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SYNTHESIS AND PROPERTIES OF 3-ARYLCYCLOHEPTA[4,5]-PYRROLO[1,2-*a*]-1,3,5-TRIAZINE-2,4(3*H*)-DIONES AND RELATED COMPOUNDS: PHOTO-INDUCED AUTORECYCLING OXIDATION OF AMINES

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Abstract - 3-Phenyl- and 3-(4-nitrophenyl)cyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones and the corresponding arylimino derivatives (**5a,b**) and (**6a,b**) were synthesized by the reaction of (1-azaazulen-2-yl)imino-triphenylphosphorane with aryl isocyanates and subsequent heterocyclization reaction with a second isocyanate. Related cation (**11a)**, which was derived from methylation of **5a**, is also prepared. The electrochemical reduction of these compounds exhibited more negative reduction potentials as compared with the related compounds. Some of these compounds underwent a photo-induced autorecycling oxidation toward some amines to give the corresponding imines in more than 100% yield.

INTRODUCTION

The utility of iminophosphoranes as useful building blocks for the synthesis of azaheterocycles has been demonstrated convincingly.[1-4] On the basis of the foregoing observations and our interest concerning the unique reactivity afforded by the vinyliminophosphoranes[3] and related compounds,[5] we have previously studied convenient preparations of 1,3-dialkylcyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-diones (**1**)[6] and 3,10-disubstituted cyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-diones (**2**) and related derivatives,[7] which are the structural isomers of 5-deazaflavin (5-deazaaloxazine or 5-deazaisoalloxazine) (Figure 1). Flavins are known to play an important role as cofactors in a wide variety of biological redox reactions. In this context, 5-deazaflavins and related

