Tetrahedron Vol 33, pp 1253 to 1262 Pergamon Press 19?? Printed in Great Britain

1,2,4-TRIAZOLES—XXXIII†

PHOTODIMERIZATION OF SOME *SYM*-Di(3-*s*-TRIAZOLO-[4,3-a]PYRIDYL)-ALKANES AND RELATED DERIVATIVES[1]

K. T. Potts,* W. C. Dunlap[c] and E. G. Brugel[d]
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181, U.S.A.

(*Received in USA* 29 *July* 1976; *Received in the UK for publication* 31 *December* 1976)

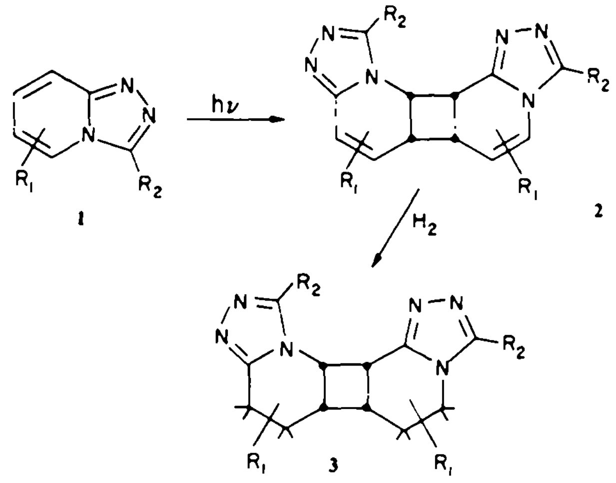
Abstract—Irradiation of 3,3'-[ethane-1,2-diyl]bis-[1,2,4-triazolo-[4,3-a]pyridine] at 300 nm gave the *cisoid*-fused cyclobutane dimer 5aα,5bα-10bα,10cα-tetrahydro-1,10-ethano-2,3,8,9,10a,10d-hexaazadicyclopenta[*a,i*]biphenylene. Under the same conditions 3,3'-[propane-1,3-diyl]bis-[1,2,4-triazolo[4,3-a]pyridine] gave the corresponding cyclobutane dimer, 5aα,5bα,10bα,10cα-tetrahydro-1,10-propano-2,3,8,9,10a,10d-hexaazadicyclopenta[*a,i*]biphenylene whereas at 254 nm the photoproduct obtained had the "cage-like" structure 3b,3c,3d,3e,6b,6c,6d,6e-octahydro-3,4-propano-1,2,3a,3f,5,6-hexaazadicyclobuta[*def,jkl*]dicyclopenta[*b,h*]biphenylene. Replacement of the hydrocarbon linkage with the oxybis(methylene) or a thiobis(methylene) unit and irradiation at 300 nm gave the corresponding *cisoid*-fused, cyclobutane dimers only. The effect of methyl substituents in the pyridine ring of the bicyclic system on the dimerization process was also studied.

In the previous publication,[2] various derivatives of 1,2,4-triazolo[4,3-a]pyridine (1) were found to undergo photodimerization to *cisoid*-fused cyclobutane derivatives by interaction of the 5,6- and 7,8-double bonds, affording 5aα,5bα,10bα,10cα-tetrahydro-1,2,3a,8,9,10a-hexaazadicyclopenta[*a,i*]biphenylene‡ (2), readily converted into 3 by hydrogenation. We have now found that dimerization occurs exclusively at the 5,6-double bond when steric constraints are imposed on the 1,2,4-triazolo[4,3-a]pyridine nucleus by incorporation into a system such as 4.

Examples of intramolecular photocycloaddition reactions involving heterocyclic systems have been reported only recently, most emphasis being placed on nonconjugated bichromophoric systems such as N,N'-[alkanediyl]bis[1$\underline{H}$-pyrrole-2,5-dione],[3] 7,7'-[alkanediylbis(oxy)]bis[2$\underline{H}$-1-benzopyran-2-one],[4] and 1,1'-[propane-1,3-diyl]bis[5-methyl-2,4(1$\underline{H}$,3$\underline{H}$)pyrimidinedione].[5] The number of carbon atoms in the chain joining the two nuclei was found to be important in determining the nature of the product formed which was also dependent to some degree on the substituents present at the dimerization centers.

Chemical results. The bichromophoric 1,2,4-triazolo[4,3-a]pyridines utilized in this study are described in Table 1, being synthesized as reported in the Experimental.[6]

Irradiation of 3,3'-[ethane-1,2-diyl]bis[1,2,4-triazolo[4,3-a]pyridine] (4) in DMF (or tetrahydrothiophene-1,1-dioxide) at 300 nm gave, after four days, the dimer 5 whose m.p. (>250° dec) was slightly higher than that of the monomer 4, (m.p. 245°). The hypsochromic shift in the UV spectrum (Table 2) is consistent with loss of some of the conjugation in the 1,2,4-triazolo[4,3-a]pyridine nucleus. At temperatures above 250° the dimer reverted to the monomer. Stability increased significantly on hydrogenation (25 psi hydrogen, Pt_2O) and the hydrogenated product 6, (m.p. 335°) showed a single absorption at 198 nm indicative of further loss of conjugation in the fused-ring system. The NMR spectrum showed only the



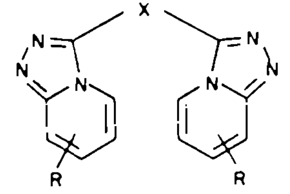
1 2 3

---

† Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

‡ This nomenclature is used here for consistency with that employed for the more complex systems described below.

