5,5-(1,2-Ethylenedioxy)-6-methoxy-1,3,4,5-tetrahydrobenz[*cd*]indole (20). The ketal **20** was prepared from the aldehyde **18** by following general procedure B in 96% yield. White prisms (from ethyl acetate–hexane): mp 141–143 °C; IR (KBr) 3330 cm^{-1}; NMR ($CDCl_3$) δ 2.2 (t, 2 H, J = 6 Hz), 3.0 (t, 2 H, J = 6 Hz) 3.9 (s, 3 H), 4.2 (m, 4 H), 6.8 (s, 1 H), 6.9 (d, 1 H, J = 9 Hz), 7.2 (d, 1 H, J = 9 Hz), 7.9 (br s, 1 H); mass spectrum (methane CI), m/e 246.

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.49; H, 6.29; N, 5.47.

3,4-Dihydrobenz[*cd*]indol-5(1*H*)-one (1). The aldehyde **17** (4.86 g, 20.0 mmol) was treated as described in general procedure B by using 3 mol % rhodium catalyst. The ketal **19** was isolated as a colorless oil:[7a] IR (NaCl film) 3420 cm^{-1}; NMR ($CDCl_3$) δ 2.2 (t, 2 H, J = 7 Hz), 3.0 (t, 2 H, J = 7 Hz), 4.2 (m, 4 H), 6.8 (s, 1 H), 7.2 (m, 3 H), 7.9 (br s, 1 H); mass spectrum (methane CI), m/e 216. The ketal **19** was dissolved in acetic acid (9 mL) and water (1 mL). After 10 min at 25 °C, water (10 mL) was added and the mixture was cooled to 0 °C for 30 min. The product was collected by filtration, washed twice with water, and dried under vacuum for 48 h at 25 °C to yield 3.04 g (89%) of the ketone **1** as red crystals: mp 161–163 °C (lit.[8] mp 162–164 °C); IR (KBr) 3260, 1655, 1620, 1605, 1495 cm^{-1}; NMR ($CDCl_3$) δ 2.9 (t, 2 H, J = 7 Hz), 3.3 (t, 2 H, J = 7 Hz), 7.1 (s, 1 H), 7.3 (t, 1 H, J = 7 Hz), 7.5 (d, 1 H, J = 7 Hz), 7.6 (d, 1 H, J = 7 Hz), 8.5 (br s, 1 H); mass spectrum (methane CI), m/e 172.

6-Methoxy-3,4-dihydrobenz[*cd*]indol-5(1*H*)-one (2). The ketal **20** (4.50 g, 18.4 mmol) was dissolved with warming in acetic acid (9 mL) and water (1 mL). After 5 min at 50 °C, the solution was diluted with water (8 mL) and cooled at 0 °C for 30 min. The product was collected by filtration, washed twice with water, and dried under vacuum for 48 h at 25 °C to yield 3.12 g (84.5%) of **2** as a light yellow powder: mp 165–166 °C, IR (KBr) 3310, 1660, 1618, 1601 cm^{-1}; NMR ($CDCl_3$) δ 2.8 (t, 2 H, J = 6 Hz), 3.1 (t, 2 H, J = 6 Hz), 3.9 (s, 3 H), 6.8 (d, 1 H, J = 9 Hz), 7.0 (s, 1 H), 7.5 (d, 1 H, J = 9 Hz), 8.9 (br s, 1 H); mass spectrum (methane CI), m/e 202.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.42; H, 5.51; N, 7.03.

Acknowledgment. We thank Dr. C. Kaiser for helpful discussions and encouragement, E. Reich for microanalyses, and Dr. S. Rottschaeffer, L. Killmer, and M. Mentzer for mass spectra.

Registry No. **1**, 3744-82-9; **2**, 90858-79-0; **11**, 90858-80-3; **12**, 65602-68-8; **13**, 65602-69-9; **15**, 90858-81-4; **16**, 90858-82-5; **17**, 90858-83-6; **18**, 90858-84-7; **19**, 89331-00-0; **20**, 90858-85-8; **24a**, 3770-50-1; **24b**, 4792-58-9; **24c**, 30933-69-8; **25a**, 19005-93-7; **25b**, 21778-81-4; **25c**, 90858-87-0; **26a**, 120-72-9; **26b**, 1006-94-6; **26c**, 90858-86-9; $Rh(dppp)_2Cl$, 53450-82-1; $(PPh_3)_2RhCOCl$, 13938-94-8; 1,3-bis(diphenylphosphino)propane, 6737-42-4.

