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Guanidinium-Based Ionic Liquids

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Cyclic ($\subset{=}N^+<$, $\subset$ = imidazolidine **3** and **4**, hexahydro-pyrimidine **7** and **8**, tetrahydro-1,3,5-oxadiazine **12**, and triazoline **15** and **16**) and acyclic [$(R_2N)_2C{=}N^+<$, **19**] guanidinium-based salts were synthesized via the quaternization of guanidine derivatives with nitric or perchloric acid or with iodomethane followed by metathesis reaction with silver nitrate, silver perchlorate, or ammonium dinitroamide. The structure of **15d** was confirmed by single-crystal X-ray analysis. Most of the salts exhibited low melting points and good thermal stabilities. Their densities range between 1.2 and 1.5 g/cm^3. Standard molar enthalpies of formation were calculated from experimentally determined constant-volume combustion energies obtained using an oxygen bomb calorimeter.

Introduction

Ionic liquids have emerged as promising alternative media for the replacement of conventional organic solvents.[1] The unique properties have already been demonstrated by their use in a wide range of stoichiometric and catalytic reactions. Much attention has been attracted through their technological applications as electrolytes in batteries, photoelectrochemical cells, and other wet electrochemical devices.[2] The number of ionic liquids that can be synthesized is essentially limitless. The variation in their properties that can be caused by small changes in molecular composition provides the opportunity for a myriad of applications. Recently, the syntheses of new heterocyclic-based energetic, low-melting salts were reported.[3] These salt-based materials often possess advantages over nonionic molecules since they tend to exhibit very low vapor pressures, essentially eliminating the risk of exposure through inhalation. Ionic compounds often exhibit higher densities than their atomically similar nonionic analogues. These results arise from the influence of Coulombic forces which encourage the formation of ordered and dense lattice structures in molecular assemblies.[3−6]

While the ionic liquid field is dominated by imidazolium salts, most high-energy ionic liquids are substituted triazolium and tetrazolium derivatives.[3] Therefore, in this work, we have extended our synthetic study to new energetic cyclic and acyclic guanidinium salts. There are only a few guanidinium compounds that have been characterized as ionic liquids.[7] Earlier studies give strong support for the guanidinium unit as a quality candidate for a new generation of diverse ionic liquids. Guanidinium salts can be prepared in a straightforward manner, are robust, and have useful solubility and thermal properties. For example, the tetraalkyl dimethyl guanidinium cation provides the opportunity to prepare a diverse range of cationic structures and thus to markedly tune the properties of these liquids with concomitant anion variation.[8] By using a cyclic hexaalkyl guanidinium cation-containing ionic liquid as both the phase transfer catalyst and the solvent, we have achieved selective oxidation of a series of substituted benzyl alcohols using sodium hypochlorite as the oxidant. The solvent was shown to be recyclable

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after the benzaldehyde product is extracted with ether.[9] Other useful applications have been found in dye-sensitized solar cells,[10] in biological and molecular recognition,[11] and as energetic materials.[12]

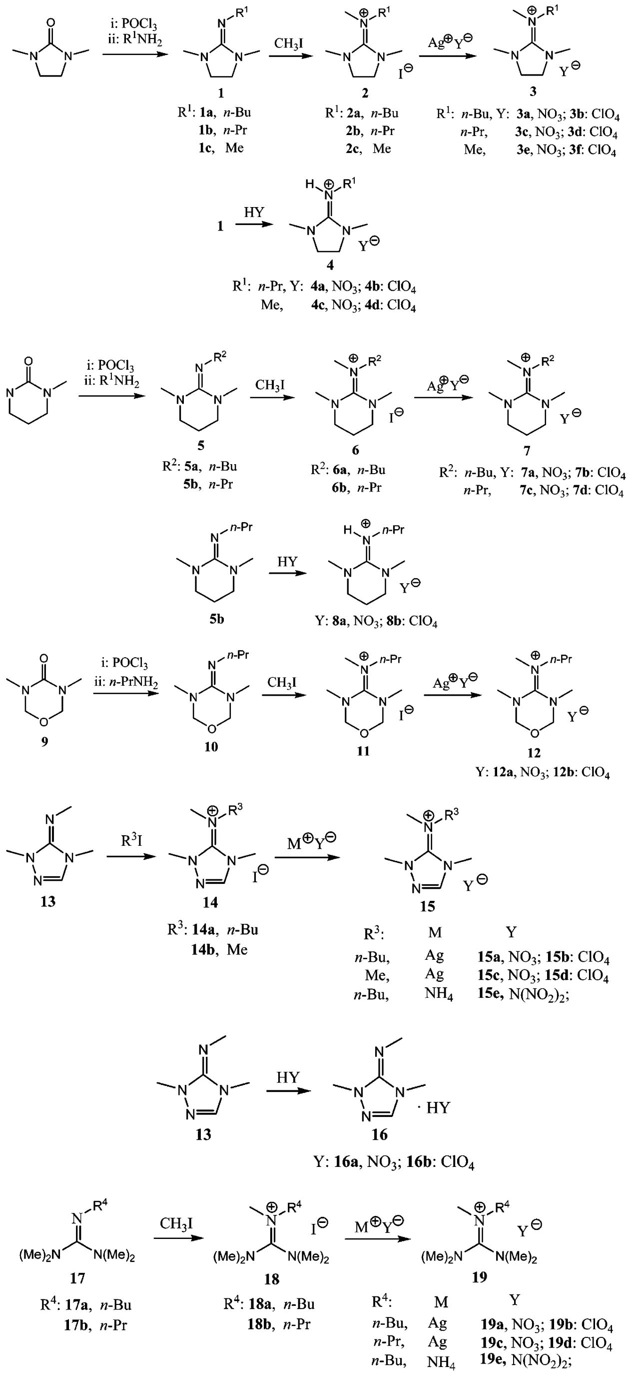
Our earlier work focused on studies on the properties of high-energy ionic liquids comprised of azido-, nitro-, and *N*-amino-substituted azolium cations with nitrate or perchlorate as anion.[3b,c] In this paper, we now report the syntheses of several new cyclic and acyclic guanidines, followed by the subsequent formation of quaternary guanidinium salts with acids or alkyl iodide. The latter are then converted to the nitrate, perchlorate, and dinitroamide ionic liquids. Their thermal, physical, and energetic properties have been studied in detail.

Results and Discussion

Cyclic and acyclic pentaalkyl guanidines were obtained from 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, tetrahydro-3,5-dimethyl-4*H*-1,3,5-oxadiazin-4-one, and tetramethylurea by a published method (Scheme 1).[9] 1,4-Dimethyl-5-methylimino-1,2,4-triazole, **13**, was prepared from *N*,*N′*,*S*-trimethylisothiourea hydroiodide and methyl hydrazine in ethyl alcohol which was then reacted with formic acid after the solvent had been removed.[13] After the reaction was neutralized with NaOH solution, the pure product was obtained by using column chromatography. Subsequent reaction with alkyl iodides resulted in the formation of iodide salts. The nitrate, perchlorate, and dintroamide salts were synthesized by metathesis of the guanidinium iodides with silver nitrate, silver perchlorate, and ammonium dinitroamide in aqueous solution, or the former two were obtained by the substituted guanidines being reacted with nitric acid and perchlorate acid directly (Scheme 1). Some of the nitrate salts were hygroscopic and were stored in a desiccator for further analysis.

