Photo-Induced Reactions of Oxime O-Ethers Derived from 3-Acyl-1,2-dihydrocinnoline-1,2-dicarboximides

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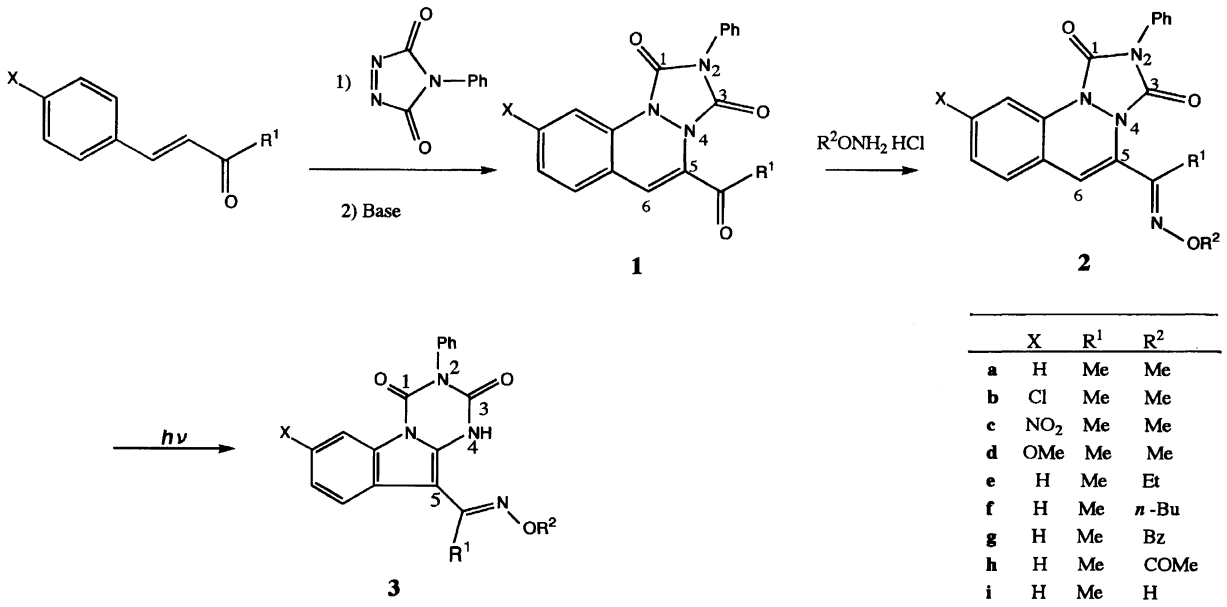
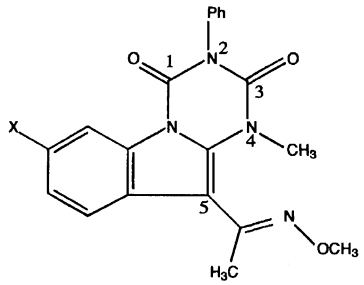
The irradiation of oxime O-ethers **2**, derived from *N*-substituted 3-acyl-1,2-dihydrocinnoline-1,2-dicarboximides in benzene, afforded rearranged products **3** possessing a [1,3,5]triazino[1,2-*a*]indole skeleton in good yields. Upon irradiation, 7-methoxy-substituted 1,2-dihydrocinnoline-1,2-dicarboximides **2** gave a novel dimer **5** together with the rearranged triazinoindole derivatives **3** in benzene, while in nucleophiles they gave the nucleophile-incorporated dihydrotriazinoindoles **6**. However, the 7-nitro-substituted one was inert under the same conditions. The dimer and dihydrotriazinoindole derivatives were thought to be formed by a nucleophilic attack of the initial photoproduct **3** and nucleophiles to **2**, respectively. From these results and the observation of a remarkable solvent-dependency of the fluorescence and UV spectra of **2**, it was suggested that these photoreactions should occur through a nitrogen–nitrogen bond cleavage at polar excited states followed by skeletal rearrangements.

In contrast to the wide-spread information concerning the photochemical reactivities of cyclic imides,[1] only a few reports concerning the photochemistry of the aza analogues (hydrazodicarboximides)and their related compounds have been published, which include [4+2] and [2+2] cycloadditions,[2] a di-π-methane rearrangement under sensitized conditions[3] and transformations to triazine derivatives.[4] Very recently, we exploited a new synthetic methodology of heterocycles using *N*-phenyl-substituted 1,2-dihydrocinnoline-1,2-dicarboximide derivatives **1**, obtained from the reaction of α-benzylidene ketones with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD).[5] In particular, successful one-pot syntheses of series of hetero analogues of angular triquinanes,[6] hetero[4.3.3]propellanes,[7] and cyanoindoles,[8] which proceed via a nucleophile-assited rearrangement of compound **1**, suggest that the hydrazodicarboximide



	X	R^1	R^2
a	H	Me	Me
b	Cl	Me	Me
c	NO_2	Me	Me
d	OMe	Me	Me
e	H	Me	Et
f	H	Me	*n*-Bu
g	H	Me	Bz
h	H	Me	COMe
i	H	Me	H
j	H	*n*-Pr	Me
k	OMe	Me	Bz

Scheme 1.



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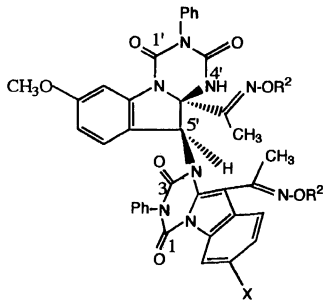
a; X=H
b; X=OMe



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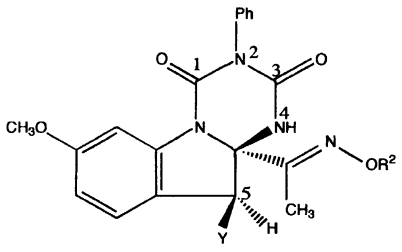
a; X=OMe, R^2=Me
b; X=OMe, R^2=Bz
c; X=H, R^2=Me



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a; Y=OEt, R^2=Me
b; Y=OMe, R^2=Me
c; Y= O-*i*-Pr, R^2=Me
d; Y= O-*t*-Bu, R^2=Me
e; Y= O-*t*-Pent, R^2=Me
f; Y=OBz, R^2=Me
g; Y=1-Phenylethoxy, R^2=Me
h; Y=*n*-BuNH, R^2=Me
i; Y=piperidino, R^2=Me
j; Y=OEt, R^2=Bz

Chart 1.

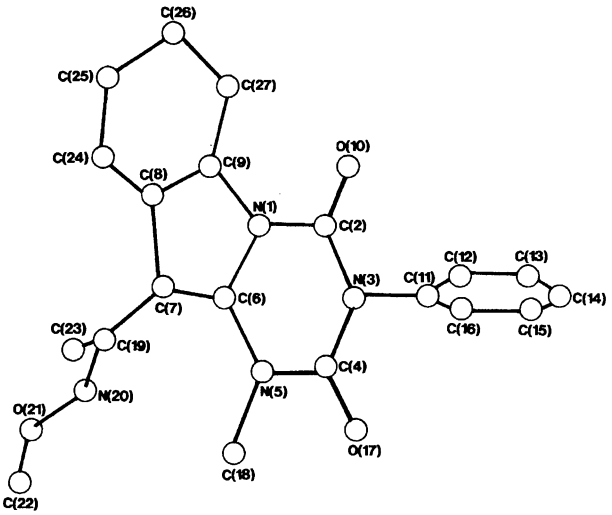

Fig. 1. Molecular structure of **4a** showing atom labelling. Hydrogen atoms are not shown for clarity.

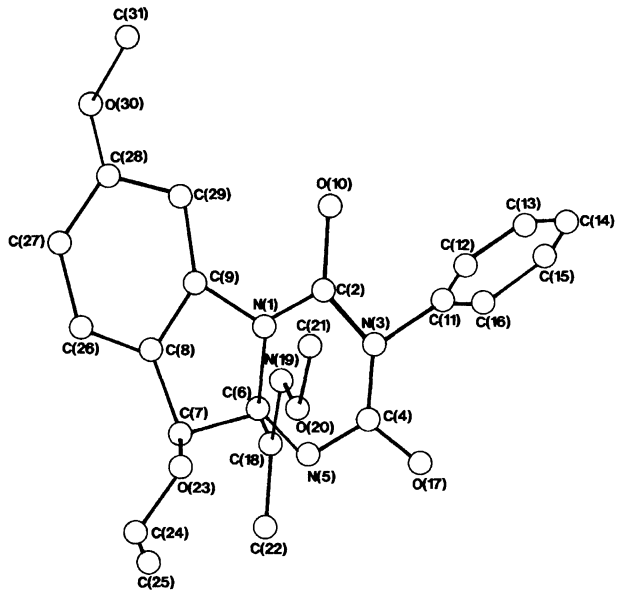

Fig. 2. Molecular structure of **6a** showing atom labelling. Hydrogen atoms are not shown for clarity.

ring should highly activate an adjacent carbon–carbon double bond, and that the nitrogen–nitrogen bond undergoes a heterolytic cleavage more easily than expected.[9] In our continuing exploration of the further synthetic potential of hydrazodicarboximides in organic syntheses, it is of great interest to investigate photoreactions assisted by the excitation of this carbon–carbon double bond. In this paper we deal with novel photo-induced rearrangements of hydrazodicarboximides **2** to triazinoindoles and nucleophile-incorporated dihydrotriazioindololes.[10]