Synthesis and Structural Study of Azidonaphtho-*as*-triazines: "Annelation Effect" in Azide–Tetrazole Equlibria[1]

Gy. Hajós, A. Messmer,* A. Neszmélyi, and L. Párkányi

Central Research Institue for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B. 17, Hungary

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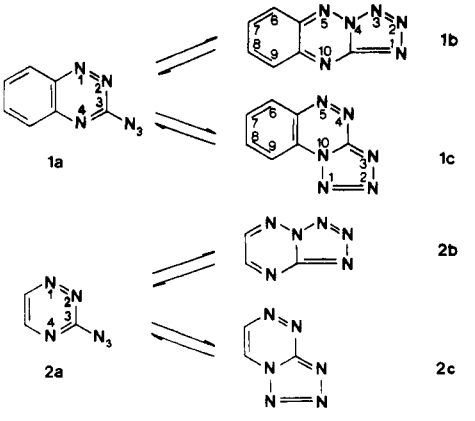
Azide derivatives of the three possible (two angular and one linear) naphtho-as-triazines **7a**, **10a**, and **15a** were prepared and the equilibria leading to fused tetrazoles were investigated by NMR spectroscopy and X-ray analysis. Comparison of the differently annelated systems (topological isomers) revealed an essential "annelation effect": while 3-azidonaphtho[2,1-*c*]-*as*-triazine (**7a**) and 3-azidonaphtho[1,2-*c*]-*as*-triazine (**10a**) formed "*b*-fused" tetrazoles **7b** and **10b**, the linear 3-azidonaphtho[2,3-*e*]-*as*-triazine (**15a**) resulted in the "*c*-fused" tetrazole compound **15c**. For the differences between behavior of the angular and the linear azidonaphthotriazines, a possible interpretation is presented by extension of Clar's principle to heteroaromatic systems.

Earlier we have shown[2,3] that isomerization of 3-azidobenzo-*as*-triazine (**1a**) affords predominantly tetrazolo[5,1-*a*]benzo-*as*-triazine (**1c**), whereas the other possible tetrazole isomer **1b** can only be detected in dipolar aprotic solvents (e.g., in dimethyl sulfoxide) in small amounts.[4] Ring closure of the monocyclic azido-*as*-triazine **2a** as reported later by Paudler et al.[5] proceeds, however, in an essentially different way: tetrazolo[1,5-*b*]-*as*-triazine (**2b**) was found exclusively as product and no trace of [5,1-*c*]-fused isomer **2c** was detected.

As the presence of the additional fused benzene ring in **1** (compared to **2**) caused a dramatic change in direction of the ring closure (i.e., cyclization occurred at N-4 rather than at N-2), the problem of whether "*b*- or "*c*-fused" types predominate in tetrazole systems having one more annelated benzene ring was of interest.

Scheme I

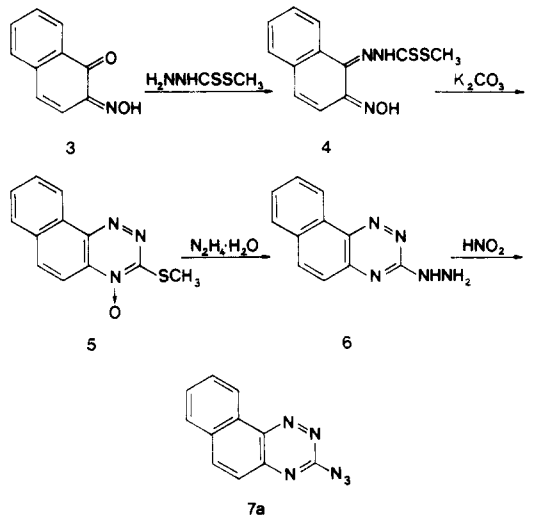


Only one of the three possible azidonaphtho-*as*-triazines (two angular and one linear ring systems) is described in the literature. Vilarrasa et al. reported in their first

(1) Presented in part at the Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, 1980; Abstr pp 115.
(2) Messmer, A., Hajós, Gy., Benkő, P.; Pallos, L. *J. Heterocycl. Chem.* **1973**, *10*, 575.
(3) Messmer, A.; Hajós, Gy.; Tamás, J.; Neszmélyi, A. *J. Org. Chem.* **1979**, *44*, 1823.
(4) Increased participation of **1b** in equilibria for substituted cases was found recently by Castillon, S.; Meléndez, E.; Pascual, C.; Vilarrasa, J. *J. Org. Chem.* **1982**, *47*, 3883.
(5) Goodman, M. M.; Atwood, J. L.; Carlin, R.; Hunter, W.; Paudler, W. W. *J. Org. Chem.* **1976**, *41*, 2860.

