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1,2,4-TRIAZOLES—XXXIV†

PHOTODIMERIZATION OF SOME 1,2,4-TRIAZO[4,3--]QUINOLINE AND 1,2,4-TRIAZOLO[3,4-a]ISOQUINOLINE DERIVATIVES[1]

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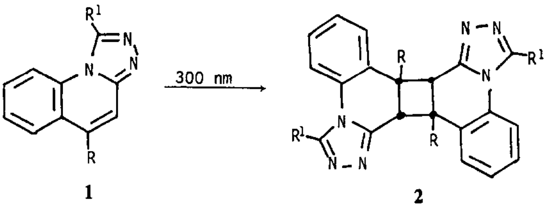
Abstract—Irradiation of 1,2,4-triazolo[4,3-a]quinoline and several Me derivatives at 300 nm afforded the *cisoid*-fused, head-to-tail cyclobutane dimers 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylenes. However, 1,2,4 - triazolo[3,4-a]isoquinolines gave analogous *cisoid*-fused, head-to-head dimers except for the 5-Me derivative where the head-to-tail dimer was obtained.

Codimerization occurred when 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline and 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline were irradiated at 300 nm, affording a *cisoid*-fused head-to-tail cyclobutane co-dimer as the single photoproduct. However, irradiation of their 5-Me substituted derivatives at 300 nm afforded the *cisoid*-fused, head-to-head, cyclobutane codimer and also a minor amount of the dimer derived from 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline. Irradiation of equimolar quantities of 2(1H)-quinolinone and 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline at 300 nm gave the known 2(1H)-quinolinone dimer and a minor amount of a *cisoid*-fused co-dimer of undetermined configuration.

In previous publications in this series, 1,2,4 - triazolo[4,3-a]pyridine derivatives were shown to undergo ready photodimerization in aprotic solvents to derivatives of the 5aα,5bα,10bα,10cα - tetrahydro - 1,3a,8,9,10a - hexaazadicyclopenta[*a,i*]biphenylene‡ ring system, dimerization occurring between the 5,6-double bond of one molecule and the 7,8-double bond in another.[2] These thermally labile dimers gave on reduction a series of extremely stable photoproducts. Dimerization at the 5,6-double bond only was observed[3] with several 3,3′ - [alkanediyl]bis[1,2,4 - triazolo[4,3-a]pyridines], this intramolecular photodimerization resulting from the conformational restraint imposed by the alkane bridge. Extension of these studies to benzologs of the 1,2,4-triazolo[4,3-a]pyridine system was of considerable interest and these results are described below.

Chemical results. The 1,2,4 - triazolo[4,3-a]quinoline and [3,4-a]isoquinoline ring systems were prepared by literature procedures.[4-6]

Irradiation of 1,2,4-triazolo[4,3-a]quinoline (1;R=R^1=H) in acetonitrile or tetrahydrofuran at 300 nm gave a crystalline photoproduct 2 (R=R^1=H) which separated from the reaction over 5 days. Its m.p. 282–284° was significantly higher than that of its precursor, 1 (m.p. 175–177°) and its UV spectrum showed a shift to shorter wavelength, indicating disruption of the conjugation in the precursor. A molecular ion, M^+ 338 (0.2%) and analytical data corresponded to the molecular formula $C_{20}H_{14}N_6 \cdot H_2O$, the presence of water being confirmed by ν_{OH} 3400 cm^{-1} and the loss of water upon heating in a vacuum could be monitored via mass spectrometry. An analysis of the 100 MHz NMR data for this photoproduct 2 (R=R^1=H) indicated that it had the dimeric structure 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylene (2; R=R^1=H).



1 **2**

Similar irradiation of 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me) at 300 nm gave dimer **2** (R=H; R^1=CH$_3$), 3,10-dimethyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a, g*]biphenylene. This photoproduct had physical characteristics analogous to those described for **2** (R=R^1=H) and these are described in Table 1.

An equally ready dimerization was observed with 5 - methyl - 1,2,4 - triazolo[4,3-a] - quinoline (**1**; R=CH$_3$; R^1=H) with a Me substituent at the site of the double bond undergoing reaction. In acetonitrile solution (300 nm) **1** (R=CH$_3$; R^1=H) gave the dimer **2** (R=Me; R^1=H) (Table 1) with comparable spectral data to that of the dimers described above. Its NMR spectrum (CF_3CO_2D) exhibited a two proton singlet corresponding to the absorption of protons H_{7c} and H_{14c} (δ 4.85), confirming the assigned chemical shifts of the cyclobutane protons in the dimers **2** (R=H; R^1=H and Me). A 6-proton singlet was observed for the C_{7b}–CH_3 and C_{14b}–CH_3 protons at δ 2.00.

Irradiation of 1,5 - dimethyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=R^1=Me) in dry THF or acetonitrile at 300 nm afforded dimer **2** (R=R^1=Me). The product likewise separated from the reaction and showed the anticipated shift to shorter wavelength in its UV spectrum as well as a molecular ion, $M^{\ddagger}$ 394 (0.8). Its NMR spectrum (CF_3CO_2D) was consistent with the structure 3,7bα,10,14bα - tetramethyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylene (**2**; R=R^1=Me). In addition to the data described in Table 1 and the NMR analyses reported

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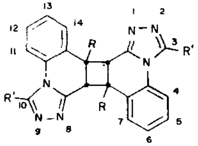
†Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

‡This nomenclature is used in this instance for consistency with that used in this paper.

