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Synthesis and Characterization of Verdazyl Radicals Bearing Pyridine or Pyrimidine Substituents: A New Family of Chelating Spin-Bearing Ligands

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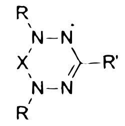
The syntheses and characterization of two new 1,5-dimethyl-6-oxoverdazyl radicals bearing 2-pyridine and 4,6-dimethyl-2-pyrimidine rings as substituents are described. The radical precursors, the corresponding 1,2,4,5-tetrazanes, were prepared by condensation of the bis(1-methylhydrazide) of carbonic acid with the appropriate aromatic aldehyde. Oxidation of 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide (**7**) with sodium periodate afforded 1,5-dimethyl-3-(4,6-dimethyl-2-pyrimidyl)-6-oxoverdazyl (**4**), which could be isolated and stored without decomposition. In contrast, attempts to oxidize the analogous 3-(2-pyridyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-oxide (**6**) with periodate produced the 1,5-dimethyl-3-(2-pyridyl)-6-oxoverdazyl (**3**) which could not be isolated. However, oxidation of this tetrazane with benzoquinone produced the pyridylverdazyl **3** as a 1:1 complex with hydroquinone. This complex is indefinitely stable in the solid state and provides a means of long-term storage of the pyridylverdazyl. The electronic properties of both radicals have been characterized by EPR spectroscopy, cyclic voltammetry, and MNDO calculations. The radicals have a wide electrochemical window of stability (>1.8 V), and the EPR and computational studies indicate a large spin density residing on N2 and N4.

Introduction

Transition metal complexes of spin-bearing ligands have been one of the more fruitful sources of molecular magnetic materials. The families of paramagnetic ligands which have been most heavily studied can be divided into two broad classes: charged and neutral radicals. The former include radical anions of nitrogen heterocycles,[1] semiquinones,[2−5] and cyanocarbons such as TCNE,[6−8] TCNQ, and related[9] species. By far the most heavily studied neutral radicals belong to the nitroxide family,[10−13] which includes imino nitroxides[14] and nitronyl nitroxides.[15] In all of these systems, discrete metal−radical complexes have allowed delineation of basic exchange coupling between ligand and metal, and radicals capable of bridging two or more metal centers have led to a rich array of one-, two-, and three-dimensional coordination polymers, some of which exhibit cooperative magnetic behavior.

Verdazyl radicals (**1**; X = CH_2, CO) are another established family of stable organic free radicals.[16] With the recent exception of a 1D chain complex of bis(verdazyl) **2** and copper(I) halides,[17] however, the coordination chemistry of verdazyls remains uncharted territory. We believe that judiciously substituted derivatives of **1** should possess a rich coordination chemistry and may ultimately lead to new examples of so-called “molecule-based” magnets. For example, pyridine and pyrimidine groups appended at the 3 position of verdazyls (i.e., **3** and **4**, respectively) afford chelating environments strongly reminiscent of 2,2′-bipyridine and 2,2′-bipyrimidine. This concept of appending remote donor atoms has been



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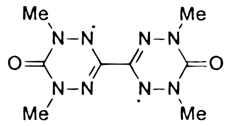

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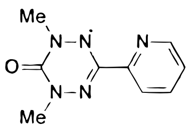

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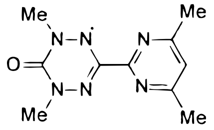

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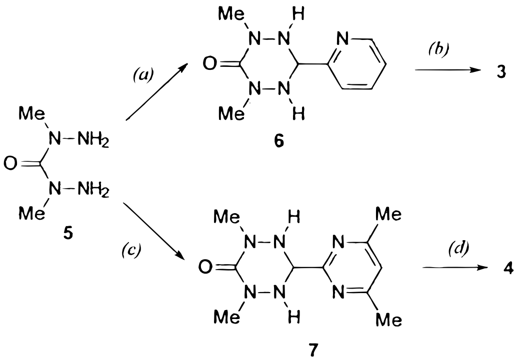
extensively employed for the nitronyl nitroxide radicals,[18-27] which are known to be fairly weak donors in the absence of assistance from the chelate effect.[28] In this paper we present the synthesis of verdazyl radicals **3** and **4**. The former should be capable of forming discrete mononuclear transition metal complexes, while the latter may also produce binuclear or 1D chain complexes. We also describe studies of these radicals which are aimed at gaining a more complete picture of their fundamental electronic properties. These data will be extremely useful in understanding the properties of subsequent transition metal complexes.

