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Syntheses and Characterization of Salts of *N,N′,N″*-Tricyanoguanidinate Dianion ($C_4N_6^{2-}$) and the Observation of a Strong Nonlinear Optical Effect by Second Harmonic Generation from $Na_2C_4N_6{\cdot}H_2O$

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Reaction of cyanamide with dimethyl cyaniminodithiocarbonate in the presence of potassium carbonate gives the potassium salt of *N,N′*-dicyano-1,3-diaza-2-thiomethoxypropenide ($KC_4H_3N_6S$). Synthesis of disodium *N,N′,N″*-tricyanoguanidinate ($Na_2C_4N_6{\cdot}H_2O$) was accomplished by the reaction of disodium cyanamide with dimethyl cyaniminodithiocarbonate in *N,N*-dimethylacetamide at 120−140 °C. This salt exhibits a very strong nonlinear optical effect as assayed by second harmonic generation. The monoguanidinium monosodium salt of *N,N′,N″*-tricyanoguanidinate was synthesized by partial cation ion exchange of the disodium salt. The crystal structure of this salt, $Na[C(NH_2)_3][C(NCN)_3]$, was solved in the space group $P\bar{3}$ with $Z = 2$, $a = 8.942(2)$ Å, $b = 8.942(2)$ Å, $c = 6.576(4)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 120.00$, and $V = 455.4(4)$ Å^3.

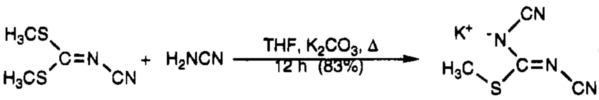
Introduction

Among the binary carbon and nitrogen compounds and ions which have been reported,[1] relatively few have alternating carbon−nitrogen connectivity, although such structures are highly stable. These include cyanamide (CH_2N_2), dicyandiamide ($C_2H_4N_2$), and melamine ($C_3H_6N_6$),[2] and salts such as disodium cyanamide (Na_2NCN),[3] sodium dicyanamide (NaC_2N_3),[4] and trisodium *N,N′,N″*-tricyanomelamine ($Na_3C_6N_9$).[5] In view of the recent prediction of β-carbon nitride (C_3N_4) as a material harder than diamond,[6] these compounds and salts may be considered as the organic precursors for the synthesis of such a hard material.[7]

As part of a general investigation of carbon/nitrogen materials, we report a new synthesis of the dianion, *N,N′,N″*-tricyanoguanidinate dianion ($C_4N_6^{2-}$), and its first chemical and structural characterization. This ion has an open chain, rather than the cyclic aromatic triazine structure common among high nitrogen compounds, and has the alternating C−N connectivity. As such, *N,N′,N″*-tricyanoguanidinate may be a useful precursor to other high nitrogen materials. Guanidine-based structures have also been recognized as having special stability due to "Y" aromaticity.[8]

Results and Discussion

Sodium and quaternary ammonium salts of 2-methylthio-*N,N′*-dicyano-1,3-diaza-2-propenide were synthesized by Blanchard at DuPont[9] for antistatic applications in hydrocarbons fuels. The potassium salt of 2-methylthio-*N,N′*-dicyano-1,3-diaza-2-propenide (**3**) was prepared by the reaction of dimethyl cyanimiodithiocarbonate (**1**) with cyanamide (**2**) in the presence of potassium carbonate (eq 1).



1 **2** **3** (1)

Blanchard apparently did not attempt to carry out the displacement of the second thiomethyl group. The substitution of the both thiomethyl groups in **1** by cyanamide (**2**) to give the salt of *N,N′,N″*-tricyanoguanidinate ($C_4N_6^{2-}$) was reported by a Japanese group using a similar reaction at higher temperatures and a stronger base, potassium hydroxide.[10] In our