0022-3263/84/1949-3199$01.50/0

Scheme II



3 4 5 6 7a

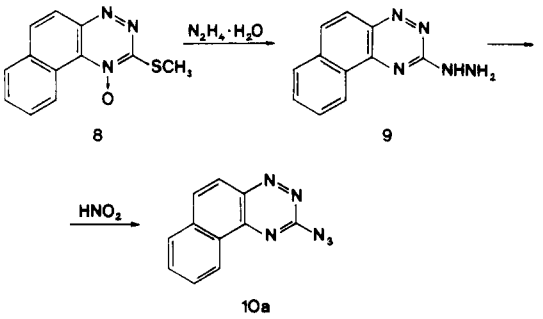
publication[6] on this subject that reaction of tetrazolediazonium salt with 2-aminonaphthalene followed by cyclization gave rise to a crystalline fused tetrazole compound which, on the basis of NMR and UV studies, was supposed to have structure **7c** ("Z-shape" molecule). The same authors recently reported[7] a reinvestigation of this structure and, on the basis of a detailed 200-MHz NMR study, they proposed structure **7b** ("L-shaped" molecule).

In the present paper we elaborated an independent route to 3-azidonaphtho[2,1-*e*]-*as*-triazine (**7a**) and/or its tetrazole isomer. Reaction of β-nitroso-α-naphthol (**3**) with methyl dithiocarbazate gave a rather unstable condensation product **4** which could be cyclized to 3-(methylthio)naphtho[2,1-*e*]-*as*-triazine 4-oxide (**5**) in moderate yield. The methylthio *N*-oxide compound **5** was treated with hydrazine hydrate and the simultaneously reduced hydrazine compound **6** was reacted with nitrous acid to give **7a**.

An infrared spectrum of the crude product **7a** contained an intense azide peak at 2100 cm^{-1}. Repeated spectroscopic control during storage in a desiccator at room temperature, however, showed that this peak gradually disappeared and in about one week after the preparation it was no longer present. The ^1H NMR spectrum of this product was found to be identical with that reported by Vilarrasa et al.,[6,7] thus, it could be regarded to have structure **7b**. The fact that the crude azide product and **7b** also gave identical NMR spectra showed that **7a** was obtained as primary, metastable azide product.

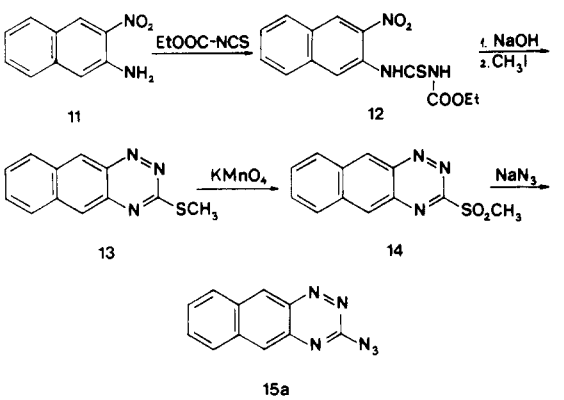
Azide derivative of the second possible angular naphtho-*as*-triazine **10a**—the [1,2-*e*]-fused system—has not been described earlier. Preparation of this product was accomplished by hydrazine hydrate treatment of 3-(methylthio)naphtho[1,2-*a*]-*as*-triazine *N*-oxide (**8**) synthesized according to Lalor et al.[8] followed by treatment of the resulting hydrazine compound[9] **9** with nitrous acid. While the infrared spectrum of the crude product **10a** recorded in KBr disks showed an intense azide peak at 2120 cm^{-1}, no azide band was observed in the spectrum of the recrystallized product which, for this evidence, was considered to have an isomeric tetrazole structure **10b** or **10c**.

Scheme III



8 9 10a

Scheme IV



11 12 13 14 15a

As far as we know, no derivative of the linearly fused naphtho[2,3-*e*]-*as*-triazine ring system has been known in the literature. Our attempts to synthesize this linear isomer similarly to the angular ones **7** and **10** were unsuccessful because of the difficult access to 2,3-naphthoquinone analogues. Application of the simplified Arndt–Rosenau *as*-triazine synthesis elaborated in our laboratory recently,[10] however, provided a suitable method for synthesis of 3-(methylthio)naphtho[2,3-*e*]-*as*-triazine (**13**).

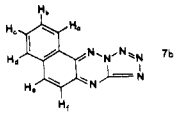
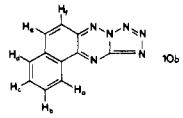
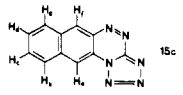
Thus, treatment of 2-nitro-3-aminonaphthalene (**11**) with ethoxycarbonyl isothiocyanate resulted in the crystalline thiourea derivative **12**, which, in the presence of aqueous sodium hydroxide solution, underwent cyclization to give 3-(methylthio)naphtho[2,3-*e*]-*as*-triazine (**13**). It is interesting to note that unlike other cases[10] the 1-oxide derivative of **13** was not detected in the reaction mixture and direct formation of the deoxy compound **13** was found.

Selective oxidation of methylthio compound **13** by potassium permanganate afforded methylsulfonyl derivative **14** which, on reaction with sodium azide, resulted in the potential azido compound **15a** under very mild conditions. (Efforts to exchange the methylthio group of **13** for hydrazine were unsuccessful because of considerable decomposition of the reaction mixture.) The crystalline solid obtained directly from the reaction mixture was considered to exist entirely in tetrazole form **15b** or **15c** because of the absence of the azide peak in the IR spectrum recorded in KBr disk.