In the ^{1}H NMR spectrum of **4d**, the imino CH_3 was observed as a doublet ($J = 5.2$ Hz). On the basis of the H−H COSY spectra, it was evident that the imino nitrogen was also bonded to a proton that coupled with the methyl group. This supports the structure as indicated in Scheme 1. However, for **16a** and **16b**, there was no evidence of coupling based on the ^{1}H NMR spectra and H−H COSY measurements. Therefore, these are apparently ordinary acid salts.[13]

Scheme 1



Phase transition temperatures (midpoints of melting points (T_m) or glass phase transition temperatures (T_g)) for all the salts were determined by differential scanning calorimetry (DSC) as given in Table 1. With a common cation, the nitrates invariably had lower T_m/T_g values than the perchlorates. With the same anion, for homologues, the longer the R alkyl chain, the lower the T_m/T_g. With the same R substituent on the cation (different cation) and the same anion, the order of T_m/T_g of the different rings was as follows: **15a** < **7a** < **3a** < **19a**, $-69 < 6 < 7 < 72$ °C; **15b** < **3b** < **7b** < **19b**, $-59 < 28 < 78 < 135$ °C; **3c** < **7c** < **12b** < **19c**, $31 < 57 < 94 < 209$ °C; **3d** < **12b** < **7d** < **19d**, $39 < 94 < 128 < 268$ °C; **15c** < **3e**, $74 < 128$ °C; **15d** < **3f**, $125 < 182$ °C. To generalize, the T_m/T_g values for (1) cyclic compounds < acylic compounds; (2) five-membered rings < six-membered rings; (3) triazolium <

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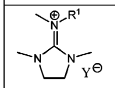
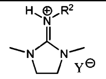
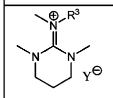
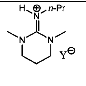
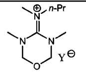
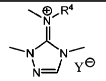
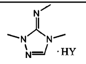
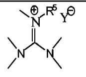
Table 1. Structure and Properties of Guanidinium Salts

comp	Y	R	No.	Tm/Tg[a]	Td[b]	d_{calcd}[c]	$-\Delta_cU_m$[d]	Δ_fH_m[e]
	NO_3	*n*-Bu	**3a**	7	246	1.20/1.23[f]	1574	-490
		n-Pr	**3c**	31	272	1.22	1592	267
		Me	**3e**	128	316	1.28	1123	-341
	ClO_4	*n*-Bu	**3b**	28	303	1.31/1.32[f]	1679	-1
		n-Pr	**3d**	39	325	1.34	1527	42
		Me	**3f**	182	292	1.41	1545	656
	NO_3	*n*-Pr	**4a**	-[g]	128	1.26/1.24[f]	1013	-1481
		Me	**4c**	3	130	1.32/1.34[f]	584	-1914
	ClO_4	*n*-Pr	**4b**	6	271	1.38/1.32[f]	1409	225
		Me	**4d**	116	285	1.46	888	-599
	NO_3	*n*-Bu	**7a**	6	292	1.19/1.31[f]	1519	-1395
		n-Pr	**7c**	57	308	1.21	1632	-245
	ClO_4	*n*-Bu	**7b**	78	276	1.29	1909	284
		n-Pr	**7d**	128	273	1.32	1859	752
	NO_3		**8a**	-[g]	127	1.24	1047	-2018
	ClO_4		**8b**	-70[h]	265	1.35	1546	120
	NO_3		**12a**	65	238	1.26	1697	704
	ClO_4		**12b**	94	244	1.37	1501	-70
	NO_3	*n*-Bu	**15a**	-69[h]	211	1.26	1515	85
		Me	**15c**	74	229	1.36	990	-80
	ClO_4	*n*-Bu	**15b**	-59[h]	284	1.37	1527	181
		Me	**15d**	125	276	1.49/1.53[i]	994	-14
	[j]	*n*-Bu	**15e**	-66[h]	197		1532	153
	NO_3		**16a**	139	222	1.42	845	-8
	ClO_4		**16b**	120	281	1.56	891	234
	NO_3	*n*-Bu	**19a**	72	314	1.17	1709	-209
		n-Pr	**19c**	209	265	1.19	1475	-509
	ClO_4	*n*-Bu	**19b**	135	322	1.28	1884	570
		n-Pr	**19d**	268	293	1.30	1780	815
	[j]	*n*-Bu	**19e**	75	196		1504	-71

[a] In °C. [b] In °C. [c] Calculated from refs 14, 15; g/cm^3. [d] Constant volume combustion energy, kcal/mol. [e] Molar enthalpy of formation, kJ/mol. [f] Measured density using a pycnometer at 25 °C. [g] Phase transition temperature less than −78 °C. [h] T_g data. [i] From X-ray structure. [j] $N(NO_2)_2^-$.

imidazolium; and (4) single oxygen six-membered rings < no oxygen six-membered rings—that is, **15** < **3** < **12** < **7** < **19**.

When the T_m/T_g of salts prepared directly from the acids is compared with those obtained from the iodides—that is, in every case where the species attached to the ring is hydrogen (alkyl iminium, $RHN{=}^+$) rather than methyl (alkyl methyl iminium, $RMeN{=}^+$)—the T_m/T_g is lower, e.g., **4a** < **3c** (less than −78 < 31 °C); **4c** < **3e** (3 < 128 °C); **4b** < **3d** (6 < 39 °C); **4d** < **3f** (116 < 182 °C); **8a** < **7c** (less than −78 < 57 °C); **8b** < **7d** (−70 < 128 °C). This indicates that there is no appreciable hydrogen bonding and that the increase in the T_m/T_g value is as would be expected with increasing molecular weight. Since **16a** and **16b** are not quaternary salts, no relationship is found when compared, for instance, with **15c** and **15d**. For homologues, the longer the alkyl chain, the lower the T_m/T_g which arises from crystal packing effects.

The nitrate and perchlorate salts obtained from the corresponding iodide compounds (alkyl methyl iminium, $RMeN{=}^+$) were thermally stable with decomposition temperatures (T_d) ranging from 211 °C for **15a** to 325 °C for **3d**. The dinitroamide salts are somewhat less thermally stable than their nitrate or perchlorate analogues. For the salts obtained by reaction with strong acids (alkyl iminium, $RHN{=}^+$), the perchlorate derivatives were very stable thermally with T_d's falling from 265 °C for **8b** to 285 °C for **4d**, while the nitrate analogues were much less stable with T_d's falling at ∼130 °C. Not unexpectedly, the presence of the *N*-methyl iminium moiety adds to the thermal stability of these salts.

The calculated densities of the liquid salts[14,15] were moderate ranging from 1.17 g/cm^3 for **19a** to 1.49 g/cm^3 for **15d**. Some of the measured densities for the room-temperature ionic liquids and the value calculated for the single-crystal structure are also listed in Table 1. The calculated and experimentally obtained densities are reasonably close. The calculated value for **15d** and that obtained from single-crystal structure calculations agree within 3%.

The standard enthalpy of formation of a compound is a measure of its thermodynamic stability. The heats of formation reported here were calculated from experimentally determined heats of combustion. Typical experimental results (averaged over three measurements each) of the constant volume combustion energy ($\Delta_c U_m$) of the new salts are given in Table 1. The standard molar enthalpy of combustion ($\Delta_c H_m^\circ$) of the samples can be derived from the constant volume combustion energy by means of the following formula:

$$\Delta_c H_m^\circ = \Delta_c U_m + \Delta nRT,\ \Delta n = \sum n_i\ (\text{products, g}) - \sum n_i\ (\text{reactants, g})$$

where $\sum n_i$ is the total molar amount of the gases in products or reactants. For nitrate and dinitroamide salts, the calculated molar enthalpy of formation was calculated from a designed Hess thermochemical cycle according to reaction (a) as follows:

$$[C_aH_bN_cO_d]\ (s) + (a + b/4 - d/2)O_2 \rightarrow aCO_2\ (g) + b/2[H_2O\ (l)] + c/2[N_2\ (g)] \quad (a)$$

$$\Delta_f H_m^\circ[C_aH_bN_cO_d,\ s] = [a\Delta_f H_m^\circ(CO_2,\ g) + b/2\Delta_f H_m^\circ(H_2O,\ l)] - \Delta_c H_m^\circ(C_aH_bN_cO_d,\ s)$$

