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N-Chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine and *N*,*N*-dichloro-*N*′,*N*′-bis(ethoxycarbonyl)hydrazine: synthesis, stability and reactions with nucleophiles

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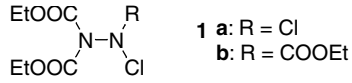
Abstract—*N*-Chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine (**1b**) was prepared in 27% yield by chlorination of *N*,*N*,*N*′-tris(ethoxycarbonyl)hydrazine anion with *t*-BuOCl. The reaction of **1b** with CN(−) gave the product of *N*-substitution. Attempts at chlorination of *N*,*N*-bis(ethoxycarbonyl)hydrazine (**2a**) with *t*-BuOCl did not yield the expected *N*,*N*-dichloro-*N*′,*N*′-bis(ethoxycarbonyl)hydrazine (**1a**), and led to the exclusive formation of ClCOOEt. The mechanism of the decomposition and the relative stability of **1a** and **1b** are assessed using DFT calculations and compared to those for the parent chlorohydrazine (**3**). © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

N-Chlorohydrazines are rare compounds and only a handful of them have been isolated as stable species.[1–3] The main reason for their observed instability is the enhanced reactivity of the N–Cl bond. This results from the $n_{N'}-\sigma_{NCl}^{*}$ interaction in which the lone pair of the N′ atom populates the antibonding N–Cl orbital, facilitating the departure of the Cl(−) anion. Thus some chlorohydrazines exist in solution as ion pairs, while many others eliminate a proton, if possible, to form imines.[1] The in-depth analysis done by Shustov et al.[1] and supported by quantum mechanical calculations,[4] led to the conclusion that stable chlorohydrazines with a covalent N–Cl bond can be obtained if the donor capabilities of the N′ nitrogen lone pair are significantly reduced either by placing a strong π acceptor or imposing conformational constraints. Also substitution at the nitrogen atom bonded to the halogen with an electron withdrawing group is predicted to increase the stability of the chlorohydrazine.

With this in mind, and in the context of our interest in new heterocycles, we designed two tetrasubstituted chlorohydrazines, **1a** and **1b**, containing ester groups and two or one chlorine atoms, respectively.



1 **a**: R = Cl
b: R = COOEt

The ester groups in **1** are intended to stabilize the chlorohydrazines by acting as π acceptors for the nitrogen lone pairs, and to provide means for further functional group transformations including deprotection of the nitrogen centers. Chlorine atoms are expected to undergo nucleophilic displacement analogous to the well documented substitution at the N-centers in *N*-chloroamides with a variety of carbon-,[5] nitrogen-,[6] sulfur-,[7–11] phosphorus-,[12] and oxygen-centered[13,14] nucleophiles. There is also a single report of nucleophilic substitution on an *N*-halohydrazine.[15] According to the report, an *N*-chloro derivative of 1,6-diazabicyclo[3.1.0]hexane-5-carboxamide reacted with the methoxide anion to give the *N*-methoxy derivative in 37% yield. However, another chlorohydrazine, *N*-chloro-2-azaquinuclidone, acts as a chlorine donor in the reaction with dimethylamine.[1]

Here we report our efforts at preparation of chlorohydrazines **1**, evaluate their thermal stabilities with the aid of DFT calculations, and investigate reactions of **1b** with several nucleophiles.

2. Results and discussion

2.1. Chlorination of *N*,*N*-bis- and *N*,*N*,*N*′-tris(ethoxycarbonyl)hydrazine

Both the di- and trisubstituted hydrazines **2a** and **2b** were

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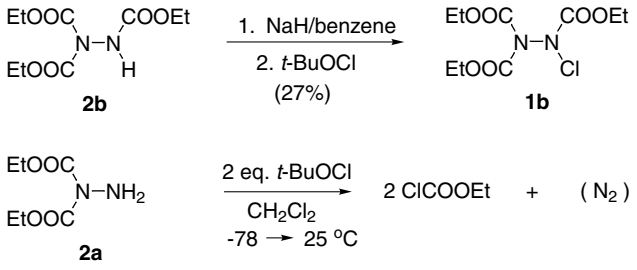


Scheme 1.