^1H NMR spectra of the products **7**, **10**, and **15** recorded at 400 MHz (Table I) showed unambiguously that, in all of the three cases, only one of three possible isomers is present in dimethyl sulfoxide solution. From the close agreement of infrared spectra recorded in the solid phase and dimethyl sulfoxide solution, we concluded, furthermore, that the same structure is present in the crystalline state and in the dimethyl sulfoxide solution, and, because

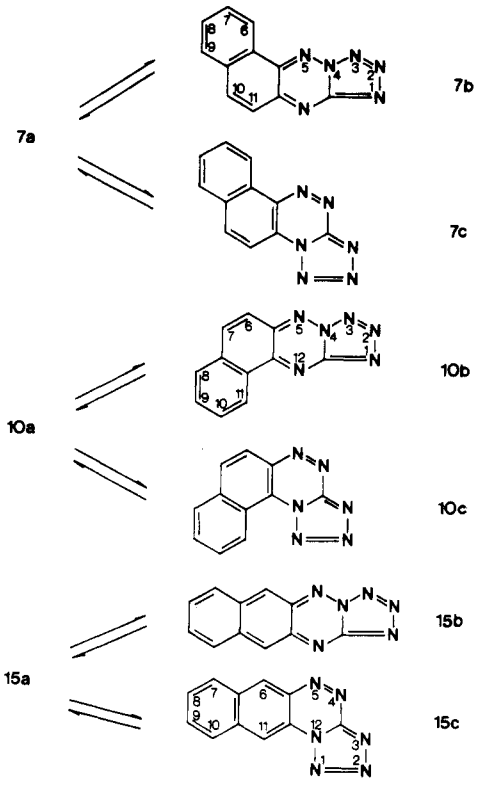
(6) Vilarrasa, J.; Granados, R. *J. Heterocycl. Chem.* **1974**, *11*, 867.
(7) Castillon, S.; Vilarrasa, J. *J. Org. Chem.* **1982**, *47*, 3168.
(8) Lalor, F. J.; Scott, F. L. *J. Chem. Soc. C* **1969**, 1034.
(9) Synthesized by another method by Fusco, R.; Bianchetti, G. *Gazz. Chim. Ital.* **1957**, *87*, 438.
(10) Messmer, A.; Hajós, Gy.; Benkő, P.; Pallos, L. *Acta Chim. Hung. (Budapest)* **1980**, *103*, 123.

Table I. ^{1}H NMR Chemical Shifts of the Tetracyclic Tetrazolo-*as*-triazine Systems (7b, 10b, and 15c)[a]

	H_a	H_b	H_c	H_d	H_e	H_f	coupling constants
 7b	9.03	8.00	7.94	8.16	8.42	7.85	J_{ab} = 7.8 Hz J_{bc} = 7.6 Hz J_{cd} = 7.5 Hz J_{ef} = 9.5 Hz J_{ac} = ~1.0 Hz[b] J_{bd} = ~1.8 Hz[b]
 10b	9.14	8.05	7.94	8.16	8.32	7.91	J_{ab} = 8.0 Hz J_{bc} = 7.0 Hz J_{ef} = 9.5 Hz J_{cd} = 8.0 Hz J_{ac} = ~1.0 Hz[b] J_{bd} = ~1.5 Hz[b]
 15c	9.79	8.59	8.08	7.92	8.51	9.27	J_{bc} = 8.7 Hz J_{cd} = 6.7 Hz J_{de} = 8.3 Hz J_{bd} = ~1.0 Hz[b] J_{ce} = ~1.0 Hz[b]

[a] Me_2SO-d_6 solutions, 60 °C, 400 MHz. [b] ±0.4 Hz.

Scheme V



of the lack of azide band at 2100 cm^{-1}, the presence of one of the possible tetrazole isomers, **7b** or **7c**, **10b** or **10c**, **15b** or **15c**, should be considered. With knowledge of these spectroscopic data, however, no decision could yet be made between the alternative (*b*- or *c*-fused) structures.

Elucidation of this structural problem was accomplished by X-ray analysis and ^{13}C NMR spectroscopy.

Suitable crystals for X-ray structure determination were prepared in cases **7** and **10**. The result (Figure 1) showed that both tetrazole systems exist as "*b*-fused" tetrazoles, i.e., **7b** and **10b**.

The structure of the third linearly fused isomeric tetrazole **15** was determined by comparison of the ^{13}C NMR shifts with those of tetrazolo[1,5-*b*]benzo-*as*-triazine (**1b**) and the angular **7b** compound.