Table 1. Some 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c*, *i*]dicyclopenta[*a*, *g*]biphenylenes (**2**)

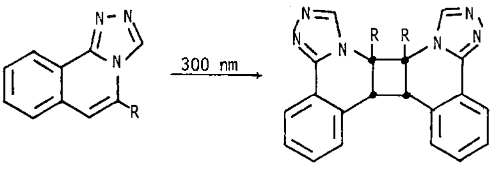


	R	R'	M.P., °C[a]	Yield,[b] %	Form	Solvent	U.V. max[c] nm (log ε)	Formula	Calcd. %			Found %		
									C	H	N	C	H	N
	H	H	282-284°	57	Small colorless needles	C_2H_5OH, H_2O	217 (4.62), 240 sh (4.17)	$C_{20}H_{14}N_6 \cdot H_2O$	67.40	4.53	23.58	67.83	4.09	23.98
Dipicrate	H	H	253-254°		Small yellow flakes	H_2O		$C_{32}H_{20}N_{12}O_{14}$	48.25	2.53	21.10	48.11	2.49	21.01
	H	CH_3	274-276°	47	Colorless micro-flakes	CH_3OH, $CH_3C_6H_5$	210 (4.55), 240 sh (4.10)	$C_{22}H_{18}N_6$	72.11	4.95	22.94	72.15	5.05	23.10
Dipicrate	H	CH_3	252-255°		Small yellow irregular prisms	H_2O		$C_{34}H_{24}N_{12}O_{14}$	49.52	2.93	20.38	49.11	2.90	20.67
	CH_3	H	316-317°	30	Small colorless flakes	C_2H_5OH, H_2O	210 (4.51), 238 (4.17), 247 (4.17)	$C_{22}H_{18}N_6 \cdot \frac{1}{2}H_2O$	70.42	5.20	22.40	70.89	5.21	22.64
Monopicrate	CH_3	H	288-290°		Fine yellow needles	H_2O		$C_{28}H_{21}N_9O_7$	56.47	3.55	21.18	56.24	3.54	21.34
	CH_3	CH_3	312-314°	44	Small colorless plates	C_2H_5OH, H_2O	212 (4.58), 242 sh (4.24)	$C_{24}H_{22}N_6$	73.07	5.62	21.31	72.82	5.64	21.26
Dipicrate	CH_3	CH_3	227-231°		Small yellow needles	H_2O		$C_{36}H_{28}N_{12}O_{14}$	50.71	3.31	19.71	50.50	3.58	19.38

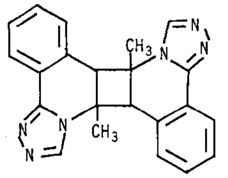
[a] Uncorrected. [b] Yield after purification (irradiation in CH_3CN solution). [c] Determined in CH_3OH.

below, all these photodimers were characterized by formation of picrates which were compared with the picrates of the respective monomers.

Photodimerization of the isomeric ring system 1,2,4 - triazolo[3,4-a]isoquinoline (**3**) was an equally facile process. In acetonitrile at 300 nm **3** (R=H) gave a crystalline photoproduct **4** (R=H) which separated from solution over 4 days and whose m.p. 282–284°, was significantly higher than that of its precursor **3** (R=H) m.p. 202–203°). The hypsochromic shift observed in the UV spectrum, a molecular ion M^{+} 338 (~ 1%), and analytical data corresponding to a molecular formula $C_{20}H_{14}N_6$, and 100 MHz NMR data indicated that this dimer was best represented as 7bα,7cα,14bα,14cα-tetrahydro - 2,3,12,13,14a,14d - hexaazadibenzo[*c,g*]dicyclopenta[a,i]biphenylene(**4**; R=H).



3 **4**



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Similar irradiation of the 5-Me derivative (**3**; R=Me) in acetonitrile at 300 nm gave a crystalline product **5** separating in an analytically pure form from the reaction over 5 days. Its physical and spectral characteristics (Experimental) suggested that the structure of this photoproduct was a *cisoid*-fused, head-to-tail dimer, 7cα,14cα - dimethyl - 7bα,7cα,14bα,14cα - tetrahydro - 2,3,7d,9,10,14d - hexaazadibenzo[*c, i*]dicyclopenta[*a, g*]-biphenylene (**5**) rather than the head-to-head isomer **4** (R=Me). This dimer showed appreciable thermal lability, reverting to monomer in the mass spectrometer.

The ready photodimerization of these isomeric ring systems suggested the possibility of co-dimer formation. Irradiation of equal molar quantities of 1-methyl-1,2,4-triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me) and 5 - methyl-1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=Me) in dry acetonitrile at 300nm gave a crystalline photo-product **6** (R=R^2=Me; R^1=H) also separating from solution in an analytically pure form. The photoproduct had an appreciably higher m.p. (290–292°) than either of its precursors and its UV spectrum showed an hypsochromic shift in comparison to those of its precursors. The mass spectrum of **6** (R=R^2=Me; R^1=H) did not show a molecular ion [M^{+} 366], the major fragment [*m/e* 183 (1000%)] corresponding to the molecular formula, $C_{11}H_9N_3$, of both precursors **1** (R=H; R^1=Me) and **3** (R=Me) but the elemental analysis confirmed an empirical formula, $(C_{11}H_9N_3)_x$. NMR data clearly showed that this photoproduct was a co-dimer of both **1** (R=H; R^1=Me) and **3** (R=Me) as an aromatic Me group (δ 2.82) and also an aliphatic Me substituent at δ 2.62 can only be accommodated by such a dimerization. An analysis of the cyclobutane proton coupling (*vide infra*) established its structure as the *cisoid*-fused, head-to-tail, cyclobutane co-dimer, 3,7cα - dimethyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,7d,9,10 - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylene (**6**; R=R^2=Me; R^1=H).