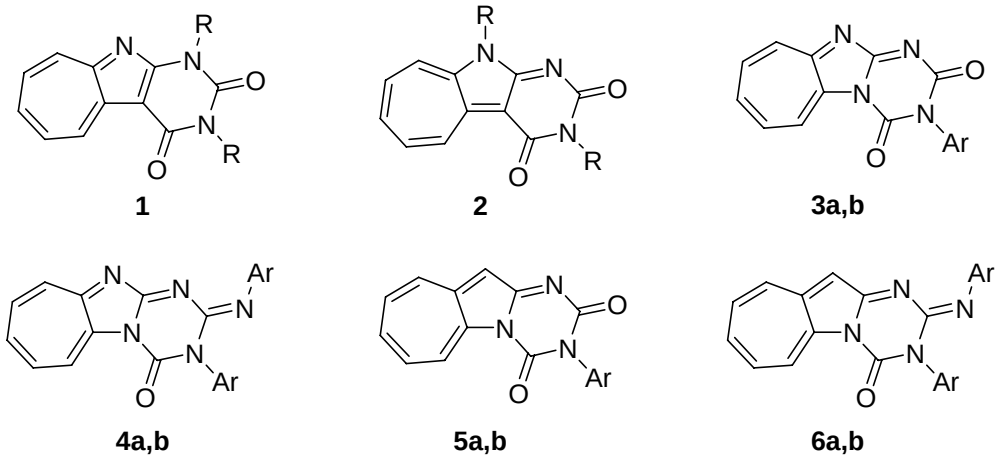
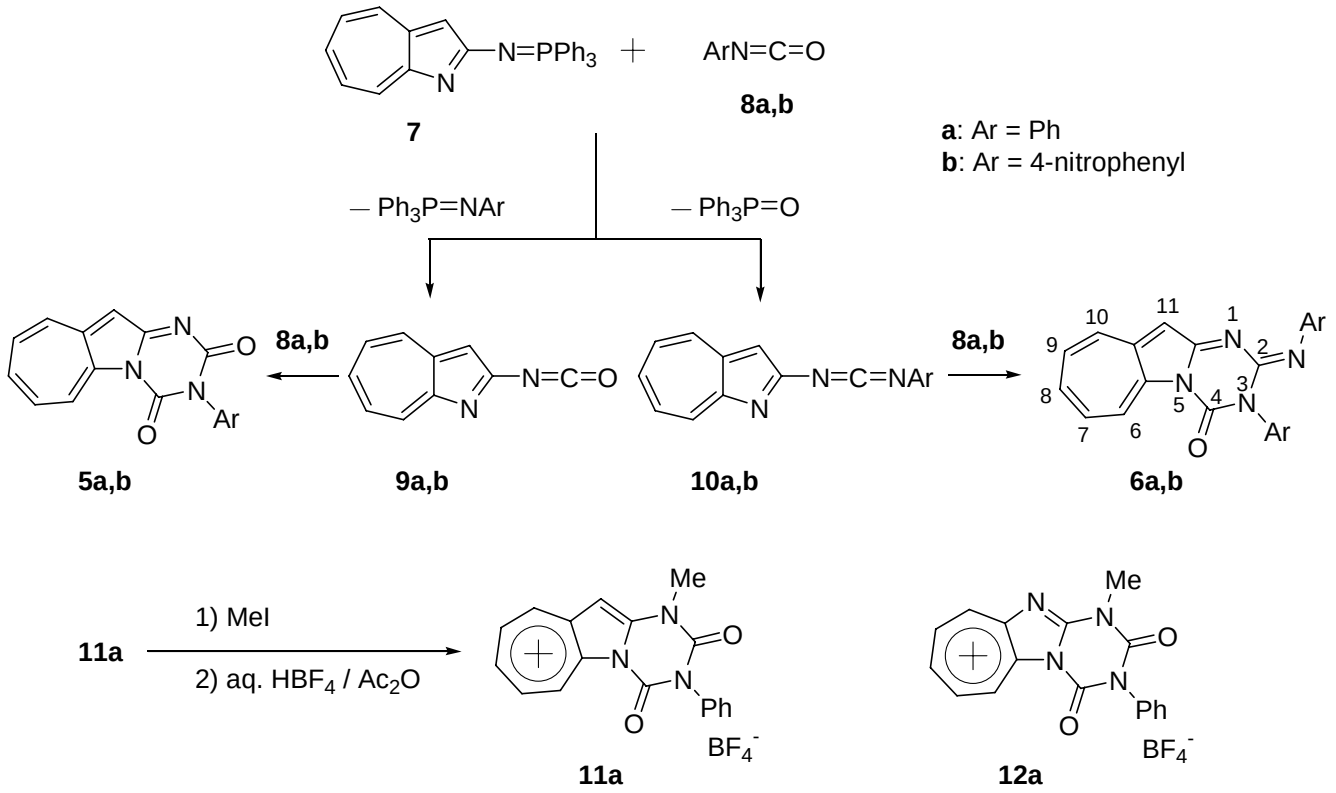


Figure 1. **a**: Ar = Ph; **b**: Ar = 4-nitrophenyl

compounds have been studied extensively in both enzymatic[9] and model systems[10,11] in the hope of providing mechanistic insight into flavin-catalyzed reactions. Recently, compound (**2**)[12] and related compounds[13] have also been demonstrated to undergo photo-induced oxidation reaction toward some amines or alcohols in an autorecycling process. For studying the properties and functions of organic molecules, structural modifications are of much interest. Thus, we have previously studied the synthesis and oxidizing function of compounds (**3**) and (**4**), which were obtained from the reaction of (1,3- diazaazaulen-2-yl)iminotriphenylphosphorane with aryl isocyanates.[14] In this context, we studied here the reaction of (1-azaazulen-2-yl)imonotriphenylphosphorane (**7**) with aryl isocyanates to provide 3-arylcyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones (**5a,b**) and related 2-arylimono derivatives (**6a,b**) in poor and moderate yields, respectively. The compounds involve the azaazulene and triazinedione skeletons instead of a 1-azaazulene and a pyrimidinedione ring systems (**1** and **2**) (Figure 1). Photo-induced autorecycling oxidation of some amines to give the corresponding imines are studied as well. We describe here the results in detail.

