Relative Reactivity and Structures of Benzoyltrimethylhydrazine and 1-Benzoyl-2-methylpyrazolidine

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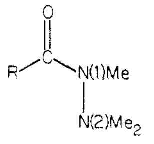
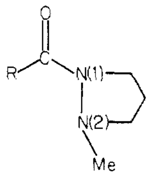
Benzoyltrimethylhydrazine (**1a**) exhibits a less nucleophilic and less basic N(2) compared with N(2) of 1-benzoyl-2-methylpyrazolidine (**2a**). The X-ray crystallographic analyses of **1a** and **2a** suggest that the reactivity differences are a consequence of the larger N(1)–N(2) lone pair–lone pair torsional angle and the greater distortion from planarity at N(1) in **2a**, as compared with those in **1a**. The configuration of **1a**, **2a** and related 1,2,2-trisubstituted hydrazines about the amide bond is *E*, as evidenced by X-ray and ^1H NMR studies. In support of the configurational results, ab initio molecular orbital calculations show that N-unsubstituted hydrazides should preferentially adopt the *Z* configuration, while fully N-substituted hydrazides should adopt the *E* form. Compound **1a** readily forms a one-to-one complex with copper(II) chloride (**7**), whose X-ray structure shows a chelating hydrazide in the *Z* configuration.

While investigating transformations of 1,2,2-trisubstituted hydrazides,[2] we observed several interesting reactivity differences between acyl derivatives of trimethylhydrazine and those of 1-methylpyrazolidine (**1** and **2**, respectively). In this paper, we detail these differences, account for them using structural information from X-ray crystallography, and examine the preferred configuration (*E* or *Z*) about the amide bond in hydrazides using ab initio molecular orbital calculations.



1a, R = Ph
b, R = *n*-C_7H_{15}



2a, R = Ph
b, R = *n*-C_7H_{15}

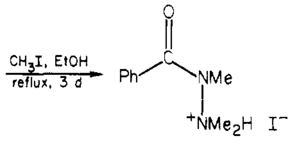
Results

When subjected to standard conditions for N(2) quaternization[3,4] (iodomethane in alcohol solution), benzoyltrimethylhydrazine (**1a**) formed its hydroiodide (**3**) instead (eq 1). 1-Benzoyl-2-methylpyrazolidine (**2a**) alkylated smoothly (**2a** → **4**, eq 2), as did 1-benzoyl-2,2-dimethylhydrazine (**5** → **6**,[4] eq 3). The same reactivity difference was observed for the corresponding octanoic acid hydrazides (**1b** and **2b**).[5]

The difference in nucleophilicity of **1a** relative to that of **2a** and **5** might be attributable to greater steric hindrance about N(2) of **1a**, although the course of reaction is responding to what appear to be minor variations in structure.

In contrast to alkylation, ease of protonation at N(2) should not be affected to any large extent by steric hindrance. Accordingly, the pK_a's of **1a**, **2a**, and benzoylhydrazine were measured in aqueous solution at 23 °C by titrating the hydrazide with hydrochloric acid. The results are shown in Table I. The cyclic hydrazide **2a** is more than 1 order of magnitude more basic than its acyclic counterpart **1a**.[6]

1a



(1)

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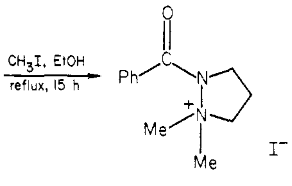
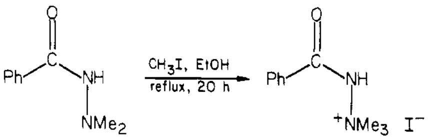
2a



(2)

4



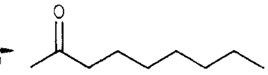
(3)

5 **6**

The reactivities of 1,2,2-trisubstituted hydrazides at the carbonyl group also show a dependence on structure. Treatment of **1b** with methyllithium in tetrahydrofuran (THF) solution at room temperature (eq 4) gave only recovered starting material. It was necessary to use a THF/hexamethylphosphoramide mixture to enable nucleophilic attack to occur. By comparison, **2b** reacted with methyllithium in THF solution within several minutes at −78 °C to give 2-nonanone in high yield (eq 5).

$$\mathbf{1b} \xrightarrow[25\ °C]{CH_3Li,\ THF} \text{no reaction} \qquad (4)$$

2b



(5)

Examination of **1** and **2** by infrared and ^{13}C NMR spectroscopy (Table II) does not indicate that the cyclic hydrazides **2** should have the more electrophilic carbonyl group. Rather, the spectral evidence is that the compounds should be similar in electronic structure, with **1a** and **1b** showing slightly higher carbonyl stretching frequencies and

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[1] Henry Rutgers Undergraduate Scholar, 1979–1980.

[2] 1,2,2-Trisubstituted hydrazides of acrylic acid undergo conjugate addition by alkyllithium reagents. S. Knapp and J. Calienni, *Synth. Commun.*, 10, 837 (1980).

[3] For a review of the chemistry of hydrazides see H. Paulsen and D. Stoye, "The Chemistry of Amides", J. Zabicky, Ed., Interscience, New York, 1970, p 515–600.

[4] J. C. Craig, J. L. Garnett, and D. M. Temple, *J. Chem. Soc.*, 4057 (1964).

[5] Alkylation of **1b** at N(2) did not occur under any of several other conditions: (a) iodomethane, 100 °C; (b) iodomethane, dimethylformamide, 100 °C; (c) trimethyloxonium tetrafluoroborate, dichloromethane; (d) dimethyl sulfate, 100 °C.

[6] For a discussion of hydrazide basicity see: (a) ref 3, p 547; (b) P. J. Kreuger, "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", Part 1, S. Patai, Ed., Wiley, New York, 1975, pp 162, 165.

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Table I. pK_a's of Benzoylhydrazines[a]

compd	pK_a	ref
1a·HCl	1.60 (5)[b]	this work
2a·HCl	2.75 (2)	this work
$PhCONHNH_2 \cdot HCl$	2.97 (3)	this work
$PhCONHNH_2 \cdot HCl$	3.03	c
$PhCONHNH_2 \cdot HCl$	3.31	d

[a] pK_a of conjugate acid in aqueous solution at 23 °C. See Experimental Section for details. [b] Value in parentheses is the logarithm of the standard deviation in K_a times 100. [c] E. V. Titov, N. G. Korzhenevskaya, and V. I. Rybachenko, *Ukr. Khim. Zh.* (*Russ. Ed.*), **34**, 1253 (1968); *Chem. Abstr.*, **70**, 109624 (1969). [d] H. Stroh and H. Tengier, *Chem. Ber.*, **101**, 751 (1968).

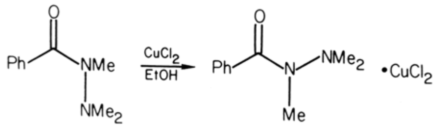
Table II. Spectral Properties of 1,2,2-Trisubstituted Hydrazides

compd	ν_{max} (C=O),[a] cm^{-1}	^{13}C NMR[b] (carbonyl C), δ
1a	1650	172.3
2a	1630	168.5
1b	1659	176.0
2b	1655	173.6

[a] Infrared spectra were obtained by using 0.04 M carbon tetrachloride solutions. [b] Carbonyl carbon chemical shifts are given in parts per million downfield from tetramethylsilane in deuteriochloroform solution.

