoquinoline (**9**) (···), tetrazolo[1,5-*b*]isoquinoline (**10**) (—), and tetrazolo[5,1-*c*]-benzo-*as*-triazine (**3**) (- - -) in ethanol at 25 °C.

Table I. Mass Spectra of Tetrazolo[5,1-*c*]benzo-*as*-triazine (3) and 4,5-Dihydrotetrazolo[5,1-*c*]benzo-*as*-triazine (5)



m/e	3	5
174		7, M
172	100, M	60, M − H_2
146		80, M − N_2
144	20, M − N_2	15, 172 − N_2
118		100, M − $2N_2$
116	50, M − $2N_2$	40, 144 − $2N_2$
91		60
90		30
89	40, 116 − HCN	30

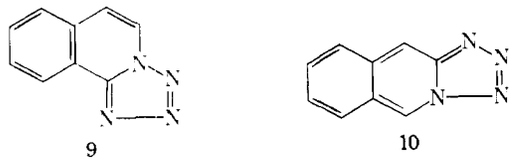
Metastable fragments

$172 \xrightarrow{-28} 144$	$172 \xrightarrow{-28} 144$
$116 \xrightarrow{-27} 89$	$118 \xrightarrow{-27} 91$
$172 \xrightarrow{-56} 116$	$116 \xrightarrow{-27} 89$

(Chart I). Figure 1 clearly shows about an 80-nm difference between the first maxima of the UV spectra of the two tetrazole ring systems fused to isoquinoline. On comparison of the spectra of the tetrazole compound **3** with these spectra, the originally proposed angular structure **3** seems to be evident.

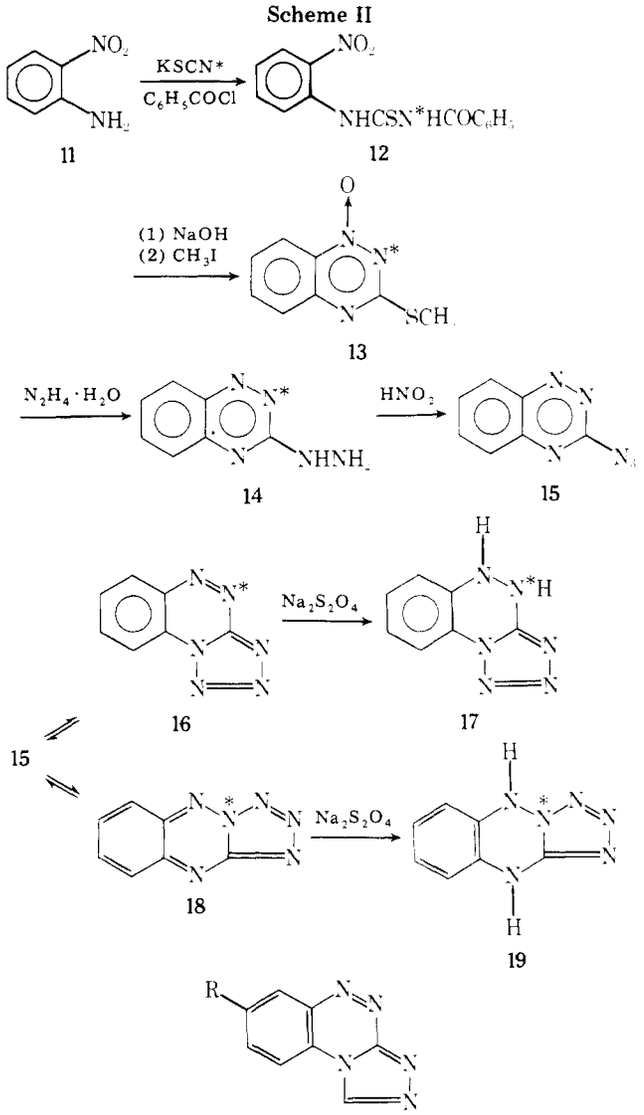
For further investigations, compound **3** containing the ^{15}N isotope in position 2 was prepared. In order to obtain the ^{15}N-labeled derivative, we started from *o*-nitroaniline (**11**), which was treated with ^{15}N-labeled benzoyl isothiocyanate generated in situ from benzoyl chloride and potassium [^{15}N]rhodanide (KSC^{15}N was prepared according to van der