Synthesis

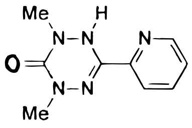
General synthetic routes to 1,5-dimethyl-6-oxoverdazyl radicals with a range of substituents have been developed by Neugebauer.[29] These methods were employed in the synthesis of **3** and **4**, although we found it necessary to make substantial modifications to some of the literature procedures. The key reagent for the synthesis of 6-oxoverdazyls, the bis(1-methyl hydrazide) of carbonic acid (**5**), is normally prepared from phosgene and methylhydrazine.[30] We have found that “triphosgene” (bis(trichloromethyl) carbonate) to be a convenient and safer alternative to phosgene, giving **5** in excellent (>90%) yields. Subsequent treatment of **5** with the appropriate aromatic aldehydes gave the corresponding 3-substituted tetrazanes **6** and **7**, respectively (Scheme 1). In the case of **7**, the required reagent 4,6-dimethyl-2-pyrimidinecarboxaldehyde was prepared from 2-bromo-4,6-dimethylpyrmidine by low-temperature (−110 °C) lithium−halogen exchange and subsequent treatment with DMF, affording the desired aldehyde in 50% yield. This is a very rare example of lithiation of a pyrimidine at the C2 carbon—the pyrimidine skeleton is normally highly susceptible to addition by organolithium reagents.[31]

Scheme 1



[a] Key: (a) 2-pyridinecarboxaldehyde, MeOH, Δ, 80%: (b) benzoquinone, C_6H_6, 95%; (c) 4,6-dimethyl-2-pyrimidinecarboxaldehyde, MeOH, Δ, 51%; (d) $NaIO_4$, $MeOH/H_2O$, 72%.

Oxidations of the tetrazanes to the corresponding verdazyls were initially attempted using a variety of oxidants which have been previously reported to generate verdazyls (ferricyanide, lead oxide, silver oxide). Although deeply colored, EPR-active solutions were easily generated, we were unable to isolate either of the desired radicals using these reagents. These reactions may have been plagued by possible coordination of the metal to the ring system. This led us to explore non-metal-based oxidants with which we have had some success for the preparation of phosphorus-containing verdazyls.[32] Sodium periodate proved to be successful for the synthesis of the pyrimidine-substituted radical **4**, which could be isolated in high yield and stored indefinitely without decomposition. The synthesis of the pyridine-based radical **3** using periodate was less successful. Attempts to purify this radical by crystallization or chromatography inevitably led to decomposition over 1−2 days, primarily to a tetrahydrotetrazine **8** (historically referred to as a “leuco” verdazyl). This compound can in fact be prepared directly from tetrazane **6** with a deficit of periodate.



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Verdazyl radicals are generally known to be very robust: They can be purified, handled, and stored indefinitely without decomposition. In this context the observed instability of pyridine-substituted radical **3** is surprising and not well understood. However, we were able to overcome these instability problems through the use of 1,4-benzoquinone as the oxidizing agent. Treatment of benzene solutions of tetrazane **6** with benzoquinone produced the desired radical **3** in near-quantitative yield as a 1:1 precipitated complex with hydroquinone (hq), the byproduct of the reaction. The two components can be separated easily by flash chromatography, giving solutions of pure **3** which then slowly degrade similarly to solutions prepared using other oxidants. In contrast, the hq adduct of **3** is indefinitely stable and requires no special handling. We have therefore fully characterized **3** as its hq adduct and find that this radical can be stored for months without decomposition in this form.