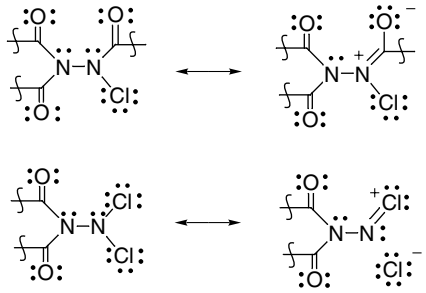


Figure 1. Selected resonance structures for **1a** and **1b**.

reacted with *t*-BuOCl under the general conditions used for preparation of *N*-chloroamides[16] and some *N*-chlorohydrazides.[1] While the disubstituted hydrazine **2a** reacted rapidly with the hypochlorite, **2b** was recovered unchanged. To increase its reactivity, **2b** was deprotonated with NaH and subsequently treated with *t*-BuOCl. The expected *N*-chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine (**1b**) was isolated in 27% yield as a stable oil (Scheme 1).

Despite the rapid reaction of *N*,*N*-bis(ethoxycarbonyl)-hydrazine (**2a**) with *t*-BuOCl, none of the desired *N*,*N*-dichloro-*N*′,*N*′-bis(ethoxycarbonyl)hydrazine (**1a**) was isolated and no residue was obtained upon removal of solvent from the reaction mixture. To investigate this unexpected result, the reaction was carried out in a NMR tube. After 10 min at −50°C, all **2a** was converted into a single compound whose ^{1}H and ^{13}C NMR spectra matched those obtained for an authentic sample of ethyl chloroformate (Scheme 1).

2.2. Stability of the chlorohydrazines

The difference in thermal stability of the two chlorohydrazines is significant. Compound **1b** is an isolable stable oil, while **1a**, presumably formed as the initial product of chlorination (vide infra), apparently decomposes rapidly to ClCOOEt and N_2 below ambient temperature. In contrast, no traces of decomposition of **1b** were detected by ^{1}H NMR analysis of a benzene solution heated at 80°C for 3 days in a sealed NMR tube.

The observed difference in stability of the two hydrazines can be rationalized in terms of a previous discussion on the subject.[1] Thus, the main factor causing instability of chlorohydrazines, the $n_{N'}-\sigma_{NCl}^{*}$ interaction, is largely eliminated in **1** since the two *geminal* carbonyl groups on N′ act as strong π acceptors for the $n_{N'}$ lone pair. The stability of the N–Cl covalent bond is enhanced further in **1b** by the presence of another carboxyl group *geminal* to chlorine and strong $n_{N}-\pi_{CO}^{*}$ interactions. Placement of a second chlorine atom in **1a** has the opposite effect. Now, through the $n_{Cl'}-\sigma_{NCl}^{*}$ interactions, the lone pair of the second chlorine populates the N–Cl antibonding orbital and activates departure of Cl(−) as shown in Fig. 1. This results in an electronegative chlorine in **1a**, while in **1b** the halogen is electropositive.

The presence of the destabilizing $n_{Cl'}-\sigma_{NCl}^{*}$ interactions suggests that the decomposition pathway for **1a** may be analogous to that of other chlorohydrazines[1,4] and involve heterolytic dissociation of the halide and the formation of an ion pair. The subsequent attack of the chloride anion on the carbonyl group leads to the formation of ethyl chloroformate and molecular nitrogen. Decomposition of **1a** through the HERON mechanism[4] is unlikely since neither diethyl azodicarboxylate nor tetrazine, the expected products, have been observed experimentally.

The above qualitative considerations are largely supported

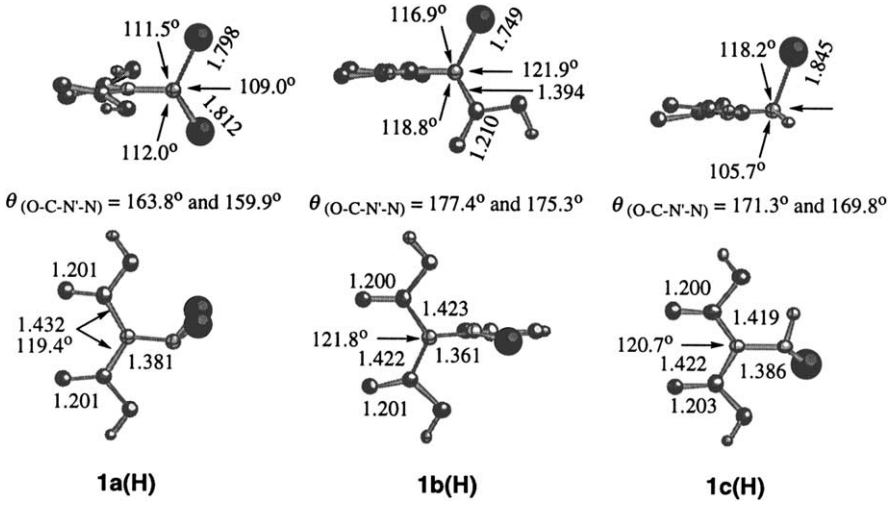
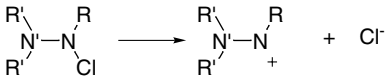