For perchlorate salts, by using a combustion calorimetric method, both chlorine gas[16] and HCl (aq) formed.[17] We also used a similar method[16] in which only 0.5% of the chlorine was found to be present as chlorine gas. When the combustion reaction was run with water added to the sample in the calorimeter, the chloride concentration was determined by the Volhard method[18] which indicates nearly quantitative chloride ion formation during combustion. Therefore, for the perchlorate salts, the designed Hess thermochemical cycle was based on reaction b:

$$[C_eH_fN_gClO_h]\ (s) + [e + (f - 1)/4 - h/2]O_2 \rightarrow eCO_2\ (g) + (f - 1)/2H_2O\ (l) + g/2N_2\ (g) + HCl\ (g) \quad (b)$$

Using the above formula and the literature values for the standard molar enthalpies of formation of CO_2 (g) and H_2O (l) [$\Delta_f H_m^\circ(CO_2,\ g) = -393.51$ kJ/mol, $\Delta_f H_m^\circ(H_2O,\ l) = -285.83$ kJ/mol],[19,20] we determined the constant volume combustion energies and calculated heats of formation, listed in Table 1. It can be seen that some of the guanidinium salts have high constant volume combustion energies. Generally, for most compounds, the experimentally obtained combustion energies and calculated standard molar enthalpies of formation for perchlorate salts are higher than those of nitrates. The alkyl methyl iminium ($RMeN{=}^+$) derivatives exhibited higher combustion energies than the alkyl iminium ($RHN{=}^+$) salts. When compounds **3** and **15** are compared, i.e., imidazolium with triazolium derivatives with the same substituents, three of the latter compounds have higher molar enthalpies of formation. When **12** is compared with **7** where a carbon in the ring has been replaced with an oxygen atom, the molar enthalpy of formation of the nitrate became more positive while that of the perchlorate became more negative; i.e., the salts are more thermodynamically stable. In this paper, salts **3f**, **7d**, **12a**, and **19d** have relatively high molar enthalpies of formation, i.e., 656, 752, 704, and 815 kJ/mol, respectively. Well-known explosives/propellants such as RDX, TNT, and FOX-12 have $\Delta H_f = 6l.6, -74.6$, and -355 kJ/mol, respectively. Of the four salts, only **12a** falls into the ionic liquid class, i.e., melting point < 100 °C. However,

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Table 2. Crystal Data and Structure Refinement for **15d**

	15d
empirical formula	$C_6H_{13}ClN_4O_4$
fw	240.65
λ (Å)	0.71073
cryst syst, space group	orthorhombic, $P\bar{2}_1\bar{2}_1\bar{2}_1$
color, habit	colorless plate
cryst dim (mm)	0.36, 0.19, 0.06
T (°C)	86 (2)
a (Å)	12.272 (3)
b (Å)	12.454 (3)
c (Å)	13.699 (3)
V (Å^3)	2093.7 (9)
Z	8
d_{calc} (mg m^{-3})	1.527
μ (mm^{-1})	0.368
data/restraints/parameters	4104/0/280
index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
goodness of fit on F^2	1.098
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0479, wR2 = 0.0975
R indices (all data)	R1 = 0.0530, wR2 = 0.0995

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **15d**

	cation 1		cation 2
N3 C4	1.343(4)	N13 C14	1.330(4)
C4 N5	1.356(4)	C14 N15	1.342(4)
N5 C7	1.358(4)	C18 N19	1.362(4)
C7 N8	1.282(4)	N17 C18	1.290(4)
N8 N9	1.377(4)	N15 N17	1.388(4)
N9 C4	1.331(4)	N19 C14	1.362(4)
Nme$_2$ > triazole	38.7		32.9

3c, **3d**, **4b**, **8b**, **15a**, **15b**, and **15e**, all of which have positive heats of formation, are ionic liquids, and **7b** falls into the ionic liquid class.

Molecular structure. Compound **15d** crystallizes in chiral orthorhombic space group $P\bar{2}(1)\bar{2}(1)\bar{2}(1)$ (Table 2). There are two independent ion pairs in the asymmetric unit, and the solution was refined as a racemic mixture (Figure 1). When the coordinates of one cation are inverted and overlaid on the other, the weighted RMS deviation from fit is 0.0592 Å. The triazolium rings and the exocyclic NMe_2 groups are planar. This indicates that the lone pair on the exocyclic nitrogen atom is cross-conjugated with the triazolium ring. This is also reflected in the N3−C4 and N13−C14 bond lengths (Table 3) which are considerably shorter than expected and are comparable to double bond distances. The extended conjugation can also be seen in the contraction of the endocyclic bonds in both cations. Sterically the NMe_2 group cannot become coplanar with the triazolium ring due to the dimethylation of the ring. This leads to dihedral angles between the NMe_2 group and the triazolium ring ∼32−39° which are very similar to that in $[(C_2H_2CNMe)_2CNMe_2][ClO_4]$ (40.8°),[21] $[(CH_2NMe)_2CNEt_2][Me_3SiF_2]$ (30.6°),[22] and $[(CH_2N\{CH(Me)Ph\})_2CNMe_2][PF_6]$ (30.6 °).[23] The ClO_4 anions are remarkably uniform and undistorted with an average O−Cl−O angle of 109°. Nearly all the oxygen atoms are involved in weak, nonclassical hydrogen bonding with the cations with donor−acceptor distances of 3.2−3.4 Å (Figure 2).

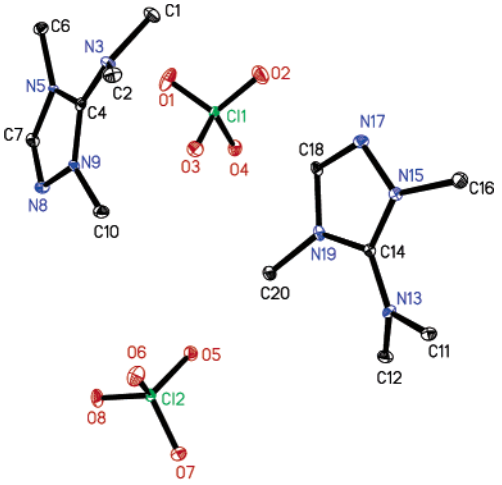

Figure 1. Thermal ellipsoid (30%) drawing of **15d**. Hydrogen atoms have been removed for clarity.

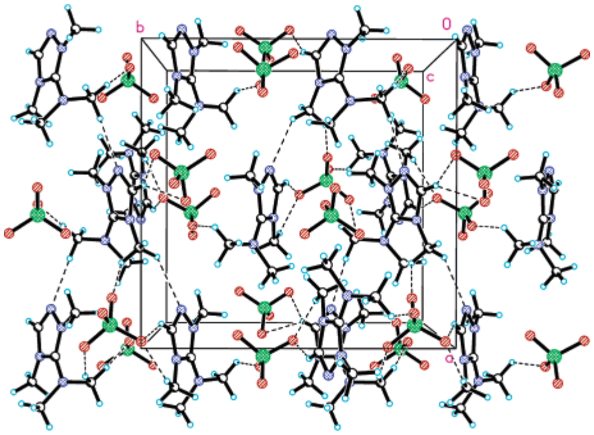

Figure 2. Packing diagram of **15d**. Dashed lines indicate hydrogen bonding.

Conclusion

Cyclic and acyclic guanidinium-based salts (**3**, **4**, **7**, **8**, **12**, **15**, **16**, and **19**) were synthesized and characterized. The structure of **15d** was confirmed by single-crystal X-ray analysis. Most of the salts exhibited low melting points of <100 °C and good thermal stabilities. They showed medium densities ranging from 1.17 to 1.49 g/cm^3. The molar enthalpies of formation were calculated from the combustion energy obtained via oxygen bomb calorimetry. Some of the guanidinium salts have high positive molar enthalpies of formation. The properties of these high-nitrogen materials make them attractive candidates for energetic materials applications.