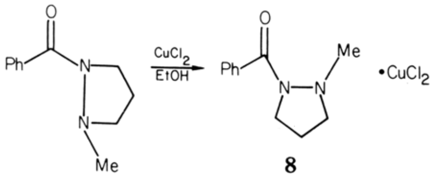
more deshielded carbonyl carbons than their respective analogues **2a** and **2b**.

The configuration about the amide [C(7)–N(1)] bond[7] of **1** and **2** was also of interest, since this aspect could contribute to the reactivity differences described above. All four hydrazides (**1a**,**b**, **2a**,**b**) show only one configurational isomer by ^1H NMR at 25 or −57 °C in deuteriochloroform solution or at 25 °C in carbon tetrachloride or methanol-d_4. Aromatic solvent induced shift (ASIS) experiments[8] (see Experimental Section) suggest that this is the *E* isomer in each case.[9] Compounds **1a** and **2a** react rapidly at room temperature with ethanolic copper(II) chloride (eq 6 and 7) to give the one-to-one copper complexes **7** and **8**. The hydrazide ligand in such a complex is assumed to have the *Z* configuration.[10] Attempts to liberate the *Z* isomer of **1a** from **7** by rapid aqueous extraction of copper(II)[11] or by precipitation of copper(II)



(6)

1a **7**



(7)

2a **8**

$$7 \xrightarrow[\text{or 2,2}'\text{-bipyridyl}]{\text{aqueous NH}_4\text{Cl}} 1a \qquad (8)$$

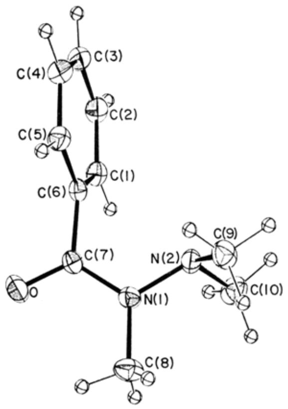


Figure 1. Computer-assisted (ORTEP) view showing the atom numbering scheme for benzoyltrimethylhydrazine (**1a**).

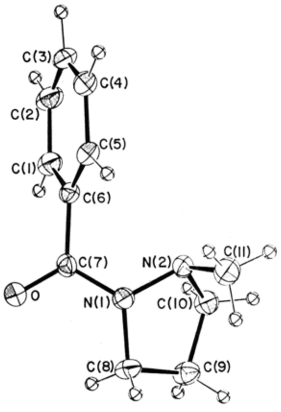


Figure 2. Computer-assisted (ORTEP) view showing the atom numbering scheme for 1-benzoyl-2-methylpyrazolidine (**2a**).

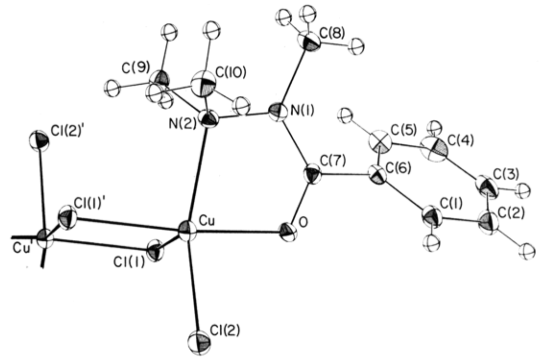


Figure 3. Computer-assisted (ORTEP) view showing the atom numbering scheme for di-μ-chloro-bis[chloro(benzoyltrimethylhydrazino)copper(II)] (**7**).

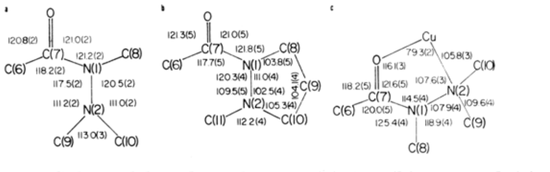


Figure 4. Selected bond angles for (a) **1a**, (b) **2a**, and (c) **7**.

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[7] For a discussion of the configurational properties of the amide bond, see M. B. Robin, F. A. Bovey, and H. Basch, "The Chemistry of Amides", J. Zabicky, Ed., Interscience, New York, 1970, p 27–34.

[8] Upon addition of benzene-d_6 to a deuteriochloroform solution of an amide, the protons of the group located trans to the carbonyl oxygen are shifted farther upfield in the ^1H NMR spectrum than are those of the group located cis. A. H. Lewin and M. Frucht, *Org. Magn. Reson.*, **7**, 206 (1975).

[9] The evidence is suggestive rather than conclusive, since the other configurational isomer is not present for comparison. However, the ASIS results are compatible with those of several model amides such as dimethylacetamide and dimethylbenzamide[8] and with both configurational isomers of 1-acetyl-2,2-dimethylhydrazine.

[10] (a). J. F. Alcock, R. J. Baker, and A. A. Diamantis, *Aust. J. Chem.*, **25**, 289 (1972); (b) M. F. Iskander, S. E. Zayan, M. A. Khalifa, and L. El-Sayed, *J. Inorg. Nucl. Chem.*, **36**, 551 (1974); (c) Y. Y. Kharitonov, R. I. Machkhoshvili, P. V. Gogoroshvili, and M. V. Karkarashvili, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **17**, 546 (1972).

Table III. Bond Distances (Å) and Angles (deg)

atoms[a]	1a	2a	7
	Distances		
C(1)-C(2)	1.382 (4)	1.379 (9)	1.399 (8)
C(1)-C(6)	1.390 (4)	1.393 (8)	1.383 (8)
C(2)-C(3)	1.373 (5)	1.324 (12)	1.381 (9)
C(3)-C(4)	1.380 (5)	1.387 (11)	1.376 (10)
C(4)-C(5)	1.379 (4)	1.404 (10)	1.385 (9)
C(5)-C(6)	1.380 (4)	1.368 (7)	1.386 (8)
C(6)-C(7)	1.495 (4)	1.485 (7)	1.490 (7)
C(7)-O	1.229 (3)	1.220 (6)	1.249 (6)
C(7)-N(1)	1.343 (4)	1.359 (6)	1.353 (7)
N(1)-N(2)	1.416 (3)	1.418 (6)	1.441 (6)
N(1)-C(8)	1.460 (4)	1.481 (6)	1.460 (7)
N(2)-C(10)	1.459 (4)	1.466 (7)	1.498 (7)
N(2)-C(11)		1.443 (9)	
C(8)-C(9)		1.515 (8)	
C(9)-C(10)		1.551 (9)	
N(2)-C(9)	1.460 (4)		1.500 (7)
Cu-O			1.974 (3)
Cu-N(2)			2.122 (4)
Cu-Cl(1)			2.735 (2)
Cu-Cl(1′)			2.258 (2)
Cu-Cl(2)			2.232 (2)
Cu···Cu′			3.631 (3)
	Angles		
C(1)-C(2)-C(3)	120.5 (3)	122.6 (8)	120.0 (6)
C(2)-C(3)-C(4)	119.7 (3)	119.6 (7)	119.7 (6)
C(3)-C(4)-C(5)	120.0 (3)	119.2 (6)	120.6 (6)
C(4)-C(5)-C(6)	120.9 (3)	120.4 (6)	120.2 (6)
C(5)-C(6)-C(1)	118.9 (3)	118.9 (5)	119.5 (5)
C(6)-C(1)-C(2)	120.1 (3)	119.2 (6)	120.0 (6)
C(1)-C(6)-C(7)	121.9 (2)	117.8 (5)	118.5 (5)
C(5)-C(6)-C(7)	119.1 (2)	123.2 (6)	121.6 (5)
N(1)-N(2)-C(10)	111.0 (2)	102.5 (4)	111.6 (4)
Cu-N(2)-C(9)			114.4 (3)
O-Cu-Cl(1)			88.96 (12)
O-Cu-Cl(1′)			172.61 (13)
O-Cu-Cl(2)			90.82 (11)
N(2)-Cu-Cl(1)			98.10 (12)
N(2)-Cu-Cl(1′)			94.98 (12)
N(2)-Cu-Cl(2)			151.23 (12)
Cl(1)-Cu-Cl(1′)			87.17 (5)
Cl(1)-Cu-Cl(2)			108.78 (5)
Cl(1′)-Cu-Cl(2)			96.38 (5)
Cu-Cl(1)-Cu′			92.83 (5)