Results and Discussion

Photoreaction of Hydrazodicarboximide. 3-Acyl-1,2-dihydrocinnoline-1,2-dicarboximide(5-acyl-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione) **1** were prepared by addition–elimination reactions of α-benzylidene ketones with PTAD.[5] The corresponding 5-[1-(alkoxyimino)alkyl] derivatives (oxime O-ethers) **2** were obtained from **1**, as shown in Scheme 1, or by the alkylation of **2i**. The irradiation of **2a** in benzene for 8 h by a 400-W high-pressure mercury lamp through a Pyrex filter resulted in the loss of its characteristic green fluorescence. A conventional work-up unexpectedly gave a rearranged product **3a** (89% yield) possessing a [1,3,5]triazino[1,2-*a*]indole skeleton. The structure of **3a** was determined based on the spectral data, elemental analyses, and chemical transformation. The mass spectrum showed a peak at *m/z* 348 (M^+), indicating **3a** to be an isomer of **2a**. Its IR spectrum showed characteristic bands at 3445 and 1702

Table 1. Photoreactions of Hydrazodicarboximide **2** in Benzene

Entry No.	Hydrazodicarboximides	Irradiation time	Product yield (%)	
	2	h	**3**	**5**
1	**2a**	4	(**3a**) 89	0
2	**2b**	9	(**3b**) 57	0
3	**2c**	17	(**3c**) 0[a]	0
4	**2d**	1	(**3d**) 21	(**5a**) 40
5	**2e**	17	(**3e**) 74	0
6	**2f**	10	(**3f**) 65	0
7	**2g**	5	(**3g**) 74	0
8	**2h**	4	(**3h**) 0[b,c]	0
9	**2j**	7	(**3j**) 65	0
10	**2k**	2	(**3k**) 30	(**5b**) 34

a) The starting material was recovered in 83 % yield. b) The stating material was recovered in 80% yield. c) *E,Z*-isomerization of the starting material was observed ($E/Z = 1$, based on ^{1}H NMR).

Table 2. Solvent Effects on Photoreactions of Hydrazodicarboximides

Entry No.	Compound	Irradiation time	Solvent	Additive (1%)	Product yield (%)		
		h			**3**	**5**	**6**
1	**2a**	17	EtOH	—	80	0	0
2	**2d**	1	PhH	EtOH	0	0	80 (**6a**)
3	**2d**	1	EtOH	—	0	0	86 (**6a**)
4	**2d**	6	PhH	MeOH	0	0	83 (**6b**)
5	**2d**	5	PhH	*i*-PrOH	5	11	52 (**6c**)
6	**2d**	1	PhH	*t*-BuOH	19	5	34 (**6d**)
7	**2d**	1	PhH	*t*-PeOH[a]	15	7	52 (**6e**)
8	**2d**	1	PhH	BzOH	0	0	63 (**6f**)
9	**2d**	1	PhH	PheOH[b]	5	0	34 (**6g**)
10	**2d**	1	PhH	*n*-$BuNH_2$	20	0	59 (**6h**)
11	**2d**	1	PhH	Piperidine	0	0	86 (**6i**)
12	**2k**	1	EtOH	—	0	0	98 (**6j**)

a) *t*-Pentyl alcohol. b) 1-Phenylethyl alcohol.

cm^{-1} due to the –CO–NH– group. The ^{1}H NMR spectrum of **3a** showed two methyl singlets at $\delta = 3.93$ and 2.40, and a –CO–NH– proton at $\delta = 10.0$, which disappeared upon the addition of D_2O. The ^{13}C NMR spectrum also supported the proposed structure. Compound **3a** was easily methylated with methyl iodide to afford **4a** in 52% yield, using a two-phase system (aq NaOH/CH_2Cl_2/*n*-Bu_4NBr). The spectral data and elemental analyses of **4a** satisfied its structure. Finally, the structure of **4a** was unambiguously determined by a single-crystal X-ray analysis (Fig. 1).

Although dicarboximide **2b**, bearing a chorine substituent on the benzene ring, also gave a similar rearranged triazinoindole derivative **3b** in 57% yield by the conventional work-up after the disappearance of its fluorescence, **2c** possessing an electron-withdrawing nitro group was inert upon irradiation for over 17 h. The starting material was recovered without *Z,E*-isomerization of the oxime O-ether moiety. In contrast, more photosensitive **2d** possessing an electron-donating methoxyl group on the benzene ring afforded an intriguing compound **5a** in 40% yield together with the expected rearranged product **3d** in 21% yield upon irradiation for only 1 h. The methylation of **3d** gave **4b** by a two-phase system as described above (Chart 1). The structures of **3d**, **5a**, and **4b** were also confirmed on the basis of their spectral data and elemental analyses. In particular, the 2D NOESY spectra of **3d** and **4b** showed clear correlation crosspeaks, as expected from their structures, between the C-methyl pro-

Table 3. Absorption and Emission Maxima of **2a** in Various Solvents

	Solvent	E_T[a]	λ_{max}/nm	Em_{max}/nm	SS[b]/nm
1	MeOH	55.5	360	510	150
2	EtOH	51.9	361	506	145
3	*n*-BuOH	50.2	363	508	145
4	*i*-PrOH	48.6	357	500	143
5	Acetonitrile	46.0	365	494	129
6	DMSO	45.0	372	508	136
7	DMF	43.8	370	506	136
8	Acetone	42.2	366	502	136
9	Chloroform	39.1	362	490	128
10	Ethyl acetate	38.1	369	500	131
11	THF	37.4	369	500	131
12	1,4-Dioxane	36.0	370	496	126
13	Benzene	34.5	371	490	119
14	CCl_4	32.5	370	490	120

a) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York (1968), Chap. 2.6. b) Stokes shift.

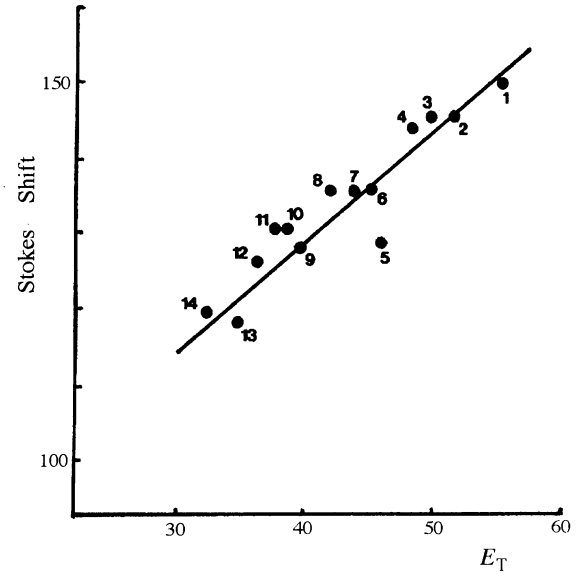

Fig. 3. Relation between Stokes shifts and E_T values of the solvents.

tons of the 1-(methoxyimino)ethyl groups and the protons *meta* to the methoxyl groups on the benzene rings. On the other hand, the mass spectrum of **5a** showed M^+ at *m/z* 756, which indicated a dimer structure. The ^1H NMR spectrum of **5a** showed the presence of four methoxyl and two methyl groups ($\delta = 3.72$, 3.80, 3.83, 3.92, 2.08, and 2.43), and a methine proton at $\delta = 6.15$ (s, 5-H). The ^{13}C NMR spectrum of **5a** showed a doublet ($\delta = 64.3$, C-5′) and a singlet ($\delta = 77.7$, C-4′a) signals in addition to signals which were assigned to the skeleton of **3d**. In addition, the irradiation of **2d** in benzene containing 1% ethanol (v/v) gave an ethanol-incorporated adduct **6a** predominantly, while no reaction

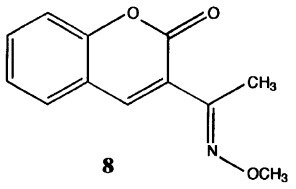

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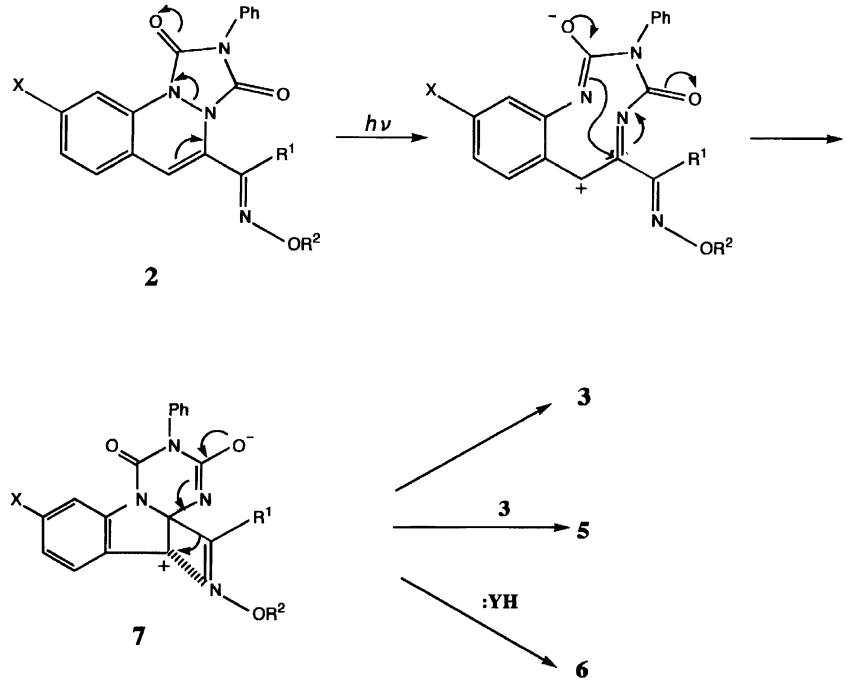
Chart 2.

occurred in dark. The structure of **6a** was unambiguously determined by a single-crystal X-ray analysis (Fig. 2). These facts suggested that the framework of **5a** comprised those of **3d** and **6a**. It thus seemed that the photo-transformation of **2d** to **5a** proceeded through an intermediate **7**, which could accept **3d** or ethanol as a nucleophile to give indolinylindole **5a** or dihydrotriazinoindole **6a**, as discussed later on.