Characterization of Verdazyl Radicals. The solution EPR spectrum of **4** is shown in Figure 1; the corresponding spectrum of **3** is essentially identical. Both radicals have *g*-values of 2.0037. The observed hyperfine structure for both radicals arises due to coupling of the

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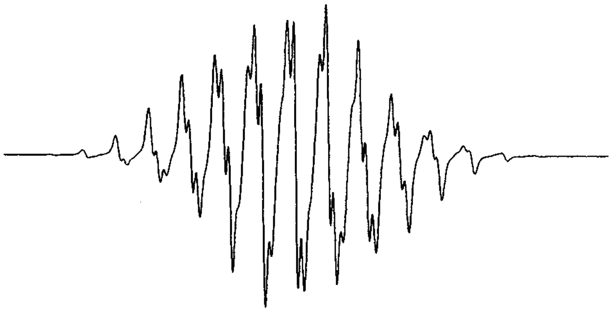


Figure 1. EPR spectrum of **4** in CH_2Cl_2 at 298 K. The total spectral width is 100 G.

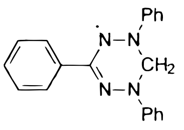
Table 1. Redox Potentials of Selected Verdazyl Radicals with All Values in V vs SCE

compd	E_{ox}	E_{red}
3	$+0.60^a$	-1.25^b
4	$+0.60^a$	-1.26^b
9	$+0.30^a$	c
TEMPO	$+0.70$	c

[a] Quasi-reversible. [b] Irreversible. [c] Not measured.

odd electron to the four verdazyl ring nitrogens and the six methyl protons on the verdazyl ring. Spectral simulation afforded hyperfine coupling constants as follows: $a(N_{2,4}) = 6.5$ G (2N), $a(N_{1,5}) = 5.3$ G (2N), $a(CH_3) = 5.3$ G (6H). The larger of the two nitrogen hyperfine constants is assigned to the two-coordinate nitrogen atoms.[29] Hyperfine coupling to the pyridine or pyrimidine ring atoms is not observed in these systems. Collectively these features are wholly typical of 4,6-dimethyl-6-oxoverdazyls with aryl groups in the 3 position; proton coupling constants for the 3-aryl protons are known from NMR measurements to be well under 1 G.[33]

The redox properties of verdazyl radicals have not been extensively investigated, and to our knowledge no such studies on 6-oxverdazyls have been reported. Given that verdazyls might be expected to be readily oxidized and/or reduced to closed-shell cations/anions, and that there are important implications of this in the context of possible ground-state electron transfer between verdazyl ligands and a transition metal, we decided to investigate the electrochemical behavior of **3** and **4** by cyclic voltammetry. Our results are summarized in Table 1, which also includes literature data for the 1,3,5-triphenylverdazyl radical **9** and TEMPO, a prototypical nitroxide radical.[34−36] Compounds **3** and **4** exhibit oxidation processes at 0.60 V vs SCE that are irreversible at low scan rates (<100 mV s^{-1}) but appear more reversible (ratio of anodic and cathodic peak potentials ≈1) at higher scan rates (1 V s^{-1}). This qualitatively mirrors the behavior of **9**, although **3** and **4** are considerably more difficult to oxidize. We believe the most likely reason for the increase in oxidation potentials in the present compounds is the presence of the electron-withdrawing carbonyl group, although there may also be minor contributions arising from the differing substituents at the two nitrogens (methyl in **3**, **4** vs phenyl in **9**) and at C3 (N-aromatic in **3**, **4** vs phenyl in **9**). Finally, we observed irreversible reduction processes for **3** and **4** at ∼−1.20 V, indicating that these radicals are fairly difficult to reduce.



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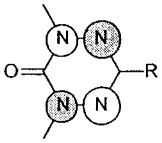
Discussion and Summary

Within the verdazyl family, those possessing a carbonyl group at C6 are known to be rigorously planar,[37,38] while verdazyls with methylene bridges (e.g. **9**) are bent at C6.[39] Previous calculations on verdazyl diradical **2**[37,40] indicate that the unpaired electrons reside in delocalized π-symmetry orbitals, and our own MNDO calculations on a simplified 1,5-dimethyl-6-oxoverdazyl (**1**, X=CO, R = Me, R′ = H) with structural parameters taken from the literature[37] mirror these findings: The singly occupied molecular orbital is a π orbital (**10**) spanning the four nitrogen atoms. Notably there is a nodal plane passing through C3 and C6, which rationalizes the very small hyperfine coupling to C3 substituents in a range of verdazyls.