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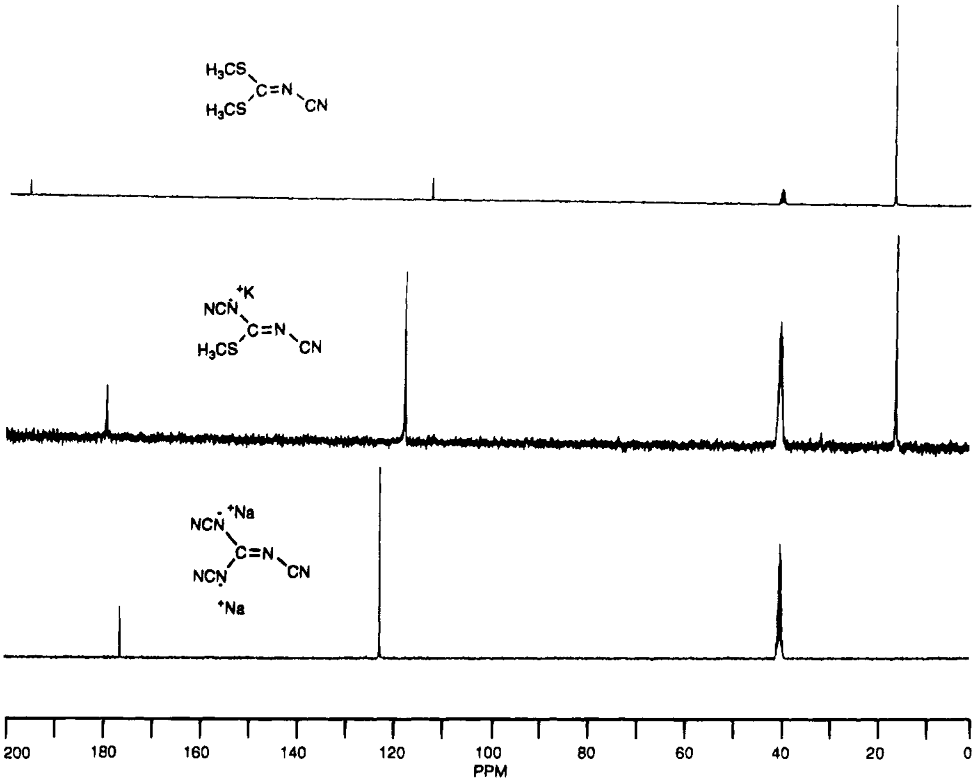
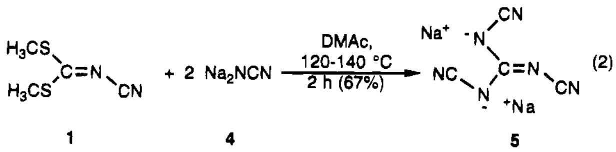


Figure 1. ^{13}C NMR spectra of dimethyl cyaniminodithiocarbonate (**1**), potassium 2-methylthio-*N,N'*-dicyano-1,3-diaza-2-propenide (**3**), and disodium *N,N',N''*-tricyanoguanidinate (**5**) in DMSO-d_6.

hands, their procedure was found to lead mainly to the dimerization of cyanamide to dicyandiamide followed by nucleophilic substitution of the thiomethyl groups by the dicyandiamide, affording a mixture of several cyclic and acyclic products. In our approach this dimerization is avoided by the use of disodium cyanamide, Na_2NCN (**4**, eq 2) as the nucleophile, without the addition of a base. The $C_4N_6^{2-}$ salts are obtained cleanly as shown by the ^{13}C NMR (Figure 1).



(2)

Disodium tricyanoguanidinate (**5**) appears to bind a single water tightly, and although it can be dried by heating at 150 °C in vacuum for several hours, it quickly restores any lost water upon grinding with KBr or on standing. The infrared spectrum of **5** shows a strong band at 3564 cm^{-1} in addition to weak bands at 3384 and 3264 cm^{-1}, suggesting that the water may be hydrogen bonded to the dianion. The bound water also could be detected in ^1H NMR spectrum. The dried material showed a small loss of water in the thermogravimetric analysis (TGA) presumably picked up during transfer. The TGA also shows that the salt is remarkably stable, up to nearly 600 °C, under nitrogen. The ^{13}C NMR data of the starting material **1** and of the salts **3** and **5** (see Figure 1) show a definite trend in the chemical shifts upon substitution of the thiomethyl groups by the cyanamido groups.