The photoreaction of **1** (R=H; R^1=Me) and **3** (R=Me) gave co-dimer **6** (R=R^2=Me; R^1=H) as the single photoproduct. Neither dimer **2** (R=H; R^1=Me) derived from two molecules of 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me) or dimer **5** derived from two molecules of 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline was obtained.

Co-dimerization of 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me) and 1,2,4-triazolo[3,4-a]isoquinoline (**3**; R=H) was also found to occur readily in dry acetonitrile at 300 nm, a single crystalline photoproduct **6** (R=R′=H; R^2=Me) m.p. 302–304° separating from solution. The mass spectrum of **6** R=R^1=H; R^2=Me) was devoid of a molecular ion [M^{+} 352] but codimerization was indicated by two major fragments observed in the mass spectrum: *m/e* 183 (100%), corresponding to $C_{11}H_9N_3$, 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me), and *m/e* 169 (46%), corresponding to $C_{10}H_7N_3$, 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=H). NMR data showed that the structure of this photoproduct was best represented as 3 - methyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,7d,9,10 - hexaazadibenzo[*c, i*]dicyclopenta[*a, g*]biphenylene (**6**; R=R^1=H; R^2=Me).

This co-dimerization was extended to include Me substituted derivatives of both ring systems. Thus irradiation of equal molar quantities of 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H) and 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=Me) in dry acetonitrile at 300 nm gave a solid crystallizing in two forms which were separated mechanically. The major product **7**, m.p. 299–300°, was found to be a co-dimer derived from **1** (R=Me; R^1=H) and **3** (R=Me). The minor product, m.p. 315–317° was identical to the dimer, 7bα,14bα-dimethyl - 7bα,7cα,14bα,14cα-tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylene (**2**; R=Me; R^1=H) derived from 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H). Dimer **5** derived from 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=Me) was not obtained in this reaction. The UV spectrum of co-dimer **7** indicated chromophore disruption in the photoproduct and the mass spectrum of **7** did not show a molecular ion [M^{+} 366]; however, the major fragment [*m/e* 183 (100%)] corresponded to the molecular formula, $C_{11}H_9N_3$, of both precursors, **1** (R=Me; R^1=H) and **3** (R=Me). An analysis of the NMR spectrum (*vide infra*) of this co-dimer established its structure as a head-to-head, cyclobutane co-dimer, 7bα,14bα - dimethyl - 7bα,7cα14bα,14cα - tetrahydro - 1,2,3a,12,13,14a - hexaazadibenzo[*c,g*]dicyclopenta[*a,i*]biphenylene (**7**).

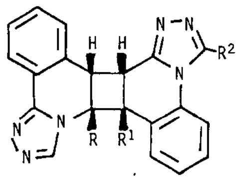
The 1,2,4-triazolo[4,3-a]quinoline system was also found to undergo co-dimerization with 2(1H)-quinolinone (**8**). Thus irradiation of equimolar amounts of 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H) and **8** in dry acetonitrile at 300 nm gave a solid product consisting of two components which separate slowly from solution. Fractional crystallization from aqueous trifluoroacetic acid gave the dimer of 2(1H)-quinolinone, 6bα,6cβ,12aβ,12bα - tetrahydrocyclobuta[1,2-c:4,3-c′] - diquinoline - 1,12(2H,11H)dione[7] (**9**) as the major fraction

(63%). Crystallization of the minor fraction by the addition of acetone to the filtrate gave a product, m.p. 158–160° (9% yield). A hypsochromic shift in the UV spectrum, a ν_{CONH} 1670 cm^{-1}, and two major fragments at *m/e* 183 (100%), corresponding to the molecular formula, $C_{11}H_9N_3$, of 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H), and at *m/e* 145 (94%), corresponding to the molecular formula, C_9H_7NO, of 2(1H)-quinolinone (**8**) in its mass spectrum, together with analytical data established that this produce was a co-dimer of the reactants. Additional evidence for this co-dimer was obtained from the 100 MHz NMR spectrum (*vide infra*) and, because the configuration could not be determined from the NMR data, it may be represented by structure **10** or **10a**.

Under similar conditions, the photoreaction of 2(1H)-quinolinone (**8**) and 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=CH$_3$) gave only the dimer **9** derived from 2(1H)-quinolinone (**8**).

tetrahydro - 1,2,3a,5,9,10a - hexaazadibenzo[*c,i*]dicyclopenta[*a,g*]biphenylene (**2**; R=R^1=H) exhibited a downfield 2-proton singlet (δ 9.62) assigned to the protons H_3 and H_{10}, and an 8-proton multiplet containing the aromatic protons H_4, H_5, H_6, H_7, H_{11}, H_{12}, H_{13}, H_{14} (δ 6.9–7.6). The protons of the cyclobutane ring absorbed as two virtual triplets, the downfield triplet being assigned to the H_{7c} and H_{14c} protons (δ 5.49). Similarly protons H_{7b} and H_{14b} are also equivalent and correspond to the triplet at δ 4.88. The NMR data were consistent with dimerization occurring at the 4,5-double bond of the 1,2,4 - triazolo[4,3-a]quinoline nucleus.