Table 1. Some dichromophoric 1,2,4-Triazolo[4,3-a]pyridines



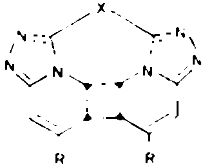
R	Mp, °C[a]	Yield[b], %	Form[c]	UV_{max} nm[d] (log ε)	Formula	Calc. % C	Calc. % H	Calc. % N	Found % C	Found % H	Found % N
				3,3'-[Ethane-1,2-diyl]bis[1,2,4-triazolo[4,3-a]pyridines], X = $-(CH_2CH_2)-$							
H	245-246[e]	74	Colorless plates	212 (4.67), 259 (3.74), 263 (3.74), 269 (3.81), 288 (3.74)	$C_{26}H_{18}N_{12}O_{14}$[f]	43.22	2.51	23.26	43.03	2.42	23.39
5-CH₃	335-336	86	Tan micro-needles	213 (4.74), 264 (3.95), 273 (3.98), 288 (3.95)	$C_{16}H_{16}N_6$	65.73	5.52	28.75	65.37	5.47	28.51
7-CH₃	249-250	87	Small colorless plates	211 (4.79), 272 (3.97), 288 (3.95)	$C_{16}H_{16}N_6$	65.73	5.52	28.75	65.65	5.46	28.69
8-CH₃	278-279	80	Colorless irreg. prisms	212 (4.61), 262 (3.88), 271 (3.95), 283 (3.87)	$C_{16}H_{16}N_6$	65.73	5.52	28.75	65.80	5.60	28.67
				3,3'-[Propane-1,3-diyl]bis[1,2,4-triazolo[4,3-a]pyridines], X = $-(CH_2CH_2CH_2)-$							
H	168-169[g]	39	Tan prisms	212 (4.77), 259 (3.74), 263 (3.75), 269 (3.81), 288 (3.75)	$C_{27}H_{20}N_{12}O_{14}$[h]	44.03	2.74	22.82	44.18	2.91	22.79
5-CH₃	224-225	80	Colorless small plates	213 (4.72), 266 (3.88), 273 (3.96), 288 (3.92)	$C_{17}H_{18}N_6$	66.64	5.92	27.43	66.31	5.89	27.19

7-CH_3	214-215	83	Small colorless needles	211 (4.86), 267 (3.97), 270 (3.99), 287 (3.82)	$C_{17}H_{18}N_6$ $C_{23}H_{21}N_9O_7$	66.64 51.59	5.92 4.00	27.43 23.54	66.47 51.81	5.93 3.80	27.31 23.39
8-CH_3	235-236	63	Tan irreg. prisms	211 (4.65), 262 (3.85), 270 (3.94), 284 (3.88)	$C_{17}H_{18}N_6$	66.64	5.92	27.43	66.51	5.92	27.38
5,7-(CH_3)	249-250	70	Pale, yellow-green needles	213 (4.77), 269 (3.95), 279 (3.99)	$C_{19}H_{22}N_6$	68.24	6.63	25.13	67.85	6.51	25.13
			3,3'-[Butane-1,4-diyl]bis[1,2,4-triazolo[4,3-a]pyridine], X =		-$(CH_2CH_2CH_2CH_2)$-						
H	227-228	47	Colorless irreg. prisms	211 (4.80), 258 (3.78), 262 (3.79), 268 (3.87), 290 (3.83)	$C_{16}H_{16}N_6$	65.73	5.52	28.75	65.44	5.39	28.58
			3,3'-[Oxybis(methylene)]bis[1,2,4-triazolo[4,3-a]pyridine], X =		-(CH_2OCH_2)-						
H	184-185	78	Colorless irreg. prisms	208 (4.70), 263 (3.91), 272 (3.96), 283 (3.84)	$C_{14}H_{12}N_6O$ $C_{26}H_{18}N_{12}O_{15}$	59.99 42.28	4.32 2.46	29.99 22.76	60.07 42.23	4.25 2.46	29.84 22.68
			3,3'-[Thiobis(methylene)]bis[1,2,4-triazolo[4,3-a]pyridine], X =		-(CH_2SCH_2)-						
H	209-212	62	Colorless needles^{ℓ}	211 (4.64), 264 (3.93), 273 (3.97), 285 (3.78)	$C_{14}H_{12}N_6S$ $C_{20}H_{15}N_9O_7S^{k}$	56.75 45.22	4.08 2.82	28.37 23.80	56.81 45.12	4.30 2.88	28.48 23.90

---

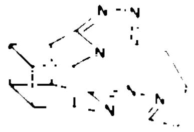
[a] Uncorrected. [b] Calculated on the basis of converted dicarboxylic acid. [c] All crystallized from ethanol except compound ℓ which crystallized from $CH_3OH:(C_2H_5)_2O$. [d] Determined in CH_3OH. [e] Lit.,[6] mp 234-235°. [f] Dipicrate, yellow needles from H_2O, mp 275-276°. [g] Lit.,[6] mp 170-171° [h] Dipicrate fine, yellow leafs from H_2O; mp 214-215°. [i] Picrate, small, yellow leafs from H_2O, mp 277-278°. [j] Dipicrate; fine, yellow leafs from H_2O, mp 199-200°. [k] Picrate, yellow micro-needles from H_2O, mp 251-253°.