[a] Primed atoms are related to unprimed atoms by a center of symmetry at the origin.

as its 2,2′-bipyridyl complex led only to the recovery of **1a** having the original NMR spectrum (eq 8). Presumably this is the *E* isomer, which is restored by rapid isomerization of the *Z* isomer under these conditions.

The factors controlling the reactivity differences between **1** and **2** are apparently subtle and not readily identified from the infrared and ^{13}C NMR spectra. Therefore **1a** and **2a** were subjected to X-ray crystallographic analysis to determine if there is a structural basis for the greater reactivity of the cyclic hydrazides **2**. The copper complex **7** was also studied to verify the postulated configurational changes about the amide bond of **1a**.

Crystallography. The crystal structures of **1a**, **2a**, and **7** have been determined (see Experimental Section for details). Figures 1–3 show ORTEP views of the molecules and give the numbering schemes of the atoms. Bond distances and angles are listed in Table III except for angles associated with the N—N—C=O fragments which are displayed in Figure 4.

Both **1a** and **2a** appear as discrete molecules in the crystalline state with no interactions stronger than those arising from van der Waals forces suggested by intermolecular contacts. In each structure, the C(6)–C(7)–O–N(1) amide-type fragment is planar to within ±0.01 Å. For **1a**, N(2) is 0.177 Å removed from this plane, while for **2a**, the deviation (0.337 Å) is substantially larger. The phenyl groups are essentially planar and, as suggested by the phenyl/CC(=O)N dihedral angles (70.9° and 64.8° for **1a** and **2a**, respectively), appear to be only weakly conjugated to the CC(=O)N fragments. In both structures, the configuration is *E* about the N(1)–C(7) amide bond.

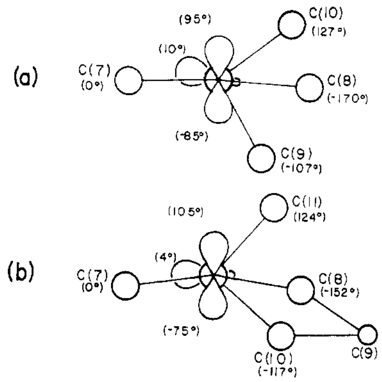

Figure 5. Newman projections along the N(1)–N(2) bonds showing torsional angles [measured clockwise from C(7)] and probable positions of nitrogen lone pairs for (a) **1a** and (b) **2a**.

The five-membered ring of **2a** constrains the N(2)–N(1)–C(8) angle to 111.0 (4)° as compared with 120.5 (2)° for **1a**. Nitrogen 1 of **2a** is thereby *significantly distorted from planar* (*sp*^{2}) *hybridization.* This is displayed graphically in Figure 5, which shows Newman projections down the N(1)–N(2) axes. From Figure 5, one may derive nitrogen lone pair–lone pair angles of 85° (**1a**) and 101° (**2a**), if it is assumed that the nitrogen lone pair orbitals bisect the appropriate torsional angles.[12] Finally, the deviation from planarity at N(1) in **2a** is accompanied by small changes in bond lengths within the C(=O)—N—N fragments. By use of the 2σ criterion, the N(1)—C(7) length in **2a** [1.359 (4) Å] is significantly longer than that in **1a** [1.343 (6) Å], while the C=O and N—N bond distances are equivalent within experimental error. These distances are all similar to those reported for other hydrazides.[13,14]

Compound **7** crystallizes as discrete $(CuLCl_2)_2$ (L = benzoyltrimethylhydrazide) dimers with point symmetry C_i. Each Cu(II) ion is five-coordinate and is bound to two bridging chloride ions [Cl(1), Cl(1′)], a terminal chloride ion [Cl(2)], and a bidentate hydrazide ligand. The coordination geometry is reminiscent of that reported for $[Cu(BuSCH_2CH_2SBu)Cl_2]_2$[15] (**9**) and for $[Cu(CH_3)_2NCH_2CH_2N(CH_3)_2Cl_2]_2$[16] (**10**) and may be described either as square pyramidal with Cl(1) apically bound to a pseudoplanar Cu–O–Cl(2)–Cl(1′)–N(2) fragment or as trigonal

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[11] H. S. Gutowsky, J. Jonas, and T. H. Siddall, *J. Am. Chem. Soc.*, **89**, 4300 (1967).

[12] Y. Shvo, "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", Part 2, S. Patai, Ed., Wiley, New York, 1975, p 1019.

[13] For a discussion of hydrazide structural features see ref 3, p 518.

[14] Recent hydrazide structures: (a) *N*-benzyl-β-(N^2-isonicotinoylhydrazino)propionamide hydrochloride, J. L. de Lerma, S. Garcia-Blanco, J. Fayos, and J. G. Rodriguez, *Acta Crystallogr.*, **B33**, 2311 (1977); (b) malonic dihydrazide, C. Miravitlles, J. L. Brianso, F. Plana, and M. Font-Altaba, *Cryst. Struct. Commun.*, **4**, 81 (1975); (c) *N*-picolinylidene-*N*′-salicyloylhydrazine, P. Domiano, A. Musatti, C. Pelizzi, and G. Predieri, *ibid.*, **3**, 531 (1974); (d) cyanoacetohydrazide, P. C. Chieh, *J. Chem. Soc., Perkin Trans. 2*, 1825 (1973); (e) bis(*N*-benzoylhydrazine)copper(II) pentachlorotricuprate(I), R. J. Baker, S. C. Nyburg, and J. T. Szymanski, *Inorg. Chem.*, **10**, 138 (1971).

[15] B. Cohen, C.-C. Ou, R. A. Lalancette, W. Borowski, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, **18**, 217 (1979).

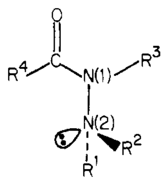
[16] E. D. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 106 (1975).

bipyramidal with O and Cl(1′) apical. As with the bidentate thioether complex **9**, analysis[15] of the bond angles with Cu as vertex does not permit an unambiguous choice between these alternatives, although angular deviations from ideal values are slightly smaller for the square-pyramidal model. The Cu–Cl(1′) and Cu–Cl(2) distances are within ±0.02 Å of those reported for **9** and **10**, while the longer bridging Cu–Cl distance in **7** [2.735 (2) Å] is substantially shorter than corresponding values reported for **9** [2.825 (2) Å] and **10** [3.147 (3) Å]. This shortening is reflected in the Cu···Cu separation [3.631 (3) Å] and Cu–Cl–Cu bridging angle [92.83 (5)°], both of which are significantly smaller than those reported for **9** and **10**. The Cu–N(2) distance is about 0.1 Å longer than the value reported[14e] [2.009 (19) Å] for bis(benzoylhydrazine)copper(II) pentachlorocuprate, which contains tetragonal copper bound to two unsubstituted hydrazine ligands and more nearly resembles the values obtained [2.054 (4), 2.081 (3) Å] for the tertiary amine Cu(II) complex **10**.