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The experimental and theoretical results indicate that these verdazyl radicals possess features which make them attractive as ligands. Cyclic voltammetry studies indicate a large potential window of stability for the radicals, which should make them versatile ligands for a wide range of metals and oxidation states. More importantly, the EPR and theoretical studies indicate a significant amount of spin density at the two-coordinate nitrogens—the atoms which form half of the chelating environment. It has been established that there is a relationship between spin density on the donor atoms of a radical ligand and the magnitude of exchange interactions between unpaired electrons on the ligand and the metal.[41,42] This correlation is evident in nitroxide and nitronyl nitroxide complexes in which metals bound directly to the nitroxide oxygen atom exhibit much stronger exchange coupling than complexes in which the nitroxide functional group is not directly bound to the metal. In the latter case, radical−metal exchange interactions must occur indirectly by a superexchange mech-

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anism and are considerably weaker.[43−46] In this context the design of new materials with magnetic ordering at higher temperatures should greatly benefit from ligands which (a) have large spin densities on the coordination sites and (b) have the ability to simultaneously bridge more than one metal center. Compound **4** fulfills both criteria nicely. We are currently actively pursuing discrete complexes of **3** and **4** as well as 1-dimensional chain complexes of **4** and will report on these in due course.

Experimental Section

General Methods. Unless stated otherwise, all reactions and manipulations were carried out under an argon atmosphere using standard Schlenk line or glovebox techniques. Solvents were dried and distilled under argon prior to use (CH_2Cl_2, from CaH_2; benzene, toluene, and THF, from sodium/benzophenone). All reagents were purchased from Aldrich and used as received except as stated otherwise. NMR spectra were recorded on 360 or 250 MHz instruments. Infrared spectra were recorded as Nujol mulls on KBr plates or as KBr pressed pellets. EPR spectra were recorded on a Varian E6S instrument, and the spectra so obtained were simulated using the WinEPR SimFonia program. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC, Canada. Semiempirical MO calculations were carried out with HyperChem 5.0.1. Cyclic voltammetry experiments were performed with a Bioanalytical Systems CV50 voltammetric analyzer. Typical electrochemical cells were consisted of a three electrode setup containing acetonitrile solutions of analyte ($\sim$1 mM), electrolyte (0.1 M $Bu_4N^+BF_4^-$), and ferrocene (0.5−1 mM), the last of which was added as an internal reference.

Synthesis of Carbonic Acid Bis(1-methylhydrazide) (5). A solution of triphosgene (5.00 g, 17.2 mmol) in 60 mL of benzene was added dropwise to a solution of methylhydrazine (9.507 g, 0.206 mol) in 120 mL of CH_2Cl_2 at −42 °C (dry ice/acetonitrile bath) under argon. The reaction mixture was stirred for 15 h, and then the white precipitate of methylhydrazine hydrochloride was filtered out in vacuo and washed with 2 × 10 mL of hexanes. The filtrate was evaporated in vacuo to give **5** as a very hygroscopic white solid, yield 5.776 g (95%). The solid was stored at −35 °C in a drybox. ^1H NMR ($CDCl_3$): δ 4.13 (br s, 4H), 2.92 ppm (s, 6H). ^{13}C NMR ($CDCl_3$): δ 165.6, 41.65 ppm. IR (Nujol): ν(NH) 3310, 3198, ν(C=O) 1633 cm^{-1}.