Experimental Section

Caution: While we have experienced no difficulties with shock and friction sensitivity of these compounds with high nitrogen content and rather high heats of formation, they should be synthesized in mmole amounts and handled with extreme care.

General. ^1H, ^{13}C, and H−H COSY NMR spectra were recorded in acetone-d_6 unless otherwise indicated on a 300 MHz spectrometer

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(Bruker AMX 300) operating at 300.1, 75.5, and 300.1 MHz, respectively. ^{14}N NMR spectra were recorded on a 500 MHz spectrometer (Bruker AMX 500) operating at 36.1 MHz. Chemical shifts are reported in parts per million relative to the appropriate standard (Me_4Si for ^1H and ^{13}C NMR; $MeNO_2$ for ^{14}N NMR). J values are in hertz. T_m and T_g were determined using a differential scanning calorimeter (DSC) (TA Instruments TA10) at a scan rate of 10 °C/min. TGA (TA Instruments TA50) measurements were recorded as 5% weight loss temperature at a scan rate of 10 °C/min. IR spectra (BioRad FTS 3000 Excalibur series infrared spectrometer) were obtained using KBr plates for neat liquids and KBr pellets for solids. Densities were measured at 24 °C using a pycnometer. HRMS spectra were obtained with a JEOL JMS-AX505HA mass spectrometer (cation only). Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ, and the Shanghai Institute of Organic Chemistry.

Calorimetry Apparatus and Procedure. The heat of combustion was determined using a Parr (series 1425) semi micro oxygen bomb calorimeter. The substances were combusted in an oxygen atmosphere at a pressure of 3.04 MPa. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39i, NIST). Parr 45C10 alloy fuse wire was used. A correction of 2.3 (IT) cal per cm of wire burned was applied in all standardization and calorific value determinations. Acid corrections have been omitted for all semi micro samples. The bomb was examined for evidence of noncombusted carbon for each run. If more than a slight trace was present, the run was discarded. The dinitroamide salts burn particularly cleanly. The enthalpy of combustion was determined using the formula $\Delta_c H_m^\circ = \Delta_c U_m + \Delta nRT$, where $\Delta_c U_m$ is the constant volume combustion energy and Δn is the increase in the number of moles of gas during the reaction. The enthalpy of formation, $\Delta_f H_m^\circ$, for each of the corresponding salts was calculated at 298.15 K using designed Hess thermochemical cycles.

X-ray Crystallographic Studies. Crystals of compound **15d** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[24] Data for **15d** were collected at 86 (2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2132 frames was collected with a final resolution of 0.73 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[25] software and refined using SAINTPlus[26] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[27] The structure was solved by direct methods and refined by a least-squares method on F^5 using the SHELXTL program package. All atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in the Supporting Information.

Cyclic and acyclic pentaalkylguanidines **1**, **5**, **10**, **13**, and **17** were obtained from 1,3-dimethyl-2-imidazolidinone,1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, *N*,*N*′-dimethyl-4-oxooxadiazinane (**9**),[28] and tetramethylurea reacted with phosphorus oxychloride or oxalyl chloride to yield a chloroformamidinium salt, followed by reaction with corresponding amines by modified published methods.[7] 5-Methylamino-1,4-dimethyl-1,2,4-triazole (**13**) was prepared by using a modified literature procedure.[13] *N*,*N*′,*S*-trimethylisothiourea hydroiodide[29] (0.1 mol) and methylhydrazine (0.1 mol) in 100 mL of ethyl alcohol were refluxed for 20 h. The solvent was removed, 30 mL of formic acid added, the mixture refluxed for 30 h, and the excess formic acid removed in vacuo. Then 20 mL of water and 40 mL of 15% NaOH solution were added. The solution was extracted with 3 × 60 mL of methylene chloride and dried with Na_2SO_4, and the solvent was removed. **13** was isolated by column chromatography (alumina; hexanes−diethyl ether, 7:3) to give 5.9 g (yield 47%). The iodide salts **2**, **6**, **11**, **14**, and **18** were obtained from guanidine derivatives and corresponding alkyl iodides. The nitrate, perchlorate, and dinitroamide salts were synthesized by metathesis of the guanidinium iodide salts with silver nitrate, silver perchlorate, and ammonium dinitroamide in water (**3**, **7**, **12**, **15**, and **19**) or by reacting the guanidines with nitric acid and perchloric acid directly (**4**, **8**, and **16**).

Typically pentaalkylguanidines were prepared from 30 mmol of 1,3-dimethyl-2-imidazolidinone, which was reacted with 33 mmol of phosphorus oxychloride in 5 mL of dry toluene at 65 °C for 20 h. The mixture was cooled, and 15 mL of dry methylene chloride was added. At 0 °C, 120 mmol of *n*-$PrNH_2$ was added and the mixture was refluxed for 10 h. After the mixture had cooled to 0 °C, 20 mL of 15% NaOH solution was added, and then the solution was extracted with 3 × 40 mL of methylene chloride and dried with Na_2SO_4. The solvent was removed, and the product was isolated by column chromatography (alumina; hexanes−diethyl ether, 9:1) to give **1b**: 2.0 g, 43% yield, colorless liquid; ^1H NMR ($CDCl_3$) δ 0.94 (t, $J = 7.4$, 3H), 1.56 (dt, $J_1 = 7.4$, $J_2 = 7.2$, 2H), 2.70 (s, 3H), 2.90 (s, 3H), 3.15 (s, 4H), 3.32 (d, $J = 7.2$, 2H); ^{13}C NMR ($CDCl_3$) δ 157.9, 51.76, 50.39, 49.01, 39.28, 35.46, 27.41, 12.64.

1c: 1.4 g, 37% yield, colorless liquid. ^1H NMR ($CDCl_3$) δ 2.64 (s, 3H), 2.91 (s, 3H), 3.10 (s, 4H), 3.12 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.5, 51.74, 48.43, 39.01, 36.02, 35.09.

5a: 2.8 g, 51% yield, colorless liquid; IR (KBr) 3390, 2957, 2873, 1620, 1451, 1365, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, $J = 7.2$, 3H), 1.35 (tq, $J_1 = 7.2$, $J_2 = 7.4$, 2H), 1.48 (tt, $J_1 = 7.2$, $J_2 = 6.9$, 2H), 1.86 (tt, $J_1 = 6.3$, $J_2 = 6.3$, 2H), 2.77 (s, 6H), 3.06 (t, $J = 6.4$, 4H), 3.12 (t, $J = 6.9$, 2H); ^{13}C NMR ($CDCl_3$) δ 157.6, 49.26, 49.13, 39.34, 36.48, 21.47, 21.17, 15.00.

5b: 2.4 g, 47% yield, colorless liquid; IR (KBr) 3398, 3196, 2953, 2871, 1616, 1448, 1366, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, $J = 7.3$, 3H), 1.54 (dt, $J_1 = 7.3$, $J_2 = 6.9$, 2H), 1.83−1.92 (m, 2H), 2.80 (s, 6H), 3.10 (t, $J = 6.5$, 4H), 3.12 (t, $J = 6.9$, 2H); ^{13}C NMR ($CDCl_3$) δ 157.6, 51.47, 49.12, 39.30, 27.24, 21.18, 12.84.

17a: 2.6 g, 51% yield, colorless liquid; IR (KBr) 2926, 2868, 1624, 1494, 1454, 1363, 1142 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, $J = 7.3$, 3H), 1.35 (tq, $J_1 = 7.0$, $J_2 = 7.3$, 2H), 1.50 (tt, $J_1 = 7.0$, $J_2 = 6.8$, 2H), 2.64 (s, 6H), 2.73 (s, 6H), 3.10 (t, $J = 6.8$, 2H); ^{13}C NMR ($CDCl_3$) δ 161.0, 49.44, 40.50, 39.90, 35.36, 21.32, 14.77.