An analysis of the cyclobutane proton resonances (an AA′XX′ spin system) eliminated a head-to-head structure for dimer **2** (R=R^1=H). The large magnitude of the coupling, $|J_{AX} + J_{AX'}| = 17.0$ Hz is consistent with a *cisoid*-fused, head-to-tail structure in which the J_{AX} and $J_{AX'}$ protons are both *cis* vicinal coupled ($J_{AX} \simeq J_{AX'}$) and, moreover, the two cyclobutane triplets result from equal



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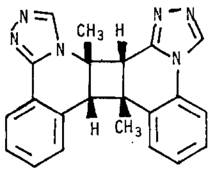

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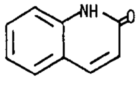

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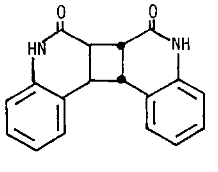

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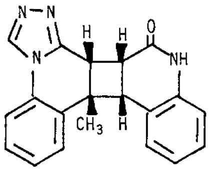

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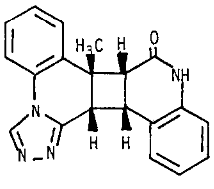


10a

The facile photodimerization of derivatives of the 1,2,4 - triazolo[4,3-a]quinoline and 1,2,4 - triazolo[3,4-a]isoquinoline ring systems suggested the study of the photochemical behavior of several nitrogen analogs. Of particular interest was whether introduction of a N atom in the reactive 4,5-double bond of the 1,2,4 - triazolo[4,3-a]quinoline or the 5,6-double bond of the 1,2,4 - triazolo[3,4-a]isoquinoline ring system would give a diazetidine photo-adduct via a $[2\pi + 2\pi]$-dimerization at these reactive sites.

Irradiation of 1,2,4 - triazolo[4,3-a]quinoxaline[8] which is isoelectronic with the 1,2,4 - triazolo[4,3-a]quinoline ring system, in acetonitrile solution with 300 nm UV light did not give a photoproduct, the fused system always being recovered unchanged.

Irradiation of 1,2,4 - triazolo[4,3-c]quinazoline[9] or 1,2,4 - triazolo[3,4-a]phthalazine,[10] both of which are isoelectronic with the 1,2,4 - triazolo[3,4-a]isoquinoline ring system, under analogous conditions also did not give photoproducts. Unchanged starting compounds were recovered in both cases.

Structure and stereochemical assignments. As in previous papers in this study, structure and stereochemical assignments for these photoproducts were made principally on the basis of their 100 MHz NMR spectral data whose most important characteristics only are described here. The spectrum (CF_3CO_2D) of 7bα,7cα,14bα,14cα -

values of J_{AX} and $J_{AX'}$ which can only occur when the cyclobutane is *cisoid*-fused. When $J_{AX} = J_{AX'}$, the two protons pairs, A,A′ and X,X′, are magnetically equivalent (an A_2X_2 spin system) and the coupling ($J_{AX} = 8.5$ Hz) was measured directly from the NMR spectrum. Similar data have been observed[11] for the *cisoid*-fused, head-to-tail dimer derived from 7,7′ - [propane - 1,3 - diyl - bis(oxy)]bis[(2H) - 1 - benzopyran - 2 - one].

A NMRCAL analysis of the H_{7c}, H_{14c} and H_{7b},H_{14b} proton resonances of (**2**; R=R^1=H) revealed that the cyclobutane protons do not resonate as an exact first-order A_2X_2 spin system, approximating an A_2B_2 spin system, and the calculated spectrum was consistent with the experimental spectrum.

The NMR spectrum (CF_3CO_2D) of **2** (R=H; R^1=CH$_3$) was nearly identical to that of dimer **2** (R=R^1=H) with C_3–CH_3 and C_{10}–CH_3 absorbing as a 6-proton singlet at δ 2.98. The cyclobutane protons resonated as an A_2X_2 spin system ($J_{AX} = 8.5$ Hz) as they did in dimer **2** (R=R^1=H). Irradiation at the resonance frequency of protons H_{7c} and H_{14c} (δ 5.39) caused the H_{7b}, H_{14b} triplet (δ 4.76) to collapse to a singlet. Irradiation at the H_{7b}, H_{14b} resonance resulted in a similar singlet for the H_{7c}, H_{14c} protons.

The photodimers derived from the *s* - triazolo[3,4-a]isoquinoline system were equally amenable to NMR analysis, the spectrum (CF_3CO_2D) of dimer **4** (R=H) (Table 2) being consistent with the assigned structure. The

Table 2. Some hexaazadibenzodicyclopentabiphenylene photodimers derived from 1,2,4 - triazolo[3,4-a]isoquinoline derivatives

Compound Number	M.P., °C[a]	Yield[b] %	Form	Solvent	U.V. max nm (log ε)[d]	Formula	Calcd. %			Found %		
							C	H	N	C	H	N
4; R=H	313-315°	54	Colorless needles	aq. EtOH (Norit)	211 (4.52), 250 (4.35), 257 (4.38)	$C_{20}H_{14}N_6$	70.99	4.17	24.84	70.81	4.26	24.79
Picrate	274-276°	—	Yellow, irreg. prisms	H_2O	—	$C_{26}H_{17}N_9O_7$	55.02	3.02	22.21	54.92	3.01	22.10
5	>350° (dec)	76	Large, flat, colorless needles[c]	—	214 (4.59), 253[e] (4.31), 258 (4.45)	$C_{22}H_{18}N_6$	72.11	4.95	22.94	72.19	4.84	23.00
Dipicrate	238-240°	—	Yellow needles	H_2O	—	$C_{34}H_{24}N_{12}O_{14}$	49.52	2.93	20.38	49.67	3.00	20.18
6; $R=R^2=CH_3$; $R^1=H$	290-292°	65	Colorless, rectangular plates[c]	—	208 (4.65), 212 (4.65), 255 (4.24), 252 (4.26), 280[e] (3.82)	$C_{22}H_{18}N_6$	72.11	4.95	22.94	72.19	5.16	23.10
6; $R=R^1=H$; $R^2=CH_3$	302-304°	51	Light tan microprisms	toluene:methanol	207 (4.61), 245 (4.16), 252 (4.17), 268[e] (3.87)	$C_{21}H_{16}N_6$	71.57	4.58	23.85	71.92	4.76	23.59
7	299-300°	52	Colorless, irreg. prisms[c]	—	207 (4.56), 245 (4.25), 252 (4.29), 275[e] (3.71)	$C_{22}H_{18}N_6$	72.11	4.95	22.94	71.78	5.15	23.00
10	258-260°	9	Colorless cubes	$CF_3COOH:(CH_3)_2CO$	212 (4.59), 247 (4.17), 290[e] (3.22)	$C_{20}H_{16}N_4O\cdot 1/2H_2O$	71.25	5.07	16.61	71.44	4.84	16.69