Synthesis of 3-(2-Pyridyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-Oxide (6). A solution of freshly vacuum-distilled 2-pyridinecarboxaldehyde (1.81 g, 16.9 mmol) in 55 mL of methanol was added dropwise to a solution of **5** (1.993 g, 16.9 mmol) in 110 mL of hot methanol. After the addition was complete, the solution was heated to reflux for 24 h. The solvent was then removed under reduced pressure, and the solid residue was recrystallized from methanol/ethyl acetate to give **6** as large transparent blocks, yield 2.75 g (79%). ^1H NMR ($CDCl_3$): δ 8.5 (d, 1H, J = 2.9 Hz), 7.7 (td, 1H, J = 5.9, 1.7 Hz), 7.4 (d, 1H, J = 8.1 Hz), 7.3 (dd, 1H, J = 7.0, 5.5 Hz), 4.85 (br s, 3H), 3.14 ppm (s, 6H). ^{13}C NMR ($CDCl_3$): δ 154.6, 153.7, 149.7, 137.4, 124.4, 123.7, 69.6, 38.2 ppm. IR (KBr): ν(NH) 3240 (m), 3183 (s), ν(C=O) 1630 (s) cm^{-1}. Mp: 148−149 °C. Anal. Calcd for $C_9H_{13}N_5O$: C, 52.16; H, 6.32; N, 33.79. Found: C, 52.33; H, 6.36; N, 33.68. MS (CI methane): *m/z* 208 (M + 1, 100%).

Synthesis of 3-(2-Pyridyl)-1,5-dimethyl-1,2,5,6-tetrahydro-1,2,4,5-tetrazine 6-Oxide (8). To a stirred solution of **6** (330 mg, 1.59 mmol) in 5 mL of water was added a solution of $NaIO_4$ (260 mg, 1.22 mmol) in 7 mL of water. The solution immediately turned bright yellow/orange, and within 5 min of stirring a fine yellow solid precipitated. The reaction mixture was then diluted into 100 mL of water and extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel using ethyl acetate as eluent to give **8** as yellow needles from chloroform/petroleum ether, yield 130 mg (40%). The starting tetrazane **6** was also recovered from the column in 40% yield. ^1H NMR ($CDCl_3$): δ 8.5 (d, 1H, J = 5.1 Hz), 8.0 (d, 1H, J = 8.1 Hz), 7.8 (td, 1H, J = 7.7, 1.5 Hz), 7.3 (dd, 1H, J = 7.4, 5.9 Hz), 3.3 (s, 3H), 3.1 ppm (s, 3H). ^{13}C ($CDCl_3$): 155.6, 147.8, 146.6, 145.2, 136.3, 124.4, 120.0, 36.6, 35.7 ppm. Mp: 90−92 °C. Anal. Calcd for $C_9H_{11}N_5O$: C, 52.67; H, 5.40; N, 34.13. Found: C, 52.88; H, 5.43; N, 34.33. IR (KBr): ν(NH) 3215 (s), ν(C=O) 1675 (s) cm^{-1}. λ_{max} (CH_2Cl_2): 357 nm. MS (EI LR): *m/z* 205 (M^+, 100%), 190 ($(M - CH_3)^+$, 10), 78 ($C_5H_4N^+$, 35).

Synthesis of 3-(2-Pyridyl)-1,5-dimethyl-6-oxoverdazyl (3) (as 1:1 Complex with Hydroquinone). To a stirred solution of **6** (806 mg, 3.89 mmol) in 20 mL of hot benzene was added 1,4-benzoquinone (630 mg, 5.82 mmol). The solution immediately turned yellow and then became increasingly darker in color. After being stirred for 1 h, the resulting maroon microcrystalline solid was isolated by vacuum filtration and recrystallized from ethyl acetate/benzene to give **3**−$C_6H_6O_2$ as maroon needles, yield 1.16 g (95%). Mp: 90−92 °C. Anal. Calcd for $C_{15}H_{16}N_5O_3$: C, 57.32; H, 5.13; N, 22.28. Found: C, 57.33; H, 5.17; N, 22.23. IR (KBr): ν(OH) 3294 (br, w), ν(C=O) 1683 (s) cm^{-1}. λ_{max} (CH_2Cl_2): 238, 269, 409 nm. MS (CI methane): *m/z* 205 (M + 1, 28%), 111 ($(hq + 1)^+$, 100).