In order to further comfirm the structure of this novel dimer **5a**, a photo-crossover experiment was performed using an equimolar mixture of **2d** and **3a** in benzene. A careful chromatographic separation of the product mixture afforded a crossover dimer **5c** together with the rearranged oxime O-ether **3d** and the dimer **5a**. No reaction occurred in the dark, and **3a** itself was quite stable upon irradiation. This observation also supported the proposed structure of the dimer. An ORTEP projection (Fig. 2) showed the stereochemistry of **6a** to be (4a*R**, 5*S**). The stereochemistry of **5a** was also determined to be (4′a*R**, 5′*S**) by an analysis of the NOESY spectrum, which showed the NOEs between 5′-H and C-methyl proton of C-4′a-[1-(methoxyimino)ethyl]group. A quite similar NOEs relationship was observed for **6a**.

In parallel to the above-mentioned remarkable C7-substituent effects on the course of the present photoreactions, substituents around the imino group exhibited similar effects on the photoreactivities of **2**. When an alkoxyl group



Scheme 2.

on imino nitrogen was replaced by an electron-withdrawing acetoxyl group (compound **2h**), the expected photoreaction did not occur in benzene and ethanol at all, and *Z,E*-isomerization of a carbon–nitrogen double bond was observed ($Z/E = 1$, based on ^{1}H NMR), whereas changing the alkyl groups on the imino methyl carbon resulted in slight effects on the photoreactivities (see Table 1).

In order to elucidate the formation mechanism of the nucleophile-incorporated adduct **6** in more detail, the photoreactions in some nucleophiles were investigated using **2a**, **2d**, and **2k**. The results are shown in Table 2. Although irradiation of the parent 1,2-dihydrocinnoline-1,2-dicarboximide **2a** (X = H) in ethanol or benzene yielded only **3a**, that of **2d** (X = OMe) and **2k** (X = OMe) in ethanol or in benzene containing primary alcohols and amines afforded the respective nucleophile-incorporated indoline derivatives **6** in high yields. However, when more crowded alcohols were employed as additives (Entry No.5, 6, 7, and 9), the rearranged products **3** and dimeric products **5** were formed in yields of 5—19% together with the expected alcohol-incorporated products **6**. Accordingly, the dimers **5** should be formed by a nucleophilic attack of the photoproduct **3** to an intermediate **7**, which was in competition with a nucleophilic attack of the solvent molecules to give **6**.

Fluorescent Properties. In order to examine the nature of the excited state, the solvent effects on the absorption and fluorescence spectra of **2a** were investigated using fourteen solvents. The observed absorption maxima (λ_{max}) and the emission maxima (Em_{max}) are listed in Table 3. The Stokes shift (SS) denotes the difference in the wavelength between the emission maxima and the absorption maxima. The observed Stokes shifts were unusually high, and the linear correlation between the Stokes shifts and the solvent polarity (E_T) shown in Fig. 3 indicates that the excited state is more polar than ground state.[11] An intramolecular charge separation at the singlet excited state may be responsible for the observed large Stokes shifts.

Reaction Mechanism. The structures of the isolated products suggested that a nitrogen–nitrogen bond cleavage played a definitive role in the present photoreactions. To confirm this unique participation of the hydrazodicarboximide ring, similar photoreactions were performed using 3-[1-(methoxyimino)ethyl]coumarin **8** (Chart 2), prepared by the oxime etherification of 3-acetylcoumarin, which possessed a lactone ring in place of a hydrazodicarboximide ring in **2a.** Although compound **8** showed quite similar absorption and fluorescence bands to those of **2a**, the irradiation of **8** in benzene or ethanol resulted only in, *Z,E*-isomerization of the carbon–nitrogen double bond. This difference in the photoreactivities may result from differences in the bond energies of a nitrogen–nitrogen bond and an oxygen–carbonyl carbon bond.[12]

From both remarkable substituent and solvent effects on the present photoreactions, the differences in the photoreactivities of **2a** and **8**, and as well as the solvent effects on the fluorescent properties of **2a**, the reaction mechanism can be most likely explained by the following Scheme 2. A photochemical nitrogen–nitrogen bond cleavage in the hydrazodicarboximide moiety occurs through a polar singlet excited state of the carbon–carbon double bond,[13] and a transannular nucleophilic attack of the isourea anion to the carbon–nitrogen double bond gives an intermediate **7** stabilized by an electron-donating group and a methoxy group at the benzene ring. The 1,2-shift of the 1-(alkoxyimino)alkyl group of **7** followed by prototropy gives triazinoindole derivative **3**. A nucleophilic attack of a nucleophile or compound **3** to **7** gives the corresponding indolines **6** or dimeric products **5**. The results obtained from the photo-crossover experiment support the proposed mechanism. An alternative mechanism via aziridine[4] cannot explain the rearrangement of the alkoxyiminoalkyl group.

Thus, the carbon–carbon double bond of the excited state of **2** should have a highly polar character affected by the adjacent hydrazodicarboximide group. The presence of the imino nitrogen group highly stabilizes the rearranged intermediate **7** by its electron-donating ability.

Experimental

All of the melting point were uncorrected. The IR spectra were recorded on a Shimadzu R-460 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Hitachi R-1900 and a JEOL FX-200 spectrometers. The chemical shifts are given in δ with tetramethylsilane as an internal standard. Mass spectra were obtained using a JEOL JMX-DX-303 spectrometer. Elemental analyses were performed using a Yanagimoto Model MT-3 CHN analyzer. UV and fluorescence spectra were measured on Shimadzu UV-265 and Hitachi 650-10S spectrometers, respectively. Column chromatography was conducted on silica gel (Wakogel C-200).

Preparations of Hydrazodicarboximides 1. Hydrazodicarboximides were prepared according to the previous paper.[5] The properties of **1a,b** and **1d** were given in the previous paper.[5]

5-Acetyl-9-nitro-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (1c). Red needles; mp 252—253 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.53 (3H, s, Me), 6.17 (1H, s, 6-H), 7.23 (1H, d, Ph), 7.44—7.57 (5H, m, Ph), 7.95 (1H, dd, Ph), 9.02 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 28.6 (q), 110.5 (s), 110.7 (d, C-6), 121.1 (d), 125.7 (d), 125.8 (d), 128.2 (d), 129.2 (d), 129.3 (d), 129.5 (d), 130.0 (s), 135.0 (s), 136.2 (s), 143.8 (s), 145.9 (s, C=O), 148.8 (s, C=O), 190.6 (s, C=O); IR (KBr) 1765, 1726, 1630, 1613, 1521, 1427, 1280, 1207, 1168 cm^{-1}; MS (70 eV) *m/z* (%) 364 (M^+; 100), 322 (3), 245 (3), 217 (39), 189 (15), 175 (17), 119 (39). HRMS: Found: *m/z* 364.0809. Calcd for $C_{18}H_{12}N_4O_5$: M, 364.0810.

5-Butyryl-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (1j). Yellow powder; mp 172—173 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 0.96 (3H, t, Me), 1.57—1.96 (2H, m, CH_2), 2.75 (2H, t, CH_2), 6.17 (1H, s, 6-H), 6.97—7.63 (8H, m, Ph), 8.03—8.30 (1H, m,Ph); ^{13}C NMR ($CDCl_3$) δ = 13.7 (q), 17.7 (t), 42.7 (t), 113.7 (s), 115.3 (d, C-6), 119.7 (s), 125.7 (d), 125.9 (d), 128.2 (d), 128.7 (d), 129.3 (d), 130.6 (d), 131.2 (d), 133.4 (s), 134.7 (s), 143.9 (s, C=O), 146.2 (s, C=O), 193.9 (s, C=O); IR (KBr) 1756, 1704, 1425, 1331, 1182 cm^{-1}; MS (70eV) *m/z* (%) 347 (M^+; 100), 200 (15), 185 (10), 172 (14), 157 (13), 130 (45). HRMS: Found: *m/z* 347.1285. Calcd for $C_{20}H_{17}N_3O_3$: M, 347.1270.

Preparations of Oxime Ethers of Hydrazodicarboximides. 2. Oxime O-ethers **2** were prepared by the following two methods: (1) Oximation of hydrazodicarboximide **1** with O-alkylhydroxylamine to give **2a—d** and **2g—k**. An ethanol solution of hydrazodicarbox-

imide **1** (1.57 mmol), hydroxylamine hydrochloride, or O-methyl-, or O-benzylhydroxylamine hydrochloride (7.85 mmol), and sodium acetate trihydrate were refluxed for 8 h, or heated at 100 °C for 100 h in an autoclave.[14] After cooling, the resulting precipitates were filtered by suction, and recrystallized from ethanol. (2) Alkylation of hydrazodicarboximide **2i** with alkyl bromide to give **2e—f**. A dichloromethane solution of oxime **2i** (1.50 mmol), alkyl bromide (15.0 mmol), and an aqueous sodium hydroxide solution were mixed and stirred vigorously in the presence of a catalytic amount of tetrabutylammonium bromide at 25 °C for 24 h.[15] The dichloromethane layer was separated, washed with water, and concentrated by a rotary evaporator. The residual solid was chromatographed on silica gel with dichloromethane as an eluent.