Chart I



9 **10**

Scheme II



20, R = H
21, R = CH_3
22, R = OCH_3

Plas[6]) (Scheme II). Further steps of the synthesis were carried out as described elsewhere.[7] Thus, 1-benzoyl-2-(*o*-nitrophenyl)[1-^{15}N]thiourea (**12**) was first treated with sodium hydroxide. Treatment with methyl iodide resulted in 3-(methylthio)[2-^{15}N]benzo-*as*-triazine (**13**), which was, by the action of hydrazine hydrate, converted to 3-hydrazino[2-^{15}N]-benzo-*as*-triazine (**14**). The reaction of compound **14** with nitrous acid led through the azide derivative **15** to the labeled tetrazolobenzo-*as*-triazine (**16**).

This compound (**16**) as well as its dihydro derivative (**18**) obtained by reaction with sodium dithionate was investigated by mass spectroscopy. Table I shows the main peaks as well as their origins for the reference compounds of natural isotopic composition (**3** and **5**).

As seen from Table I, the dihydro compound **5** is fragmented in two pathways: in the first procedure it is aromatized by H_2 loss followed by the same fragmentation as that of the aromatic compound **3**; the second path proceeds through N_2 loss and leads to similar fragments with two additional hydrogens.

The results achieved with the ^{15}N-containing compounds are summarized in Table II. It can be seen that fragmentations of the aromatic and dihydro compounds differ in their N_2 loss. The fragment remaining after loss of a nitrogen molecule contains practically no isotope; this means that the N-1–N-2 fragment left the molecule. In the case of the dihydro deriv-

Table II. ^{15}N Content of Fragments of Labeled 16 and 18 of 10% Enrichment

ion	^{15}N content, % 16	18
M^+	9.5 ± 1	9 ± 1
$(M - 28)^+$	2 ± 1	10 ± 1
$(M - 56)^+$	0	not evaluateable

Table III. ^{13}C Chemical Shifts (ppm) of s-Triazolo[3,4-c]-benzo-as-triazine (20) and the Azide–Tetrazole Equilibrium Mixture in Dimethyl Sulfoxide

	model (20)	tetrazole A (3)	azide 2	tetrazole B (4)
C-6	128.1	130.5	129.0	128.6
C-7	130.6	131.1	130.0	134.9
C-8	135.6	137.8	137.3	137.6
C-9	116.2	115.4	126.8	127.0

ative **18**, however, the first N_2 fragment is derived from another part of the molecule. This difference can only be explained by the fact that in compound **18** N-2 is attached to a hydrogen atom and is therefore not able to split off in the first fragment. If the structures of the two molecules **17** and **19** corresponded to the linear structure, the isotope-containing N_2 fragment and the observed difference between the aromatic (**16**) and dihydro compounds (**18**) would not appear.

With the help of the MS study of the molecules in the vapor phase, the structure of only the dihydro compound **18** was clarified. For the structure of the aromatic tetrazole compound **16**, only probable conclusions could be drawn. If the tetrazole originally had a linear structure (**4**), it could also furnish the above fragmentation by shifting the isomer equilibrium. The angular structure of dihydrotetrazolobenzo-*as*-triazine (**5**), however, does not exclude the possibility of a linear tetrazolobenzo-*as*-triazine. Compound **5** might be formed by reduction of the angular isomer resulting through equilibrium. In order to obtain direct information on the ring-closed product in question, the tetrazole compound **3** itself has been investigated. The study of the compound was made more difficult due to the fact that no crystals suitable for X-ray analysis could be obtained.