17b: 2.8 g, 60% yield, colorless liquid; IR (KBr) 2951, 2872, 1624, 1492, 1360, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, $J =$

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7.4, 3H), 1.51 (tq, $J_1 = 7.4$, $J_2 = 7.0$, 2H), 2.64 (s, 6H), 2.73 (s, 6H), 3.06 (t, $J = 7.0$, 2H); ^{13}C NMR ($CDCl_3$) δ 160.7, 52.42, 40.46, 39.63, 26.74, 12.85.

10. Compound **10** was obtained in 75% yield after being isolated using Al_2O_3 column chromatography. It was reacted with iodomethane without further purification. The resulting product, **11**, was crystallized from acetonitrile/ethyl acetate (1:1; 70% yield).

13: colorless liquid; IR (KBr) 3403, 3082, 2957, 2873, 1647, 1575, 1405, 1314, 1067, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 3H), 3.14 (s, 3H), 3.54 (s, 3H), 7.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 148.2, 136.6, 36.52 (br), 33.28, 29.66 (br).

Typical preparation of iodide salt was to dissolve 5 mmol of **1b** in 2 mL of ethyl acetate, add 6 mmol of methyl iodide, and stir at 25 °C for 24 h. The precipitate was washed with 3 × 5 mL of ethyl acetate and dried under vacuum for 24 h to give **2b**: 1.46 g, 98% yield, colorless solid; mp 91.4 °C; IR (KBr) 2962, 2876, 1624, 1566, 1459, 1412, 1304, 1157, 932 cm^{-1}; ^{1}H NMR (D_2O) δ 0.83 (t, $J = 7.4$, 3H), 1.60 (dt, $J_1 = 7.1$, $J_2 = 7.4$, 2H), 2.94 (s, 9H), 3.24 (t, $J = 7.1$, 2H), 3.64 (s, 4H); ^{13}C NMR (D_2O) δ 165.2, 54.89, 50.26, 37.89, 36.93, 21.14, 11.00.

2c: 1.33 g, 99% yield, colorless solid; mp 183.6 °C; IR (KBr) 2946, 2896, 2809, 1642, 1566, 1468, 1411, 1304, 1161, 912 cm^{-1}; ^{1}H NMR (D_2O) δ 2.92 (s, 6H), 2.96 (s, 6H), 3.61 (s, 4H); ^{13}C NMR (D_2O) δ 165.1, 50.51, 40.70, 37.02.

6a: 1.59 g, 98% yield, colorless solid; mp 52.8 °C; IR (KBr) 2956, 2933, 2871, 1597, 1571, 1455, 1410, 1321, 1252, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.3$, 3H), 1.28 (tq, $J_1 = 7.5$, $J_2 = 7.3$, 2H), 1.55 (tt, $J_1 = 7.6$, $J_2 = 7.6$, 2H), 2.12−2.23 (m, 2H), 2.97 (s, 3H), 3.07 (s, 6H), 3.13 (t, $J = 7.6$, 2H), 3.43−3.51 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 162.1, 53.51, 50.26, 42.43, 39.61, 30.75, 23.81, 20.76, 14.64.

6b: 1.51 g, 97% yield, colorless solid; mp 137.9 °C; IR (KBr) 2959, 2869, 1597, 1411, 1319, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, $J = 7.4$, 3H), 1.60 (dt, $J_1 = 7.4$, $J_2 = 7.6$, 2H), 2.11−2.19 (m, 2H), 2.94 (s, 3H), 3.06 (s, 6H), 3.08 (t, $J = 7.6$, 2H), 3.44 (t, $J = 5.7$, 2H), 3.46 (t, $J = 5.7$, 2H); ^{13}C NMR ($CDCl_3$) δ 162.1, 55.35, 50.25, 42.41, 39.52, 23.80, 22.02, 12.00.

11: 1.52 g, 97% yield, colorless solid; mp 90.1 °C; IR (KBr) 3473, 2964, 2935, 2877, 1606, 1573, 1412, 1353, 1101, 1038, 938 cm^{-1}; ^{1}H NMR (D_2O) δ 0.90 (t, $J = 7.4$, 3H), 1.69 (tq, $J_1 = 7.4$, $J_2 = 7.3$, 2H), 2.99 (s, 3H), 3.09 (s, 6H), 3.27 (t, $J = 7.3$, 2H), 4.86 (s, 4H); ^{13}C NMR (D_2O) δ 161.9, 80.88, 54.69, 38.74, 37.92, 21.32, 11.32.

14a: 1.50 g, 97% yield, colorless solid; mp 83.9 °C; IR (KBr) 3460, 3059, 2959, 1622, 1562, 1458, 1413, 1232, 1075 cm^{-1}; ^{1}H NMR (D_2O) δ 0.82 (t, $J = 7.4$, 3H), 1.24 (tq, $J_1 = 7.4$, $J_2 = 7.5$, 2H), 1.60 (tt, $J_1 = 7.5$, $J_2 = 7.4$, 2H), 3.04 (s, 3H), 3.31 (t, $J = 7.4$, 2H), 3.62 (s, 3H), 3.78 (s, 3H), 8.22 (s, 1H); ^{13}C NMR (D_2O) δ 153.3, 143.2, 53.48, 38.35, 38.00, 34.18, 30.02, 19.93, 13.87.

14b: 1.31 g, 98% yield, colorless solid; mp 151.0 °C; IR (KBr) 3464, 3009, 2959, 1635, 1566, 1406, 1465, 1242, 1067 cm^{-1}; ^{1}H NMR (D_2O) δ 3.16 (s, 6H), 3.69 (s, 3H), 3.84 (s, 3H), 8.23 (s, 1H); ^{13}C NMR (D_2O) δ 152.0, 141.7, 39.63, 37.07, 32.93.

18a: 1.53 g, 98% yield, colorless solid; mp 149.4 °C; IR (KBr) 2955, 2874, 1585, 1466, 1408, 1254, 1153, 897 cm^{-1}; ^{1}H NMR (D_2O) δ 0.89 (t, $J = 7.3$, 3H), 1.23−1.33 (m, 2H), 1.54−1.64 (m, 2H), 2.89 (s, 3H), 2.91 (s, 12H), 3.21 (t, $J = 6.7$, 2H); ^{13}C NMR (D_2O) δ 164.3, 52.79, 40.33, 38.10, 29.81, 20.28, 13.85.

18b: 1.45 g, 97% yield, colorless solid; mp 271.7 °C; IR (KBr) 2959, 2873, 1585, 1468, 1408, 1255, 1153, 899 cm^{-1}; ^{1}H NMR (D_2O) δ 0.88 (t, $J = 7.4$, 3H), 1.53−1.73 (m, 2H), 2.90 (s, 3H), 2.92 (s, 12H), 3.17 (t, $J = 7.6$, 2H); ^{13}C NMR (D_2O) δ 164.3, 54.80, 40.29, 37.96, 21.18, 11.33.

To 2 mmol of **1b** was added 0.18 g of 70% HNO_3 which was stirred for 24 h, and the water was pumped off. After the residue was washed with 3 × 2 mL of ethyl acetate, it was dried under vacuum for 24 h to give **4a**: 0.42 g, 97% yield, colorless liquid; $d = 1.24$ g cm^{-1}; IR (KBr) 3299, 2969, 2883, 1641, 1601, 1409, 1377, 1351, 1304, 1148, 957 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, $J = 7.3$, 3H), 1.71 (dt, $J_1 = 7.3$, $J_2 = 7.2$, 2H), 3.07 (s, 6H), 3.40 (dt, $J_1 = 7.3$, $J_2 = 6.0$, 2H), 3.68 (s, 4H), 7.28 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 159.9, 50.27, 47.02, 35.41, 24.40, 11.71. HRMS calcd for $C_8H_{18}N_3$: 156.1500. Found: 156.1503.