Table 2. Photoproducts derived from some bichromophoric 1,2,4-triazolo[4,3-a]pyridines: 5aα,5bα,10bα,10cα-tetrahydro-2,3,8,9,10a,10d-hexaazadicyclopenta[a,i]biphenylenes



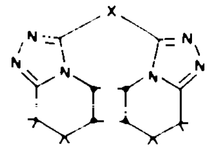
Compound Number	X	R	Yield %	M.p. °C	Form	Solvent	UV λmax (log ε)	NMR	Formula	Calc. % C	Calc. % H	Calc. % N	Found % C	Found % H	Found % N
5 Dipicrate	CH [illegible]	H H	[illegible]	[illegible]dec 275-276	Colorless needles Yellow microneedles	[illegible] [illegible]	[illegible]	[illegible]	$C_{14}H_{12}N_6$ $C_{26}H_{18}N_{12}O_{14}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8 Dipicrate	[illegible]	[illegible] H	55	[illegible]dec 228-230	Colorless needles Yellow powder	[illegible] H_2O	[illegible]	[illegible]	$C_{15}H_{14}N_6$ $C_{27}H_{20}N_{12}O_{14}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] Monopicrate	[illegible]	[illegible]	[illegible]	242-243 [illegible]	Colorless needles Yellow microneedles	[illegible]	245 [illegible]	[illegible]	$C_{16}H_{16}N_6$ $C_{22}H_{19}N_9O_7$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] Dipicrate	[illegible]	[illegible] H	[illegible]	232-234 [illegible]-240	Colorless irregular prisms; Yellow needles	[illegible]	248 [illegible]	[illegible]	$C_{17}H_{18}N_6$ $C_{29}H_{24}N_{12}O_{14}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
14 Dipicrate	[illegible]	[illegible] H	[illegible]	[illegible]	Colorless leafs Fine yellow leafs	[illegible]	249 [illegible]	[illegible]	$C_{14}H_{12}N_6O$ $C_{26}H_{18}N_{12}O_{15}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] Dipicrate	[illegible] [illegible]	H H	[illegible]	[illegible]-254 [illegible]-242	Colorless microflakes Yellow leafs	[illegible]	[illegible]	[illegible]	$C_{14}H_{12}N_6S$ $C_{26}H_{18}N_{12}O_{14}S$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]



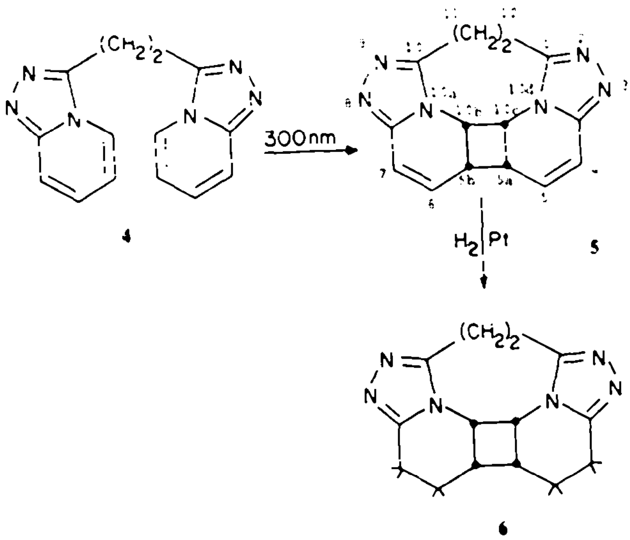
Compound Number	Yield, %[a]	M.p., °C[b]	Form	Solvent	λ max nm (log ε)	[illegible][d]	[illegible][c]	Formula	Analysis % Calcd C	H	N	Found C	H	N
13	74.5	241dec	Fine colorless needles	CH₃OH, H₂O	205 (4.81)	[illegible]	[illegible]	$C_{15}H_{14}N_6$	64	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Dipicrate		228-229	Yellow leafs					$C_{27}H_{20}N_{12}O_{14}$	45	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]



Compound Number	X	Yield %[a]	M.p., °C[b]	Form	Solvent	λ max nm (log ε)	[illegible][d]	Formula	Analysis % Calcd C	H	N	Found C	H	N
[illegible]	[illegible]	[illegible]	[illegible]dec	Colorless irregular prisms	[illegible]	[illegible]	[illegible]	$C_{14}H_{16}N_6 \cdot \frac{1}{2}H_2O$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Dipicrate			250dec	Yellow leafs				$C_{26}H_{22}N_{12}O_{14}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	Fine colorless needles	[illegible]	[illegible]	[illegible]	$C_{15}H_{18}N_6 \cdot (H_2O)_x$[e]						
Dipicrate	[illegible]		270dec	Yellow needles				$C_{27}H_{24}N_{12}O_{14}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
15	[illegible]	64.5	346-349	Fine colorless needles	[illegible]	199 (4.91)	9.[illegible] Hz	$C_{14}H_{16}N_6O$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Dipicrate	[illegible]		>250dec	Yellow irregular prisms				$C_{26}H_{22}N_{12}O_{15}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Yield after purification. [b] Uncorrected. [c] Determined in [illegible]. [d] [illegible] NMR [illegible]. [e] Indefinite hydrate.