5- [1- (Methoxyimino)ethyl]- 2- phenyl- 1*H*- [1, 2, 4]triazolo-[1,2-*a*]cinnoline-1,3(2*H*)-dione (2a). Pale yellow powder; mp 197—198 °C (from EtOH); ^{1}H NMR($CDCl_3$) δ = 2.09 (3H, s, Me), 3.96 (3H, s, OMe), 5.85 (1H, s, 6-H), 6.93—7.53 (9H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.6 (q), 62.3 (q), 110.1 (d, C-6), 115.1 (d), 120.8 (s), 125.7 (d), 125.9 (d), 126.9 (d), 128.6 (d), 129.2 (d), 129.7 (d), 130.7 (s), 130.9 (s), 133.6 (s), 143.2 (s, C=O), 145.4 (s, C=O), 150.6 (s, C=N); IR (KBr) 1759, 1712, 1594, 1502, 1457, 1416, 1362, 1057 cm^{-1}; MS (70 eV) *m/z* (%) 348 (M^+; 100), 317 (16), 201 (17), 157 (23), 130 (28). Found: C, 65.39; H, 4.58; N, 15.85%. Calcd for $C_{19}H_{16}N_4O_3$: C, 65.49; H, 4.63; N, 16.09%.

9-Chloro-5-[1-(methoxyimino)ethyl]-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (2b). Yellow powder; mp 247—249 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.08 (3H, s, Me), 3.95 (3H, s, OMe), 5.80 (1H, s, 6-H), 6.90—7.07 (1H, m, Ph), 7.33—7.90 (6H, m, Ph), 8.17—8.27 (1H, m,Ph); ^{13}C NMR ($CDCl_3$) δ = 15.5 (q), 62.3 (q), 109.2 (d, C-6), 115.6 (d), 119.4 (s), 125.4 (d), 125.9 (d), 127.5 (d), 128.8 (d), 129.3 (d), 130.5 (s), 131.2 (s), 134.3 (s), 135.2 (s), 143.1 (s, C=O), 145.4 (s, C=O), 150.3 (s, C=N); IR (KBr) 1755, 1718, 1413, 1356, 1055 cm^{-1}; MS (70 eV) *m/z* (%) 384 (M^++2; 40), 382 (M^+; 100), 351 (20), 235 (20), 191 (34), 164 (36). HRMS: Found: *m/z* 382.0830. Calcd for $C_{19}H_{15}ClN_4O_3$: M, 382.0830.

5-[1-(Methoxyimino)ethyl]-9-nitro-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (2c). Red powder; mp 273—275 °C (from EtOH); ^{1} NMR ($CDCl_3$) δ = 2.10 (3H, s, Me), 3.97 (3H, s, OMe), 5.80 (1H, s, 6-H), 7.38—7.53 (6H, m, Ph), 7.73—7.80 (1H, m, Ph), 8.34—8.37 (1H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.5 (q), 62.5 (q), 107.9 (d), 110.3 (d, C-6), 121.1 (d), 125.8 (d), 126.7 (d), 127.3 (s), 129.0 (d), 129.4 (d), 130.2 (s), 134.2 (s), 134.3 (s), 143.0 (s), 145.3 (s, C=O), 147.9 (s, C=O), 149.9 (s, C=N); IR (KBr) 1756, 1718, 1414, 1330, 1046 cm^{-1}; MS (70eV) *m/z* (%) 393 (M^+; 100), 326 (51), 335 (4), 246 (22), 201 (14), 175 (51), 119 (36). HRMS: Found: *m/z* 393.1072. Calcd for $C_{19}H_{15}N_5O_5$: M, 393.1070.

9-Methoxy-5-[1-(methoxyimino)ethyl]-2-phenyl-1*H*-[1,2,4]-triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (2d). Pale yellow powder; mp 190—191 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.10 (3H, s, Me), 3.80 (3H, s, OMe), 3.95 (3H, s, OMe), 5.83 (1H, s, 6-H), 6.57 (1H, dd, Ph), 7.33—7.53 (6H, m, Ph), 7.90 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.7 (q), 55.6 (q), 62.2 (q), 101.5 (d), 110.4 (d, C-6), 111.4 (d), 113.4 (s), 125.9 (d), 128.0 (d), 128.6 (d), 128.8 (s), 129.2 (d), 130.7 (s), 134.8 (s), 143.2 (s, C=O), 145.6 (s, C=O), 150.7 (s, C=N), 160.8 (s); IR (KBr) 1750, 1706, 1418, 1361, 1048, 1033 cm^{-1}; MS *m/z* (%) 378 (M^+; 100), 187 (77), 160 (42). Found: C, 63.53; H, 4.62; N, 14.70%. Calcd for $C_{20}H_{18}N_4O_4$: C, 63.46; H, 4.80; N, 14.82%.

5-[1-(Ethoxyimino)ethyl]-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]-cinnoline-1,3(2*H*)-dione (2e). Pale yellow needles; mp 158—159 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.26 (3H, t, Me), 2.06 (3H, s, Me), 4.16 (2H, q, CH_2), 5.80 (1H, s, 6-H), 6.83—7.60 (8H, m, Ph), 7.93—8.30 (1H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 14.6 (q), 15.7 (q), 70.2 (t), 109.9 (d, C-6), 115.2 (d), 120.9 (s), 125.6 (d), 125.9 (d), 126.8 (d), 128.6 (d), 129.2 (d), 129.7 (d), 130.7 (s), 131.3 (s), 133.7 (s), 143.3 (s, C=O), 145.4 (s, C=O), 150.2 (s, C=N); IR (KBr) 1761, 1710, 1415, 1360, 1048 cm^{-1}; MS (70 eV) *m/z* (%) 362 (M^+; 100), 317 (33), 290 (9), 215 (10), 198 (13), 157 (41), 130 (52), 119 (24). HRMS: Found: *m/z* 362.1373. Calcd for $C_{20}H_{18}N_4O_3$: M, 362.1373.

5-[1-(Butoxyimino)ethyl]-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]-cinnoline-1,3(2*H*)-dione (2f). Pale yellow powder; mp 114—115 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 0.91 (3H, t, Me), 1.40—1.73 (4H, m, CH_2), 2.07 (3H, s, Me), 4.13 (2H, t, CH_2), 5.80 (1H, s, 6-H), 6.93—7.10 (8H, m, Ph), 7.30—8.30 (1H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 13.9 (q), 15.7 (q), 19.2 (t), 31.2 (t), 74.6 (t), 110.0 (d, C-6), 115.2 (d), 120.9 (s), 125.6 (d), 126.0 (d), 126.8 (d), 128.6 (d), 129.2 (d), 129.6 (d), 130.7 (s), 131.3 (s), 133.7 (s), 143.3 (s, C=O), 145.4 (s, C=O), 150.7 (s, C=N); IR (KBr) 1760, 1712, 1414, 1360, 1052 cm^{-1}; MS (70 eV) *m/z* (%) 390 (M^+; 100), 317 (8), 198 (9), 157 (19), 130 (10). HRMS: Found: *m/z* 390.1689. Calcd for $C_{22}H_{22}N_4O_3$: M. 390.1690.

5- [1- (Benzyloxyimino)ethyl]- 2- phenyl- 1*H*- [1, 2, 4]triazolo [1,2-*a*]cinnoline-1,3(2*H*)-dione (2g). Pale yellow needles; mp 174—175 °C (from EtOH); ^{1}H NMR($CDCl_3$) δ = 2.13 (3H, s, Me), 5.20 (2H, s, CH_2), 5.83 (1H, s, 6-H), 6.93—7.63 (13H, m, Ph), 8.17 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.9 (q), 76.6 (t), 110.2 (d, C-6), 115.2 (d), 120.9 (s), 125.6 (d), 125.8 (d), 125.9 (d), 126.8 (d), 127.8 (d), 127.9 (d), 128.4 (d), 128.6 (d), 129.2 (d), 129.7 (d), 130.8 (s), 131.1(s), 133.7 (s), 137.6 (s), 143.3 (s, C=O), 145.4 (s, C=0), 151.1 (s, C=N); IR (KBr) 1764, 1715, 1593, 1488, 1452, 1410, 1145, 1023, 1006 cm^{-1}; MS (70 eV) *m/z* (%) 424 (M^+; 100), 317 (7), 292(8), 260(8), 157 (19), 146 (13), 119(10). Found: C, 70.32; H, 4.62; N, 13.23%. Calcd for $C_{25}H_{20}N_4O_3$: C, 70.72; H, 4.75; N, 13.21%.

5-[1-(Acetoxyimino)ethyl]-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]-cinnoline-1,3(2*H*)-dione (2h). Pale yellow powder; mp 183 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.20 (3H, s, Me), 2.30 (3H, s, Me), 5.97 (1H, s, 6-H), 6.93—7.50 (8H, m, Ph), 8.07—8.30 (1H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 17.1 (q), 19.5 (q), 111.5 (d, C-6), 115.4 (d), 120.3 (s), 125.9 (d), 127.3 (d), 128.8 (d), 129.3 (d), 129.4 (s), 130.4 (d), 130.6 (s), 133.7 (s), 143.5 (s, C=O), 145.3 (s, C=O), 158.4 (s, C=N), 167.8 (s, C=O); IR (KBr) 1764, 1709, 1417, 1361, 1233, 1194 cm^{-1}; MS (70 eV) *m/z* (%) 376 (M^+; 100), 334 (20), 318 (18), 187 (36), 157 (46), 130 (14), 119 (19). HRMS: Found: *m/z* 376.1175. Calcd for $C_{20}H_{16}N_4O_4$: M, 376.1170.