In our earlier publication[3] we described that the ^{13}C chemical shift of C-9 in tetrazoles **1c** and **1b** is of diagnostic importance in respect to the type of annelation ("*b*-fused" or "*c*-fused" systems): the chemical shift at 115 ppm found in the ^{13}C NMR spectrum of **1c** was attributed to the "*c*-fused" annelation and the shift of the corresponding carbon atom in the linear ring system **1b** appeared at

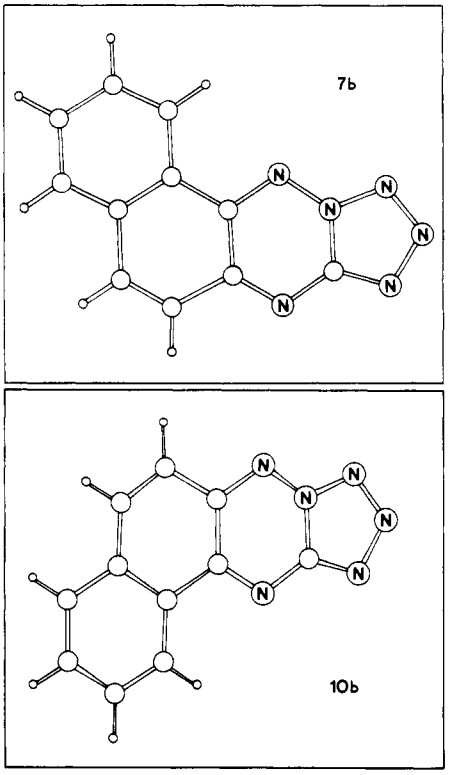


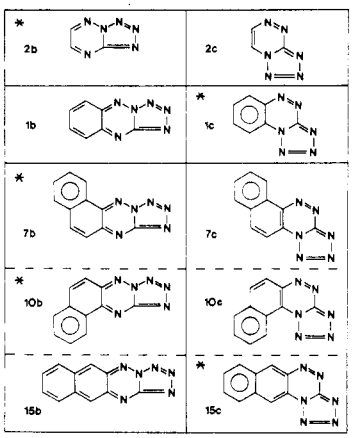
Figure 1. The structures of **7b** (above) and **10b** (below). Only one of the molecules of the asymmetric unit is shown.

Table II. ^{13}C Shifts of Tertiary Carbon Atoms in Differently Annelated Tetrazolobenzo-*as*-triazines (1b and 1c) and in Tetracycles 7b and 15c[a]

1b	1c	7b	15c
137.6 C-6	137.8 C-6	140.4 C-6	133.4
134.9 C-7	131.1 C-7	132.4 C-10	131.3
128.6 C-8	130.5 C-8	129.7 C-7,8	130.0 C-6,7,8,9,10
127.0 C-9	115.4 C-9	129.4	127.8
		124.9 C-11	127.9
		124.5 C-9	112.8 C-11

[a] The carbon shift of diagnostic importance[3] in **1b** and **1c** (C-9) as well as the shifts of the corresponding carbon atoms in the tetracycles (i.e., C-11 in **7b** and C-7 in **15c**) appear in boldfaced print.

Table III. Representation of the Possible Bicyclic, Tricyclic, and Tetracyclic Fused Tetrazolo-*as*-triazines (2, 1, 7, 10, and 15, respectively) by Clar's Notation[a]



[a] Circles stand for benzene π sextets. Asterisks indicate the experimentally found isomers.

significantly lower field (δ <125).

Table II contains ^{13}C NMR shifts of the corresponding carbon atoms for compounds **1b**, **1c**, and **7b** as well as for the new linear system **15**. This comparison clearly shows that **7b**, having a shift similar to **1b**, has a "*b*-fused" annelation as proved by X-ray, while the shift of product **15** is very close to that of "*c*-fused" **1c**. This spectroscopic evidence supports structure **15c**.

The behavior of the differently fused (two-, three-, and four-ring) tetrazolo-*as*-triazine systems is compared in Table III. This table reveals that change of annelation of the fused benzene ring plays an important role in orientation of the ring closure of azide tetrazole.

A general interpretation of this essential "annelation effect" can be obtained by consideration of the heteroaromatic stability of the isomer pairs. In Table III we used the Clar sextet notation:[11] each separate real benzene unit, when possible, is demonstrated by a Clar circle (one circle stands for three benzene type double bonds, i.e., for the π-electron sextet). According to Clar's theorem, the greater number of Clar's circles in a polyfused carbocycle, the higher degree of aromatic stability expected. Support for this principle has recently been provided by Staab et al.[12]

By application of Clar's rule elaborated originally for carbocycles, an easy estimation can be made for the difference between stabilities of the *b*- and *c*-fused topological isomers in cases **1** and **15**: with these equilibria, the *c*-fused ring systems are highly favored because of their enhanced aromatic character, whereas **1b** and **15b** can not be described by formulas having at least one Clar's circle at all.