Figure 2. Ball and Stick models for DFT-optimized chlorohydrazines with selected bond lengths and angles.

Table 1. Calculated molecular parameters and gas-phase dissociation energies for selected hydrazines



Compound	R′	R	N–Cl (Å)	BO[a]	θ (deg)[b]	Q_{Cl}[c]	ΔH_{298}	ΔG_{298}
1a(H)	COOH	Cl	1.800/1.810	0.51/0.49	35	0.12/0.13	133.6	124.9
1b(H)	COOH	COOH	1.743	0.55	9.6	0.17	148.7	139.9
1c(H)	COOH	H	1.845	0.47	36	0.01	143.9	135.3
3	H	H	1.969	0.37	37	−0.18	138.8	131.1

B3LYP/6-31+G(d)//B3LYP/6-31G(d) level calculations. Energies in kcal/mol.
[a] Total of atom–atom overlap-weighted NAO bond order for chlorine atom.
[b] Pyramidalization of the nitrogen atom measured as the dihedral angle defined by N–N′–Cl–R atoms.
[c] Natural charge on chlorine atom.

by computational results for three related chlorohydrazines **1(H)**, in which the ester ethyl groups were replaced with hydrogen atoms (Fig. 2), and parent chlorohydrazine (**3**). The *syn* pseudocoplanar orientation of the two *geminal* carboxyl groups was found to be most favorable energetically in derivatives **1** and **2**. The diazenium ions derived from chlorohydrazines **1(H)** can be described as the corresponding *trans* azocarboxylic acids with a carboxyl cation coordinated to nitrogen atom lone pair.

Generally, the lone pairs of the two nitrogen atoms are orthogonal to each other, which leads to two distinct molecular subunits in **1** and **2**. The nitrogen N′ bearing two carboxyl groups is almost planar and the dihedral angle θ defined by N′–N–R′–R′ atoms, ranges from 0.0° in **2a(H)** to 4.8° in **2b(H)**. The pyramidalization of the other nitrogen atom N is significantly higher, about 36°, except for the tricarboxy derivatives **1b(H)** and **2b(H)** for which the $n_N-\pi_{CO}^*$ interactions result in low pyramidalization of about 10 and 14°, respectively. The planar structures represent low energy transition states (about 0.5 kcal/mol) for inversion at the nitrogen atom.

The variation in the pyramidalization angle can be rationalized using either electrostatic interaction arguments or the Hückel MO model. In the latter, the planar O=C–N′–C=O, O=C–N–Cl and Cl–N–Cl can be viewed as a 6π electron pentadienyl, butadiene and allyl system, respectively. The first π system is energetically favorable and expected to remain planar. In contrast, the presence of an electron pair on the antibonding orbital of butadiene and allyl destabilizes the planar structures and results in pyramidalization to avoid unfavorable π conjugation.