5- [1- (Hydroxyimino)ethyl]- 2- phenyl- 1*H*- [1, 2, 4]triazolo [1,2-*a*]cinnoline-1,3(2*H*)-dione (2i). Pale yellow powder; mp 252 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.13 (3H, s, Me), 5.80 (1H, s, 6-H), 6.90—7.10 (1H, m, Ph), 7.37—7.57 (7H, m, Ph), 8.07—8.30 (1H, m, Ph); ^{13}C NMR (DMSO-d_6) δ = 14.4 (q), 108.7 (d, C-6), 113.9 (d), 120.9 (d), 125.4 (d), 126.7 (d), 126.9 (d), 128.4 (s), 128.7(d), 129.0 (d), 130.9 (s), 131.4 (s), 133.9 (s), 142.7 (s), 145.7 (s), 149.4 (s); IR (KBr) 3230, 1759, 1708, 1489, 1407, 1359, 1026, 1006 cm^{-1}; MS (70 eV) *m/z* (%) 334 (M^+, 100), 318 (10), 198 (20), 187 (76), 157 (13), 130 (36). HRMS: Found: *m/z* 334.1071. Calcd for $C_{18}H_{14}N_4O_3$: M, 334.1070.

5- [1- (Methoxyimino)butyl]- 2- phenyl- 1*H*- [1, 2, 4]triazolo-[1,2-*a*]cinnoline-1,3(2*H*)-dione (2j). Pale yellow powder; mp 119—120 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 0.93 (3H, t, Me), 1.33—1.80 (2H, m, CH_2), 2.52 (2H, t, CH_2), 3.93 (3H, s, OMe), 5.78 (1H, s, 6-H), 6.90—7.67 (9H, m, Ph); ^{13}C NMR ($CDCl_3$)

δ = 14.2 (q), 19.0 (t), 31.1 (t), 62.2 (q), 110.4 (d, C-6), 113.7 (s), 115.2 (d), 120.9 (s), 125.6 (d), 125.9 (d), 126.7 (d), 128.6 (d), 129.1 (d), 129.6 (d), 130.7 (s), 133.6 (s), 143.3 (s, C=O), 145.2 (s, C=O), 154.7 (s, C=N); IR (KBr) 1765, 1716, 1405, 1355, 1047 cm^{-1}; MS (70 eV) *m/z* (%) 376 (M^+; 100), 345 (10), 226 (6), 198 (14), 157 (22). HRMS: Found: *m/z* 376.1535. Calcd for $C_{21}H_{20}N_4O_3$: M, 376.1540.

5-[1-(Benzyloxyimino)ethyl]-9-methoxy-2-phenyl-1*H*-[1,2,4]-triazolo[1,2-*a*]cinnoline-1,3(2*H*)-dione (2k). Pale yellow powder; mp 154 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.18 (3H, s, Me), 3.85 (3H, s, OMe), 5.25 (2H, s, CH_2), 5.88 (1H, s, 6-H), 6.90—7.13 (1H, dd, Ph), 7.16—7.60 (12H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 15.9 (q), 55.6 (q), 76.5 (t), 101.5 (d), 110.5 (d, C-6), 111.4 (d), 113.5 (s), 125.9 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.4 (d), 128.5 (s), 128.6 (d), 129.2 (d), 130.8 (s), 134.9 (s), 137.6 (s), 143.2 (s, C=O), 145.6 (s, C=O), 151.3 (s, C=N), 160.8 (s); IR (KBr) 1750, 1699, 1605, 1504, 1409, 1362, 1238, 1000 cm^{-1}; MS (70 eV) *m/z* (%) 454 (M^+; 100), 347 (5), 322 (10), 290 (9), 202 (22), 187 (33), 175 (17). HRMS: Found: *m/z* 454.1643. Calcd for $C_{26}H_{22}N_4O_4$: M, 454.1640.

General Procedure of Photochemical Reaction. A solution of hydrazodicarboximide **2** (0.29 mmol) in 30 cm^3 of benzene or other solvents in a Pyrex tube was irradiated using a 400-W high-pressure mercury lamp (Riko Co.). The progress of the reaction was followed by thin-layer chromatography (TLC) and the disappearance of the fluorescence of hydrazodicarboximide **2**. After removing the solvent, the residue was separated by chromatography on silica gel with dichloromethane used as an eluent. The final purification was usually accomplished by chromatography on silica gel (Merck, type No. 7794) using a centrifugal Harrison Chromatotron, or recrystallization from appropriate solvents.

5-[1-(Methoxyimino)ethyl]-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3a). Colorless powder; mp 239—240 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.40 (3H, s, Me), 3.93 (3H s, OMe), 7.13—7.73 (9H, m, Ph), 10.00 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.1 (q), 62.2 (q), 93.9 (s,C-5), 115.3 (d), 118.9 (d), 123.1 (d), 125.1 (d), 127.6 (s), 128.8 (d), 129.3 (d), 129.5 (d), 130.8 (s), 130.9 (s), 133.7 (s), 146.0 (s, C=O), 147.6 (s, C=O), 153.4 (s, C=N); IR (KBr) 3445, 1746, 1702, 1630, 1493, 1464, 1374, 1055 cm^{-1}; MS (70 eV) *m/z* (%) 348 (M^+; 100), 317 (25), 290 (3), 229 (16), 178 (37), 179 (12). HRMS: Found: *m/z* 348.1226. Calcd for $C_{19}H_{16}N_4O_3$: M, 348.1220.

8-Chloro-5-[1-(methoxyimino)ethyl]-2-phenyl[1,3,5]triazino-[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3b). Colorless powder; mp 262—264 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.47 (3H, s, Me), 4.00 (3H, s, OMe), 7.27—7.67 (7H, m, Ph), 8.28—8.53 (1H, m, Ph), 10.00 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.0 (q), 62.3 (q), 93.7 (s, C-5), 115.6 (d),119.6 (d), 125.5 (d), 126.1 (s), 128.7 (d), 128.9 (s), 129.4 (d), 129.5 (d), 131.0 (s), 131.1 (s), 133.4 (s), 145.9 (s, C=O), 147.3 (s, C=O), 152.9 (s,C=N); IR (KBr) 3280, 1744, 1700, 1636, 1489, 1449, 1317 cm^{-1}; MS (70 eV) *m/z* (%) 384 (M^++2; 40), 382 (M^+; 100), 351 (13), 263 (12), 232 (27), 204 (9), 191 (6). HRMS: Found: *m/z* 382.0834. Calcd for $C_{19}H_{15}ClN_4O_3$: M, 382.0830.

8-Methoxy-5-[1-(methoxyimino)ethyl]-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3d). Colorless powder; mp 238—239 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.47 (3H, s, Me), 3.83 (3H, s, OMe), 4.00 (3H, s, OMe), 6.87 (1H, dd, Ph), 7.27—7.63 (6H, m, Ph), 7.83 (1H, d, Ph), 10.00 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.0 (q), 55.7 (q), 62.2 (q), 93.7 (s, C-5), 99.6 (d), 114.0 (d), 119.5 (d), 120.9 (s), 128.8 (d), 129.3 (d), 129.4 (s), 129.5 (d), 131.7 (s), 133.7 (s), 146.5 (s, C=O), 147.6 (s, C=O), 153.4 (s, C=N), 156.6 (s); IR (KBr) 3285, 1742, 1700, 1634, 1490, 1455, 1372, 1277, 1227, 1157, 1056 cm^{-1}; MS (70 eV) *m/z* (%) 378 (M^+; 100), 347 (17), 228 (13), 200 (7). HRMS: Found: *m/z* 378.1326. Calcd for $C_{20}H_{18}N_4O_4$: M, 378.1330.

5-[1-(Ethoxyimino)ethyl]-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3e). Colorless powder; mp 235—236 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.40 (3H, t, Me), 2.50 (3H, s, Me), 4.20 (2H, q, CH_2), 6.87—7.87 (8H, m, Ph), 8.00—8.33 (1H, m, Ph), 10.00 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.2 (q), 14.6 (q), 69.9 (t), 94.1 (s, C-5), 115.3 (d), 119.0 (d), 123.0 (d), 125.0 (d), 127.7 (s), 128.8 (d), 129.3 (d), 129.5 (d), 130.7 (s), 130.9 (s), 133.7 (s), 146.2 (s, C=O), 147.6 (s, C=O), 153.1 (s, C=N); IR (KBr) 3285, 1740, 1700, 1629, 1458, 1372, 1157, 1046 cm^{-1}; MS (70 eV) *m/z* (%) 362 (M^+; 100), 317 (29), 277 (7), 243 (17), 215 (18), 198 (37), 170 (17), 149 (27). HRMS: Found: *m/z* 362.1381. Calcd for $C_{20}H_{18}N_4O_3$: M, 362.1380.