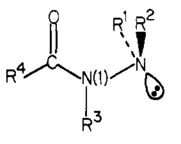
In the ligand, the CC(=O)N fragment is planar to within 0.02 Å, while the configuration about the N(1)–C(7) amide bond is *Z*, as expected. Although the differences are small, both the C(7)–O and N(1)–N(2) distances in **7** are significantly longer than those in the free ligand **1a**, presumably as a result of coordination to the metal.

The *E* configurations observed for **1a** and **2a** are unprecedented, and this led us to undertake a theoretical examination of the relative stabilities of the *E* and *Z* configurations for simple N-substituted hydrazides.

Calculations. Ab initio calculations were performed on formhydrazide (**11a**; $R^1 = R^2 = R^3 = R^4 = H$) and



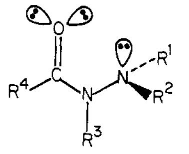
(*E*)-**11**



(*Z*)-**11**

various N-substituted hydrazides (see Experimental Section for details). The optimized bond lengths and angles in the *E* and *Z* (in parentheses) forms of **11a** are similar: $R_{C=O} = 1.223$ Å (1.223), $R_{CN} = 1.412$ (1.413) Å, $R_{NN} = 1.421$ (1.422) Å, ∠CN(1)N(2) = 122.1° (120.2°), ∠HN(2)H = 106.0° (106.9°), and ∠HN(2)N(1) = 108.3° (109.4°). Where comparisons can be made, the agreement generally is good between the calculated structure (*E*)-**11** and the structure of **1a** determined by X-ray crystallography (Table III). The main exception is the carbonyl–N(1) bond, which is calculated to be 0.07 Å longer than that observed for **1a**. This basis set defect, which has been noted previously in the case of formamide,[17] should not affect our relative energy comparisons significantly. The local geometry around N(2) is strongly pyramidal, and the N(2) lone pair and the carbonyl carbon are anti relative to the N–N bond in the *Z* isomer but *eclipsed* in the *E* isomer. The *Z* isomer of **11a** is calculated to be 1.0 kcal/mol more stable than the *E* isomer (Table IV). The inversion barrier at N(2) for hydrogen motion passing through a planar NH_2 group is larger than 9.0 kcal/mol, and fully conjugated 6π-electron structures[18,19] lie about 15 kcal/mol above the pyramidal structures.

Methyl groups were chosen to represent the energetic effects of alkyl substitution at C, N(1), and N(2). The relative energies of the various methyl-bearing hydrazides are given in Table IV. Methyl substitution does not appreciably affect the favored geometry in the *E* configuration [(*E*)-**11**], but the conformer in the *Z* configuration in which the N(2) lone pair and carbonyl carbon are eclipsed with respect to the N(1)–N(2) bond (**12**) is favored over (*Z*)-**11** by 0.9 kcal/mol for **11e** ($R^3 = R^4 = H$, $R^1 = R^2 = CH_3$).



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Based upon the energy differences shown in Table IV, the following predictions can be made. (1) Unsubstituted hydrazides of alkanoic acids (**11b**; $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$) should be, as formhydrazide itself, mixtures of both configurations with the *Z* configuration dominant. (2) Hydrazides with an alkyl group at N(1) (**11c**; $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$) should occur also as mixtures, but with the *E* configuration dominant. (3) Alkyl substituents at N(2) (**11e**; $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$) should favor the *E* form. (4) 1,2,2-Trisubstituted hydrazides (**11f**; $R^1 = R^2 = R^3 = CH_3$, $R^4 = H$) should be mixtures with the *E* isomer strongly dominating. (5) Substitution at C and twice at N(2) (**11g**; $R^1 = R^2 = R^4 = CH_3$, $R^3 = H$) should result in mixtures with the *E* configuration by far the major component. (6) Fully substituted hydrazides of alkanoic acids (**11h**; $R^1 = R^2 = R^3 = R^4 = CH_3$) should be *virtually exclusively E*.

Since these computational results refer to an idealized gas-phase situation at 0 K, effects such as preferential solvation, finite temperature, differences in vibrational frequencies, and intermolecular hydrogen bonding are neglected. The limitations inherent in the minimal basis set and the lack of geometry relaxation in the substituted structures also introduce some uncertainty as to the accuracy of the energy differences obtained. Since these differences are small, the *E*/*Z* ratios actually measured in solution will differ from those predicted by the calculated energy differences and a Boltzmann distribution. With consideration of these factors, the experimental isomer ratios measured by ^1H NMR spectroscopy (shown in Table IV) actually correspond reasonably well to the calculated energy differences.

Discussion

The enhanced nucleophilicity and basicity of N(2) of **2a** and the greater reactivity of the carbonyl group of **2b** compared with that of **1b** may be explained on the basis of structural differences between the two types of hydrazides. Cyclic hydrazide **2a** accomodates its five-membered ring by widening the lone pair–lone pair torsional angle[20] and by distortion of N(1) from planarity. Accompanying the partial change from sp^2 toward sp^3 hybridization is a decrease in conjugation between the lone pair of N(1) and the carbonyl group, as evidenced by the longer bond length. This effect is small—it is not apparent in the NMR or IR spectra or in the C=O or N—N bond lengths.

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[17] N. R. Carlsen, L. Radom, N. V. Riggs, and W. R. Rodwell, *J. Am. Chem. Soc.*, **101**, 2233 (1979).

[18] P. Bouchet, J. Elguero, R. Jacquier, and J.-M. Pereillo, *Bull. Soc. Chim. Fr.*, 2264 (1972).

[19] I. P. Bezhan, V. A. Khrustalev, K. N. Zelenin, and B. P. Nikolaev. *J. Org. Chem. USSR*, (*Engl. Transl.*), 14, 696 (1978).

[20] A similar effect has been observed upon comparison of the lone pair-lone pair angle, as estimated by photoelectron spectroscopy, of 1,2-dimethylpyrazolidine and acyclic hydrazines: (a) S. F. Nelson and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 6982 (1974); (b) P. Rademacher, *Tetrahedron Lett.*, 83 (1974).

Considerations such as steric hindrance and ability to coordinate lithium ion may also play a role in determining the relative reactivities, and it is difficult to assess their importance. Nevertheless, the reactions of **2** show less influence of the hydrazine portion on the carbonyl group, and vice versa, compared with those of **1** under the same conditions.