Our experimental findings seem to be in accordance with this consideration. In the case of **1**, **1c** was found as the major component both in solutions and in the solid phase,[3] and the four-ring system **15c** seems to be the only component in solution and in crystalline form.

The equilibria[17] of angular systems **7** and **10** may, however, be interpreted by extension of Clar's principle to heteroaromatics: the energetic preference of **2b** over **2c**, found experimentally,[5] may account for the preference of formation of **7b** and **10b** instead of the *c* isomers, as **7b** and **10b** do involve the more stable heteroaromatic moiety.

As conclusion we can point out that the heteroaromatic character of the polyfused tetrazoles can be regarded as one of the main factors governing direction in the cyclization of azido-*as*-triazines. Formation of "*c*-fused" isomers were found in cases **1c** and **15c** where an enhanced stability of the *c*-fused isomers are predicted on Clar's basis. In the other cases like the two-ring system **2** as well as tetracycles **7** and **10** formation of the *b*-fused tetrazoles are favored. This experimental finding could be rationalized by application of Clar's theorem to the heteroaromatic unit of the polyfused system. Work on further study of this annelation effect with different types of heteroaromatics is in progress.

Experimental Section

X-ray Structure Analysis. Crystals of both compounds **7b** and **10b** were mounted on a glass fiber and the determinations of unit cell parameters and intensity data collections were performed on an Enraf-Nonius CAD-4 four-circle computer-controlled diffractometer.

7b: $C_{11}H_6N_6$, F wt = 222.21, a = 15.355 (4) Å, b = 7.639 (5) Å, c = 17.223 (8) Å, β = 104.22 (2)°, $p2_1/n$, Z = 8, d_{exp} = 1.50, d_x = 1.507 g cm^{-3}, μ(Mo K$_\alpha$, λ = 0.7107 Å) = 1.10 cm^{-1}, approximate crystal size = 0.08 × 0.11 × 0.16 mm. 2253 independent intensities were collected by using graphite-monochromated Mo K$_\alpha$ radiation ($1.5 \lesssim \varphi \gtrsim 22$).

10b: $C_{11}H_6N_6$, F wt = 222.21, a = 15.467 (1) Å, b = 7.650 (1) Å, c = 20.108 (1) Å, β = 124.40 (2)°, $P2_1/c$, Z = 8, d_{exp} = 1.51, d_x = 1.504 g cm^{-1}, μ(Cu K$_\alpha$, λ = 1.5418 Å) = 8.41 cm^{-1}, approximate crystal size: 0.18 × 0.20 × 0.30 mm. 2791 independent intensities were collected by using graphite-monochromated Cu K$_\alpha$ radiation ($1.5 \lesssim \varphi \gtrsim 70$).

Structure Solution and Refinement. Both structures were routinely solved by direct methods[13] and were refined by anisotropic full-matrix least-squares analysis, **7b**: Due to the rather poor quality of the crystal and the small number (1743) of observed reflections ($I \geq 1.0\ \sigma(I)$) the refinement was terminated at R_{obsd} = 0.134 (1743) and R_{tot} = 0.151 for all data. Hydrogen positional parameters were generated from assumed geometries.

10b: 2265 reflections ($I \geq 1.0\ \sigma(I)$) were used in the refinement. Hydrogen positional parameters were generated from assumed geometries. The final R values were R_{obsd} = 0.049 and R_{tot} = 0.065 for all data. The highest peak in the final difference map was 0.24 e Å^{-3}.

The final values of positional and thermal parameters of **7b** and **10b** are given in the microfilm supplement.[14]

Preparation of Compounds 4–15. Melting points were obtained on a Büchi apparatus and are uncorrected. IR spectra were obtained on Specord IR 75 instrument. The 60-MHz ^1H NMR spectra were obtained on Varian EM-360, and ^{13}C NMR spectra and 100-MHz ^1H NMR spectra on Varian XL-100 spectrometers; chemical shifts are reported in parts per million with respect to internal Me_4Si.

Methyl *N*-[(β-Hydroximino-α-naphthylidene)amine]dithiocarbamate (4). A mixture of β-nitroso-α-naphthol (1.6 g, 9.2 mmol), methyl dithiocarbazate[15] (1.2 g, 9.9 mmol), ethanol (40 mL), and hydrochloric acid (0.8 mL) was stirred in an inert atmosphere at room temperature for 48 h. The precipitated red crystals were filtered off to give 0.9 g (35%) of crude product. A high degree of decomposition was observed with any effort for recrystallization and the crude product was not suitable for elemental analysis; however, it proved to be pure enough for further reaction.