5-[1-(Butoxyimino)ethyl]-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3f). Colorless powder; mp 219 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.03 (3H, t, Me), 1.37—1.80 (4H, m, CH_2), 2.50 (3H, s, Me), 4.20 (2H, t, CH_2), 7.27—7.83 (8H, m, Ph), 8.20—8.43 (1H, m, Ph), 10.10 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 13.9 (q), 14.2 (q), 19.3 (t), 31.3 (t), 74.4 (t), 94.1 (s, C-5), 115.3 (d), 119.0 (d), 123.0 (d), 125.0 (d), 127.7 (s), 128.8 (d), 129.3 (d), 129.5 (d), 130.7 (s), 130.9 (s), 133.7 (s), 146.2 (s, C=O), 147.6 (s, C=O), 153.0 (s, C=N); IR (KBr) 3255, 1740, 1698, 1632, 1458, 1373 cm^{-1}; MS (70 eV) *m/z* (%) 390 (M^+; 100), 334 (5), 317 (12), 215 (13), 198 (8). HRMS: Found: *m/z* 390.1689. Calcd for $C_{22}H_{22}N_4O_3$: M, 390.1690.

5-[1-(Benzyloxyimino)ethyl]-2-phenyl[1,3,5]triazino[1,2-*a*]-indole-1,3(2*H*,4*H*)-dione (3g). Colorless powder; mp 248—249 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.53 (3H, s, Me), 5.16 (2H, s, CH_2), 7.13—7.53 (13H, m, Ph), 8.33 (1H, d, Ph), 10.53 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.3 (q), 76.4 (t), 94.1 (s, C-5), 115.3 (d), 118.9 (d), 123.0 (d), 125.0 (d), 127.6 (d), 128.2 (s), 128.5 (d), 128.8 (d), 128.9 (d), 129.3 (d), 129.5 (d), 130.9 (s), 133.7 (s), 137.7 (s), 146.2 (s, C=O), 147.4 (s, C=O), 153.7 (s, C=N); IR (KBr) 3255, 1737, 1696, 1630, 1458, 1373, 1222, 1156, 1024 cm^{-1}; MS (70 eV) *m/z* (%) 424 (M^+; 100), 407 (14), 367 (8), 333 (19), 318 (11), 303 (34), 199 (18), 184 (19). Found: C, 70.66; H, 4.62; N, 13.11%. Calcd for $C_{25}H_{20}N_4O_3$: C, 70.72; H, 4.75; N, 13.21%.

5-[1-(Methoxyimino)butyl]-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3j). Colorless powder; mp 167—168 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.10 (3H, t, Me), 1.47—2.00 (2H, m, CH_2), 2.92 (2H, t, CH_2), 4.00 (3H, s, OMe), 7.13—7.60 (8H, m, Ph), 8.13—8.40 (1H, m, Ph), 10.23 (1H, bs, NH); ^{13}C NMR (CDC_3) δ = 14.0 (q), 20.0 (t), 29.3 (t), 62.7 (q), 92.7 (s, C-5), 115.3 (d), 119.3 (d), 123.3 (d), 125.3 (d), 127.3 (s), 128.7 (d), 129.3 (d), 129.7 (d), 130.7 (s), 131.3 (s), 136.7 (s), 146.0 (s, C=O), 148.0 (s, C=O), 158.0 (s, C=N); IR (KBr) 3320, 1747, 1695, 1627, 1462, 1154, 1047 cm^{-1}; MS (70 eV) *m/z* (%) 376 (M^+; 100), 345 (44), 226 (30), 183 (56), 128 (27). HRMS: Found: *m/z* 376.1538. Calcd for $C_{21}H_{20}N_4O_3$: M, 376.1540.

5-[1-(Benzyloxyimino)ethyl]-8-methoxy-2-phenyl[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (3k). Colorless powder; mp 238 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.47 (3H, s, Me), 3.43 (3H, s, OMe), 5.17 (2H, s, CH_2), 6.93 (1H, dd, Ph), 7.20—7.67 (12H, m, Ph), 9.70 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ = 14.3 (q), 55.7 (q), 76.4 (t), 93.9 (s, C-5), 99.6 (d), 113.9 (d), 119.5 (d), 120.9 (s), 128.2 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.3 (d), 129.5 (d), 131.8 (s), 133.7 (s), 137.7 (s), 146.5 (s, C=O), 147.4 (s, C=O), 153.6 (s, C=N), 156.5 (s); IR (KBr) 3255, 1736, 1692, 1631, 1489, 1455, 1372, 1274 cm^{-1}; MS (70 eV) *m/z* (%) 454 (M^+; 100), 437

(9), 363 (40), 333 (33), 244 (10), 214 (27), 202 (5), 171 (5). HRMS: Found: *m/z* 454.1639. Calcd for $C_{26}H_{22}N_4O_4$: M, 454.1640.

(4′a*R,5′*S**)-8,8′-Dimethoxy-5,4′a-di[1-(methoxyimino)ethyl]-2,2′-diphenyl-4′a,5′-dihydro-4,5′-bi[1,3,5]triazino[1,2-*a*]indole-1,3,1′,3′(2*H*,4*H*,2′*H*,4′*H*)-tetraone (5a).** Colorless powder; mp 215 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.08 (3H, s, Me), 2.43 (3H, s, Me), 3.72 (3H, s, OMe), 3.80 (3H, s, OMe), 3.83 (3H, s, OMe), 3.92 (3H, s, OMe), 6.15 (1H, s, 5′-H), 6.50—7.50 (14H, m, Ph, NH), 7.83—8.00 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.0 (q), 17.5 (q), 55.5 (q), 55.8 (q), 61.9 (q), 62.3 (q), 64.3 (d, C-5′), 77.7 (s, C-4′a), 99.4 (s), 99.6 (d), 102.9 (d), 112.6 (d), 114.6 (d), 117.6 (s), 119.3 (d), 122.2 (s), 124.7 (d), 128.6 (d), 128.8 (d), 129.0 (d), 129.1 (d), 129.2 (d), 129.4 (d), 129.9 (s), 131.8 (s), 133.8 (s), 134.7 (s), 144.5 (s), 146.3 (s), 147.9 (s), 151.6 (s), 151.7 (s), 151.8 (s), 153.1 (s), 157.9 (s), 161.8 (s); IR (KBr) 3200, 1744, 1716, 1697, 1672, 1607, 1487, 1455, 1429, 1271, 1048, 1030 cm^{-1}; MS (70 eV) *m/z* (%) 756 (M$^+$; 21), 637 (7), 419 (27), 378 (100), 347 (26), 337 (11), 307 (8), 228 (14), 119 (16). HRMS: Found: *m/z* 756.2659. Calcd for $C_{40}H_{36}N_8O_8$: M, 756.2660.

(4′a*R,5′*S**)-5,4′a-Di[1-(benzyloxyimino)ethyl]-8,8′-dimethoxy-2,2′-diphenyl-4′a, 5′-dihydro-4,5′-bi[1,3,5]triazino[1,2-*a*]indole-1,3,1′,3′(2*H*,4*H*,2′*H*,4′*H*)-tetraone (5b).** Colorless powder; mp 212—215 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.10 (3H, s, Me), 2.43 (3H, s, Me), 3.73 (3H, s, OMe), 3.83 (3H, s, OMe), 5.03 (2H, s, CH_2), 5.20 (2H, s, CH_2), 6.20 (1H, s, 5′-H), 6.73—7.47 (25H, m, Ph, NH), 7.87—7.97 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.3 (q), 17.9 (q), 55.5 (q), 55.8 (q), 64.3 (d, C-5′), 76.7 (t), 77.2 (t), 77.9 (s, C-4′a), 99.3 (s), 99.6 (d), 102.9 (d), 112.7 (d), 114.5 (d), 117.7 (s), 119.2 (d), 122.3 (d), 124.6 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.1 (d), 129.2 (d), 129.3 (d), 129.9 (s), 131.8 (s), 133.8 (s), 134.6 (s), 136.8 (s), 136.9 (s), 144.4 (s), 146.2 (s), 148.0 (s), 149.4 (s), 151.9 (s), 152.6 (s), 153.9 (s), 157.9 (s), 161.8 (s); IR (KBr) 3200, 1744, 1697, 1672, 1487, 1271, 1030 cm^{-1}; MS (70 eV) *m/z* (%) 908 (M$^+$; 3), 495 (23), 454 (51), 348 (22), 333 (17), 307 (42), 229 (25), 214 (21), 187 (18), 173 (20). HRMS (SIMS, *m*-NBA): Found: *m/z* (M+H$^+$) 909.3360. Calcd for $C_{52}H_{45}N_8O_8$: M, 909.3367.

(4′a*R, 5′*S**)-5,4′a-Di[1-(methoxyimino)ethyl]-2,2′-diphenyl-8′-methoxy-4′a,5′-dihydro-4,5′-bi[1,3,5]triazino[1,2-*a*]indole-1,3,1′,3′(2*H*,4*H*,2′*H*,4′*H*)-tetraone (5c).** Colorless powder; mp 251 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.03 (3H, s, Me), 2.33 (3H, s, Me) 3.67 (3H, s, OMe), 3.90 (3H, s, OMe), 4.00 (3H, s, OMe), 5.23 (1H, s, 5′-H), 6.20 (1H, s, NH), 6.83—7.63 (17H, m, Ph); ^{13}C NMR (DMSO-d_6) δ = 10.0 (q), 17.7 (q), 55.2 (q), 61.4 (q), 61.9 (q), 64.7 (d, C-5′), 77.6 (s, C-4′a), 97.0 (s), 109.9 (d), 114.2 (s) 118.4 (s), 123.2 (d), 124.4 (d), 125.6 (d), 127.9 (d), 128.1 (d), 128.4 (d), 128.8 (d), 129.2(d), 129.5 (d), 134.4 (s), 134.9 (s), 143.3 (s), 148.5 (s), 151.0 (s), 153.9 (s), 160.4 (s), IR (KBr) 3120, 1747, 1726, 1702, 1467, 1421, 1281, 1248, 1046 cm^{-1}; MS (70 eV) *m/z* (%) 726 (M$^+$; 25), 419 (20), 379 (86), 348 (100), 306 (50), 277 (26), 229 (45), 198 (37), 187 (47), 170 (15), 158 (27), 119 (30). HRMS: Found: *m/z* 726.2549. Calcd for $C_{39}H_{34}N_8O_7$: M, 726.2550.