Compounds **1a** and **2a** are to our knowledge the first examples of hydrazides shown to have the *E* configuration about the N(1)–carbonyl bond in the crystalline state. Previous structures[13,14] have shown intermolecular hydrogen bonding in the crystal (in no case was the hydrazide fully substituted on the nitrogens). The 1,2,2-trisubstituted hydrazides **1a** and **2a** cannot form hydrogen bonds; therefore, this consideration is removed. It is apparent that, with the absence of noticeable intermolecular effects, 1,2,2-trisubstituted hydrazides are inherently more stable in the *E* configuration. The calculations on acetyltrimethylhydrazine (**11h**, Table IV) support this observation, as do the ASIS experiments on solutions of **1a**,**b**, **2a**,**b**, and **11h**. While the evidence does not indicate exactly what the "reasons" for this configurational preference might be,[18,19,21,22] we nevertheless offer the following speculations. A 1,2,2-trisubstituted hydrazide in the *Z* configuration would be expected to experience a lone pair–lone pair repulsion between oxygen and N(2), as in **12**, or steric crowding as in (*Z*)-**11**. If R^1 and/or R^2 are H instead of alkyl, rotation about the N(1)–N(2) bond would reduce the lone-pair repulsion [see (*Z*)-**11**]. In support of this idea, the calculations in Table IV indicate that the preference of **11e** for the *E* isomer is much greater than that of **11d**, which in turn is greater than that of **11a**. A weak intramolecular attraction between oxygen and N(2)–H may also help stabilize the *Z* form of **11a** and **11d**, although the OHN(2) angle (83°) and O–H distance (2.7 Å) do not permit a full hydrogen bond.

Experimental Section

Reagents. Solvents and reagents were obtained commercially and used as received, except as noted below. Dichloromethane, triethylamine, and hexamethylphosphoramide were distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from benzophenone ketyl. Benzoyl chloride was distilled under vacuum. Water for pK_a studies was distilled, passed through ion-exchange and charcoal columns, and degassed. Commercial benzoylhydrazine was recrystallized twice from absolute alcohol. Trimethylhydrazine[24] and 1-methylpyrazolidine[25] were prepared by following literature procedures.

Apparatus. Infrared spectra were obtained by using a Perkin-Elmer 727B spectrometer. NMR spectra were obtained by using Varian Associates T-60 (^1H) and CFT-20 (^{13}C) spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane in deuteriochloroform solution except as indicated otherwise, and the *J* values are given in hertz. For aromatic solvent induced shift experiments, the upfield shift in parts per million of a given signal in benzene solution compared with that in chloroform solution is given in brackets after the chemical shift. A Fischer Acumet 525 pH meter with a combination glass electrode was used for the titration studies. Melting points were determined by using sealed, evacuated capillaries and are uncorrected. Precoated silica gel plates (E. Merck 5765) were used for analytical thin-layer chromatography (TLC). Visualization of products was by ultraviolet fluorescence or staining with ethanolic phosphomolybdic acid. Glassware was generally dried in an oven at 100 °C, assembled while hot, evacuated, and filled with argon. Solvents and liquid reagents were transferred by syringe through rubber septa. Organic solutions were dried over anhydrous magnesium sulfate, filtered, and concentrated to constant weight by using a rotary evaporator and vacuum pump.

Benzoyltrimethylhydrazine (1a). A solution of 2.82 g (20 mmol) of benzoyl chloride and 2.02 g (20 mmol) of triethylamine in 20 mL of dichloromethane was stirred at 0 °C. Trimethylhydrazine (1.48 g, 20 mmol) was added dropwise. After 30 min the reaction was warmed to room temperature, quenched with saturated aqueous sodium bicarbonate, extracted with dichloromethane, dried, and concentrated. Crystallization of the residue from 20 mL of petroleum ether/ether gave 2.83 g (79%) of colorless prisms: mp 89–90 °C (lit.[26] mp 87–89 °C); ^1H NMR 2.49 [0.52] (s, 6 H), 3.09 [0.30] (s, 3 H), 7.2–7.7 (m, 5 H).

Benzoyl-2-methylpyrazolidine (2a). The procedure described above applied to 60 mmol of *N*-methylpyrazolidine gave a crude procuct which was crystallized from 50 mL of ether, giving 5.48 g (58%) of colorless plates, mp 59–60 °C. Concentration of the mother liquor gave a second crop: 1.25 g; mp 50–56 °C; ^1H NMR 2.18 [0.75] (apparent q, 2 H, *J* = 7), 2.44 [0.50] (s, 3 H), 3.01 [0.67] (apparent t, 2 H, *J* = 7), 3.77 [0.10] (apparent t, 2 H, *J* = 7), 7.1–7.5 [0.10] (m, 3 H), 7.5–7.8 [–0.50] (m, 2 H).

Octanoyltrimethylhydrazine (1b). A solution of 3.7 g (40 mmol) of trimethylhydrazine and 6.12 mL (44 mmol) of triethylamine in 40 mL of dichloromethane was stirred at –78 °C. Octanoyl chloride (6.82 mL, 40 mmol) was added dropwise. After the addition, the reaction was warmed to 0 °C, stirred for 10 min, and then treated with saturated aqueous sodium bicarbonate solution. Extractive workup as before gave an oil which was distilled at 113 °C (3 mm), affording 6.88 g (86%) of **1b**: ^1H NMR 0.90 (br t, 3 H, *J* = 6), 1.1–1.9 (m, 10 H), 2.48 [0.52] (s, 6 H), 2.49 [–0.03] (t, 2 H, *J* = 6), 2.85 [0.22] (s, 3 H).

Octanoyl-2-methylpyrazolidine (2b). The procedure described above applied to 80 mmol of 1-methylpyrazolidine gave 15.09 g (89%) of **2b**: bp 145 °C (3 mm); ^1H NMR 0.90 (br t, 3 H, *J* = 6), 1.0–2.1 (m, 12 H), 2.56 [–0.03] (br t, *J* = 7, 2 H), 2.56 [0.48] (s, 3 H), 3.00 [0.62] (apparent t, 2 H, *J* = 7), 3.70 [0.23] (apparent t, 2 H, *J* = 7).

Acetyltrimethylhydrazine:[18] ^1H NMR 2.15 [0.05] (s, 3 H), 2.46 [0.58] (s, 6 H), 3.94 [0.27] (s, 3 H).

1-Acetyl-2,2-dimethylhydrazine:[18] ^1H NMR [of major (*E*) isomer] 2.10 [0.13] (s, 3 H), 2.55 [0.38] (s, 6 H); ^1H NMR [of minor (*Z*) isomer] 1.91 [0.32] (s, 3 H), 2.58 [0.20] (s, 6 H).

Benzoyltrimethylhydrazine Hydroiodide (3). A solution of 0.356 g (2 mmol) of **1a** and 1 mL of iodomethane in 5 mL of absolute ethanol was heated at reflux in the dark. After 3 days the solvents were removed, and the resulting yellow solid was triturated twice with 10 mL of anhydrous ether. Crystallization of the residue from 15 mL of absolute ethanol gave 0.320 g (54%) of cream-colored solid, mp 181–196 °C dec. A second crystallization gave white crystals: mp 202–204 °C dec; NMR (D_2O) 3.12 (s, 6 H), 3.28 (s, 3 H), 7.46 (s, 5 H). Anal. Calcd for $C_{10}H_{15}N_2OI$: C, 39.23; H, 4.94; N, 9.15. Found: C, 39.03; H, 5.22; N, 8.92. Reactions conducted for a shorter period of time gave mixtures of **3** and recovered **1a**.

Regeneration of 1a from 3. A solution of 0.160 g (0.5 mmol) of **3** in 3 mL of water was treated with 0.092 g (1.1 mmol) of solid sodium bicarbonate. When the bubbling had subsided the solution was extracted with dichloromethane, which was dried and concentrated to give 0.090 g (100%) of **1a**.