RESULTS AND DISCUSSION

The aza-Wittig reaction of iminophosphoranes with isocyanate has proven to be one of the most useful methodologies for the synthesis of nitrogen-containing heterocycles.[4,16-18] In this context, we report a minor abnormal and a major normal aza-Wittig reactions observed in our program directed toward the synthesis of **5a,b** along with the corresponding arylimino derivatives (**6a,b**). The abnormal aza-Wittig reaction involves the formation of an isocyanate instead of a carbodiimide intermediate, and the studies reported on this reaction are very limitted.[17,19] Upon treatment of the iminophosphorane (**7**) with phenyl and 4-nitrophenyl isocyanates (**8a,b**) afforded **5a,b** (**a**: 5%; **b**: 3%) and **6a,b** (**a**: 64%;**b**: 86%).



Scheme 1

Compound (**5a**) is known[20] and the structures of new compounds (**5b**) and (**6a,b**) are confirmed on the basis of the ^{1}H and ^{13}C NMR spectra, IR, UV-VIS, and MS spectral data, as well as elemental analyses. In the structural similarity of **6a,b** and **4a,b,** of which the structures were confirmed by X-Ray analysis, the aryl groups on the arylimino group would be anti to the N3Ar group. The proposed mechanistic pathways for the formation of **5a,b** and **6a,b** are outlined in Scheme 1. Both intermediates (**9a,b**) and (**10a,b**) can be formed upon treatment of **7** with **8a,b**. Formation of **9a,b** involves loss of aryliminotriphenylphosphorane as the abnormal aza-Wittig product. The isocyanates can undergo an intermolecular reaction with a second aryl isocyanate providing compounds (**5a,b**). In contrast, carbodiimides (**10a,b**) as the normal aza-Wittig product, which predominates over the formation of **9a,b**, undergo subsequent reaction with a second aryl isocyanate to result in the formation of compounds (**6a,b**). The controlling factor for the abnormal and normal aza-Wittig reactions has been obscure. 2-Amino-1-azaazulene is known to react with **8a** to give N-(1-azaazulen-2-yl)-N'-phenylurea and **5a**;[20] however, attempted reaction of 2-aminio-1-azaazulene with **8b** afforded **5b** in a minute amount (1 % yield), and the main product is an unseparable mixture of 2-(4-nitrophenylcarbamoyl)amino- and 2-bis(4-nitrophenylcarbamoyl)amino-1-azaazulenes. In relation to the studies of oxidizing ability, compound (**5a**) was converted to **11a** upon treatment with MeI and followed by counter ion exchange

Table 1. ^{1}H NMR spectral data (600 MHz) of **5a,b**, **6a,b**, and **11a**

Compd		H5		H6		H7		H8		H9	H10	Remaining signals
5a[a]	δ_H	9.07		----------		7.36-7.44		----------		7.79	6.70	7.34 (2H, d, *J*=7.4), 7.47 (2H, t, *J*=7.4)
	J		9.2	----------		m		----------	10.8			7.53 (1H, t, *J*=7.4)
5b[a]	δ_H	8.92		7.49-7.54		7.44		7.49-7.54		8.02	6.78	7.76 (2H, d, *J*=9.0), 8.38 (2H, d, *J*=9.6)
	J		9.5		11.0		8.4		10.8			
6a[b]	δ_H	8.60		7.00		6.87		6.95-6.99		7.36	6.25	6.96 (2H, d, *J*=7.3), 6.95-6.99 (1H, m),
	J		9.4		11.0		11.0		11.2			7.23 (2H, dd, *J*=8.8, 7.3), 7.40
												(2H, d, *J*=7.9), 7.42 (2H, t, *J*=7.6),
												7.52 (2H, dd, *J*=7.9, 7.6)
6b[b]	δ_H	8.72		7.36-7.44		7.29		7.36-7.44		7.83	6.64	7.04 (2H, d, *J*=9.2), 7.80 (2H, d, *J*=9.2),
	J		9.2		10.8		8.7		11.0			8.09 (2H, d, *J*=9.2), 8.39 (2H,d, *J*=9.2)
11a[a]	δ_H	10.10		8.43		8.51		8.46		8.93	7.27	7.42-7.45 (2H, m), 7.59-7.6 (3H, m)
	J		10.0		10.0		10.2		10.2			