(4a*R, 5*S**)-5-Ethoxy-8-methoxy-4a-[1-(methoxyimino)ethyl]2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6a).** Colorless powder; mp 184—185 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.23 (3H, t, Me), 1.72 (3H, s, Me), 3.56 (2H, q, CH_2), 3.77 (3H, s, OMe), 3.83 (3H, s, OMe), 4.80 (1H, s, 5-H), 6.30 (1H, s, NH), 6.47—6.71 (1H, dd, Ph), 7.06—7.60 (7H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.4 (q), 15.2 (q), 55.6 (q), 62.6 (q), 64.5 (t), 77.9 (s), 79.3 (d, C-5), 100.2 (d), 111.4 (d), 118.3 (s), 126.8 (d), 128.5 (d), 128.9 (d), 129.3 (d), 134.8 (s), 143.2(s), 148.8 (s, C=O), 152.5 (s, C=O), 152.6 (s, C=N), 162.4 (s); IR (KBr) 3215, 1723, 1686, 1480, 1451, 1256, 1048 cm^{-1}; MS (70 eV) *m/z* (%) 424 (M$^+$; 5), 393 (100), 350 (23), 322 (36), 306 (12), HRMS: Found: *m/z* 424.1749. Calcd for $C_{22}H_{24}N_4O_5$: M, 424.1750.

(4a*R,5*S**)-5,8-Dimethoxy-4a-[1-(methoxyimino)ethyl]-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (6b).** Colorless powder; mp 215—216 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.89 (3H, s, Me), 3.42 (3H, s, OMe), 3.81 (3H, s, OMe), 3.87 (3H, s, OMe), 4.78 (1H, s, 5-H), 6.28 (1H, s, NH), 6.65 (1H, dd, Ph), 7.13—7.63 (7H, m, Ph): ^{13}C NMR ($CDCl_3$) δ = 10.7 (q), 55.9 (q), 56.1 (q), 62.6 (q), 79.3 (s), 80.7 (d, C-5), 101.4 (d), 110.1 (d), 119.7 (s), 128.0 (d), 128.5 (d), 129.1 (d), 130.5 (d), 136.1 (s), 144.0 (s), 149.0 (s, C=O), 152.3 (s, C=O), 153.4 (s, C=N), 162.8 (s); IR (KBr) 3200, 1727, 1687, 1500, 1439, 1354, 1291, 1255 cm^{-1}; MS (70 eV) *m/z* (%) 410 (M$^+$; 1), 379 (100), 217 (54), 187 (54), 176 (32). HRMS: Found: *m/z* 410.1588. Calcd for $C_{21}H_{22}N_4O_5$: M, 410.1590.

(4a*R,5*S**)-5-Isopropoxy-8-methoxy-4a-[1-(methoxyimino)-ethyl]-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6c).** Colorless needles; mp 219 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.23 (3H, d, Me), 1.32 (3H, d, Me), 1.89 (3H, s, Me), 3.79 (3H, s, OMe), 3.88 (3H, s, OMe), 3.87—4.23 (1H, m, CH), 4.88 (1H, s, 5-H), 6.29 (1H, s, NH), 6.57—6.73 (1H, dd, Ph), 7.17—7.63 (7H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.7 (q), 22.1 (q), 23.2 (q), 55.6 (q), 62.6 (q), 71.9 (d), 77.8 (s), 78.8 (d, C-5), 100.0 (d), 111.6 (d), 119.1 (s), 126.3 (d), 128.5 (d), 128.9 (d), 129.2 (d), 130.0 (s), 134.6 (s), 152.0 (s, C=O), 152.6 (s, C=N), 161.3 (s); IR (KBr) 3225, 1726, 1685, 1609, 1474, 1255, 1107, 1046 cm^{-1}; MS (70 eV) *m/z* (%) 438 (M$^+$; 1), 407 (40), 365 (25), 322 (100), 176 (76). HRMS: Found: *m/z* 438.1897. Calcd for $C_{23}H_{26}N_4O_5$: M, 438.1990.

(4a*R,5*S**)-5-*t*-Butoxy-8-methoxy-4a-[1-(methoxyimino)ethyl]-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6d).** Colorless powder; mp 209 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.37 (9H, s, Me), 1.87 (3H, s, Me), 3.77 (3H, s, OMe), 3.91 (3H, s, OMe), 5.03 (1H, s, 5-H), 5.97 (1H, s, NH), 6.66 (1H, dd, Ph), 7.11—7.57 (7H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.7 (q), 29.0 (q), 55.6 (q), 62.7 (q), 74.5 (d, C-5), 76.5 (s), 77.4 (s), 99.7 (d), 111.9 (d), 120.1 (s), 126.4 (d), 128.5 (d), 128.9 (d), 129.2 (d), 134.6 (s), 142.6 (s), 149.3 (s, C=O), 152.3 (s, C=N), 153.3 (s, C=O), 161.8 (s); IR (KBr) 3265, 1734, 1692, 1491, 1315, 1030 cm^{-1}; MS (70 eV) *m/z* (%) 452 (M$^+$; 1), 421 (34), 395 (100), 365 (88), 320 (44), 233 (38), 176 (94). Found: C, 63.69; H, 6.11; N, 12.41%. Calcd for $C_{24}H_{28}N_4O_5$: C, 63.70; H, 6.24; N, 12.38%.

(4a*R,5*S**)-8-Methoxy-4a-[1-(methoxyimino)ethyl]-5-*t*-pentyloxy-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6e).** Colorless powder; mp 192 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 0.96 (3H, t, Me), 1.27 (3H, s, Me), 1.34 (3H, s, Me), 1.67 (2H, q, CH_2), 1.84 (3H, s, Me), 3.74 (3H, s, OMe), 3.87 (3H, s, OMe), 5.04 (1H, s, 5-H), 6.00 (1H, s, NH), 6.66 (1H, dd, Ph), 7.12—7.57 (7H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 9.0 (q), 10.6(q), 25.9 (q), 26.0 (q), 35.1 (t), 55.5 (q), 62.6 (q), 74.1 (d, C-5), 77.5 (s), 78.9 (s), 99.6 (d), 111.8 (d), 120.1 (s), 126.4 (d), 128.2 (d), 128.4 (d), 128.9 (d), 129.1 (d), 134.6 (s), 142.6 (s), 149.3 (s, C=O), 152.2 (s, C=N), 153.2 (s, C=O), 161.8 (s); IR (KBr) 3300, 1732, 1689, 1492, 1313, 1038 cm^{-1}; MS (70 eV) *m/z* (%) 466 (M$^+$; 1), 435 (17), 395 (100), 365 (95), 320 (54), 233 (27), 176 (79). Found: C, 64.64; H, 6.52; N, 12.07%. Calcd for $C_{25}H_{30}N_4O_5$: C, 64.36; H, 6.48; N, 12.01%.

(4a*R,5*S**)-5-Benzyloxy-8-methoxy-4a-[1-(methoxyimino)-ethyl]-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6f).** Colorless powder; mp 192 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.84 (3H, s, Me), 3.80 (3H, s, OMe), 3.85

(3H, s, OMe), 4.61 (1H, s, CH), 4.69 (1H, s, CH), 4.94 (1H, s, 5-H), 5.32 (1H, s, NH), 6.67 (1H, dd,Ph), 6.86—7.77 (12H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.4 (q), 55.5 (q), 62.5 (q), 70.6 (t), 75.6 (d, C-5), 78.4 (s), 100.0 (d), 111.3 (d), 117.9 (s), 126.8 (d), 128.2 (d), 128.3 (d), 128.5 (d), 128.8 (d), 129.2 (d), 129.4 (d), 134.5 (s), 136.6 (s), 143.1 (s), 148.6 (s, C=O), 151.9 (s, C=O), 152.7 (s, C=N), 162.2 (s); IR (KBr) 3300, 1732, 1689, 1492, 1313 cm^{-1}; MS (70 eV) *m/z* (%) 486 (M^+; 1), 455 (26), 395 (22), 322 (20), 176 (38), 91 (100). Found: C, 66.93; H, 5.46; N, 11.48%. Calcd for $C_{27}H_{26}N_4O_5$: C, 66.66; H, 5.39; N, 11.52%.