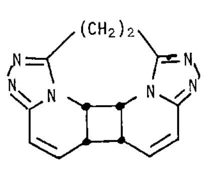
[a] Uncorrected. [b] Yield of analytically pure product after irradiation in CH_3CN at 300 nm. [c] Separated in analytically pure form. [d] Determined in methanol. [e] Shoulder.

configuration and stereochemical assignment of the cyclobutane fusion in dimer **4** (R=H) were readily determined as the two cyclobutane multiplets resembled those observed for the cyclobutane protons in the head-to-head dimers derived from bichromophoric 1,2,4 - triazolo[4,3-a]pyridines,[3] such as 5aα,5bα,10bα,10cα - tetrahydro - 1,10 - ethano - 2,3,8,9,10a,10d - hexa-azadicyclopenta[*a*, *i*]biphenylene (**11**), which resonated as an AA'XX' spin system. The coupling, $J_{AX}+J_{AX'}=$ 10.0 Hz, indicated that the cyclobutane ring was also *cisoid*-fused with the same stereochemistry as in dimer **11**. Irradiation at the center resonance frequency of the H_{7b}, H_{7c} multiplet caused the collapse of the H_{14b}, H_{14c} absorption to a singlet and likewise, irradiation of the H_{14b}, H_{14c} multiplet caused a singlet to appear for the H_{7b}, H_{7c} proton absorption. These data are consistent with **4** (R=H) being represented as a *cisoid*-fused, head-to-head dimer.

In contrast, the photodimer **5** derived from 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=CH_3) was found to have a head-to-tail configuration. Its spectrum (CF_3CO_2D) exhibited a 2-proton singlet (δ 8.16; H_1 and H_8), an 8-proton multiplet (δ 7.7–8.3) containing the aromatic protons H_4–H_7 and H_{11}–H_{14} and two, equivalent protons of the cyclobutane ring (H_{7b} and H_{14b}) resonated as a singlet at δ 4.97. The Me groups located on the cyclobutane ring also absorbed as a singlet at δ 2.18.

Differences in the chemical shifts of the aromatic protons of dimer **5** and those of dimer **4** (R=H) may be attributed to the differences in the magnetic shielding of the fused triazole ring, which has a larger charge density[4] than that associated with the fused benzo-ring, and to accomodate these observed differences the photoproduct **5** must have the head-to-tail configuration. Moreover, this difference in chemical shifts can only occur if both dimers are *cisoid*-fused so that the aromatic nuclei fused to the cyclobutane ring can interact magnetically. An inspection of a molecular model of dimer **5** showed that the triazole nuclei impose a non-symmetrical magnetic environment on the benzene nuclei resulting in a non-symmetrical multiplet for the benzenoid protons of dimer **5** in contrast to the aromatic protons of dimer (**4**; R=H) which resonate as a symmetrical multiplet.

The chemical shifts and coupling constants of the cyclobutane protons in the dimer from **3** (R=CH_3) do not immediately provide any structural information regarding the configuration of the photoproduct. The two magnetically equivalent cyclobutane protons absorbed as a singlet (δ 4.97) and could arise from either protons H_{7b} and H_{7c} of the head-to-head dimer **4** (R=CH_3) or from protons H_{7b} and H_{14b} of the head-to-tail dimer **5**. However, conclusive evidence for the configuration of this photoproduct was obtained from the coupling constant, $J_{H,H}$, between the two equivalent vicinal cyclobutane protons by the use of the naturally abundant C^{13}–H satellite proton spectrum according to the method established by Anet.[12] It was anticipated that the C^{13}–H satellite proton spectrum for dimer **4** (R=CH_3) would have shown coupling[13] between the vicinal protons H_{7b} and H_{7c} as well as the C^{13}–H coupling, and a doublet of doublets would have resulted. Similar C^{13}–H satellite spectra have been observed[14] for the head-to-head dimer **12** derived from 1,5 - dimethyl - 2,4 - (1H̲,3H̲)pyrimidinedione. In contrast to the above result, the C^{13}–H satellite proton spectrum for dimer **5** derived from 5 - methyl - 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=CH_3) showed only a doublet for the C^{13}–H coupling ($J_{C^{13}\text{-}H}=148$ Hz) and no interproton coupling ($J_{7b,14b}\cong 0$). Similar C^{13}–H satellite spectra were observed[14] for the head-to-tail dimer **13** derived also from 1,5 - dimethyl - 2,4(1H̲,3H̲)pyrimidinedione and, accordingly the structure of the photoproduct from **3** (R=CH_3) must have the head-to-tail configuration represented by **5**.