[a] Recorded in DMSO-d_6. [b] Recorded in CD_3CN.

reaction using 42% HBF_4 in Ac_2O, in good yield. The structure of **11a** was confirmed from an inspection of the spectral data including ^1H NMR and IR spectral data, HRMS data and finally X-Ray analysis (Figure 2). The X-Ray analysis revealed that the methyl group is introduced on the N1 of **5a**. The ^1H NMR spectra of two series of **5a,b** and **6a,b** are similar each other, respectively, and the chemical shifts of the protons of the seven-membered ring and the aryl group and the selected coupling constants are listed in Table 1. The characteristic H5 signal appearing at lower field is due to the anisotropy effect of the oxygen atom of the triazinedione moieties. The vicinal coupling constants of protons of the seven-membered ring of neutral compounds (**5a,b**) and (**6a,b**) suggest bond alternation in the cycloheptatriene moiety, while significant bond alternation is not observed in cation (**11a**). The UV-VIS spectra of compounds (**5a,b**), (**6a,b**), and cation (**11a**) are listed in Table 2. The two series of **5a,b** and **6a,b** are similar each other, respectively. The spectrum of cation (**11a**) exhibits a marked blue-shift as compared with that of compound (**5a**), suggesting the substantial lowering of the HOMO.

Table 2. UV-VIS spectral data of **5a,b**, **6a,b**, and **11a**

Compd	λ_{max} (CH_3CN)/nm (log ε/$dm^3mol^{-1}cm^{-1}$)
5a	428 (4.08), 277 (4.23)
5b	428 (4.26), 281 (4.49)
6a	445 (4.33), 280 (4.42)
6b	454 (4.45) 275 (4.48)
11a	408 (4.26), 285 (4.55), 234 (4.30)

The reduction potentials of **5a,b**, **6a,b**, and **11a** are determined by cyclic voltammetry (CV) in MeCN. The reduction waves of **5a,b**, **6a,b** and **11a** are irreversible under conditions of the CV measurements, and thus, their peak potentials are summarized in Table 3, together with those of the reference compounds (**3a,b**), (**4a,b**), and (**12a**).[14] As expected, the $E1_{red}$ of phenyl-substituted compounds (**5a**) and **(6a)** is more negative than that of 4-nitophenyl substituted derivatives (**5b**) and **(6b**), respectively, due to the electron-withdrawing nature of the 4-nitrophenyl group. The $E1_{red}$ of a series of these compounds is more negative than that of the reference compound (**3a,b**), (**4a,b**), and (**12a**), respectively. The affinity