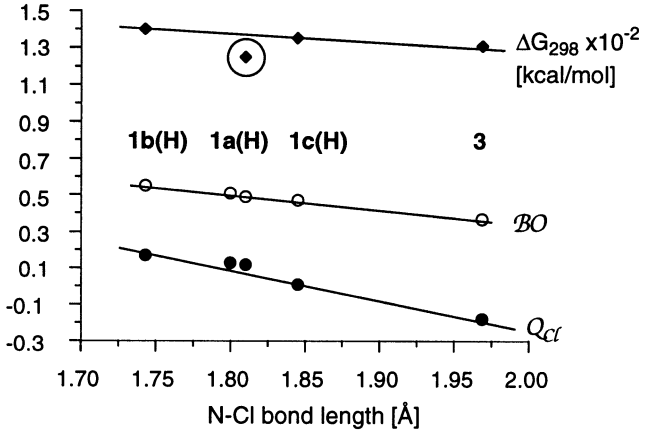


Figure 3. Correlation between the N–Cl bond length $\mathscr{L}$ and bond order BO (open circles), natural charge Q_{Cl} on Cl (full circles) and bond heterolytic dissociation energy ΔG_{298} (diamonds). The best fit functions: BO=−0.80$\mathscr{L}$+1.94 ($\mathscr{R}^2$=0.996); Q_{Cl}=−1.65$\mathscr{L}$+3.08 ($\mathscr{R}$=0.963); ΔG_{298}=−38.8$\mathscr{L}$+207.2 ($\mathscr{R}$=0.993, for three points; **1a(H)** is excluded).

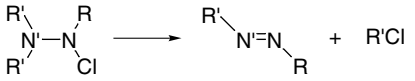
The bond lengths, bond orders and atomic charges calculated for **1(H)** are shown in Table 1. The chlorine–nitrogen distance in **1b(H)** (d_{NCl}=1.743 Å) is typical for *N*-chloroamines (e.g.[17] 1.736(3) Å) and *N*-chloroamides (e.g.[18] 1.683(3)–1.713(2) Å). This distance is longer by about 0.1 Å in **1c(H)**, and it reaches d_{NCl}=1.969 Å in chlorohydrazine (**3**) indicating a significantly weakened N–Cl bond. The increase in the bond length in the chlorohydrazines is paralleled by the proportional decrease of bond order (BO) and increase of the negative charge Q on the halogen (Table 1). Correlations in Fig. 3 show that the N–Cl bond vanishes (BO=0) at a distance of 2.43 Å, at which the chlorine carries a charge of −0.92.

The bond length also correlates well with the ability of chlorohydrazines, except for **1a(H)**, to form ion pairs in gas phase. Thus, results in Table 1 show that introduction of three carboxyl groups into chlorohydrazine (**3**) to form **1b(H)** disfavors heterolytic dissociation by about 10 kcal/mol. As a consequence, the dissociative pathway for decomposition is practically shut down, as is experimentally observed for **1b**. Results also suggest that the dicarboxyl derivative **1c** also may be sufficiently stable for isolation.

The data in Table 1 show that dichlorohydrazine **1a(H)** is exceptional. With a pyramidalized nitrogen center, a slightly elongated N–Cl bond, and a positive charge on the halogens, **1a(H)** resembles monochlorohydrazine **1c(H)** and fits well to the series of other chlorohydrazines (Fig. 3). However, dichlorohydrazine **1a(H)** has a significantly lower heterolytic dissociation energy than **1c(H)**, even lower than parent chlorohydrazine (**3**). This suggests that **1a** undergoes decomposition more readily than chlorotrialkylhydrazines, which are known to form ion pairs as the first step in decomposition in solutions.[1,4]

It can be estimated that the calculated dissociation energy is 12.3 kcal/mol lower than that expected from the correlation in Fig. 3. Since the molecular parameters of **1a(H)** fit the other three chlorohydrazines well (Fig. 3), it is likely that the difference in the dissociation energies is due to the

Table 2. Calculated gas-phase energies for elimination reactions of selected hydrazines



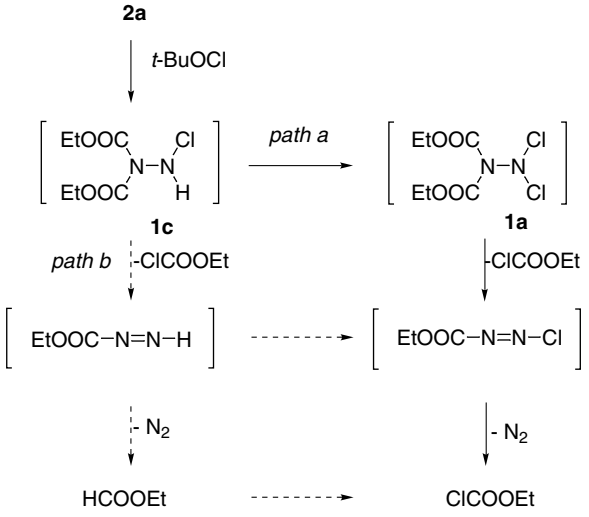
Compound	R′	R	ΔH_{298}	ΔG_{298}
1a(H)	COOH	Cl	−21.9	−35.1
1b(H)	COOH	COOH	+2.0	−12.0
1c(H)	COOH	H	+0.3	−12.6
3	H	H	−4.6	−14.1

B3LYP/6-31+G(d)//B3LYP/6-31G(d) level calculations. Energies in kcal/mol.