1-Benzoyl-2,2-dimethylpyrazolidinium Iodide (4). A solution of 0.416 g (2.19 mmol) of **2a** in 10 mL of absolute ethanol and 2.28 mL (16.06 mmol) of iodomethane was heated at reflux in the dark for 15 h. The solution was cooled and the solvents were removed. The residue was washed with 10 mL of ether and then crystallized from absolute ethanol, giving 0.546 g (75%) of a hygroscopic tan powder, mp 151–155 °C. A portion was recrystallized three times from ethanol, giving white crystals: mp

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[21] H. Lumbroso and J. Barassin, *Bull. Soc. Chim. Fr.*, 3190 (1964).

[22] (a) M. J. S. Dewar and W. B. Jennings, *J. Am. Chem. Soc.*, **95**, 1562 (1973); (b) W. Walter and K.-J. Reubke, *Chem. Ber.*, **103**, 2197 (1970); (c) U. Anthoni, C. Larsen, and P. H. Nielsen, *Acta Chem. Scand.*, **23**, 3513 (1968).

[23] 1-Acetyl-1,2,2-trimethylhydrazine shows a single isomer in the NMR spectrum which has been assigned the *Z* configuration on the basis of a comparison of steric effects with 1-acetyl-2,2-dimethylhydrazine and 1-acetyl-1,2-dimethylhydrazine.[18] Our NMR and calculational results suggest that the configuration is in fact *E*.

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[25] M. J. Kornet, *J. Pharm. Sci.*, **56**, 963 (1967).

[26] G. Zinner, W. Kliegel, W. Ritter, and H. Bohlke, *Chem. Ber.*, **99**, 1678 (1966).

Table IV. Relative Energies of Hydrazide Configurational Isomers

hydrazide 11	calcd energy[a] *E*	calcd energy[a] *Z*	% *E* obsd (solvent)[b]	ref
a, $R^1 = R^2 = R^3 = R^4 = H$	1.0	0.0	25 (Me_2SO)	18
b, $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$	1.3	0.0	<5 (Me_2SO)	18
			<5 ($CDCl_3$)	18
c, $R^1 = R^2 = R^4 = H$; $R^3 = CH_3$	0.0	1.0	60 ($CDCl_3$)	18
			30 (Me_2SO)	18
			52 (CCl_4)	19
d, $R^2 = R^3 = R^4 = H$; $R^1 = CH_3$	0.0	1.7		
e, $R^3 = R^4 = H$; $R^1 = R^2 = CH_3$	0.0	5.1	95 (CCl_4)	18
			80 ($CDCl_3$)	18
			70 (Me_2SO)	18
			72 ($CDCl_3$)[c]	22b
			85.5 (CS_2)	22b
f, $R^4 = H$; $R^1 = R^2 = R^3 = CH_3$	0.0	2.2		
g, $R^3 = H$; $R^1 = R^2 = R^4 = CH_3$	0.0	4.6	85 (CCl_4)	18
			65 ($CDCl_3$)	18
			40 (Me_2SO)	18
			65.5 ($CDCl_3$)	22b
			84 (CS_2)	22b
h, $R^1 = R^2 = R^3 = R^4 = CH_3$	0.0	6.3	>95 ($CDCl_3$)	this work[23]

[a] Calculated energies (in kilocalories per mole) are relative for the two configurational isomers of a given hydrazide. [b] Isomer composition was measured by ^1H NMR at approximately 25 °C and 10% concentration by weight. [c] This measurement was made at −50 °C.

Table V. Crystal Data and Data Collection Details

	1a	2a	7
formula	$C_{10}H_{14}N_2O$	$C_{11}H_{14}N_2O$	$CuCl_2C_{10}H_{14}N_2O$
fw, g/mol	178.33	190.24	312.58
a, Å	5.959 (6)	17.96 (2)	8.795 (7)
b, Å	12.55 (2)	6.073 (7)	11.402 (9)
c, Å	14.12 (2)	9.59 (1)	6.830 (6)
α, deg	90.0	90.0	101.24 (2)
β, deg	105.60 (5)	90.0	96.31 (3)
γ, deg	90.0	90.0	106.33 (3)
space group	$P2_1/c$	$Pna2_1$	$P\bar{1}$
Z	4	4	2
d_{obsd}, g/cm^3 [a]	1.15 (1)	1.21 (1)	1.644 (2)
d_{calcd}, g/cm^3	1.164	1.208	1.636
crystal size, mm	0.50 × 0.60 × 0.70	0.10 × 0.35 × 0.65	0.07 × 0.19 × 0.44
linear abs coef (μ), cm^{-1}	0.83	0.85	21.93
unique rflctns collected	2968	1222	3158
rflctns used (cutoff)	1175 (3σ)	681 (2σ)	1703 (3σ)
data/parameter ratio	7.3	5.4	11.7
final R_F [b]	0.060	0.060	0.052
final R_{wF} [c]	0.068	0.057	0.057

[a] Determined by flotation with cyclohexane/CCl_4 (1a, 2a) and cyclohexane/dibromomethane (7). [b] $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

160–161 °C; ^1H NMR 2.62 (apparent q, 2 H, *J* = 7), 4.19 (s, 6 H), 4.26 (apparent t, 2 H, *J* = 7), 4.90 (apparent t, 2 H, *J* = 7), 7.3–7.6 (br m, 3 H), 7.74 (apparent dd, 2 H, *J* = 2, 6); IR (KBr) 1661 cm^{-1}. Anal. Calcd for $C_{12}H_{17}IN_2O$: C, 43.39; H, 5.16; I, 38.20; N, 8.43. Found: C, 43.15; H, 5.16; I, 38.47; N, 8.38.

1-Benzoyl-2,2,2-trimethylhydrazonium Iodide (6). A solution of 0.328 g (2 mmol) of 1-benzoyl-2,2-dimethylhydrazine in 4 mL of iodomethane and 10 mL of absolute ethanol was heated at reflux for 20 h in the dark. TLC showed no more starting material. Evaporation of the iodomethane, followed by cooling to −15 °C, gave 0.512 g (84%) of **6** as white needles: mp 179–180 °C; ^1H NMR 4.02 (s, 9 H), 7.4–8.1 (m, 6 H). Anal. Calcd for $C_{10}H_{15}N_2OI$: C, 39.23; H, 4.94; N, 9.15. Found: C, 39.15; H, 5.05; N, 8.98.

Determination of pK_a's. The general procedure of Albert and Serjeant was followed.[27] A 0.01 M aqueous solution of hydrazide was titrated with ten portions of standardized 0.984 N hydrochloric acid under a nitrogen atmosphere. For each addition, a pK_a value was calculated from the measured pH. The average K_a and standard deviation in K_a were determined, and the values were converted to logarithm units. The results are displayed in Table I.

Reaction of 2b and 1b with Methyllithium. A solution of 1.272 g (6 mmol) of **2b** in 10 mL of tetrahydrofuran was stirred at −78 °C. Methyllithium solution (4.71 mL of a 1.4 M solution in ether, 6.6 mmol) was added over 2 min. After 10 min, TLC indicated that conversion to 2-nonanone was complete. The reaction was quenched with saturated aqueous sodium bicarbonate solution, and the tetrahydrofuran was removed. The residue was partitioned between water and dichloromethane, and the organic layer was dried and concentrated. The resulting 2-nonanone was isolated as its semicarbazone: mp 118 °C (lit.[28] mp 119 °C); 91% yield.

The same reaction conditions applied to **1b** gave no reaction at −78, 0, or 23 °C, as judged by TLC, and **1b** was recovered upon workup. The reaction was repeated by using **1b**, 10 mL of tetrahydrofuran, and 2.5 mL of hexamethylphosphoramide. After 10 min at −78 °C, TLC indicated that conversion to 2-nonanone was complete, and the semicarbazone was isolated in 86% yield.