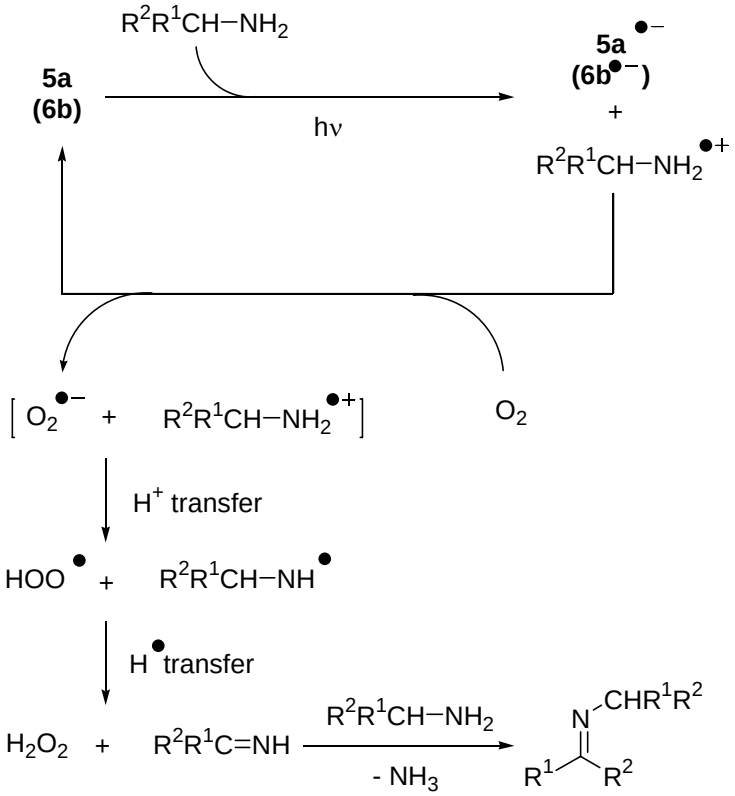
Table 3. pK_{R+} Values and reduction potentials[a] of **5a,b**, **6a,b**, **11a** and reference compounds[b] **(3a,b**), (**4a,b**), and (**12a**)

Compd	**5a**	**5b**	**6a**	**6b**	**11a**	**3a**	**3b**	**4a**	**4b**	**12a**
$E1_{red}$	-1.38	-1.34	-1.50	-1.30	0.88	-1.15	-1.12	-1.24	-1.14	-0.66
pK_{R+}					9.6					6.8

[a] Peak potential in V *vs* $Ag/AgNO_3$. [b] Ref. 14.

of carbocation toward the hydroxide ion, expressed by the pK_{R+} value, is the common criterion of carbocation stability.[21] The value of cation (**11a)** was determined spectrophotometrically as 9.6 in buffer solutions prepared in 50% MeCN and is indicated also in Table 2, along with that of the reference cation (**12a**). The value indicates that cation (**11a**) is much more stable than the reference compound **12a**, which involves imidazole instead of a pyrrole ring.

Compounds (**3a**), (**12a**),[14] and related compounds undergo photo-induced autorecycling oxidations toward some amines. In this context, we examined the oxidation of some amines by using **5a, 6a,b**, and **11a** under aerobic and photo-irradiation (RPR100, 350 nm lamps) conditions. In the amine oxidation, imine is produced at first; however, it reacts with another amine to result in the formation of $R^1R^2C{=}N\text{-}CHR^1R^2$ and NH_3 (Scheme 2). Then the reaction mixture was diluted with ether and filtered and the filtrate was treated with 2,4-dinitrophenylhydrazine in 6%N HCl to give the corresponding 2,4-dinitrophenylhydrazone. The results are summarized in Table 4 together with those of the reference compounds (**3a**) and (**12a**) under similar conditions.[14] Direct irradiation of amines in the absence of **5a**, **6a,b**, and **11a** (named "blank") gives the corresponding oxidized product in low to modest yields under similar conditions. Thus, the yields are calculated by subtraction of the "blank" yield from the total yield of the oxidized product in the presence of **5a**, **6a,b**, and **11a**. More than 100% yields are obtained based on **5a**, **6b**, and **11a**, and thus, autorecycling oxidation clearly proceeds;



Scheme 2

Table 4. Results for the photo-induced autorecycling oxidation of amines by **5a, 6a,b,** and **11a** and reference compounds (**3a**) and (**12a**)

Compd[a]	$PhCH_2NH_2$ (Yield)[b,c]	$PhCH(Me)NH_2$ (Yield)[b,c]	Hexylamine (Yield)[b,c]	Cyclohexylamine (Yield)[b,c]
5a	1364	113	550	36
6a	0	0	---	---
6b	3902	2473	2450	1423
11a	2315	1160	1686	295
3a	8322	6733	2000	862
12a	11818	8457	3143	909