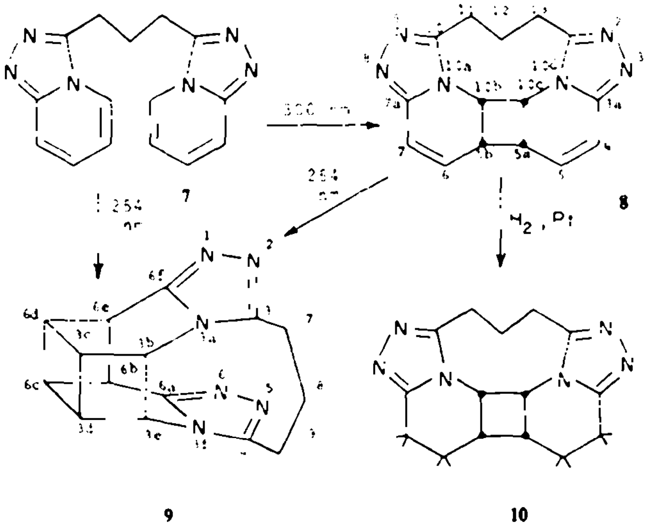


presence of hydrocarbon protons which, together with a molecular ion at $\underline{M}^{+}$ 268 and analytical data established a molecular formula of $C_{14}H_{16}N_6$ and were consistent with structure **6** for the hydrogenated dimer. Irrespective of the solvent, irradiation of **4** at 254 nm resulted in highly insoluble, non-crystalline, polymeric-type products.

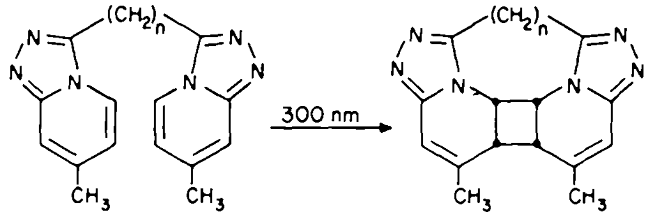
Irradiation of 3,3'-[propane-1,3-diyl]bis[1,2,4-triazolo[4,3-a]pyridine] (**7**) in DMF (or tetrahydrothiophene-1,1-dioxide) at 330 nm also gave a dimer, assigned structure 5aα,5bα,10bα,10cα-tetrahydro-1,10-propano-2,3,8,9,10a,10d-hexaazadicyclopenta[*a,i*]biphenylene (**8**). Its UV spectrum (Table 2) and other characterization data (Table 2), together with the absorption of two molecules of hydrogen to give a reduced product, **9**, ($\underline{M}^{+}$ 282) are consistent with structure **8** for this photoproduct.

At 254 nm 3,3' - [propane - 1,3 - diyl]bis[1,2,4 - triazolo[4,3 - a]pyridine] (**7**) gave a different photoproduct, assigned structure 3b,3c,3d,3e,6b,6c,6d,6e - octahydro - 3,4 - propano - 1,2,3a,3f,5,6 - hexaazadicyclobuta[*def,jkl*]dicyclopenta[*b,h*]biphenylene (**10**). Photodimer **10** did not absorb hydrogen, and its molecular ion $\underline{M}^{+}$ 278, the presence of only hydrocarbon protons in its NMR spectrum and a single absorption at 205 nm indicating that the pyridine ring is fully saturated as in the hydrogenated dimer **9**, are consistent with the formation of an intramolecular dimer. On heating above 200° in tetrahydrothiophene-1,1-dioxide solution, **10** reverted to **7** precluding any photo-induced rearrangements. Additional chemical evidence for structure **10** comes from the intramolecular dimerization of **8** (which is a likely precursor of **10**) at 254 nm in dry tetrahydrothiophene-1,1-dioxide to afford the cage dimer **10**. The intramolecular photodimerization of **8** strongly suggests the presence of a *cisoid*-fused cyclobutane ring system necessary for a second intramolecular photoprocess to occur. However consideration of the data below is necessary to exclude an alternative [4 + 4] followed by a subsequent [2 + 2] process which would also adequately explain the observed product.

An inspection of molecular models gave evidence that when the alkyl chain connecting the two chromophores consisted of two methylene units, the additional strain imposed by the ethano bridge prevented the second intramolecular photoreaction from occurring. Hence, on irradiation of **4** or its dimer **5** with 254 nm light, only polymeric type products were obtained.



The effect of introducing methyl substituents into the pyridine ring of **4** and **7** was also studied. Irradiation of the bicyclic system **11** (n = 2) or **11** (n = 3) at 300 nm in DMF gave the corresponding dimers **12** (*n* = 2) and **12** (*n* = 3), respectively, whose spectral characteristics are shown in Table 2. These data are consistent with dimerization having occurred at the 5,6-double bonds of both chromophores resulting in a *cisoid*-fused cyclobutane. Both dimeric products were totally resistant to hydrogenation (60 psi, H_2/Pt) of the 4,5- and 6,7-unsaturated bonds, no doubt due to the unfavorable steric crowding resulting from addition of hydrogen at the unhindered side of the double bonds which prevents reduction from occurring.



11 **12**

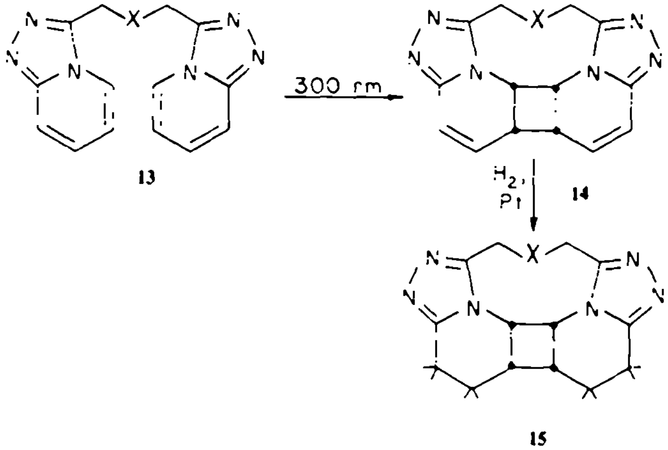
Irradiation of **11** (n = 2) and **11** (n = 3) or their respective dimers, **12** (n = 2) and **12** (n = 3), with 254 nm light gave highly insoluble non-crystalline material. The steric hindrance of the C_5 and C_6-Me groups in these dimers could possibly prevent sufficient orbital overlap for an intramolecular photodimerization to occur, with the resultant excited species reacting in an intermolecular fashion to form a polymeric species.