3-(Methylthio)naphtho[2,1-*e*]-*as*-triazine 4-Oxide (5). The mixture of the crude methyl ester **4** (0.7 g, 2.6 mmol) and aqueous potassium carbonate solution (20%, 56 mL) was refluxed for 10 min. The mixture was then cooled and the precipitated dark solid was filtered off. Recrystallization from glacial acetic acid afforded

(11) Clar, E. "Aromatic Sextet"; Wiley: New York, 1972.
(12) These authors carried out a thorough structure analysis of kekulene and found that "formulation employing Clar's sextet notation is undoubtedly the best representative of the actual bond situation of kekulene": Krieger, C.; Diederich, F.; Schweitzer, D.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 699.
(13) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B26*, 274.
(14) See paragraph at the end of paper regarding supplementary material.
(15) Kőrősi, J. Ger. Patent 1 934 809, Jan 29, 1970; *Chem. Abstr.* **1970**, *72*, 100334s.

brilliant yellow needles: 0.38 g (60%); mp 189–190 °C; ^{1}H NMR (TFA) δ 9.1–8.9 (m, 1 H, H_{10}), 8.5–8.0 (m, 5 H, H_{5-9}), 2.8 (s, 3 H, CH_3); IR (KBr) 3080, 3000, 2920 (CH), 1610, 1590, 1510, 1500 cm^{-1} (C=N, C=C).

Anal. Calcd for $C_{12}H_9N_3OS$: N, 17.27; S, 13.18. Found: N, 17.09; S, 13.24.

3-Hydrazinonaphtho[2,1-*e*]-*as*-triazine (6). A mixture of 3-(methylthio)naphtho[2,1-*e*]-*as*-triazine 4-oxide (**5**) (0.3 g, 1.2 mmol), 100% hydrazine hydrate (3 mL), and butanol (3 mL) was refluxed for 2 h. Long yellow needles separated from the cooled reaction mixture which, after recrystallization from acetonitrile, resulted in 0.18 g (69 %) of **6**: mp 208–209 °C; IR (KBr) 3300–3000, 1630, 1610, 1580 cm^{-1}.

Anal. Calcd for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N 33.15. Found C, 62.43; H, 4.52; N, 32.91.

Naphtho[2,1-*e*]tetrazolo[1,5-*b*]-*as*-triazine (7b). A mixture of hydrazino compound **6** (0.16 g, 0.76 mmol), glacial acetic acid (10 mL), and water (5 mL) was treated with sodium nitrite (0.06 g) in small portions. The reaction mixture became first a clear solution from which a cream colored solid separated. Recrystallization from dimethyl formamide gave rise to 0.09 g (50%) of tetrazole compound **7b**: mp 187–189 °C; IR (KBr) of the crude product 3050 (CH_{Ar}), 2150, 2120 (N_3), 1600, 1560, 1530 (C=N, C=C); IR after recrystallization from ethanol 3050 (CH_{Ar}), 1590, 1530, 1510 (C=N, C=C) cm^{-1}. The same spectrum (the latter one) was obtained from the crude product after a 6 day storage; IR (Me_2SO) 3050, 1600, 1540, 1520 cm^{-1}; UV (Me_2SO) 427 (sh), 410, 380, 285 nm.

Anal. Calcd for $C_{11}H_6N_6$: C, 59.46; H, 2.72; N, 37.82. Found: C, 59.15; H, 2.59; N, 37.54.

2-Hydrazinonaphtho[1,2-*e*]-*as*-triazine (9). A mixture of 2-(methylthio)naphtho[1,2-*e*]-*as*-triazine 1-oxide (**8**) (0.43 g, 1.8 mmol), butanol (5 mL), and 100% hydrazine hydrate (5 mL) was heated at reflux for 2 h. The resulting brown solution was cooled, and the separated yellow crystals were filtered off to give 0.54 g (69%) of **9**: mp 216–218 °C; IR (KBr) 3300, 3250 (NH), 3040 (CH_{Ar}), 1610, 1570, 1540 (C=N, C=C) cm^{-1}; NMR (TFA) δ 9.35 (d, 1 H, H_{10}), 8.94–7.7 (m, 5 H, H_{5-9}).

Anal. Calcd for $C_{11}H_9N_5$: N, 33.16. Found: N, 33.04.

Naphtho[1,2-*e*]tetrazolo[1,5-*b*]-*as*-triazine (10b). A mixture of 2-hydrazinonaphto[1,2-*e*]-*as*-triazine (**9**) (1.0 g, 4.7 mmol), glacial acetic acid (10 mL), and water (5 mL) was treated with sodium nitrite (0.43 g, 6.0 mmol) in small portions. Upon the addition, pale yellow crystals separated from the reaction mixture which were recrystallized from dimethylformamide to yield 0.65 g (62%) of **10b**: mp 193–194 °C; IR (KBr) of the crude product 3050 (CH_{Ar}), 2120 (N_3), 1620, 1570, 1550, 1530, 1500 (C=N, C=C) cm^{-1}; IR after recrystallization from dioxane 3050 (CH_{Ar}), 1610, 1560, 1540 cm^{-1}; IR (Me_2SO) 360, 1610, 1570, 1550 cm^{-1}; IR (CH_2Cl_2) obtained both from the metastable **10a** and from **10b** 3060, 2150 (m), 1610, 1570, 1555, 1525 cm^{-1}; UV (Me_2SO) 430 (sh), 382 nm; UV (CH_2Cl_2) 410 (sh), 382, 287, 279 nm.