[a] MeCN solution was irradiated by RPR100, 350 nm lamps. [b] Product was isolated by converting to the corresponding 2,4-dinitrophenylhydrazone. [c] Based on catalyst used; the yield is calculated by subtraction of the "blank" yield from the total yield in the presence catalyst.

however, **6a** does not undergo oxidation toward even benzylamine and 1-phenethylamine. The postulated mechanistic pathways for the oxidation of amines ($R^1R^2CHNH_2$) are depicted in Scheme 2. The electron transfer from amines to the excited singlet state of **5a** (**6b**) would occur to produce a radical anion **5a**$^{\bullet-}$ (**6b**$^{\bullet-}$) and $R^1R^2CHNH_2^{\bullet+}$. In the presence of oxygen, an electron transfer from **5a**$^{\bullet-}$ (**6b**$^{\bullet-}$) to O_2 may give the radical ion pair [$R^1R^2CHNH_2^{\bullet+}$ $O_2^{\bullet-}$] and **5a** (**6b**). Then a proton transfer from $R^1R^2CHNH_2^{\bullet+}$ to $O_2^{\bullet-}$ may occur, followed by formation of product $R^1R^2CH{=}NH$ and H_2O_2.[22] In the case of oxidation by **11a**, photo-induced cleavage of the initially formed amine-adduct of **11a** probably occurs to generate **11a**$^{\bullet}$ and $R^1R^2CHNH_2^{\bullet+}$.[14] An electron transfer from **11a**$^{\bullet}$ to O_2 gives the radical ion pair [$R^1R^2CHNH_2^{\bullet+}$ $O_2^{\bullet-}$] and **11a**; the former ion pair would follow the pathway described.[14]

In conclusion, 3-phenyl- and 3-(4-nitrophenyl)cyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones and the corresponding imino derivatives (**5a,b**), (**6a,b**), and 1-methyl-2,4-dioxo-1,2,3,4-tetrahydrocyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazinium tetrafluoroborate (**11a**) were synthesized. Compounds (**5a**), (**6b**), and (**11a**) were demonstrated to oxidize some amines to give the corresponding imines in more than 100% yield under aerobic and photo-irradiation conditions. The oxidation reaction of these compounds seems to proceed less efficiently as compared with that of the corresponding imidazole-containing compounds.

EXPERIMENTAL

IR spectra were recorded on a HORIBA FT-710 spectrophotometer. UV-VIS spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. MS spectra and HRMS were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE 600 spectrometer, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. Photo-irradiation was carried out by using RPR-100 fitted with 350 nm lamps though a Pyrex filter.

Preparation of 5a and 6a. A solution of iminophosphorane (**7**)[14] (162 mg, 0.4 mmol) and **8a** (143 mg, 1.2 mmol) in benzene (10 mL) was heated under reflux for 30 min. After evaporation of the solvent, the residue was separated by column chromatography on SiO_2. Fractions eluted with CH_2Cl_2-AcOEt (5/1-2/1) afforded **5a** (6.0 mg, 5%). Fractions eluted with acetone afforded **6a** (93.0 mg, 64%). For 3-phenyl-2-phenyliminocyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine- 4(3*H*)-one (**6a**): red prisms; mp 239-240 ºC (decomp) (from $CHCl_3$); ^{13}C NMR(CD_3CN) δ106.7, 120.6, 122.7, 122.8, 128.3, 128.8, 129.4, 131.7, 133.1, 133.5, 134.5, 136.6, 143.4, 148.5, 148.5, 149.2, 157.1; IR($CHCl_3$, cm^{-1}) 1722, 1634; MS m/z 364 (M^+, 18%), 362 (M-2, 100). *Anal*. Calcd for $C_{23}H_{17}N_4O$+1/10 $CHCl_3$: C, 73.53; H, 4.43; N, 15.37. Found: C, 73.49; H, 4.30; N, 14.91.