Introduction of methyl substituents into the 5- or 8-positions of the *s*-triazolo-[4,3-a]pyridine nucleus had a pronounced effect on the dimerization process. Irradiation of 3,3'-[ethane-1,2-diyl]bis[5-methyl-1,2,4-triazolo[4,3-a]pyridine] or 3,3'-[propane-1,3-diyl]bis-[5-methyl-1,2,4-triazolo[4,3-a]pyridine] at 300 nm in either DMF or tetrahydrothiophene-1,1-dioxide did not give a photoproduct and the starting compounds were recovered in near quantitative amounts. At 254 nm a highly insoluble, non-crystalline material was formed on the walls of the quartz reaction vessel. It appears that the 5-Me substituent can cause sufficient steric hinderance to the intramolecular photoreaction involving the 5,6-double bonds that no dimerization occurs. Similar results were obtained with the corresponding 8-Me substituted monomers and also with 3,3'-[propane-1,3-diyl]bis[5,7-dimethyl-1,2,4-triazolo-[4,3-a]pyridine]. In the last instance, however, no polymeric product was obtained at 254 nm, the starting material being recovered.

Although introduction of additional C atoms into the chain separating the two nuclei is possible through the use of the appropriate dicarboxylic acids, the propane chain represents the limit for systems suitable for solution photochemistry. 3,3'-[Butane-1,4-diyl]bis[1,2,4-triazolo[4,3-a]pyridine] was found to be insufficiently soluble in non-protic solvents to preclude its further study.

Utilizing the appropriate dicarboxylic acid and 2-pyridylhydrazine, it was possible to introduce an O and S atom into the alkane chain, these products also readily yielding analogous photoproducts. Thus irradiation of 3,3' - [oxybis(methylene)]bis[1,2,4 - triazolo[4,3 - a]pyridine] (**13**; X = O) in acetonitrile or tetrahydrothiophene-1,1-dioxide at 254 or 300 nm gave the *cisoid*-fused dimer 5aα,5bα,10bα,10cα - tetrahydro - 1,10 - propano - 2,3,8,9,10a,10d - hexaaza - 12 - oxadicyclopenta[*a,i*]biphenylene (**14**; X = O) (Table 2). This product showed the anticipated shift to shorter wavelength in its UV spectrum when compared to its precursor. In DMF no photoproduct was formed, and further irradiation of the dimer (**14**; X = O) at 254 nm did not give an intramolecular cyclized photoproduct of type **10** described above. Hydrogenation of **14** (X = O) gave the corresponding tetrahydro product **15** (X = O) (Table 2).

Irradiation of 3,3'-[thiobis(methylene)]bis[1,2,4-triazolo[4,3-a]pyridine] (**13**; X = S) at 300 nm in DMF gave the *cisoid* fused dimer 5aα,5bα,10bα,10cα - tetrahydro - 1,10 - propano - 2,3,8,9,10a,10d - hexaaza - 12 - thiadicyclopenta[*a,i*]biphenylene (**14**; X = S) (Table 2). The dimer did not absorb hydrogen, probably due to the sulfur atom in the thiobis(methylene) group poisoning the hydrogenation catalyst. At 254 nm in DMF solution **13** (X = S)



13 **14** **15**

gave a highly insoluble, non-crystalline, polymer-like product.

Characterization of these photoproducts was also possible by ready picrate formation. These are described in Table 2.

Structural and stereochemical assignments. NMR data (100 MHz) were used extensively in structure determinations of these photoproducts. In the substrate **4** the enthano bridge between the two chromophores is too short to allow the formation of a head-to-tail isomer and the dimer should consequently have a head-to-head configuration. However, two regioisomers are still possible depending on whether the cyclobutane is *cisoid* or *transoid* fused and, in addition, two structural isomers are possible depending on whether the cyclobutane is fused between the 5,6-bonds or 7,8-bonds of the 1,2,4-triazolo[4,3-a]pyridine nuclei. The position of the cyclobutane fusion was assigned on the basis of the chemical shift data which were compared to that obtained[5] for the cyclobutane protons in the intermolecular dimers **2** obtained from 1,2,4-triazolo[4,3-a]pyridines. In all of these cases, the cyclobutane proton fused at the 5-position absorbed at δ 5.7, and the cyclobutane proton fused at the 7-position absorbed at δ 3.8. Since the downfield cyclobutane protons assigned to H_{10b} and H_{10c} resonated at δ 5.98, these protons must be located at the 5-position of the 1,2,4-triazolo[4,3-a]pyridine nuclei consistent with dimerization having occurred at the 5,6-double bonds.