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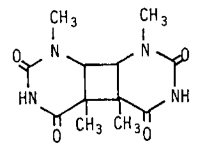

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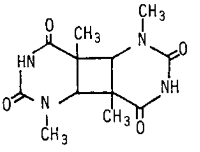

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A head-to-tail configuration for dimer **6** (R=R^2=CH_3; R^1=H) was also evident from the NMR data (Table 1). The downfield 1-proton singlet (δ 9.49; H_8), and an 8-proton multiplet (δ 6.7–8.1)containing the aromatic protons H_4–H_7 and H_{11}–H_{14} and the protons of the cyclobutane ring, a 1-proton triplet (δ 5.01) and a two proton doublet (δ 4.54), are in accord with the assigned structure. The downfield triplet (δ 5.01) was assigned to proton H_{14c} as it is in the deshielding region of the triazole ring and the higher field 2-proton doublet (δ 4.54) was assigned to the cyclobutane protons, H_{7b} and H_{14b} which are chemically and symmetrically non-equivalent. However, the magnetic environments of these protons are very nearly equivalent, causing them to absorb as "accidentally equivalent" nuclei. The observed, virtual AB_2 spectrum for this cyclobutane spin-system can only occur if the configuration of the co-dimer is oriented head-to-tail with the coupling, $J_{14b,14c'}$, being nearly equivalent to $J_{7b,14c}$. The H_{14c} triplet closely resembles the cyclobutane AB_2 triplets observed for the head-to-tail dimer **2** (R=R^1=H) derived from 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=R^1=H). The coupling ($J_{AB}=8.4$ Hz) for this AB_2 spin-system is also of nearly equal magnitude to that observed for dimer **2** (R=R^1=H) ($J_{AB}=8.5$ Hz). Hence, codimer **6** (R=R^2=CH_3; R^1=H) must also be fused with cisoid stereochemistry. Irradiation at the center resonance frequency of the H_{14c} triplet (δ 5.01) caused the collapse of the H_{7b},H_{14b} doublet at δ 4.54 to a slightly broadened singlet in a spin-decoupling experiment. Likewise, irradiation of the H_{7b}, H_{14b} doublet (δ 4.54) also decoupled the H_{14c} triplet at δ 5.01 to a singlet.

Similarly the NMR spectrum of dimer **6** (R=R^1=H; R^2=CH_3) (Table 3) showed a downfield singlet at δ 9.54 (H_8), and eight benzenoid, aromatic protons absorbed as a 6-proton overlapping multiplet in the region δ 7.2–7.9, a 1-proton doublet at δ 8.03, and a shielded, 1-proton doublet at δ 6.67. The assignment of the upfield aromatic doublet (δ 6.67) was verified by a spin-decoupling experiment. The cyclobutane protons absorbed as a lowfield triplet at δ 6.24 and a higher field 3-proton, overlapping multiplet (δ 4.6–5.1). The lowfield triplet (δ 6.24) was assigned to proton H_{7c} which resonates in the deshielding zone of the bridgehead nitrogen, N_{7d}. The *cis*-coupling ($J_{7b,7c}=J_{7c,14b}=8.5$ Hz) of proton H_{7c} requires the "accidental" equivalency of protons H_{7b} and H_{14b} as did codimer **14**.

Table 3. NMR data for some photodimers derived from 1,2,4 - triazolo[4,3-a]quinolines and 1,2,4 - triazolo[3,4-a]isoquinolines[a]

Compound Number	Chemical Shifts (δ)	Coupling Constants (Hz)
2; R=R^1=H	9.62 (s, 2, H_3, H_{10}), 7.6-6.9 (m, 8, H_4, H_5, H_6, H_7), 5.49 (t, 2, H_7, H_{14c}), 4.88 (t, 2, H_{7b}, H_{14b})	$J_{7c,7b}$=$J_{7c,14b}$=8.5; $J_{14c,14b}$=$J_{14c,7b}$=8.5; $J_{7b,7c}$= $J_{7b,14c}$=8.5; $J_{14b,7c}$=$J_{14b,14c}$=8.5
2; R=H; R^1=CH$_3$	7.6-6.9 (m, 8, H_{4-7}, H_{11-14}), 5.39 (t, 2, H_{7c}, H_{14c}), 4.76 (t, 2, H_{7b}, H_{14b}), 2.98 (s, 6, C_3-CH_3, C_{10}-CH_3)	$J_{7c,7b}$=$J_{7c,14b}$=8.5; $J_{14c,7b}$=$J_{14c,14b}$=8.5; $J_{7b,14c}$= $J_{14b,7c}$=8.5
2; R=CH$_3$; R^1=H	9.54 (s, 2, H_3, H_{10}), 7.5-6.8 (m, 8, H_{4-7}, H_{11-14}), 4.85 (s, 2, H_{7c}, H_{14c}), 2.00 (s, 6, C_{7b}-CH_3, C_{14b}-CH_3)	
2; R=R^1=CH$_3$	7.6-6.8 (m, 8, H_{4-7}, H_{11-14}), 4.68 (s, 2, H_{7c}, H_{14c}), 3.05 (s, 6, C_3-CH_3, C_{10}-CH_3), 1.94 (s, 6, C_{7b}-CH_3, C_{14b}-CH_3)	
4; R=H	9.19 (s, 2, H_1, H_{14}), 8.1-7.0 (m, 8, H_{4-11}), 6.27 (AA'XX' m, 2, H_{14b}, H_{14c}), 5.14 (AA'XX' m, 2, H_{7b}, H_{7c})	$\lvert J_{14b,7c}+J_{14b,7b}\rvert$=10.0; $\lvert J_{14c,7b}+J_{14c,7c}\rvert$=10.0; $\lvert J_{7b,14c}+J_{7b,14b}\rvert$=10.0; $\lvert J_{7c,14b}+J_{7c,14c}\rvert$=10.0
5	8.16 (s, 2, H_1, H_8), 8.3-7.6 (m, 8, H_{4-7}, H_{11-14}), 4.97 (s, 2, H_{7b}, H_{14b}), 2.18 (s, 6, C_{7c}-CH_3, C_{14c}-CH_3)	$J_{C^{13}-H_{7b},\ H_{14b}}$=148 Hz
6; R=R^2=CH$_3$; R^1=H	9.49 (s, 1, H_8), 8.1-6.7 (m, 8, H_{4-7}, H_{11-14}), 5.0 (t, 1, H_{14c}), 4.54 (d, 2, H_{7b}, H_{14b}), 2.82 (s, 3, C_3-CH_3), 2.62 (s, 3, C_{7c}-CH_3)	$J_{14c,7b}$=$J_{14c,14b}$=8.4; $J_{7b,14c}$=$J_{14b,14c}$=8.4
6; R=R^1=H; R^2=CH$_3$	9.54 (s, 1, H_8), 8.1-6.6 (m, 8, H_{4-7}, H_{11-14}), 6.24 (t, 1, H_{7c}), 5.1-4.6 (AB_2 m, 3, H_{7b}, H_{14b}, H_{14c}), 2.82 (s, 3, C_3-CH_3)	$J_{7b,7c}$=$J_{7c,14b}$=8.5
7	10.03 (s, 1, H_{14}), 8.59 (s, 1, H_3), 8.1-6.4 (m, 8, H_{4-11}), 5.01 (s, 1, H_{14c}), 4.75 (s, 1, H_{7c}), 2.18 (s, 3, C_{14b}-CH_3), 1.98 (s, 3, C_{7b}-CH_3)	
10	9.89 (s, 1, $H_{1'}$), 8.1-7.0 (m, 8, H_{5-8}, $H_{6'-9'}$), 4.49 (d, 1, $H_{4'}$), 4.29 (or 4.12) (d, 1, H_3), 4.12 (or 4.29) (dd, 1, H_4)	$J_{4',3}$ (or $J_{4',4}$)=7.5; $J_{3,4'}$=7.5; $J_{3,4}$=9.4