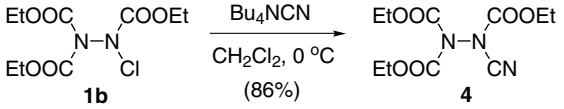
unusually high relative stability of the corresponding diazenium ion. Indeed, the $(HOOC)_2NNCl(+)$ cation is unique among the carboxyldiazenium cations. Analysis of its molecular structure shows a nearly planar HOOC–N=N–Cl fragment ($\theta_{(O-C-N-N)}$=174.1°). The natural bond order (NBO) calculations indicate that the BO of Cl–N increases from 0.51 to 0.68 upon ionization of **1a(H)**, while the BO for the C=O group in the cation is 1.35, the lowest for all carbonyl groups in the series of the diazenium cations. This suggests π conjugation and weak donor–acceptor interactions in the cation,[19] which additionally stabilizes the cation and facilitates the dissociation process.

The unusually high propensity of **1a** to form ion pairs is paralleled by the high exothermicity of the elimination reaction to form the chloride R′–Cl and azene (Table 2). While for **1b(H)**, **1c(H)** and **3** the process is almost thermoneutral, the first step in the decomposition of **1a(H)** is exothermic by almost −22 kcal/mol. The subsequent step, elimination of chloroformate from chloroazocarboxylate and formation of molecular nitrogen, is even more exothermic. Thus the total change of enthalpy is −86.5 kcal/mol which provides a significant driving force for decomposition.

The computational results in Tables 1 and 2 strongly suggest that the formation of ethyl chloroformate upon chlorination of **2a** proceeds through dichlorohydrazine **1a** (path a in Scheme 2), rather than through monochlorohydrazine **1c** (path b in Scheme 2). Both the dissociation energy and the exothermicity of the formation of the azene appear to be much more favorable for **1a** than for **1c**. Path b would also involve the formation of ethyl formate, which could undergo subsequent chlorination. This is not supported by ^{1}H NMR analysis of the reaction mixture since no signals other that those for ethyl chloroformate and *t*-butanol were detected.



Scheme 2.



Scheme 3.

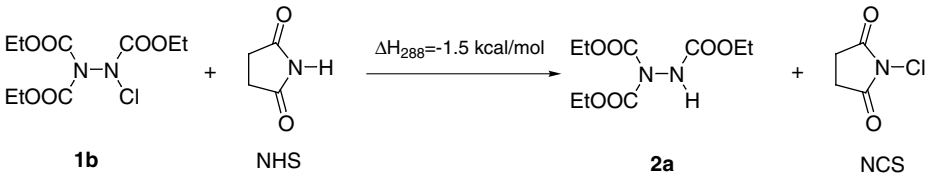
2.3. Reactions of *N*-chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)-hydrazine with nucleophiles

N-Chlorohydrazine **1b** was reacted with several typical nucleophiles. The *N*-substituted product was obtained only in a reaction with the cyanide anion (Scheme 3) which gave the *N*-cyano derivative **4** isolated in high yield. The formal substitution product **4** could be formed however, by initial chlorine transfer from **1b** to CN(−) and subsequent reaction of the resulting cyanogen chloride with the N-anion of **2b**. A similar mechanism (inverse nucleophilic substitution) was postulated for an analogous reaction of 1-chlorobenzotriazole.[20]

Reactions of **1b** with other nucleophiles gave hydrazine **2b**, a reduction product of **1b**, accompanied by various amounts of tetrakis(ethoxycarbonyl)hydrazine (**5**).[21] No *N*-substitution products were observed. For instance, a reaction of **1b** with *n*-C_3H_7SH in Et_3N/benzene, conducted according to a literature procedure,[9] and 4-$CH_3C_6H_4S^-Me_4N^+$ in MeCN led to the formation of the corresponding disulfides in quantitative yields and a mixture of **2b** and **5**. In the former case **2b** was isolated in 67%, while the reaction with the thiocresolate salt gave **2b** and **5** in 1:9 ratio, according to GC–MS. A similar mixture of hydrazine tri- and tetraesters, **2b** and **5**, was also obtained from the reaction of **1b** with the acetate anion, an oxygen-centered nucleophile, used for the preparation of an *N*-acetoxy urea.[13] The reaction of **1b** with morpholine led to the predominant formation of *N*,*N*,*N*′-tris(ethoxycarbonyl)hydrazine (**2b**), isolated in 60% yield, accompanied by about 30% of unidentified product derived from **1b**.[22]

Reaction of **1b** with ethanol in the presence of equimolar amount of AgOTf also resulted in the formation of the hydrazine **2b** as the sole product.