4b. This preparation is identical to that given for **4a** with the exception that 70% $HClO_4$ is used: 50 g, 98% yield, colorless liquid; $d = 1.32$ g cm^{-1}; mp 6.2 °C; IR (KBr) 3595, 3345, 2968, 2881, 2020, 1638, 1603, 1462, 1305, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.4$, 3H), 1.64 (dt, $J_1 = 7.4$, $J_2 = 7.2$, 2H), 3.00 (s, 6H), 3.33 (t, $J = 7.3$, 2H), 3.64 (s, 4H), 5.76 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 159.6, 50.20, 46.87, 35.28, 24.34, 11.71. Anal. Calcd for $C_8H_{18}N_3ClO_4$: C, 37.58; H, 7.10; N, 16.43. Found: C, 37.36; H, 6.80; N, 16.34.

4c: 0.37 g, 97% yield, colorless liquid; $d = 1.51$ g cm^{-1}; mp 3.0 °C; IR (KBr) 3312, 2955, 2901, 1648, 1600, 1408, 1378, 1302, 1160, 949 cm^{-1}; ^{1}H NMR (D_2O) δ 2.85 (s, 6H), 2.92 (s, 3H), 3.47 (s, 4H); ^{13}C NMR (D_2O) δ 160.5, 49.90, 34.37, 30.72. HRMS calcd for $C_6H_{14}N_3$: 129.1188. Found: 129.1190.

4d: 0.44 g, 97% yield, colorless solid; mp 115.8 °C; IR (KBr) 3541, 3358, 3205, 2952, 2022, 1647, 1598, 1493, 1408, 1302, 1095 cm^{-1}; ^{1}H NMR δ 3.12 (s, 6H), 3.19 (d, $J = 5.20$, 3H), 3.74 (s, 4H), 6.83 (brs, 1H); ^{13}C NMR δ 160.5, 50.18, 34.53, 31.17. Anal. Calcd for $C_6H_{14}N_3ClO_4$: C, 31.66; H, 6.20; N, 18.46. Found: C, 31.45; H, 6.21; N, 18.08.

8a: 0.44 g, 95% yield, colorless liquid; IR (KBr) 3318, 2968, 2881, 1622, 1579, 1418, 1326, 1231, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $J = 7.4$, 3H), 1.68 (tq, $J_1 = 7.4$, $J_2 = 7.3$, 2H), 2.07 (tt, $J_1 = 6.1$, $J_2 = 6.1$, 2H), 3.11 (s, 6H), 3.15 (dt, $J_1 = 3.4$, $J_2 = 7.3$, 2H), 3.33 (t, $J = 6.1$, 4H), 6.13 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 159.1, 49.42, 48.44, 40.61, 24.44, 22.61, 11.92. HRMS calcd for $C_9H_{20}N_3$: 170.1657. Found: 170.1664.

8b: 0.52 g, 96% yield, colorless liquid; T_g −70.4 °C; IR (KBr) 3358, 2965, 2880, 1621, 1576, 1454, 1323, 1231, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $J = 7.4$, 3H), 1.70 (tq, $J_1 = 7.4$, $J_2 = 7.3$, 2H), 2.07 (tt, $J_1 = 6.1$, $J_2 = 6.1$, 2H), 3.13 (s, 6H), 3.15 (dt, $J_1 = 5.8$, $J_2 = 7.3$, 2H), 3.35 (t, $J = 6.1$, 4H), 5.69 (t, $J = 5.8$, 1H); ^{13}C NMR ($CDCl_3$) δ 159.0, 49.35, 48.27, 40.68, 24.29, 22.60, 11.97. Calcd for $C_9H_{20}N_3ClO_4$: C, 40.08; H, 7.47; N, 15.58. Found: C, 39.89; H, 7.30; N, 15.61.

16a: 0.37 g, 98% yield, colorless solid; mp 139.0 °C; IR (KBr) 3423, 3172, 2968, 1658, 1591, 1458, 1378, 1338, 1172, 1068 cm^{-1}; ^{1}H NMR (CD_3CN) δ 3.29 (s, 3H), 3.67 (s, 3H), 3.89 (s, 3H), 7.96 (s, 2H); ^{13}C NMR (CD_3CN) δ 151.0, 141.2, 37.74, 33.03, 30.74. Anal. Calcd for $C_5H_{11}N_5O_3$: C, 31.75; H, 5.86; N, 37.02. Found: C, 31.79; H, 5.91; N, 37.00.

16b: 0.44 g, 97% yield, colorless solid; mp 120.4 °C; IR (KBr) 3346, 3139, 2967, 1655, 1590, 1463, 1172, 1099 cm^{-1}; ^{1}H NMR δ 3.39 (s, 3H), 3.81 (s, 3H), 3.98 (s, 3H), 6.08 (brs, 1H), 8.27 (s, 1H); ^{13}C NMR δ 150.9, 141.3, 37.52, 32.85, 30.79. Anal. Calcd for $C_5H_{11}N_4ClO_4$: C, 26.50; H, 4.89; N, 24.72. Found: C, 26.48; H, 4.98; N, 24.67.

In a metathesis reaction, 2 mmol of iodide salt **2a** in 5 mL of water was titrated with 2 mmol of silver nitrate in 3 mL of water. The AgI was filtered off, the water pumped off, and the residue dried under vacuum for 24 h to give **3a**: 0.48 g, 97% yield, colorless liquid; $d = 1.23$ g cm^{-1}; mp 7.2 °C; IR (KBr) 2958, 1624, 1566, 1462, 1351 cm^{-1}; ^{1}H NMR (D_2O) δ 0.83 (t, $J = 7.3$, 3H), 1.23

(dt, $J_1 = 7.3$, $J_2 = 7.4$, 2H), 1.55 (dd, $J_1 = 7.4$, $J_2 = 7.2$, 2H), 2.91 (s, 6H), 2.92 (s, 3H), 3.25 (t, $J = 7.1$, 2H), 3.61 (s, 4H); ^{13}C NMR (D_2O) δ 165.2, 52.91, 50.22, 37.78, 36.76, 29.78, 19.90, 13.77. HRMS calcd for $C_{10}H_{22}N_3$: 184.1814. Found: 184.1806.

3b: 0.55 g, 97% yield, colorless liquid; $d = 1.32$ g cm^{-1}; mp 28.2 °C; IR (KBr) 2959, 1624, 1567, 1464, 1413, 1307, 1090 cm^{-1}; ^{1}H NMR δ 0.93 (t, $J = 7.3$, 3H), 1.36 (dt, $J_1 = 7.3$, $J_2 = 7.5$, 2H), 1.69 (dd, $J_1 = 7.5$, $J_2 = 7.4$, 2H), 3.10 (s, 6H), 3.11 (s, 3H), 3.42 (t, $J = 7.4$, 2H), 3.83 (s, 4H); ^{13}C NMR δ 165.2, 53.09, 50.38, 37.92, 36.78, 30.29, 20.26, 14.04. Anal. Calcd for $C_{10}H_{22}N_3ClO_4$: C, 42.33; H, 7.81; N, 14.81. Found: C, 42.20; H, 7.66; N, 14.94.

3c: 0.45 g, 97% yield, colorless solid; mp 30.9 °C; IR (KBr) 3965, 1624, 1566, 1458, 1379, 1157, 1091 cm^{-1}; ^{1}H NMR (D_2O) δ 0.82 (t, $J = 7.4$, 3H), 1.58 (dt, $J_1 = 7.1$, $J_2 = 7.4$, 2H), 2.93 (s, 9H), 3.22 (t, $J = 7.1$, 2H), 3.63 (s, 4H); ^{13}C NMR (D_2O) δ 165.2, 54.85, 50.18, 37.66, 36.72, 21.08, 10.86. HRMS calcd for $C_9H_{20}N_3$: 170.1657. Found: 170.1664.