[a] Determined at 100 MHz in CF_3CO_2D

Proton H_{7c} resonated as the X portion of the cyclobutane AB_2X spin-system and protons H_{7b}, H_{14b} and H_{14c} are assigned to the close AB_2 multiplet at δ 4.6–5.1.

The 3-proton singlet at δ 2.82 is assigned to the triazole C_3–CH_3 methyl substituent. The integrated 1:3 ratio of the H_8 singlet to that of the C_3–Me singlet is additional evidence that **6** (R=R^1=H; R^2=Me) is derived from the codimerization of 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=H; R^1=Me) and 1,2,4 - triazolo[3,4-a]isoquinoline (**3**; R=H). These data are consistent with its representation as 3 - methyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,7d,9,10 - hexaazadibenzo[*c*, *i*]dicyclopenta[*a*, *g*]biphenylene (**6**; R=R^1=H; R^2=Me).

In contrast the codimer **7** formed from 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H) and 5 - methyl - 1,2,4 - triazolo[4,3-a]isoquinoline (**3**; R=Me) was found to have a head-to-head configuration. The NMR spectrum showed two non-equivalent, cyclobutane protons and two non-equivalent, cyclobutane Me substituents. The low field cyclobutane absorption (δ 5.01) was assigned to proton H_{14c} as it resonated in the deshielding region of a fused triazole ring. The H_{7c} cyclobutane proton resonated at δ 4.75. The two non-equivalent, cyclobutane protons are not coupled and appear as singlets. The lack of coupling between these protons indicated that the structure of codimer **7** did not have a head-to-tail configuration and must, therefore, be fused head-to-head. The lack of coupling between these protons did not provide any stereochemical information for the cyclobutane fusion but it was assumed that this codimer is *cisoid*-fused as were the dimers derived from 1,2,4 - triazolo[4,3-a]pyridines and 1,2,4 - triazolo[3,4-a]isoquinolines. A similar change in the orientation mode of dimerization occurred with 5 - methyl - 1,2,4 - triazolo[3.4-a]isoquinoline (**3**; R=Me), presumably to relieve the vicinal steric interaction of a dimethyl-substituted cyclobutane which would have resulted from dimerization in the manner described above.

Analysis of the NMR spectrum (CF_3CO_2D) of codimer **10** derived from 2(1$\underline{H}$) - quinolinone (**8**) and 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline (**1**; R=Me; R^1=H) showed a low field 1-proton singlet at δ 9.89 attributed to the triazole proton, a high field, cyclobutane methyl absorption at δ 2.52 and eight aromatic protons forming a multiplet in the region δ 7.08–8.1. The three cyclobutane protons of **10** resonate as a multiplet in the region δ 4.0–4.6 and, on expansion of the spectrum, appeared as a doublet (J = 7.5 Hz) at δ 4.49, a doublet (J = 9.4 Hz) at δ 4.29 and a doublet of doublets (J = 7.5 Hz, J = 9.4 Hz) at δ 4.12. Considering that the cyclobutane protons of the dimer derived from 2(1$\underline{H}$)-quinolinone resonated at δ 4.12, the low field doublet (δ 4.49) can be assigned to the proton at the cyclobutane and 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline ring fusion. The 7.5 Hz coupling of this doublet thus indicates a *cisoid* cyclobutane fusion of the 5 - methyl - 1,2,4 - triazolo[4,3-a] quinoline and the 2(1$\underline{H}$)-quinolinone nuclei. The configuration of codimer **10** can be determined only if the absolute chemical shift assignments for the two 2(1$\underline{H}$)-quinolinone protons at the cyclobutane ring-fusion can be realized to correlate with the known coupling (and chemical shift) of the 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline, cyclobutane-fused proton (δ 4.49). The small difference in chemical shifts for these two protons ($\Delta\nu$ = 17 Hz) in the NMR spectrum of **10** is reflected in the collapsed AA'BB' singlet for the cyclobutane protons found in the dimer derived from 2(1$\underline{H}$)-quinolinone.