Synthesis of 4,6-Dimethyl-2-pyrimidinecarboxaldehyde. *tert*-Butyllithium (10.7 mL of a 1.7 M pentane solution, 18.2 mmol) was added very slowly to a stirred solution of 2-bromo-4,6-dimethylpyrimidine[47−49] (1.705 g, 9.11 mmol) in 75 mL of anhydrous diethyl ether at −110 °C. The clear light yellow solution turned deep orange and slightly turbid. During the addition the temperature was maintained below −90 °C. The solution was stirred at low temperature for 1 h, and then a solution of anhydrous dimethylformamide (DMF) (1.42 mL, 18.4 mmol) in 20 mL anhydrous diethyl ether was added dropwise over 0.5 h. The solution was warmed to room temperature for 1.5 h, poured into ice, and diluted with water. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The resulting dark red oil was subjected to chromatography (silica gel, 3:1 CH_2Cl_2/acetonitrile) to afford 4,6-dimethyl-2-pyrimidinecarboxaldehyde as an off-white solid which was further purified by vacuum sublimation, yield 600 mg (48%). ^1H NMR ($CDCl_3$): δ 10.04 (s, 1H), 7.19 (s, 1H), 2.59 ppm (s, 6H). ^{13}C NMR ($CDCl_3$): δ 192.0, 168.1, 139.8, 122.5, 23.9 ppm. Anal. Calcd for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.57. Found: C, 61.53; H, 5.88; N, 20.49. MS (CI methane): *m/z* 137 (M + 1, 100%).

Synthesis of 3-(4,6-Dimethyl-2-pyrimidyl)-1,5-dimethyl-1,2,4,5-tetrazane 6-Oxide (7). A solution of 4,6-dimethyl-2-pyrimidinecarboxaldehyde (0.173 g, 1.46 mmol) in 40 mL of methanol was added dropwise to a solution of **5** (0.198 g, 1.47 mmol) in 30 mL of hot methanol. After the addition was complete, the solution was heated to reflux for 15 h. The solvent was then removed under reduced pressure, and the solid residue was recrystallized from ethyl acetate to give **7** as large pale yellow crystals, yield 0.176 g (51%). Mp: 158−160 °C. ^1H NMR ($CDCl_3$): δ 7.01 (s, 1H), 4.90 (br s, 3H), 3.16 (s, 6H), 2.46 ppm (s, 6H). ^{13}C NMR ($CDCl_3$): δ 167.7, 162.3, 154.7, 120.2, 70.9, 38.1, 23.8 ppm. IR (KBr): ν(NH) 3249 (br,

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w), 3210 (s), ν(C=O) 1630 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_6O$: C, 50.83; H, 6.82; N, 35.57. Found: C, 50.84; H, 6.91; N, 35.53. MS (CI methane): *m*/*z* 237 (M + 1, 66%).

Synthesis of 3-(4,6-dimethyl-2-pyrimidyl)-1,5-dimethyl-6-oxoverdazyl (4). To a stirred solution of **7** (257 mg, 1.08 mmol) in 10 mL of water was added a solution of $NaIO_4$ (345 mg, 1.61 mmol) in 17 mL of water. Immediately thereafter the solution turned bright orange and was stirred for an additional 0.5 h, after which time the reaction mixture was diluted into 100 mL of water and the product was extracted with CH_2Cl_2, dried over $MgSO_4$, and evaporated under reduced pressure. The brown/red solid residue was subject to flash chromatography on silica gel using acetonitrile as eluent to give **4** as brown/red needles from ethyl acetate, yield 180 mg (72%). Mp: 126−128 °C. Anal. Calcd for $C_{10}H_{13}N_6O$: C, 51.48; H, 5.62; N, 36.02. Found: C, 51.34; H, 5.76; N, 35.17. IR (KBr): ν(C=O) 1685 (s) cm^{-1}. λ_{max} (CH_2Cl_2): 400, 450 (sh) nm. MS (EI LR): *m*/*z* 233 (M$^+$, 100%).

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