Di-μ-chloro-bis[chloro(benzoyltrimethylhydrazine)copper(II)] (7). A solution of 0.322 g (2.39 mmol) of copper(II) chloride in 10 mL of absolute ethanol was stirred at room temperature. Benzoyltrimethylhydrazide (**1a**; 0.427 g, 2.39 mmol) was added, and the mixture was stirred for 0.5 h. The resulting blue-green solid was filtered, washed with ethanol, and dried in vacuo, giving 0.739 g (99%) of **7**: mp 209–210 °C; IR (KBr) 1587, 1568 cm^{-1}. Anal. Calcd for $C_{10}H_{14}Cl_2CuN_2O$: C, 38.41; H, 4.51; Cl, 22.67; Cu, 20.32; N, 8.95. Found: C, 38.76; H, 4.76; Cl, 22.68; Cu, 20.51; N, 8.92.

Bis(1-benzoyl-2-methylpyrazolidine)copper(II) Chloride (8). By use of the same procedure, the copper complex of **2a** was prepared in 83% yield: mp 196–197 °C dec; IR (KBr) 1590, 1571 cm^{-1}. Anal. Calcd for $C_{11}H_{14}Cl_2CuN_2O$: C, 40.69; H, 4.35; Cl, 21.84; Cu, 19.57; N, 8.63. Found: C, 40.68; H, 4.50; Cl, 21.54; Cu, 19.30; N, 8.63.

Regeneration of 1a from 7. By Extraction. A sample of **7** (0.040 g, 0.128 mmol) was partitioned between 1 mL of deuteriochloroform and 5 mL of 5% aqueous sodium bicarbonate

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[27] A. Albert and E. P. Serjeant, "The Determination of Ionization Constants", Chapman and Hall Ltd., London, 1971.

[28] L. Ruzicka, and W. Brugger, *Helv. Chim. Acta*, **9**, 353 (1926).

Table VI. Fractional Atomic Coordinates[a]

atom	x	y	z	B_{eq}[b] Å^2 (or B, Å^2)
Compound **1a**				
O	0.3999 (4)	0.1762 (2)	0.22687 (15)	7.4
N(1)	0.6675 (3)	0.0479 (2)	0.27472 (14)	5.0
N(2)	0.8516 (4)	0.0093 (2)	0.3529 (2)	5.1
C(1)	0.9050 (5)	0.2593 (2)	0.3817 (2)	5.2
C(2)	1.0008 (6)	0.3248 (2)	0.4609 (3)	6.2
C(3)	0.8905 (6)	0.3391 (3)	0.5338 (3)	6.8
C(4)	0.6815 (6)	0.2883 (3)	0.5273 (2)	6.8
C(5)	0.5840 (6)	0.2240 (2)	0.4477 (2)	5.5
C(6)	0.6943 (4)	0.2081 (2)	0.3746 (2)	4.3
C(7)	0.5757 (4)	0.1430 (2)	0.2868 (2)	4.7
C(8)	0.5579 (7)	−0.0210 (3)	0.1919 (3)	6.8
C(9)	0.7727 (7)	−0.0775 (3)	0.4049 (3)	6.9
C(10)	1.0532 (6)	−0.0194 (4)	0.3183 (3)	7.7
H(C1)	0.986 (5)	0.246 (3)	0.329 (2)	4.9
H(C2)	1.147 (7)	0.363 (3)	0.464 (2)	6.2
H(C3)	0.950 (7)	0.387 (3)	0.589 (3)	6.2
H(C4)	0.589 (6)	0.296 (3)	0.583 (3)	6.8
H(C5)	0.435 (6)	0.193 (3)	0.439 (2)	5.2
H(C8-1)	0.501 (6)	−0.082 (3)	0.211 (3)	6.3
H(C8-2)	0.417 (6)	0.011 (3)	0.150 (3)	6.3
H(C8-3)	0.638 (6)	−0.016 (3)	0.142 (3)	6.3
H(C9-1)	0.729 (7)	−0.148 (3)	0.364 (3)	7.1
H(C9-2)	0.913 (7)	−0.100 (3)	0.463 (3)	7.1
H(C9-3)	0.633 (7)	−0.050 (3)	0.430 (3)	7.1
H(C10-1)	1.106 (7)	0.048 (4)	0.283 (3)	7.2
H(C10-2)	1.178 (7)	−0.035 (4)	0.377 (3)	7.2
H(C10-3)	1.025 (7)	−0.083 (3)	0.274 (3)	7.2
Compound **2a**				
O	0.9128 (2)	0.3895 (8)	0.0640	7.2
N(1)	0.9923 (2)	0.1406 (8)	0.1527 (7)	5.3
N(2)	1.0131 (2)	0.0139 (8)	0.2706 (7)	5.2
C(1)	0.8415 (3)	0.3237 (10)	0.3469 (8)	6.5
C(2)	0.7855 (3)	0.263 (2)	0.4374 (9)	8.1
C(3)	0.7531 (3)	0.067 (2)	0.4325 (10)	7.8
C(4)	0.7775 (3)	−0.0876 (12)	0.3365 (11)	7.1
C(5)	0.8359 (3)	−0.0330 (10)	0.2456 (8)	6.1
C(6)	0.8674 (3)	0.1718 (10)	0.2496 (8)	4.7
C(7)	0.9255 (3)	0.2457 (10)	0.1498 (7)	5.0
C(8)	1.0586 (3)	0.2306 (11)	0.0810 (8)	6.0
C(9)	1.1195 (3)	0.2159 (11)	0.1900 (9)	7.0
C(10)	1.0788 (3)	0.1318 (12)	0.3222 (8)	6.4
C(11)	1.0306 (3)	−0.2075 (13)	0.2271 (10)	7.5
H(C1)	0.865	0.468	0.351	7.0
H(C2)	0.764	0.371	0.509	7.4
H(C3)	0.712	0.026	0.488	6.3
H(C4)	0.754	−0.235	0.332	6.2
H(C5)	0.856	−0.150	0.181	5.8
H(C8-1)	1.051	0.378	0.054	5.7
H(C8-2)	1.070	0.134	0.000	5.7
H(C9-1)	1.143	0.349	0.206	6.2
H(C9-2)	1.157	0.098	0.161	6.2
H(C10-1)	1.065	0.251	0.378	6.2
H(C10-2)	1.110	0.025	0.373	6.2
H(C11-1)	1.072	−0.206	0.158	6.9
H(C11-2)	1.047	−0.300	0.302	6.9
H(C11-3)	0.990	−0.278	0.181	6.9
Compound 7				
Cu	0.20586 (8)	−0.00129 (6)	−0.00127 (10)	3.0
Cl(1)	−0.0675 (2)	−0.11272 (12)	0.1341 (2)	3.4
Cl(2)	0.3657 (2)	0.15666 (13)	0.2486 (2)	3.7
O	0.3051 (4)	−0.1203 (3)	0.0928 (5)	3.1
N(1)	0.2196 (5)	−0.2401 (4)	−0.2295 (6)	2.9
N(2)	0.1696 (5)	−0.1373 (4)	−0.2769 (6)	2.7
C(1)	0.4672 (7)	−0.2972 (5)	0.1757 (9)	3.5
C(2)	0.5019 (8)	−0.3904 (6)	0.2619 (10)	4.5
C(3)	0.3938 (10)	−0.5103 (6)	0.2143 (11)	4.7
C(4)	0.2514 (9)	−0.5373 (6)	0.0833 (11)	5.0
C(5)	0.2165 (7)	−0.4456 (6)	−0.0034 (10)	4.0
C(6)	0.3249 (6)	−0.3253 (5)	0.0418 (8)	2.7
C(7)	0.2851 (6)	−0.2212 (5)	−0.0328 (8)	2.7
C(8)	0.2269 (7)	−0.3395 (5)	−0.3955 (9)	3.9
C(9)	−0.0015 (7)	−0.1899 (6)	−0.3857 (9)	3.6
C(10)	0.2733 (7)	−0.0720 (6)	−0.4080 (9)	3.9
H(C1)	0.542	−0.215	0.208	4.4