The well-defined O–H/N–H bands in the infrared spectrum of **5** suggested an unusual pattern of hydrogen bonding between the bound water molecule and the $C_4N_6^{2-}$ ion. In an effort to determine its crystal structure, transparent, colorless crystals of **5** were grown from ethanol/water (4:1 v/v) by slow evaporation. However, the structure determination was hampered by disorder and/or twinning, and a satisfactory refinement could not be obtained. A superlattice seems unlikely since long exposure photographs of relatively large crystals showed no sign of superlattice reflections. Crystals of the partially metathesized, anhydrous salt sodium guanidinium tricyanoguanidinate (**7**) were prepared by slow evaporation of an aqueous solution of **5** with guanidinium carbonate (**6**). The crystal structure of **7** was solved in the $P\bar{3}$ space group. Crystallographic data are listed in Table 1. This is the first structural report on tricyanoguanidinate dianion, $C_4N_6^{2-}$, which is found to be planar with a triskelion shape and a C2–N1–C1 angle of 119° (see Figure 2).

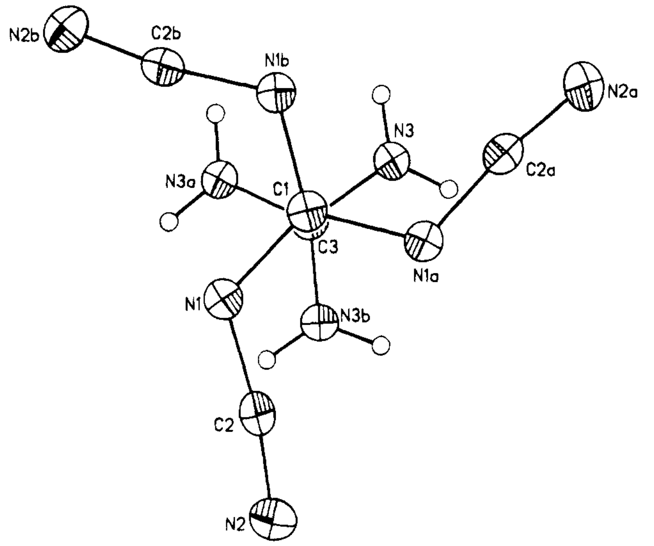


Figure 2. ORTEP diagram of guanidinium monocation and sodium *N,N',N''*-tricyanoguanidinate (**7**) dianion.

Table 1. Crystallographic Data for Compounds 5 and 7

properties	compound **5**	compound **7**
empirical formula	$C_4H_2N_6ONa_2$	$C_5H_6N_9Na$
cryst dimensions (nm)		0.32 × 0.50 × 0.36
a	9.063(1) Å	8.942(2) Å
b	9.063(1) Å	8.942(2) Å
c	6.468(2) Å	6.576(4) Å
α	90°	90°
β	90°	90°
γ	120°	120°
V	460.2(2) $Å^3$	455.4(4) $Å^3$
Z		2
Q_{calcd}		1.571 g cm^{-3}
space group		trigonal, $P\bar{3}$ (no. 147)
$F(000)$		220 electrons
μ(Mo Kα)		0.78 cm^{-1}
no. of data collected		4339
no. of unique reflections		694 (full matrix least-squares on F^2 was used in the refinement)
R_{int}		0.0310
final R indexes ($I \geq 2\sigma(I)$)		$R1 = 0.0296$, $wR2 = 0.0826$
R indexes (all data)		$R_1 = 0.0302$, $wR2 = 0.0933$
GOF		1.101

Table 2. Average Bond Lengths (Å) in 7

N2−C2	1.122(7)	Na−N	2.5328(9)
N1−C1	1.3461(8)	C3−N3	1.3249(8)
N1−C2	1.301(2)		

Significant bond lengths of $C_4N_6^{2-}$ are listed in Table 2, and the remainder of the data are in the supporting information. The two planar ions pack on sites of 3-fold symmetry in an alternating staggered stack separated by a repeat distance of 3.28 Å (Figure 3). While this distance is understandably short for oppositely charged ions, it contrasts with most guanidinium structures which tend to be dominated by hydrogen-bonding interactions. Thus, the guanidinium salt of tricyanomethanide anion, $[C(CN)_3^-]$, has a more complex stacking which involves hydrogen bonding between the nitrile nitrogens and the guanidinium cation, and the two triangular ions are eclipsed but at a significantly greater distance of 3.58 Å.[11] There is evidence for a moderate hydrogen bond in our structure as well, since the interstack N1−N3 distance, with its implicit hydrogen bond, is 3.01 Å, not as short as the N-N hydrogen bonded distance of 2.78 Å found for histidine[12] but shorter than the sum of bond and van der Waal's radii for N−H···N of 3.7 Å. The packing diagram for the *ab* plane, showing the hydrogen bonding, is given in the supporting information.