The sterochemistry of dimer **5** was established by considering the NMR coupling of the cyclobutane protons. Protons H_{10b}, H_{10c} (δ 5.98) and protons H_{5a}, H_{5b} (δ 4.74) form two pairs of symmetrically equivalent but magnetically non-equivalent nuclei and the spectrum may be interpreted in terms of an AA'XX' spin-system analysis.[7] The magnitude, $|J_{AX} + J_{AX'}| = 11.5$ Hz, obtained for **5** indicates that this spin system is *cis* vicinal (J_{AX}) coupled and *cis* diagnoal ($J_{AX'}$) coupled as it is in accord with the values and signs found for the vicinal[8] and diagonal[9] coupling constants of the cyclobutane protons in similar systems. Thus, a *cisoid*, head-to-head configuration seems most probable for dimer **5**. A similar doublet of doublets ($|J_{AX} + J_{AX'}| = 10.3$ Hz) was observed[4] for the cyclobutane protons of the *cisoid*, head-to-head dimer 7,7' - [propane - 1,3 - diylbis(oxy)]bis[2H - 1 - benzopyran - 2 - one] (**16**), whereas, in the case of the transoid dimer, 1,2,4,4aα,4bα,5,7,8aα,8bα - decahydro - 2,7 - dimethyl - cyclobuta[1,2 - c; 4,3 - c']dipyridine - 3,6 - dione (**17**), the value $|J_{AX} + J_{AX'}| = 7.5$ Hz was observed.[10]

The NMR spectrum of 5aα,5bα,10bα,10cα - tetrahydro - 1,10 - propano - 2,3,8,9,10a,10d, - hexaazadicyclopenta[*a,i*]biphenylene (**8**) with a propano bridge is very similar to that of **5**, with the major difference being attributed to the proton absorptions of the propano bridge. The protons at each terminus of the propano bridge are non-equivalent and give rise to complex, overlapping multiplets in the NMR region δ 1.95–δ 3.05.

The NMR spectrum of 3b,3c,3d,3e,6b,6c,6d,6e - octahydro - 3,4 - propano - 1,2,3a,3f,5,6 - hexaazadicyclobuta[*def,jkl*]dicyclopenta[b,h]biphenylene (**10**) was significantly different from those of dimers **5** and **8** in that no olefinic protons appeared in the δ 6.4–δ 6.8 region. The low field absorption at δ 6.00 was assigned to the two equivalent cyclobutane protons H_{3b} and H_{3e} having nearly identical chemical environments and thus chemical shifts to those observed for the $H_{10}b$ and $H_{10}c$ protons of dimers **5** and **8**. Protons H_{3b} and H_{3e} resonated as an AA'XX' system similar to the cyclobutane protons of dimers **5** and **8**, and appeared as a doublet of doublets being coupled with protons H_{3c} and H_{3d} ($|J_{3b,3c} + J_{3b,3d}| = 7.8$ Hz; $|J_{3e,3d} + J_{3e,3c}| = 7.8$ Hz).

The value of the $|J_{AX} + J_{AX'}|$ coupling for this photoproduct (7.8 Hz) is significantly smaller than that of dimers **5** and **8** (11.5 Hz and 11.3 Hz, respectively). The rigidity of structure **10** requires almost complete eclipsing of the vicinal, cyclobutane protons and, hence, would maximize the proton coupling rather than reduce them. However, the small coupling constants can be attributed on theoretical grounds[12] to a change in bond angles (and, thus, degree of hybridization[12]) in that an increase in the magnitude of the angles H–C–C' and C–C'–H' in the fragment H–C–C'–H' without any change in the dihedral angle will lead to a diminution of the vicinal coupling constant $J_{HH'}$.

The NMR spectrum of dimer **12** (n = 2) shows the C_5–CH_3 and C_6–CH_3 Me substituents to be equivalent, resonating at δ 2.17. The shift of the methyl absorption indicates that the Me groups are bonded to an olefinic carbon and thus confirms that dimerization indeed occurs

Table 3. NMR data for photoproducts obtained from several sym-di[(3-s-triazolo[4,3-a]pyridyl]alkanes

Dimer No.	H_7,H_8 (ABX)	H_5,H_6 (ABX)	H_{10b},H_{10c}	H_{5a},H_{5b}	H_{11},H_{12} [illegible]	[illegible]	C_5-CH_3	C_6-CH_3	Coupling Constants (Hz)
5	[illegible]	6.65	5.98	[illegible]	[illegible]				[illegible]
8	6.83	6.55	5.98	4.80		1.95-3.05			[illegible]
12, n = 2	6.66		5.98	4.82	3.70		[illegible]	[illegible]	[illegible]
12, n = 3	6.56		[illegible]	4.78		[illegible]	[illegible]	[illegible]	[illegible] $= 10.9$, [illegible] $= 10.8$, [illegible] $= 10.8$
16, X = O	[illegible]	[illegible]	6.03	4.80		[illegible] AB q ($J_{AB} = 16.8$)			[illegible]
16, X = S	[illegible]	[illegible]	[illegible]	[illegible]		[illegible] AB q			[illegible] $= 10.4$

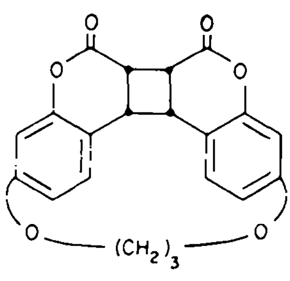
at the 5,6-bonds in both 1,2,4-triazolo[4,3-a]-pyridine chromophores. The Me absorption showed a small allylic coupling (1.3 Hz), verified by spin-decoupling experiments, with the H_4 and H_7 olefinic protons (δ 6.66) and some broadening due to small spin interactions with the H_{5a} and H_{5b} protons. The H_{10b} and H_{10c} protons (δ 5.98) formed part of an AA'XX' spin system with H_{5a} and H_{5b} (δ 4.82) and irradiation at the center frequency of the H_{10b} and H_{10c} doublet of doublets caused protons H_{5a} and H_{5b} to appear as a slightly broadened singlet due to the small coupling interaction with the olefinic Me protons. Conversely, irradiation of the H_{5a} and H_{5b} resonance caused collapse of the H_{10b} and H_{10c} absorption to a singlet at δ 5.98. The ethano bridge absorbed as a close A_2B_2 multiplet centered at δ 3.70. The corresponding dimer with a propano bridge **12** (n = 3) had an NMR spectrum nearly identical to the spectrum of **12** (n = 2) with the major difference being the absorption of the propano bridge which resonated as overlapping multiplets between δ 2.5–3.6.