These results demonstrate that *N*-chloro-*N*,*N*′,*N*′-tris-(ethoxycarbonyl)hydrazine (**1b**) is a powerful donor of electrophilic chlorine. The DFT calculations show significant positive charge density on the chlorine atom in **1b(H)** (+0.17) which is very similar to that calculated for NCS. Further analysis of computational results shows that chlorohydrazine **1b(H)** is a more potent donor of Cl^+ than NCS



Scheme 4.

since the chlorination of succinimide (NHS) with **1b(H)** is moderately exothermic (Scheme 4).

3. Conclusions

Chlorination of two ethoxycarbonylhydrazines, **2a** and **2b**, gave an exceptionally stable chlorohydrazine **1b** and a particularly unstable dichlorohydrazine **1a** postulated as a transient species. The presence of the carbonyl groups generally stabilizes the covalent N–Cl bond in chlorohydrazines through $n_N-\pi_{CO}^*$ interactions, which effectively compete with the detrimental $n_{N'}-\sigma_{NCl}^*$ interactions. In contrast, the presence of a *geminal* halogen has a strong destabilizing effect on the N–Cl bond in **1a**, which appears to be less stable to heterolytic dissociation than the parent chlorohydrazine (**3**). The results of DFT calculations suggest that the instability of **1a** is related to the relatively high stability of the corresponding diazenium ion rather than to the destabilizing $n_{Cl'}-\sigma_{NCl}^*$ interactions.

The experimental and computational results suggest that the two *geminal* carbonyl groups are sufficient to stabilize chlorohydrazines against dissociative decomposition pathways. Thus, some *N*-alkyl derivatives of **1c** may be sufficiently stable for isolation, which would significantly expand the small number of known halohydrazines. In addition, the chlorine atom in such *N*-alkyl-*N*-chloro derivatives should be less electropositive than that in **1b** and should more readily undergo nucleophilic displacement giving a variety of N-substituted hydrazines and heterocycles.

4. Computational details

Quantum-mechanical calculations were carried out at the B3LYP/6-31G(d) level of theory using the Linda–Gaussian 98 package[23] on a Beowulf cluster of 16 processors. Geometry optimizations were undertaken without symmetry constraints, except for NCS and NHS, and default convergence limits. Global conformational minima for **1**, **2** and the ions were located at the B3LYP/3-21G(d) and subsequently on the B3LYP/6-31G(d) level of theory by systematic changes of orientation for the COOH groups. Vibrational frequencies were used to characterize the nature of the stationary points and to obtain thermodynamic parameters. Zero-point energy (ZPE) corrections were scaled by 0.9806.[24] Following general recommendations,[25] dissociation energies of chlorohydrazines were derived as the differences of SCF energies of individual species computed using the diffuse function-augmented 6-31+G(d) basis set at the geometries obtained with the 6-31G(d) basis set (single point calculations). Thermodynamic corrections were obtained using the 6-31G(d) basis set. Atom–atom overlap-weighted NAO bond order and natural atomic charges were calculated using the NBO method in Gaussian 98.[26]

5. Experimental

5.1. General

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, on Bruker instruments in $CDCl_3$ and referenced to the solvent unless specified otherwise. IR spectra were recorded using an ATI Mattson Genesis FT-IR by deposition of a thin film onto sodium chloride disks. HRMS analysis was performed at the Mass Spectrometry facilities of the University of Notre Dame. Elemental analysis was provided by Atlantic Microlab in Norcross, GA. Liquid chromatography separations were carried out on Silica Gel 60 (230–400 mesh). Bu_4NCN was purchased from Fluka.