The sodium cations in the crystal lattice are also at sites of 3-fold symmetry. The sodium ions are six coordinate occupying octahedral holes formed by the cyano nitrogens from tricyanoguanidinates. The tricyanoguanidinate is disordered with N1 and C2 occupying slightly different positions which result in a different handedness to the propeller shape of the ion. The positions of the central point atom C1 and the terminal cyano nitrogen are shared in common with the two orientations. The refined site occupancies are 0.896(4) and 0.104(4).

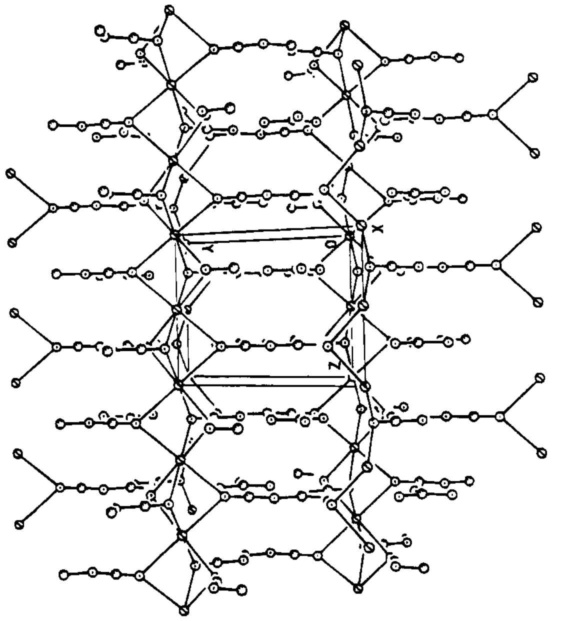


Figure 3. Crystal packing arrangement of monoguanidinium monosodium *N,N′,N″*-tricyanoguanidinate (**7**).

Table 3. Nonlinear Optical Effect Data

sample							average value	Na/KDP ratio
series 1	KDP	4.4[a]	1.5	1.45	1.3		1.42	
	Na(1)	15.5	15.4	15.5			15.5	10.9
	KDP	0.4	0.41	0.48	0.59	0.56	0.49	
	Na(2)	7.2	7.6	7.9	8.9	10.9	8.5	17.3
series 2	KDP(1b)	0.29	0.4	0.15	0.33	0.35	0.30	
	Na(1b)	5.9	5.2	4.1	5.1	5.1	5.1	17
	Na(2b)	2.6	1.0				1.8	6
								av ratio 12.8

[a] Discarded from average.

The feature of the metal cation coordinated to cyano groups is similar to that found in the structure of the calcium salt of hexacyanoisobutylene hexahydrate which was solved in the $P\bar{3}m1$ space group.[13] The calcium ions occupy octahedral sites formed by three cyano groups and three water molecules.

Although the structure of **7** is centric, the structure of **5** which remains unsolved, is clearly not. The generation of second harmonic light from a 1053 nm laser pulse was measured for powered samples of **5**. The data are shown in Table 3 for two different preparations and sample thickness relative, in each case, to samples of comparable thickness of potassium dihydrogen phosphate (KDP).

Although the data show some variation, the results of 15 trials give an average value of second harmonic generation for **5** that is 13 times greater than KDP. Since crystals of **5** are thermally stable and optically transparent up to 266 nm in the ultraviolet this result is of some interest. In future work we intend to grow large single crystals and test this material for phase matchability.