From these data, the absolute chemical shift assignments for the 2(1$\underline{H}$)-quinolinone cyclobutane-fused protons cannot be made in **10** and a head-to-head or head-to-tail configuration cannot be determined with certainty.

EXPERIMENTAL†

The following compounds were all prepared by the method described in the lit.[4] 2 - hydrazinoquinoline, 2 - hydrazino - 4 - methylquinoline, 1,2,4 - triazolo[4,3-a]quinoline, 1 - methyl - 1,2,4 - triazolo[4,3-a]quinoline, 5 - methyl - 1,2,4 - triazolo[4,3-a]quinoline, 1,5 - dimethyl - 1,2,4 - triazolo[4,3-a]quinoline and 1,2,4 - triazolo[3,4-a]isoquinoline.[4,5] The physical and spectroscopic properties of the above compounds were found to be in agreement with those reported earlier. The most convenient source of 1-chloroisoquinoline used for the preparation of the hydrazine was the reaction of isoquinoline - N - oxide with $POCl_3$.[6]

The following examples illustrate the photochemical procedures used.

Photodimerization of some 1,2,4 - *triazolo*[4,3-*a*]*quinolines*

The formation of 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,8,9,10a - hexaazadibenzo[c,i]*dicyclopenta*[a,g]*biphenylene* (**2**; R=R^1=H). Compound **1** (R=R^1=H; 3.0 g) was dissolved in acetonitrile (250 ml, dried over molecular sieves) (or THF freshly distilled from LAH). The soln was filtered into a Pyrex Erlenmeyer flask, flushed with dry N_2, and irradiated for 5 days at 300 nm during which time the product crystallized from the reaction. The solid was collected, washed with a small volume of acetonitrile, and recrystallized twice from aqueous EtOH (Norit) giving small, colorless needles: 1.71 g (57%); m.p. 282–284°; ($M^{\dot{+}}$ 338 (0.2) (Table 1).

With the other *s*-triazoloquinolines slight warming was occasionally needed to effect complete solution before starting the irradiations.

Photodimerization of some 1,2,4 - *triazolo*[3,4-*a*] *isoquinolines*

The formation of 7bα,7cα,14bα,14cα - tetrahydro - 2,3,12,13,14a,14b - hexaazadibenzo[c,g]*dicyclopenta*[a,i]*biphenylene* (**4**; R=H). Compound **3** (R=H; 3.0 g) was dissolved in acetonitrile (200 ml, dried over molecular sieves). The soln was filtered into a Pyrex Erlenmeyer flask and flushed with dry N_2. The soln was irradiated for 4 days with 300 nm UV light during which time the photoproduct crystallized from aqueous EtOH (Norit) giving small, colorless needles: 1.61 g (54%); m.p. 313–315° (Table 2).

Codimerization of some 1,2,4 - *triazolo*[4,3-*a*]*quinolines and* 1,2,4 - *triazolo*[3,4-*a*]*isoquinolines*

The formation of 3,7cα - dimethyl - 7bα,7cα,14bα,14cα - tetrahydro - 1,2,3a,7d,9,10 - hexaazadibenzo[c,i]*dicyclopenta*[a,g]*biphenylene* (**6**; R=R^2=Me; R^1=H). Compound **1** (R=H; R^1=Me; 1.0 g, 5.5 × 10^{-3} mole) and **3** (R=Me; 1.0 g, 5.5 × 10^{-3} mole) were dissolved in acetonitrile (100 ml, dried over molecular sieves). The soln was filtered into a Pyrex Erlenmeyer flask and flushed with dry N_2. The soln was irradiated for 5 days with 300 nm UV light during which time the photoproduct crystallized from the reaction in an analytically pure form as colorless, rectangular plates: 1.30 g (65%); m.p. 290–292° (Table 2).

The photoproduct from the dimerization of **1** (R=Me; R^1=H; 1.1 g, 6.0 × 10^{-3} mole) and **3** (R=Me; 1.1 g, 6.0 × 10^{-3} mole) precipitated from the reaction in two different crystalline forms. This was collected and mechanical separation gave codimer **7** in analytically pure form as soft, colorless, opaque, irregular prisms: 1.13 g (52%); m.p. 299–300° (Table 2).

The minor component separated from the mixture was obtained

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†Instrumentation and other experimental parameters are described in the preceding paper. Infrared data were consistent with the observed structures.

as large, hard, light-tan, translucent prisms: 0.38 g [(34%, based on converted **1** (R=Me; R^1=H)]; m.p. 316–317° identical with **2** (R=H; R^1=Me) derived from **1** (R=Me; R^1=H).

Codimer **10** *derived from* 2 (1H)-*quinolinone* (**8**) *and* 5 - *methyl* - 1,2,4 - *triazolo*[4,3-*a*]*quinoline* (**1**; R=Me; R^1=H)

Compound **8** (1.45 g, 0.01 mole) and **1** (R=Me; R^1=H; 1.83 g, 0.01 mole) were dissolved in acetonitrile (200 ml, dried over molecular sieves). The soln was filtered into a Pyrex Erlenmeyer flask and irradiated 6 days with 300 nm UV light. The solid which precipitated was collected, washed with a small volume of acetonitrile and dissolved in trifluoroacetic acid (20 ml). Crystallization was induced by the addition of water (20 ml) giving a colorless, micro-crystalline solid: 0.91 g [63%, based on converted **8**], m.p. 297–298°, identical with dimer **9**.

Codimer **10** crystallized over 3 days from the filtrate after addition of acetone (40 ml), giving light yellow cubes which turned

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