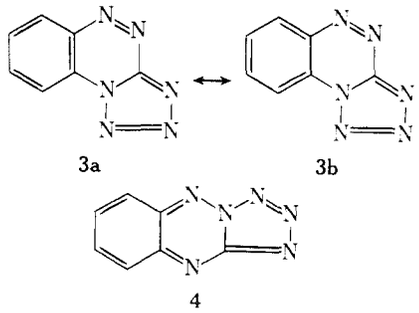
In agreement with the earlier IR observations,[1] the ^{13}C NMR spectrum of a chloroform solution of **3** showed only two sets of lines: those of azide **2** and tetrazole **3** isomers. However, in dimethyl sulfoxide solution three sets of lines appeared in the ^{13}C NMR spectrum. With the aid of variable temperature studies we found these sets to be in equilibrium. In other words, dimethyl sulfoxide solution contains, besides the azide isomer **2**, also the two possible tetrazole isomers (**3** and **4**). The intensity ratio of the compounds in equilibrium was tetrazole A 65%, azide 25%, and tetrazole B 10%.

Comparison of spectra recorded from dimethyl sulfoxide and deuteriochloroform solutions showed that the only tetrazole peak system appearing in chloroform solution corresponds to the major component of the Me_2SO spectrum, tetrazole A. This implies that also a tetrazole B component of lower intensity appears in dimethyl sulfoxide, and it had to be determined to which tetrazole (A or B) the angular (**3**) and linear (**4**) structures could be attributed.

For the purpose of structure assignment, the ^{13}C NMR spectra of *s*-triazolo[3,4-*c*]benzo-*as*-triazine (**20**) as well as its 7-methyl (**21**) and 7-methoxy derivatives (**22**) were investigated. These compounds were prepared according to a procedure published elsewhere.[7] Taking into consideration the well-known effects of CH_3 and OCH_3 groups, we identified the chemical shifts of the tertiary aromatic carbon atoms.

Table III shows the chemical shifts of *s*-triazolo[3,4-*c*]-benzo-*as*-triazine (**20**) and those of the three isomers appearing in the dimethyl sulfoxide solution. It can be clearly seen from the table that the lines of the major component of the dimethyl sulfoxide solution, tetrazole A, are strongly similar to those of the model compound **20**, particularly regarding the chemical shifts of C-9 atoms. This comparison supports our original proposal; the main component of the equilibrium mixture in dimethyl sulfoxide solution, the tetrazole A isomer has the angular structure similar to that of *s*-triazolo[3,4-*c*]benzo-*as*-triazine (**20**), and the tetrazole B isomer of linear structure appears as a minor component of the equilibrium. It should be noted that the strikingly high field shift of C-9 seems to be characteristic for five-membered ring systems angularly fused to benzo-*as*-triazine.[8]

Scheme III



3a 3b

4

The linear tetrazolo[1,5-*b*]benzo-*as*-triazine (**4**) was detected only in dimethylformamide and dimethyl sulfoxide solutions, and its concentration in the equilibrium decreased with the temperature.

Our study reveals that 3-azidobenzo-*as*-triazine (**2**) is principally in equilibrium with the angular tetrazolo[5,1-*c*]-benzo-*as*-triazine (**3**). The linear tetrazolo[1,5-*b*]benzo-*as*-triazine (**4**) supposed by Paudler et al.[3] can be detected only in exceptional cases: in strongly polar aprotic solvents.

In our opinion, the formation of the angular isomer, in the case of the fused benzo-*as*-triazine system, is not striking. The same consideration, such as resonance stability of the product by which Paudler et al. explained the formation of tetrazolo[1,5-*b*]-*as*-triazine (**8b**) from the isomer azide compound **7**, can be applied in considering the behavior of our system.

By use of classical valence-bond structure, the angular ring (**3a,b**) can be described by two neutral equivalent formulas ("benzenoid structures"), whereas the linear system **4** can be formulated only by one neutral valence-bond structure ("quinonoid structure") (Scheme III). Thus, the fact that the angular system is the major component of the equilibrium seems unambiguously proven.

Experimental Section

Compounds were synthesized according to the given references. Enrichment of the ^{15}N-labeled derivatives was 10% and was controlled by mass spectroscopy. UV spectra were recorded by a Unicam SP 800 spectrometer and NMR spectra by a Varian XL-100 apparatus. Mass spectra were obtained with an AEI MS-902 spectrometer with a direct inlet system.

Registry No.—**2**, 69365-63-5; **3**, 50275-24-6; **4**, 69365-64-6; **5**, 49739-45-9; **9**, 1443-60-3; **10**, 33459-64-2; **16**, 69365-61-3; **18**, 69365-62-4; **20**, 24477-89-2.

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