Conclusions

We have reported a new and improved synthesis of *N,N′,N″*-tricyanoguanidinate dianion, $C_4N_6^{2-}$, and have characterized it structurally for the first time. The *N,N′,N″*-tricyanoguanidinate dianion has alternate carbon−nitrogen connectivity and very high thermal stability. The guanidinium sodium *N,N′,N″*-tricyanoguanidinate has an unusual alternate charged stacking of

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guanidinium and *N,N',N''*-tricyanoguanidinate ions. The cyano nitrogens form the corners of an octahedron within which each sodium cation is located, thereby forming an infinite chain through the crystalline structure. The disodium monohydrate salt of *N,N',N''*-tricyanoguanidinate has a strong second-order nonlinear optical effect. The facile preparation of the $C_4N_6^{2-}$ suggests that this ion may be a useful starting point for other stable materials with a very high nitrogen content.

Experimental Section

General Procedure. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded using a Nicolet 5-DX FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded using Bruker AM-300 or AM-360 or AC-200 spectrometers. Chemical shift values are reported relative to appropriate solvents. All ^{13}C NMR spectra were done using broad-band proton decoupling. Fast atom bombardment (FAB) mass spectra were recorded on a VG analytical Model 70-250S mass spectrometer. Elemental analyses were performed at University of Michigan on a Perkin-Elmer 2400 CHN analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer 7/DX thermal analysis system. UV–vis spectra were recorded on Shimadzu UV-2101PC or Shimadzu UV-160U UV–visible spectrophotometers. Solvents were purified and distilled under nitrogen prior to use. All reagents were purchased from Aldrich Chemical Co. or Lancaster Synthesis, Inc.

Measurement of Nonlinear Optical Effects. Second harmonic measurements were made using the method developed by Kurtz and Perry.[14] A mode-locked Quantronix Model 416 YLF laser, operating at 1053 nm, was used to generate a train of 90 ps pulses at 76 MHz. A Quantronix Model 366 stabilizer was employed to minimize variations in laser power. The average mode-locked (TEM_{00}) output power was approximately 8.9 W. The beam was modulated at 200 Hz by a mechanical chopper, passed through a Schott RG-850 glass filter to remove wavelengths shorter than 850 nm, and then divided by a CVI beam-splitter so that approximately half the output beam was directed to a reference standard and half to the experimental sample. Light scattered from the sample and reference materials could be separately collected, filtered, and detected by duplicate systems consisting of a large aperture lens (*f*/1), an Oriel 530 ± 10 interference filter to isolate the second harmonic at 527 nm, and a 1P28 photomultiplier tube. In practice, measurements were made in the single-beam mode, alternately recording second harmonic signal from the reference material and the sample. The signal from the phototube was demodulated by a lock-in amplifier referenced in phase and frequency to the mechanical chopper.

The test samples of $Na_2C_4N_6\cdot H_2O$ will be abbreviated below and in Table 3 as Na. There were two samples of this compound, a pure white "first crop" of recrystallized material Na(1) and a second sample of pale yellow but very well-formed crystals Na(2). The standard used for comparison was potassium dihydrogen phosphate (KDP) which had been chipped off of a very large single crystal.

All samples were prepared by thorough grinding with an agate mortar and pestle followed by sieving through 200 μm mesh stainless steel sieve. Samples of sieved powder, 20 mg, were arranged in circles of 1 cm diameter between glass microscope slides. Care was taken to ensure that the thickness of sample and reference was similar. A series of observations were made by alternating the standard and test sample after each trial so that the slightly different sample locations would provide an average of surface and thickness variations. To test the effect of sample thickness, a second set (series 2) of observations were made on the same samples reduced to 10 mg of powder spread over the same area. The SHG efficiency of each sample was computed by ratioing its lock-in signal with that of the reference signal under identical conditions. The data are shown in Table 3.