5.1.1. *N*-Chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine (1b). *N*,*N*,*N*′-tris(ethoxycarbonyl)hydrazine (**2b**, 400 mg, 1.61 mmol) was dissolved in dry benzene (5 mL) and added to a stirred suspension of NaH (50 mg, 1.93 mmol) in dry benzene (2 mL). The mixture was cooled to 5°C and *t*-BuOCl (170 mg, 1.61 mmol, 170 μL) was added. Stirring continued for 1 h at 5°C, followed by 24 h at ambient temperature. The mixture was washed with water and dried (Na_2SO_4). Solvent was removed and the residue was separated on a silica gel column (eluent: CH_2Cl_2). Evaporation of the solvent gave 120 mg (27% yield) of a colorless oil: ^{1}H NMR δ 1.32 (t, J=7.1 Hz, 3H), 1.37 (t, J=7.1 Hz, 6H), 4.27 (q, J=7.1 Hz, 2H), 4.35 (q, J=7.2 Hz, 4H); ^{13}C NMR δ 14.0, 14.2, 64.7, 65.4, 150.3; IR ν_{max} 1776 cm^{-1}. Anal. Calcd for $C_9H_{15}ClN_2O_6$: C, 38.24; H, 5.35; N, 9.91. Found: C, 38.77; H, 5.40; N, 10.03.

5.1.2. *N*,*N*-Bis(ethoxycarbonyl)hydrazine (2a).[27] The hydrazine was obtained according to a general literature procedure in 88% yield.[27,28] ^{1}H NMR[29] (CD_2Cl_2) δ 1.31 (t, J=7.1 Hz, 6H), 4.25 (q, J=7.1 Hz, 4H), 4.30 (bs, 2H); (C_6D_6) δ 0.99 (t, J=7.1 Hz, 6H), 4.00 (q, J=7.1 Hz, 4H), 4.00 (bs, 2H); ^{13}C NMR (C_6D_6) δ 14.2, 63.2, 154.1; MS *m*/*e* 176 (M, 10), 76 (100).

5.1.3. *N*,*N*′,*N*′-Tris(ethoxycarbonyl)hydrazine (2b).[27] The hydrazine was obtained according to literature procedure[27] in 69% yield starting from **2a**. Alternatively, triester **2b** was prepared in 30% yield by ethoxycarbonylation of *N*,*N*′-bis(ethoxycarbonyl)hydrazine sodium salt (NaH) with ClCOOEt in THF, followed by chromatographic separation (eluent: CH_2Cl_2 followed by MeCN) of the

resulting mixture of starting material, byproduct **5** and product **2b**: ^{1}H NMR[29] δ 1.26 (t, J=7.1 Hz, 3H), 1.30 (t, J=7.1 Hz, 6H), 4.19 (q, J=7.0 Hz, 2H), 4.28 (q, J=7.1 Hz, 4H), 7.04 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.3, 62.4, 64.1, 152.2, 155.2; MS *m/e* 249 (M+1, 1), 59 (100).

5.1.4. *N*-Cyano-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine (4). *N*-Chloro-*N*,*N*′,*N*′-tris(ethoxycarbonyl)hydrazine (**1b**, 40 mg, 0.13 mmol) was dissolved in methylene chloride (2 mL) and the solution cooled to 0°C. Bu_4NCN (40 mg, 0.13 mmol) in methylene chloride (1 mL) was added dropwise and the stirring continued at the same temperature for 0.5 h, followed by 2 h at ambient temperature. The mixture was then washed with water, dried (Na_2SO_4) and passed through a short silica gel pad. The solvent was removed and the residue was separated on a silica gel column (eluent: CH_2Cl_2). Removal of the solvent gave 30 mg (86% yield) of the product as a colorless oil: ^{1}H NMR δ 1.32 (t, J=7.1 Hz, 3H), 1.38 (t, J=7.1 Hz, 6H), 4.32 (q, J=7.1 Hz, 2H), 4.39 (q, J=7.1 Hz, 4H); ^{13}C NMR δ 14.0, 64.2, 65.4, 66.6, 106.0, 149.4, 150.6; IR ν_{max} 2252, 1790 cm^{-1}. HRMS (FAB$^+$) *m/e* Calcd for $C_{10}H_{16}N_3O_6$: 274.1039. Found: 274.1026.

5.1.5. Tetrakis(ethoxycarbonyl)hydrazine (5).[27] ^{1}H NMR[30] δ 1.31 (t, J=7.1 Hz, 12H), 4.31 (q, J=7.1 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 14.0, 64.2, 150.5; MS *m/e* 321 ((M+1)$^+$, 3), 176 (100).

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