3d: 0.52 g, 96% yield, colorless solid; mp 39.2 °C; IR (KBr) 2966, 1625, 1566, 1462, 1413, 1306 cm^{-1}; ^{1}H NMR (D_2O) δ 0.87 (t, $J = 7.4$, 3H), 1.64 (dt, $J_1 = 7.1$, $J_2 = 7.4$, 2H), 2.97 (s, 9H), 3.27 (t, $J = 7.1$, 2H), 3.68 (s, 4H); ^{13}C NMR (D_2O) δ 165.2, 54.87, 50.23, 37.74, 36.79, 21.17, 10.98. Anal. Calcd for $C_9H_{20}N_3ClO_4$: C, 40.08; H, 7.47; N, 15.58. Found: C, 39.82; H, 7.58; N, 15.32.

3e: 0.40 g, 98% yield, colorless solid; mp 128.4 °C; IR (KBr) 2904, 1643, 1566, 1348, 1161, 913 cm^{-1}; ^{1}H NMR (D_2O) δ 2.94 (s, 6H), 2.97 (s, 6H), 3.62 (s, 4H); ^{13}C NMR (D_2O) δ 165.0, 50.40, 40.42, 36.74. Anal. Calcd for $C_7H_{16}N_4O_3$: C, 41.17; H, 7.90; N, 27.43. Found: C, 41.22; H, 7.82; N, 27.68.

3f: 0.46 g, 96% yield, colorless solid; mp 181.8 °C; IR (KBr) 2945, 1643, 1573, 1414, 1306, 1093 cm^{-1}; ^{1}H NMR δ 3.11 (s, 6H), 3.14 (s, 6H), 3.81 (s, 4H); ^{13}C NMR δ 165.0, 50.60, 40.64, 36.82. Anal. Calcd for $C_7H_{16}N_3ClO_4$: C, 34.79; H, 6.67; N, 17.39. Found: C, 34.61; H, 6.60; N, 17.45.

7a: 0.51 g, 98% yield, colorless liquid; mp 6.2 °C; IR (KBr) 2958, 2936, 2874, 1597, 1455, 1375, 1339, 1254, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, $J = 7.3$, 3H), 1.25 (tq, $J_1 = 7.5$, $J_2 = 7.3$, 2H), 1.50−1.55 (m, 2H), 2.03−2.14 (m, 2H), 2.88 (s, 3H), 3.01 (s, 6H), 3.08 (t, $J = 7.6$, 2H), 3.31−3.39 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 162.1, 53.19, 49.89, 41.48, 38.30, 30.64, 23.57, 20.74, 14.56. HRMS calcd for $C_{11}H_{24}N_3$: 198.1970. Found: 198.1974.

7b: 0.57 g, 96% yield, colorless solid; mp 78.0 °C; IR (KBr) 2963, 2936, 2863, 1593, 1448, 1417, 1321, 1252, 1082 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.3$, 3H), 1.30 (tq, $J_1 = 7.5$, $J_2 = 7.3$, 2H), 1.55−1.61 (m, 2H), 2.08−2.18 (m, 2H), 2.91 (s, 3H), 3.04 (s, 6H), 3.11 (t, $J = 7.6$, 2H), 3.36−3.41 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 162.1, 53.23, 49.84, 41.56, 38.37, 30.64, 23.47, 20.75, 14.62. Anal. Calcd for $C_{11}H_{24}N_3ClO_4$: C, 44.37; H, 8.12; N, 14.11. Found: C, 44.03; H, 7.93; N, 14.06.

7c: 0.48 g, 98% yield, colorless solid; mp 57.2 °C; IR (KBr) 3465, 2964, 2878, 1597, 1572, 1454, 1410, 1348, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70 (t, $J = 7.2$, 3H), 1.43 (dt, $J_1 = 7.2$, $J_2 = 7.5$, 2H), 1.88−1.97 (m, 2H), 2.72 (s, 3H), 2.86 (s, 6H), 2.90 (t, $J = 7.5$, 2H), 3.20 (t, $J = 5.8$, 4H); ^{13}C NMR ($CDCl_3$) δ 161.9, 54.90, 49.72, 41.31, 38.11, 23.46, 21.74, 11.80. HRMS calcd for $C_{10}H_{22}N_3$: 184.1814. Found: 184.1806.

7d: 0.54 g, 95% yield, colorless solid; mp 127.6 °C; IR (KBr) 2964, 2877, 1595, 1456, 1415, 1321, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.3$, 3H), 1.61 (dt, $J_1 = 7.3$, $J_2 = 7.6$, 2H), 2.06−2.15 (m, 2H), 2.88 (s, 3H), 3.01 (s, 6H), 3.06 (t, $J = 7.6$, 2H), 3.36 (t, $J = 6.2$, 4H); ^{13}C NMR ($CDCl_3$) δ 162.1, 55.05, 49.81, 41.52, 38.30, 23.46, 21.87, 11.91. Anal. Calcd for $C_{10}H_{22}N_3ClO_4$: C, 42.33; H, 7.81; N, 14.81. Found: C, 41.99; H, 7.84; N, 14.76.

12a: 0.48 g, 97% yield, colorless solid; mp 64.8 °C; IR (KBr) 2968, 2941, 2880, 1608, 1568, 1352, 1100, 1038, 938 cm^{-1}; ^{1}H NMR (D_2O) δ 0.91 (t, $J = 7.3$, 3H), 1.71 (tq, $J_1 = 7.3$, $J_2 = 7.3$, 2H), 3.01 (s, 3H), 3.10 (s, 6H), 3.28 (t, $J = 7.3$, 2H), 4.87 (s, 4H); ^{13}C NMR (D_2O) δ 161.9, 80.87, 54.68, 38.73, 37.92, 21.31, 11.32. Anal. Calcd for $C_9H_{20}N_4O_4$: C, 43.54; H, 8.12; N, 22.57. Found: C, 43.30; H, 8.04; N, 22.82.

12b: 0.55 g, 96% yield, colorless solid; mp 93.8 °C; IR (KBr) 3424, 2973, 2944, 2887, 1603, 1576, 1417, 1348, 1090 cm^{-1}; ^{1}H NMR δ 0.94 (t, $J = 7.4$, 3H), 1.74 (tq, $J_1 = 7.4$, $J_2 = 7.6$, 2H), 3.10 (s, 3H), 3.19 (s, 6H), 3.37 (t, $J = 7.6$, 2H), 4.98 (s, 4H); ^{13}C NMR δ 161.9, 80.93, 54.48, 38.46, 37.61, 21.50, 11.23. Anal. Calcd for $C_9H_{20}N_3ClO_5$: C, 37.83; H, 7.06; N, 14.71. Found: C, 37.44; H, 6.85; N, 14.67.

15a: 0.48 g, 98% yield, colorless liquid; T_g −69.4 °C; IR (KBr) 3075, 2960, 2874, 1624, 1562, 1462, 1350, 1234, 1075, 930 cm^{-1}; ^{1}H NMR (D_2O) δ 0.83 (t, $J = 7.4$, 3H), 1.24 (tq, $J_1 = 7.4$, $J_2 = 7.3$, 2H), 1.60 (tt, $J_1 = 7.3$, $J_2 = 7.4$, 2H), 3.05 (s, 3H), 3.33 (t, $J = 7.4$, 2H), 3.65 (s, 3H), 3.79 (s, 3H), 8.24 (s, 1H); ^{13}C NMR (D_2O) δ 153.5, 143.3, 53.50, 38.37, 38.01, 34.19, 30.02, 19.93, 13.88. Anal. Calcd for $C_9H_{19}N_5O_3$: C, 44.07; H, 7.81; N, 28.55. Found: C, 43.62; H, 7.57; N, 29.01.