Anal. Calcd for $C_{11}H_6N_6$: C, 59.46; H, 2.72; N, 37.82. Found: C, 59.37; H, 2.64; N, 38.11.

1-(Ethoxycarbonyl)-3-(2-nitro-3-naphthyl)thiourea (12). Treatment of a solution of 2-amino-3-nitronaphthalene (**11**)[16] (2.3 g, 12.2 mmol) in acetone (100 mL) with ethoxycarbonyl isothiocyanate (2.0 g, 15.2 mmol) followed by heating at reflux for 5 min resulted in a deep yellow solution. The reaction mixture was poured onto crushed ice (100 g), and the separated crystals were filtered and recrystallized from ethanol to give 3.3 g (85%) of product: mp 171–173 °C; NMR ($CDCl_3$) δ 9.0–7.1 (m, 6 H, H_{Ar}), 4.3 (q, 2 H, CH_2), 1.4 (t, 3 H, CH_3).

Anal. Calcd for $C_{14}H_{13}N_3O_4S$: N, 13.16; S, 10.04. Found: N, 13.06; S, 10.12.

3-(Methylthio)naphtho[2,3-*e*]-*as*-triazine (13). A mixture of thiourea compound **12** and 10% sodium hydroxide solution was refluxed for 10 min. The resulting deep red solution was mixed first with ice water (240 g) and then with methyl iodide (6 mL) and ethanol (20 mL), and the resulting mixture was shaken for 20 min. Extraction with dichloromethane, evaporation of the organic layer, and crystallization of the residue from acetonitrile gave rise to **13** (1.05 g, 42%): mp 134–136 °C; NMR ($CDCl_3$) δ 9.90 (s, 1 H, H_5), 8.4 (s, 1 H, H_{10}), 8.3–7.4 (m, 4 H, H_{Ar}), 3.7 (s, 3 H, CH_3).

Anal. Calcd for $C_{12}H_9N_3S$: N, 18.49; S, 14.11. Found: N, 18.12; S, 14.61.

3-(Methylsulfonyl)naphtho[2,3-*e*]-*as*-triazine (14). A solution of methylthio compound **13** (1.0 g, 4.4 mmol) in acetic acid (25 mL) and acetone (25 mL) was treated with a solution of potassium permanganate (1.0 g, 6.3 mmol) in water (60 mL). After a period of 1 h, the excess of permanganate was reduced by addition of sodium bisulfite solution, and the yellow mixture was poured onto water (200 mL) and was extracted with dichloromethane (2 × 100 mL). Evaporation of the organic layer and recrystallization of the residue from dioxane–petroleum ether resulted in **14** (0.9 g, 80%) as red crystals: mp 213–215 °C; NMR (Me_2SO-d_6) δ 9.4 (s, 1 H, H_5), 8.0 (s, 1 H, H_{10}), 8.8–7.8 (m, 4 H, H_{Ar}), 3.6 (s, 3 H, CH_3).

Anal. Calcd for $C_{12}H_9N_3O_2S$: N, 16.21; S, 12.37. Found: N, 16.08; S, 12.30.

Naphtho[2,3-*e*]tetrazolo[5,1-*a*]-*as*-triazine (15c). A mixture of methyl sulfone **14** (0.85 g, 3.3 mmol), sodium azide (0.5 g, 7.7 mmol), and dimethylformamide (20 mL) was stirred at room temperature for 10 min. The resulting yellow crystals were filtered and recrystallized from acetic acid to yield 0.42 g (58%) of **15c**: mp 216–218 °C; IR (KBr) 3050 (CH_{Ar}), 1620, 1600, 1500 (C=N, C=C) cm^{-1}; IR (Me_2SO) 3050, 1630, 1610, 1520, 1510 cm^{-1}; UV (Me_2SO) 410 (sh), 360, 288 nm; UV (CH_2Cl_2) 410, 360, 288 nm.

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Supplementary Material Available: A listing of final fractional coordinates and anisotopic thermal parameters (10 pages). Ordering information is given on any current masthead page.

(16) Crutis, R. F. Viswanath, G. *J. Chem. Soc.* **1959**, 1670.

(17) The azide–tetrazole isomerization in solution is generally considered to form an equilibrium[18]. In the case of **10a**=**10b**, the fact of the equilibrium was checked as follows: starting either from the crystalline azide compound **10a** or from the tetrazole isomer **10b**, upon dissolution in dichloromethane the same IR spectrum was obtained showing the presence of the major component **10b** together with a slight amount of azide **10a** (see Experimental Section).

(18) Tisler, M. *Synthesis* **1973**, 123.