The introduction of an O or S atom into the alkane bridge had a predictable effect on the NMR spectrum. The NMR spectrum of dimer **14** (X = 0) was similar to those of dimers **5** and **8** with the exception of those protons corresponding to the oxybis(methylene) unit which resonated as two overlapping AB multiplets (J_{AB} = 16.8 Hz) centered at δ 5.03 and δ 5.21. The H_{10b} and H_{10c} AA'XX' doublet of doublets were observed at δ 6.03 coupled to H_{5a} and H_{5b} and, as was anticipated protons H_4 and H_7 were an AB doublet at δ 6.91, coupled to protons H_5 and H_6 (δ 6.71; $J_{4,5} = J_{6,7}$ = 10.3 Hz).

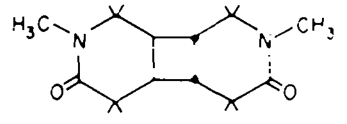
The coupling, $|J_{AX} + J_{AX'}|$ = 11.9 Hz, of the H_{10b} and H_{10c} resonances indicated that all the protons in the cyclobutane ring are in an α stereochemical position, and thus, the dimer is also cisoid-fused at the 5,6-double bonds of the 1,2,4-triazolo[4,3-a]pyridine nuclei. Spin-decoupling experiments on this dimer gave results analogous to those obtained with dimers **5** and **8**.

In contrast, the 60 MHz NMR spectrum of dimer **14** (X = S) showed a singlet for the absorption of the thiobis(methylene) protons. At this operating frequency the four protons of the thiobis(methylene) unit achieve magnetic equivalency causing the H_{10b} and H_{10c} protons to resonate in equivalent magnetic environments with identical chemical shifts (Table 2). The interrelationship of protons H_{5a}, H_{5b} (δ 4.79) to protons H_{10b}, H_{10c} and H_5, H_6 was established by double resonance experiments.

The thiobis(methylene) unit in the thioanalog **14** (X = S) showed a different NMR (100 MHz) absorption to that of its oxygen analog **14** (X = 0), resonating as two non-equivalent close AB absorptions centered at δ 4.40, the result of the thiobis(methylene) unit having a conformation in which all four protons are non-equivalent. This non-equivalency also causes the spatially adjacent protons, H_{10b} and H_{10c}, to have slightly different magnetic environments and slightly different chemical shifts, resulting in a virtual broadened doublet of doublets with the intensities of the peaks not conforming with those anticipated for a general AA'XX' spin system.



16



17

The NMR spectrum of the hydrogenated product **15** showed no olefinic protons as did the spectrum of dimer **14**. The H_{10b} and H_{10c} proton absorptions appeared as a virtual triplet ($|J_{AX} + J_{AX'}|$ = 9.6 Hz) at δ 5.64, and similar absorptions were observed in the hydrogenated products obtained from dimers **5** and **8**.

EXPERIMENTAL†

The 2-hydrazinopyridines and [alkane-1,3-diyl[bis]1,2,4-triazolo[4,3-a]pyridines] were prepared by literature procedures.[4] The following preparation illustrates the general procedure for the others whose spectral and analytical data are described in Table 1.

3,3' - [*Ethane* - 1,2 - *diyl*]*bis*[7 - *methyl* - 1,2,4 - *triazolo*[4,3 -*a*]-*pyridine* (**11**)

2-Hydrazino-4-methylpyridine (49.2 g, 0.40 mole) and butanedioic acid (23.6 g, 0.20 mole) were heated with stirring at 170° for 2 hr. The mixture was heated at 250° for an additional 4 hr and then cooled to ambient temp. The resulting solid crystallized from EtOH (Norit) to give small, colorless plates: 50.8 g (87%), m.p. 249–250°; M^+ 292 (26).

All photoreactions were carried out in anhydrous freshly distilled solvents in a Rayonet RPR-100 photochemical reactor equipped with either 300 or 254 nm UV lamps. Hydrogenations were performed in a Parr hydrogenation apparatus.

5a*α*,5b*α*,10b*α*,10c*α*-*Tetrahydro* - 1,10 - *ethano* - 2,3,8,9,10a,10d - *hexaazadicyclopenta*[*a,i*]*biphenylene* (**5**)

(a) *Using* N,N-*dimethylformamide as solvent*. Compound **4** (2.5 g) was dissolved in freshly distilled N,N-dimethylformamide (250 ml, dried over BaO) with gentle heating to effect soln. The soln was filtered into a quartz Erlenmeyer flask and irradiated 4 days with 300 nm UV light. The product which had separated from solution was collected and recrystallized from aqueous MeOH (Norit) giving colorless needles: 1.40 g (56%); m.p. > 250° (dec).

(b) *Using tetrahydrothiophene*-1,1-*dioxide as solvent*. Compound **4** (2.0 g) was dissolved in freshly distilled tetrahydrothiophene-1,1-dioxide (200 ml) and filtered into a quartz Erlenmeyer flask. The solution was irradiated 5 days with 300 nm UV light. No product had separated from this solvent. Crystallization was induced by dilution of the reaction mixture with a 3:1

---

†Spectral characteristics were determined with the following instrumentation: IR spectra Perkin–Elmer Model 337 spectrophotometer; mass spectra, Hitachi–Perkin–Elmer RMU-6E mass spectrometer at 70 eV, utilizing the direct inlet probe, with a source temp. of *ca.* 150°; NMR spectra, Varian T-60 and HA-100 spectrometers with a Varian C-1024 time averaging computer, using TMS as internal standard; UV spectra, Cary 14 spectrophotometer. M.p. determinations were performed with either a Uni-Melt Hoover capillary m.p. apparatus or a Mel-Temp capillary m.p. apparatus. NMR approximations were performed using the Nicolet NIC-05-40417 nuclear magnetic resonance spectrum calculation program (NMRCAL) with the Brüker WP-60 NMR spectrometer. Elemental microanalyses were by Instranal Laboratories, Inc., Rensselaer, N.Y. and Galbraith Laboratories, Inc., Knoxville, Tenn.