15b: 0.54 g, 96% yield, colorless liquid; T_g −59.0 °C; IR (KBr) 3147, 3096, 2961, 2872, 1624, 1562, 1462, 1416, 1231, 1094 cm^{-1}; ^{1}H NMR δ 0.94 (t, $J = 7.3$, 3H), 1.38 (tq, $J_1 = 7.3$, $J_2 = 7.5$, 2H), 1.74 (tt, $J_1 = 7.5$, $J_2 = 7.6$, 2H), 3.24 (s, 3H), 3.52 (t, $J = 7.6$, 2H), 3.83 (s, 3H), 3.95 (s, 3H), 8.46 (s, 1H); ^{13}C NMR δ 153.4, 143.3, 53.59, 38.40, 37.97, 34.05, 30.49, 20.26, 14.15. Anal. Calcd for $C_9H_{19}N_4ClO_4$: C, 38.23; H, 6.77; N, 19.82. Found: C, 37.89; H, 6.63; N, 19.74.

15c: 0.40 g, 98% yield, colorless solid; mp 73.6 °C; IR (KBr) 3467, 3081, 2956, 1639, 1567, 1351, 1237, 1073 cm^{-1}; ^{1}H NMR (D_2O) δ 3.10 (s, 6H), 3.64 (s, 3H), 3.79 (s, 3H), 8.17 (s, 1H); ^{13}C NMR (D_2O) δ 153.2, 143.0, 40.69, 38.17, 34.01. Anal. Calcd for $C_6H_{13}N_5O_3$: C, 35.47; H, 6.45; N, 34.47. Found: C, 35.16; H, 6.43; N, 34.56.

15d: 0.47 g, 98% yield, colorless solid; mp 125.4 °C; IR (KBr) 3419, 3151, 3099, 1639, 1568, 1465, 1412, 1238, 1096 cm^{-1}; ^{1}H NMR δ 3.29 (s, 6H), 3.85 (s, 3H), 3.96 (s, 3H), 8.44 (s, 1H); ^{13}C NMR δ 153.4, 143.0, 40.97, 38.39, 34.08. Anal. Calcd for $C_6H_{13}N_4ClO_4$: C, 29.95; H, 5.45; N, 23.28. Found: C, 29.63; H, 5.51; N, 23.28.

15e. To 93 mg (0.3 mmol) of **14a** dissolved in 1 mL of water was added 38 mg (0.3 mmol) of $NH_4N(NO_2)_2$ in 1 mL of water. The mixture was stirred for 1 h at room temperature, the water pumped away, and the residue purified by a short silicon gel column by elution with ethyl acetate. The solvent was removed under vacuum to give 48 mg of light yellow oil **15e**: 55% yield; T_g −66.0 °C; IR (KBr) 3142, 2961, 2872, 1622, 1514, 1443, 1183, 1009 cm^{-1}; ^{1}H NMR δ 0.94 (t, $J = 7.3$, 3H), 1.38 (tq, $J_1 = 7.3$, $J_2 = 7.5$, 2H), 1.75 (tt, $J_1 = 7.5$, $J_2 = 7.6$, 2H), 3.27 (s, 3H), 3.55 (t, $J = 7.6$, 2H), 3.90 (s, 3H), 3.99 (s, 3H), 8.67 (s, 1H); ^{13}C NMR δ 153.7, 143.4, 53.90, 38.75, 38.39, 34.52, 30.71, 20.42, 14.22; ^{14}N NMR δ −5.12, −51.54 (br), −184.11, −219.51 (br). HRMS calcd for $C_9H_{19}N_4$: 183.1610. Found: 183.1605.

19a: 0.48 g, 97% yield, colorless solid; mp 72.2 °C; IR (KBr) 2936, 2875, 1582, 1464, 1378, 1256, 1147, 1065, 900 cm^{-1}; ^{1}H NMR (D_2O) δ 0.90 (t, $J = 7.3$, 3H), 1.22−1.35 (m, 2H), 1.53−1.65 (m, 2H), 2.90 (s, 3H), 2.92 (s, 12H), 3.22 (t, $J = 6.5$, 2H); ^{13}C NMR (D_2O) δ 164.3, 52.75, 40.19, 37.94, 29.78, 20.25, 13.78. Anal. Calcd for $C_{10}H_{24}N_4O_3$: C, 48.37; H, 9.74; N, 22.56. Found: C, 48.39; H, 9.75; N, 22.64.

19b: 0.54 g, 94% yield, colorless solid; mp 134.7 °C; IR (KBr) 2963, 2879, 1583, 1470, 1411, 1252, 1146, 1087, 893 cm^{-1}; ^{1}H NMR δ 0.95 (t, $J = 7.4$, 3H), 1.32−1.40 (m, 2H), 1.65−1.75 (m, 2H), 3.08 (s, 3H), 3.10 (s, 12H), 3.33−3.42 (m, 2H); ^{13}C NMR δ 164.5, 52.96, 40.38, 38.02, 30.19, 20.53, 13.93. Anal. Calcd for $C_{10}H_{24}N_3ClO_4$: C, 42.03; H, 8.47; N, 14.70. Found: C, 41.91; H, 7.94; N, 14.54.

19c: 0.46 g, 98% yield, colorless solid; mp 208.5 °C; IR (KBr) 2963, 2878, 1584, 1409, 1379, 1336, 1153, 899 cm^{-1}; ^{1}H NMR (D_2O) δ 0.87 (t, $J = 7.3$, 3H), 1.52−1.72 (m, 2H), 2.89 (s, 3H), 2.92 (s, 12H), 3.16 (t, $J = 7.4$, 2H); ^{13}C NMR (D_2O) δ 164.3, 54.78, 40.18, 37.85, 21.17, 11.28. Anal. Calcd for $C_9H_{22}N_4O_3$: C, 46.14; H, 9.46; N, 23.91. Found: C, 45.92; H, 9.40; N, 24.09.

19d: 0.52 g, 96% yield, colorless solid; mp 267.9 °C; IR (KBr) 2963, 2879, 1586, 1410, 1249, 1153, 1090 cm^{-1}; ^{1}H NMR (CD_3CN) δ 0.92 (t, $J = 7.4$, 3H), 1.51−1.75 (m, 2H), 2.88 (s, 3H), 2.91 (s, 12H), 3.15 (t, $J = 6.7$, 2H); ^{13}C NMR (CD_3CN) δ 164.4, 54.77, 40.39, 38.03, 21.34, 11.15. Anal. Calcd for $C_9H_{22}N_3ClO_4$: C, 39.78; H, 8.16; N, 15.46. Found: C, 39.85; H, 8.18; N, 15.47.

19e: To 94 mg (0.3 mmol) of **18a** dissolved in 0.5 mL of water was added 38 mg (0.3 mmol) of $NH_4N(NO_2)_2$ in 1 mL of water solution to form a precipitate. The precipitate was removed by filtration, washed with cold water, and dried under vacuum to give a colorless solid: 78 mg, 89% yield; mp 74.8 °C; IR (KBr) 2961, 2875, 1582, 1512, 1408, 1183, 1004 cm^{-1}; ^{1}H NMR δ 0.93 (t, $J = 7.5$, 3H), 1.30−1.38 (m, 2H), 1.62−1.72 (m, 2H), 3.04 (s, 3H), 3.06 (s, 12H), 3.29−3.34 (m, 2H); ^{13}C NMR δ 164.5, 53.01, 40.51, 38.16, 30.21, 20.55, 13.99; ^{14}N NMR δ −4.51, −49.15 (br), −298.42 (br). HRMS calcd for $C_{10}H_{24}N_3$: 186.1970. Found: 186.1980.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and isotropic displacement parameters for **15d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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