(4a*R,5*S**)-8-Methoxy-4a-[1-(methoxyimino)ethyl]-2-phenyl-5-(1-phenylethoxy)-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (6g) (diastereomer).** Colorless powder; mp 228—229 °C (from EtOH); ^{1}H NMR ($CDCl_3$, diastereomeric mixture) δ = 1.47, 1.54 (3H, d, Me), 1.81, 2.14 (3H, s, Me), 3.68, 3.78 (3H, s, OMe), 4.57, 4.77 (1H, s, 5-H), 4.71, 4.81 (1H, q, CH), 6.60, 6.66 (1H, s, NH), 7.07—7.69 (13H, m, Ph); ^{13}C NMR ($CDCl_3$, diastereomeric mixture) δ = 10.3, 10.5 (q), 23.6, 23.9 (q), 55.6 (q), 62.5 (q), 75.3 (q), 75.9 (d), 77.8 (s), 78.7 (d), 79.3 (d), 100.1 (d), 111.0 (d), 118.4 (s), 126.8 (d), 126.9 (d), 128.4 (d), 128.6 (d), 128.9 (d), 129.0 (d), 129.3 (d), 134.7 (s), 141.4 (s), 142.4 (s), 143.1 (s), 148.7 (s), 151.5 (s), 152.6 (s), 162.0 (s); IR (KBr) 3230, 1724, 1685, 1489, 1438, 1044 cm^{-1}; MS (70 eV) *m/z* (%) 500 (M^+; 1), 395 (100), 365 (14), 322 (18), 233 (24), 176 (51), 105 (71). Found: C, 67.34; H, 5.44; N, 11.12%. Calcd for $C_{28}H_{28}N_4O_5$: C, 67.19; H, 5.64; N, 11.19%.

(4a*R,5*S**)-5-Butylimino-8-methoxy-4a-[1-(methoxyimino)-ethyl]-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6h).** Colorless powder; mp 126 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 0.90 (3H, t, Me), 1.28—1.63 (4H, m, CH_2), 1.86 (3H, s, Me), 2.46—3.00 (2H, m, CH_2), 3.77 (3H, s, OMe), 3.85 (3H, s, OMe), 4.14 (1H, s, 5-H), 6.63 (1H, dd, Ph), 7.10 — 7.49 (6H, m, Ph), 7.57 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.5 (q), 13.9 (q), 20.4 (t), 32.8 (t), 47.6 (t), 55.6 (q), 62.5 (q), 63.6 (d, C-5), 77.0 (s), 99.9 (d), 111.4 (d), 119.1 (d), 121.4 (s), 125.5 (d), 128.4 (d), 128.9 (d), 129.2 (d), 134.9 (s), 141.8 (s), 145.1 (s, C=O), 152.2 (s, C=N), 152.9 (s, C=O), 161.4 (s); IR (KBr) 3403, 3325, 1736, 1684, 1472, 1313, 1287, 1034 cm^{-1} MS (70 eV) *m/z* (%) 451 (M^+; 1), 420 (97), 306 (24), 301 (47), 258 (100), 228 (17), 202 (41), 187 (52). HRMS: Found: *m/z* 451.2227. Calcd for $C_{24}H_{29}N_5O_4$: M, 451.2220.

(4a*R, 5*S**)-8-Methoxy-4a-[1-(methoxyimino)ethyl]-2-phenyl-5-piperidino-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*),-dione (6i).** Colorless needles; mp 214—216 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.33—1.76 (6H, m), 1.84 (3H, s, Me), 2.37—2.87 (4H, m), 3.71 (3H, s, OMe), 3.82 (3H, s, OMe), 4.09 (1H, s, 5-H), 6.61 (1H, dd,Ph), 6.83 (1H, bs, NH), 7.16—7.49 (6H, m, Ph), 7.57 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.3 (q), 24.1 (t), 26.5 (t), 55.4 (q), 58.5 (t), 62.5 (q), 69.8 (d, C-5), 75.8 (s), 99.8 (d), 110.8 (d), 117.3 (s), 126.4 (d), 128.3 (d), 128.8 (d), 129.2 (d), 134.7 (s), 142.4 (s), 148.7 (s, C=O), 151.9 (s, C=O), 152.5 (s, C=N), 161.2 (s); IR (KBr) 3270, 1720, 1687, 1494, 1437, 1169, 1049 cm^{-1}; MS (70 eV) *m/z* (%) 463 (M^+; 5), 432 (100), 313 (85), 229 (33), 187 (42), 160 (22). Found: C, 64.58; H, 6.18;N, 14.97%. Calcd for $C_{25}H_{29}N_5O_4$: C, 64.78; H, 6.31; N, 15.11%.

(4a*R, 5*S**)-4a-[1-(Benzyloxyimino)ethyl]-5-ethoxy-8-methoxy-2-phenyl-4a,5-dihydro[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*, 4*H*)-dione (6j).** Colorless powder; mp 184—185 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.20 (3H, t, Me), 1.73 (3H, s, Me), 3.53 (2H, q, CH_2), 3.77 (3H, s, OMe), 4.72 (1H, s, 5-H), 5.00 (2H, s, CH_2), 6.35 (1H, s, NH), 6.66 (1H, dd, Ph), 6.77—7.67 (11H, m, Ph), 7.57 (1H, d, Ph); ^{13}C NMR ($CDCl_3$) δ = 10.7 (q), 15.2 (q), 55.6 (q), 64.4 (t), 76.4 (t), 78.0 (s), 79.5 (d, C-5), 100.2 (d), 111.4 (d), 118.1 (s), 126.9 (d), 128.0 (d), 128.4 (d), 128.6 (d), 128.9 (d), 129.4 (d), 134.6 (s), 137.3 (s), 143.4 (s), 148.7 (s, C=O), 152.5 (s, C=O), 152.8 (s, C=N), 162.4 (s); IR (KBr) 3215, 1728, 1686, 1607, 1480, 1256, 1048 cm^{-1}; MS (70 eV) *m/z* (%) 500 (M^+; 5), 471 (4), 409 (9),394 (31), 393 (100), 350 (17), 334 (12), 322 (31), 306 (21), 274 (12), 187 (25). HRMS: Found: *m/z* 500.2058. Calcd for $C_{28}H_{28}N_4O_5$: M, 500.2060.

Methylation of 3a and 3d. A dichloromethane solution of **3a** or **3d** (0.57 mmol) and iodomethane (2.85 mmol) and an aqueous sodium hydroxide solution were mixed and stirred vigorously in the presence of a catalytic amount of tetrabutylammonium bromide for 24 h at 25 °C.[15] The dichloromethane layer was separated and washed with water. After removing the solvent, the residue was chromatographed on silica gel with dichloromethane used as an eluent.

5-[1-(Methoxyimino)ethyl]-4-methyl-2-phenyl[1,3,5]triazino-[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (4a). Colorless powder; mp 215—216 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 2.35 (3H, s, Me), 3.57 (3H, s, NMe), 4.02 (3H, s, OMe), 7.17—7.60 (8H, m, Ph), 8.13—8.40 (1H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 17.5 (q), 33.3 (q), 62.2 (q), 98.5 (s, C-5), 115.3 (d), 118.3 (d), 123.9 (d), 124.9 (d), 128.8 (d), 129.1 (s), 129.2 (d), 129.4 (d), 130.6 (s), 134.4 (s), 146.1 (s, C=O), 148.9 (s, C=O), 149.8 (s, C=N); IR (KBr) 1734, 1687, 1620, 1592, 1459, 1421, 1295, 1044 cm^{-1}; MS (70 eV) *m/z* (%) 362 (M^+; 100), 331 (30), 212 (10), 171 (11), 143 (14). HRMS: Found: *m/z* 362.1376. Calcd for $C_{20}H_{18}N_4O_3$: M, 362.1380.

8-Methoxy-5-[1-(methoxyimino)ethyl]-4-methyl-2-phenyl-[1,3,5]triazino[1,2-*a*]indole-1,3(2*H*,4*H*)-dione (4b). Colorless powder; mp 240 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ = 1.32 (3H, s, Me), 3.52 (3H, s, NMe), 3.82 (3H, s, OMe), 4.02 (3H, s, OMe), 6.96 (1H, dd, Ph), 7.29—7.58 (6H, m, Ph), 8.40 (1H, d, Ph), ^{13}C NMR ($CDCl_3$) δ = 17.5 (q), 33.7 (q), 55.7 (q), 62.9 (q), 98.5 (s, C-5), 99.6 (d), 114.2 (d), 118.9 (d), 122.8 (s), 128.7 (d), 129.2 (d), 129.3 (s), 129.5 (d), 131.5 (s), 134.4 (s), 146.4 (s, C=O), 148.9 (s, C=O), 149.9 (s, C=N), 157.3 (s); IR (KBr) 1732, 1684, 1623, 1481, 1454, 1280, 1051 cm^{-1}; MS (70 eV) *m/z* (%) 392 (M^+; 100), 377 (5), 361 (54), 242 (15), 201 (22), 173 (29), 167 (14), 149 (34). HRMS: Found: *m/z* 392.1446. Calcd for $C_{21}H_{20}N_4O_4$: M, 392.1480.

Crystallographic Data. **6a**: M.F. = $C_{22}H_{24}N_4O_5$, M.W. = 424.46. Orthorhombic, a = 16.558 (6), b = 23.635(6), c = 11.170(2) Å, β = 90.00°, V = 4371.4(21) Å^3, space group *Pbca*, Z = 8, D_x = 1.290 g cm^{-3}. Data collection: crystal size = 0.1×0.1×0.5 mm, Cu $K\alpha$ radiation (λ = 1.15148 Å, graphite monochromater), 3442 reflections ($2\theta < 130°$).[16] **4a:** M.F. = $C_{20}H_{18}N_4O_3$, M.W. = 362.39. Monoclinic, a = 8.728(2), b = 10.664(5), c = 19.106(3) Å, β = 100.67(2)°, V = 1747.7(10) Å^3, space group *P*21/*n*, Z = 4, D_x = 1.337 g cm^{-3}. Data collection: crystal size = 0.1×0.1×0.5 mm, Cu $K\alpha$ radiation (λ = 1.15148 Å, graphite monochromater), 3442 reflections ($2\theta < 130°$).[16]

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