Preparation of 5b and 6b. A solution of **7** (80.8 mg, 0.2 mmol) and **8b** (98 mg, 0.6 mmol) in benzene(10 mL) was heated under reflux for 17 h. After evaporation of the solvent, the residue was separated by chromatography on SiO_2. Fractions eluted with CH_2Cl_2-AcOEt (5/1-1/1) afforded **5b** (1.9 mg, 3%). Fractions eluted with acetone afforded **6b** (78 mg, 86%). For 3-(4-nitrophenyl)-cyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dione (**5b**): pale yellow prisms; mp 240.0-241.0 ºC (decomp) (from CH_2Cl_2/AcOEt); ^{13}C NMR (DMSO-d_6) δ105.1, 122.9, 124.1, 128.6, 130.5, 131.4, 131.5, 133.3, 133.7, 135.8, 136.1, 141.9, 141.9, 147.0, 148.1; IR (KBr, cm^{-1}) 1723, 1681; MS m/z; HRMS calcd for $C_{17}H_{10}N_4O_4$ 335.0780 (M+H). Found: 335.0804 (M^++H). *Anal*. Calcd for $C_{17}H_{10}N_4O_4$+1/5CH_2Cl_2: C, 61.08; H, 3.02; N, 16.76. Found: C, 58.88; H, 3.05; N, 15.59. For 3-(4-nitrophenyl)-2-(4-nitrophenylimino)cyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-4(3*H*)-one (**6b**); red powder; mp 248.0-249.0 ºC (decomp) (from CH_2Cl_2/AcOEt); ^{13}C NMR (DMSO-d_6) δ105.5, 122.3, 123.8, 124.5, 124.5, 131.0, 133.1, 134.3, 135.6, 136.1, 141.8, 142.6, 143.3, 147.2, 147.6, 149.7, 150.3, 156.4, 157.7; IR (KBr, cm^{-1}) 1724; HRMS calcd for $C_{23}H_{15}N_6O_5$ 455.1104 (M+H). Found: 455.1067

(M^++H). *Anal*. Calcd for $C_{23}H_{14}N_6O_5$+1/2H_2O: C, 59.61; H, 3.26; N, 18.14. Found: C, 59.83; H, 3.26; N, 18.44.

Preparation of 11a. A solution of **5** (57.8 mg, 0.2 mmol) and MeI (4.0 mL) in 1,2-dichloroethane (4 mL) in a sealed tube was heated at 100 °C for 2 h. After evaporation of the solvent, the residue was dissolved in a mixture of Ac_2O (4 mL) and 42% aq. HBF_4 (0.8 mL) and stirred for 30 min. To the mixture was added Et_2O, and the precipitates were collected by filtration to give **11a** (63 mg, 81%). For 1-methyl-2,4-dioxo-1,2,3,4-tetrahydrocyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazinium tetrafluoroborate (**11a**): yellow prisms; mp 230-233 ºC (decomp) (from MeCN/Et_2O); ^{13}C NMR (DMSO-d_6) δ 33.6, 97.9, 129.3, 130.8, 130.9, 134.8, 135.3, 140.7, 141.4, 142.8, 143.9, 146.1, 146.7, 148.3, 150.2, 151.7; IR (KBr, cm^{-1}) 1763, 1718; MS m/z 304.1 (M^++H); HRMS calcd for $C_{18}H_{14}N_3O_2$ 304.1086 (M+H). Found: 304.1079 (M^++H). *Anal*. Calcd for $C_{18}H_{14}N_3O_2 \bullet BF_4^-$: C, 55.28; H, 3.61; N, 10.74. Found: C, 54.96; H, 3.49; N, 10.57.