Table VI (*Continued*)

atom	x	y	z	$B_{eq}{}^{b}$ Å^2 (or B, Å^2)
H(C2)	0.600	−0.371	0.354	5.4
H(C3)	0.418	−0.574	0.272	5.7
H(C4)	0.177	−0.620	0.052	5.9
H(C5)	0.118	−0.466	−0.094	4.9
H(C8-1)	0.286	−0.303	−0.488	4.8
H(C8-2)	0.279	−0.392	−0.342	4.8
H(C8-3)	0.121	−0.388	−0.462	4.8
H(C9-1)	−0.066	−0.235	−0.305	4.5
H(C9-2)	−0.040	−0.123	−0.408	4.5
H(C9-3)	−0.007	−0.244	−0.512	4.5
H(C10-1)	0.259	−0.128	−0.536	4.8
H(C10-2)	0.243	−0.001	−0.427	4.8
H(C10-3)	0.383	−0.046	−0.344	4.8

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic temperature factors, B_{eq} (Å^2), have been calculated by the equation $B_{eq} = {}^4/_3(\beta_{11}a^2 + 2\beta_{12}ab \cos\gamma + ...)$.

solution. The organic layer was drawn through a small pad of magnesium sulfate into an NMR tube and the spectrum recorded. Only peaks matching those of authentic **1a** were observed. The entire experiment was performed within 40 s at 25 °C.

By Complexation. A solution of 0.020 g (0.128 mmol) of 2,2′-bipyridyl in 1 mL of deuteriochloroform was shaken with 0.040 g (0.128 mmol) of **7** and filtered, and the ^{1}H NMR spectrum was recorded within 1 min. Only peaks matching those of authentic **1a** were observed; no bipyridyl remained.

Crystal Structure Determinations. Compound **1a** crystallized from ether/pentane as clear, multifaceted prisms. These crystals became pitted and cloudy after exposure to air for several days. Consequently, the crystal used for data collection was mounted inside a capillary tube which was subsequently sealed. Crystals of **2a** were obtained from ether/ligroin as large, clear, thin plates, one of which was cleaved for diffraction use. Bright green plates of **7** were obtained from methanol by slow evaporation.

All diffraction measurements were made at 23 (2) °C with an Enraf-Nonius CAD-3 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). For each data set, the 2θ limit was 50°. Systematic extinctions were determined from Weissenberg photographs and from diffractometer examination of the reciprocal lattices. For **1a**, this led unambiguously to space group $P2_1/c$, while for **2a**, the choice between $Pna2_1$ and $Pnma$ was resolved by successful solution and refinement of the structure. For **7**, the choice begween $P1$ and $P\bar{1}$ was resolved similarly. Intensities were corrected for Lorentz, polarization, and decay effects. Absorption corrections were applied for **1a** ($1.027 \le A \le 1.038$) and for **7** ($1.156 \le A \le 1.543$). Additional details of the data collection process and structure solution are given in Table V.

The structures of **1a** and **2a** were solved by direct methods using the program MULTAN 78.[29] In each case, the solution set with the highest combined figure of merit was used. The structure of **7** was solved by the heavy-atom method using a normal sharpened Patterson map which yielded approximate Cu and Cl coordinates. Neutral-atom scattering factors[30] were used, and anomalous dispersion corrections[30] were applied to the scattering factors of Cu and Cl in **7** and to those of O and N in the remaining structures.

All structures were refined on F by using full-matrix, least-squares techniques, and weights were derived from $\sigma(F)$. At isotropic convergence, nonmethyl H atom coordinates were calculated by assuming idealized bond geometry and a C–H bond distance of 0.95 Å.[31] Methyl H atoms were located by rotating idealized tetrahedral positions at 5° intervals and computing the electron density at these positions. The group with the highest total electron density was used in each case. At isotropic convergence, hydrogen atom temperature factors were set according to $B_H = B_n + 1$ where n is the atom bonded to H. For **1a**, in addition to the heavy-atom parameters, H atom coordinates and a secondary extinction parameter [final $g = 2.2\ (5) \times 10^{-4}$] were also refined. Final coordinates are listed in Table VI. Lists of observed and calculated structure factors and anisotropic thermal parameters are available.[32]

Calculational Details. Ab initio calculations were carried out by employing the minimal STO-3G basis set[33] and the Gaussian 70 series of programs.[34] The geometries of the E and Z conformations of formhydrazide (**11a**) were optimized by assuming idealized trigonal geometry around C, standard C–H (1.08 Å) and N–H (1.01 Å) bond lengths,[35] ∠HN(1)C = 120.0°, and overall C_s symmetry.

Geometries for the methylated hydrazides (**11b–h**) were constructed by replacing the appropriate hydrogen atom(s) in the optimized E and Z conformations of **11a**, keeping the original bond angles but using standard bond lengths for the N–C(methyl) (1.47 Å) and C–C(methyl) (1.52 Å) bonds as well as standard bond lengths and angles within the methyl groups(s) (C–H = 1.09 Å, ∠HCH = 109.47°).

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Registry No. **1a**, 3555-67-7; **1a**·HCl, 76999-27-4; **1b**, 76999-28-5; **2a**, 76999-29-6; **2a**·HCl, 76999-30-9; **2b**, 76999-31-0; **3**, 1201-57-6; **4**, 76999-32-1; **5**, 1128-86-5; **6**, 2151-88-4; **7**, 77011-23-5; **8**, 77011-24-6; **11a**, 624-84-0; **11b**, 1068-57-1; **11c**, 758-17-8; **11d**, 76530-27-3; **11e**, 3298-49-5; **11f**, 3645-44-1; **11g**, 6233-04-1; **11h**, 6261-36-5; PhCONHNH$_2$·HCl, 1452-58-0; benzoyl chloride, 98-88-4; trimethylhydrazine, 1741-01-1; N-methylpyrazolidine, 16460-04-1; octanoyl chloride, 111-64-8; 2-nonanone, 821-55-6; 2-nonanone semicarbazone, 818-06-4.

Supplementary Material Available: Listings of anisotropic thermal parameters for **1a**, **2a**, and **7** (3 pages). Ordering information is given on any current masthead page. Lists of observed and calculated structure factor amplitudes for **1a**, **2a**, and **7** are available from the authors.

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(29) In addition to local programs for the IBM 360/70 computer, local modifications of the following programs were employed: Coppens' ABSORB program; Zalkin's FORDAP Fourier program; Johnson's ORTEP II thermal ellipsoid plotting program; Busing, Martin, and Levy's ORFFE error function program; Main, Lessinger, Declercq, Woolfson, and Germain's MULTAN 78 program for the automatic solution of crystal structures; and the FLINUS least-squares program obtained from Brookhaven National Laboratories.

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