Potassium *N,N'*-Dicyano-1,3-diaza-2-methylthiopropenide (3). Into a solution of dimethyl cyaniminodithiocarbonate (**1**, 10.195 g, 0.070 mol) and cyanamide (2.919 g, 0.070 mol) in tetrahydrofuran (40.0 mL) was added anhydrous potassium carbonate (9.875 g, 0.071 mol), and the reaction mixture was set to reflux for 24 h. A white solid was precipitated in an hour. The reaction mixture was cooled to room temperature, and the solid precipitated was filtered and washed with ethanol (95%). The filtered solid was crystallized from absolute ethanol to give the product as white flakes; yield 10.234 g (83%); mp 306 °C (dec); IR (KBr) 2191, 2184, 2163, 2148, 2130, 1482, 1449, 1342, 1317, 1308, 1263, 1152, 1100, 1058, 1041, 1025, 796, 636 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.70-(s); ^{13}C NMR (DMSO-d_6) δ 179.25, 117.40, 15.40; FAB$^-$ (DTT/DTE and DMSO matrix) 139 (M$^-$); UV/vis (DMF) 267 nm (ϵ 7700). For compound **1**: UV/vis (DMF) 267 nm (ϵ 12 600). Anal. Calcd for $C_4H_3N_4SK$: C, 26.95, H, 1.70, N, 31.43. Found: C, 26.47, H, 1.54, N, 31.55.

Disodium *N,N',N''*-Tricyanoguanidinate (5). To a suspension of disodium cyanamide (**4**, 8.800 g, 0.102 mol) in *N,N*-dimethylacetamide (DMAc, 10 mL) was added 2 mL of a solution of dimethyl cyaniminodithiocarbonate (**1**, 7.52 g, 0.051 mol) dissolved in 6 mL of DMAc, and the reaction mixture was heated to 120–140 °C. The solution turned brown in 20 min. The remaining solution of **1** in DMAc was added dropwise during the next 30 min. The solution turned yellow with effervescence after each addition along with the formation of a brown solid. The reaction mixture was periodically tested for any residual **1** present, by thin-layer chromatography while the heating was continued for another hour. When no more **1** was present, the reaction mixture was stirred for an hour more, cooled to room temperature, and filtered. The filtered solid was washed with ethanol/water mixture (4/1) to remove any sodium thiomethoxide present. The undissolved solid was suspended in ethanol/water mixture (4/1, 100 mL) and was heated to give a solution. The hot solution was decolorized using charcoal. Slow cooling of the decolorized solution to room temperature gave the product as a white solid. Further purification was carried out by crystallization from ethanol/water (4:1) to give colorless needles. The product was filtered and dried in vacuum at 130 °C for 24 h; yield 6.124 g (67%); mp > 400 °C; IR (KBr) 3564, 3384, 3264, 2152, 1645, 1460, 1350, 1267, 1118, 712, 566 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.59 (H_2O); ^{13}C NMR (DMSO-d_6) δ 176.03, 122.25; FAB$^-$ (3-nitrobenzyl alcohol and DMSO matrix) 133 (AH$^-$), 155 (ANa$^-$), 233 ($A_2Na_3^-$), 511 ($A_3Na_5^-$), 689 ($A_4Na_7^-$) (A = $C_4N_6^{2-}$); UV/vis (DMF) 266 nm (ϵ 13 000). Anal. Calcd for $Na_2C_4N_6\cdot H_2O$: C, 24.50, H, 1.03, N, 42.86. Found: C, 24.71, H, 1.00, N, 42.51.

Sodium Guanidinium *N,N',N''*-Tricyanoguanidinate (7). Into a 10 mL aqueous solution of disodium tricyanoguanidine (**5**, 0.590 g, 3.315 mmol) was added 10 mL of an aqueous solution of guanidinium carbonate (**6**, 0.608 g, 3.375 mmol) and the combined solution was slowly evaporated when **7** crystallized out after a week as an off-white crystalline solid. The crystals were filtered and dried in vacuum at 100 °C for 12 h; yield 0.302 g (33%); mp > 320 °C; IR (KBr) 3435, 3379, 3367, 3255, 3200, 2144, 1678, 1589, 1442, 1119, 1115, 607, 593, 584, 579, 474 cm^{-1}. Anal. Calcd for $C_5H_6N_9Na$: C, 27.94, H, 2.79, N, 58.60, Na, 10.70. Found: 27.55, H, 2.74, N, 58.66, Na, 10.90.

Acknowledgment. The authors are grateful to the IBM Corp. for donation of the laser. This work was supported in part by a Research Opportunity Award of Research Corp.

Supporting Information Available: Full listing of bond lengths and angles for compound **7**, packing diagram in the *ab* plane, atomic coordinates, and details of data collection (5 pages); structure factor tables (2 pages). Ordering information is given on any current masthead page.

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