X-Ray crystal structure determination of 11a. Yellow prism, $C_{18}H_{14}N_3O_2BF_4$, M=391.13, monoclinic, space group $P2_1/a$, a=11.247(5), b=14.024(8), c=12.043(6) Å, β=110.94(4) °, V=1774.0(2) $Å^3$, Z=4, Dc=1.464 gmL^{-1}, crystal dimensions 0.80×0.60×0.30 mm. Data were measured on a Rigaku RAXIS-RAPID radiation diffractomater with graphite monochromated Mo-Kα radiation. Total 13354 reflections were collected, using the ω-2θ scan technique to a maximum 2θ value of 55.0 º. The structure was solved by direct methods and refined by a full-matrix least-squares method using SIR92 structure analysis software, with 267 variables and 2212 observed reflections [I>3.00σ(I)]. The non-hydrogen atoms were refined anisotropically. The weighting scheme w= [1.0000×$\sigma_c(F_0{}^2)$ + 0.0010×F_0^2+0.5000]$^{-1}$ gave satisfactory agreement analysis. The final R and Rw values were 0.0620 and 0.0960. The maximum peak and minimum peak in the final difference map were 0.39 and -0.38e^-/ $Å^3$.

Determination of pK_{R+} value of cation (11a). Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1M) and HCl (0.1 M) (for pH 2.2-4.0), potassium hydrogen phthalate (0.1M) and NaOH (0.1 M) (for pH 4.1-5.9), KH_2PO_4 (0.1M) and NaOH (0.1 M) (for pH 6.0-8.0), Na_2B_4H7 (0.025 M) and HCl (0.1 m) (for pH 8.0-9.1), and $Na_2B_4O_7$ (0.025 M) and NaOH (0.1 M) (for pH 9.0-11.0) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 3-5 mg of compound (**11a)** in

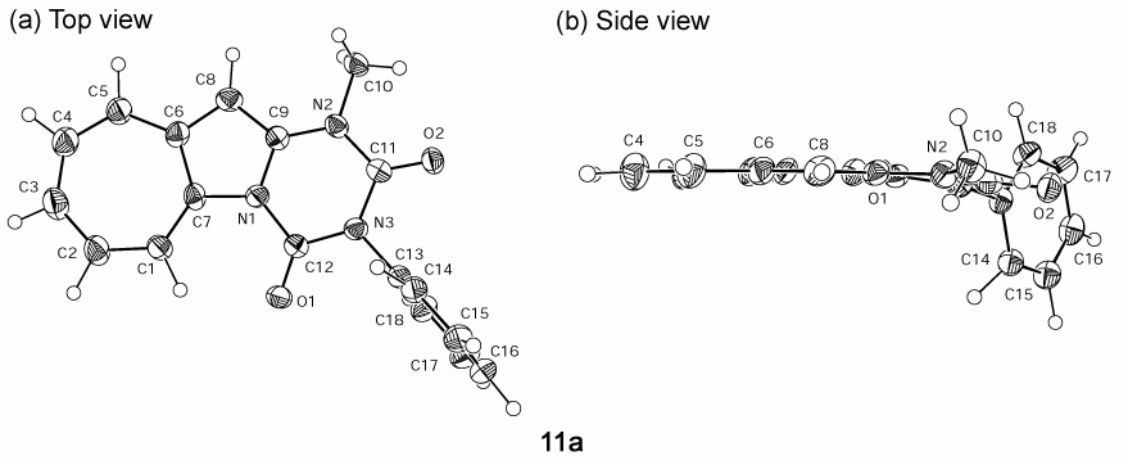


Figure 2. ORTEP drawing of **11a** with thermal ellipsoid plot (50% probability).

MeCN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and MeCN (1 mL). The UV-VIS spectrum was recorded for cation (**11a**) in 20 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelength (500 nm) of cation (**11a)** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

Cyclic Voltammetry of 5a,b, **6a,b and 11a.** The reduction potentials of **5a,b**, **6a,b** and **11a** were determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and an $Ag/AgNO_3$ reference electrode. Nitrogen was bubbled through a MeCN solution (4 mL) of each samples (1 mmol dm^{-3}) and Bu_4NClO_4 (100 mmol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1}, and the voltammograms were recorded on an X-Y recorder. Immediately after the measurements, ferrocene (0.2 mmol dm^{-3}) ($E_{1/2}$ = +0.083 V) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard.

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