2-propanone, 1,1'-oxybisethane solution (400 ml) and cooled to 0° for 24 hr. The product was collected and recrystallization from aqueous MeOH (Norit) gave colorless needles: 0.82 g (41%); m.p. > 250° (dec), identical in all respects to *a*. above.

4,5,5aα,5bα,6,7,10bα,10cα - *Octahydro* - 1,10 - *ethano* - 2,3,8,9,10a,10d - *hexaazadicyclopenta*[*a*,*i*]*biphenylene* (**6**)

Compound **5** (0.6 g) was dissolved in AcOH (50 ml) in a Parr hydrogenation flask and platinum oxide (20 mg) was added. A H_2 pressure of 40 psi was maintained with continuous shaking for 14 hr. The soln was filtered (Celite) and the solvent was evaporated under reduced pressure. The residue was recrystallized twice from methanolic 1,1'-oxybisethane (Norit) giving colorless, irregular prisms: 0.49 g (82%); m.p. > 300° dec.; M^+ 228 (8).

3b,3c,3d,3e,6b,6c,6d,6e - *Octahydro* - 3,4 - *propano* - 1,2,3a,3f,5,6 - *hexaazadicyclobuta*[*def*,*jkl*]*dicyclopenta*[*b*,*h*]*biphenylene* (**10**)

Compound **7** (3.0 g) in tetrahydrothiophene-1,1-dioxide (250 ml) was irradiated at 254 nm for 5 days. The crystalline solid that had separated crystallized from aqueous MeOH (Norit) as fine, colorless needles: 2.24 g (75%), m.p. > 240° (dec). When DMF was used as solvent the original mother liquor had to be concentrated to obtain all the product. NMR (CF_3CO_2D) δ 6.00 (2, dd, AA'XX', H_{3b}, H_{3e}; $|J_{3b,3c} + J_{3b,3d}| = 7.8$ Hz; $|J_{3e,3d} + J_{3e,3c}| = 7.8$ Hz); 5.21 (2, dd, H_{6b}, H_{6e}; $|J_{6b,6c} + J_{6b,6d}| = 7.8$ Hz; $|J_{6e,6d} + J_{6e,6c}| = 7.8$ Hz); 3.78 – 4.18 (4, m centered at 3.98); 2.0–3.8 (3, m).

Acknowledgements—We wish to express our indebtedness to J. VanEpp for his help with our NMR spectral determinations and to Dr. K. Loening, Chemical Abstracts Service, for his help deriving the systematic names for these photoproducts.

REFERENCES

[1a] Support of this work by U.S. Public Health Service Research Grant CA08495, National Cancer Institute, is gratefully acknowledged; [b]Abstracted from the Ph.D. Dissertations of E. B. (1970) and W. D. (1975) presented to the Graduate School, Rensselaer Polytechnic Institute; [c]Corning Glass Foundation Fellow, 1974–75; [d]NSF Trainee 1968–70; [e]First presented at the XXIII International Congress of Pure and Applied Chemistry, Boston (1971).

[2] K. T. Potts, E. Brugel and W. C. Dunlap, *Tetrahedron* **33**, 1247 (1977).

[3] F. C. De Schryver and J. Put, *Angew. Chem.* Intern. Ed. Engl. **8**, 213 (1969); F. C. De Schryver, W. J. Feast and G. Smets, *J. Polym. Sci.*, Part A-1, *Polymer Chem.*, **8**, 1939 (1970); F. C. De Schryver, W. J. Feast and G. Smets, *J. Polymer Sci.*, Part A-1, *Polymer Chem.*, **10**, 1687 (1972); J. Put and F. C. De Schryver, *J. Am. Chem. Soc.* **95**, 137 (1973).

[4] L. Leenders and F. C. De Schryver, *Angew. Chem.* Intern. Ed. Engl. **10**, 338 (1971); L. H. Leenders, E. Schouteden and F. C. De Schryver, *J. Org. Chem.* **38**, 957 (1973).

[5] N. J. Leonard, K. Golankiequicz, R. S. McCredie, S. M. Johnson and I. C. Paul, *J. Am. Chem. Soc.* **91**, 5855 (1969).

[6] K. T. Potts and H. R. Burton, *J. Org. Chem.* **31**, 251 (1966).

[7] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.* **39**, 216 (1961); R. J. Abraham, W. G. Schneider and H. J. Bernstein, *Ibid.* **35**, 1060 (1967).

[8] I. Fleming and D. H. Williams, *Tetrahedron* **23**, 2747 (1967).

[9] A. Gamba and R. Mondelli, *Tetrahedron Letters* 2133 (1971).

[10] F. Liberatoe, A. Casini and V. Carelli, *J. Org. Chem.* **40**, 559 (1975).

[11] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Vol. 5, p. 129. International Series of Monographs in Organic Chemistry, Pergamon, New York (1969).

[12] H. Rottendorf and S. Sternhell, *Tetrahedron Letters* 1289 (1963).