Single Crystal X-ray Structures of 2-Pyridinecarboxaldehydeazine and Biacetylazine: Implications of the Conjugation in Systems with Carbon−Nitrogen Double Bonds

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Crystal structures were determined for two compounds, 2-pyridinecarboxaldehydeazine, **1**, and biacetylazine, **2**. 2-Pyridinecarboxaldehydeazine crystallizes in space group $P2_1/c$ with $a = 10.0487(7)$ Å, $b = 4.6452(7)$ Å, $c = 11.6700(11)$ Å, $\beta = 91.030(6)°$, V = 544.65(10) Å^3, $Z = 2$, $R = 0.0345$. Biacetylazine crystallizes in space group $C2/c$ with $a = 9.879(7)$ Å, $b = 12.409(4)$ Å, $c = 7.950(6)$ Å, $\beta = 98.44(6)°$, $V = 964.0(11)$ Å^3, $Z = 4$, $R = 0.0496$. Comparison of the imine bond lengths of these and other azine and diimine systems found in the literature suggests that conjugation of imines is better through the carbon−carbon bond than through the nitrogen−nitrogen bond. Semiempirical structural calculations demonstrate that the N−N bond in these azines is rotationally soft, thereby allowing significant twisting at little energy cost. This accounts for the observation that **1** is planar and **2** is not.

Introduction

We have been studying polyazines[1] which are nitrogen-containing, conjugated polymers that can be doped with iodine to give moderately conducting materials. The repeat unit of a polyazine can be viewed as either a diimine, $-(\mathrm{N{=}C(R){-}C(R){=}N})_x-$, or an azine, $-(\mathrm{C(R){=}N{-}N{=}C(R)})_x-$. Theoretical calculations[2] indicate that these materials should be both planar and conjugated. However, to understand the bulk structural properties of these noncrystalline polymers, characterization of model compounds is required.

We have previously structurally characterized the dihydrazone model compounds 2,3-butanedione dihydrazone (BDDH)[1a] and glyoxal dihydrazone (GDH).[1c] These dihydrazones contain both a diimine linkage and a N−N bond. Both BDDH and GDH are planar and the imine and carbon−carbon bond lengths suggest some conjugation of the π system. However, the amine end groups are also strongly conjugated to the diimines, so it is unclear if the hydrazone bond is an adequate model for the azine linkage.

In this paper, we report the structural determination of two azine model compounds, 2-pyridinecarboxaldehydeazine, **1**, and biacetylazine, **2**. **1** is planar and appears to be a reasonable model for polyazines. In contrast, **2** has an unexpected twisted structure where the lone pair of each azine N is conjugated into the π bond of the adjacent imine, reminiscent of the hydrazone amines in BDDH and GDH. Semiempirical structural calculations (AM1 and PM3) suggest that the nonplanar structure in **2** is accounted for by the soft rotational mode of the N−N bond of the azine.

Experimental Section

All reagent grade reactants were purchased from Aldrich and used as received. Elemental analyses were run by M−H−W Laboratories, Phoenix, AZ. Infrared spectra were run as KBr pellets between 400 and 4000 cm^{-1} on a Perkin-Elmer 1650 FTIR spectrometer at 2 cm^{-1} resolution. ^{1}H NMR spectra were run on a Bruker AM300 spectrometer at 300 MHz, referenced to TMS. UV−vis spectra were run on a Perkin-Elmer Lambda2 spectrometer in methanol between 200 and 1100 nm.

Syntheses. *Compound **1**.* A 250.0 μL (5.1 mmol) portion of $N_2H_4{\cdot}H_2O$ was stirred in 5 mL of 95% ethanol. To this was added 1.0 mL (11 mmol) of 2-pyridinecarboxaldehyde in 10 mL of 95% ethanol over a 30 min time period. The solution was cooled on an ice/salt bath, and the yellow precipitate was collected by vacuum filtration and washed with 20 mL of cold 95% ethanol to yield 77%: mp, 150 °C (very sharp); IR, 1631, 1586, 1565, 1466, 1434 cm^{-1}; ^{1}H NMR (DMSO-d_6), δ vs TMS, 8.71 (1H, d of d of d, $J = 4.8$, 1.6, 1.1 Hz), 8.55 (1H, d, $J = 1.3$

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Hz), 8.11 (1H, d of d, $J = 7.3$, 1.1 Hz), 7.94 (^{1}H, t of d, $J = 7.3$, 1.6 Hz), 7.52 (1H, m); UV−vis (CH_3OH) λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$), 299 (31 500), 260 (14 000). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.64. Found: C, 68.54; H, 5.02; N, 26.64.

Table 1. Data for the X-ray Diffraction Studies of 1 and 2[a]

chemical formula	**1**, $C_{10}H_{12}N_4$	**2**, $C_8H_{12}O_2N_2$
a, Å	10.0487(7)	9.879(7)
b, Å	4.6452(7)	12.409(4)
c, Å	11.6700(11)	7.950(6)
β, deg	91.030(6)	98.44(6)
V, Å^3	544.65(10)	964.0(11)
Z	2	4
formula wt	210.24	168.20
space group	$P2_1/c$ (C^5_{2h}, No. 14)	$C2/c$ (C^6_{2h}, No. 15)
T, °C	21(1)	21(1)
λ, Å	1.54178	0.71073
ρ_{calc}, g cm^{-3}	1.282	1.159
μ, cm^{-1}	6.171	0.791
transmission factors	b	0.963−1.00
R	0.0345	0.0496
R_w	0.0464	0.0613

[a] $R = \sum|F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. [b] Absorption correction not made for **1**.

*Compound **2**.* The literature procedure was used as described previously.[1a,3]

X-ray Structure Determination of 1 and 2. Crystals of **1** and **2** were grown by slow evaporation from methanol solutions. Crystallographic data for compounds **1** and **2** are summarized in Table 1. Data for **1** were collected on an Enraf-Nonius CAD4-U diffractometer (Cu radiation); data for **2** were collected on a CAD4-Turbo diffractometer (Mo radiation).[4] Data were processed using the Enraf-Nonius MolEN package;[5] structures were solved by direct methods (SHELXS-86).[6] Full-matrix least squares refinement was carried out using the Oxford University CRYSTALS-PC system.[7] Both compounds contain one-half molecule in the asymmetric unit. In **1**, the full molecule has crystallographic *1* symmetry; in **2** the full molecule has crystallographic C_2 symmetry. For both structures, all nonhydrogen atoms were refined using anisotropic displacement parameters. In **1**, hydrogen atoms were refined using isotropic displacement parameters. The data in compound **2** were of lower quality; a data/parameter ratio of ca. 5:1 was obtained. Consequently, in **2** H−H contacts were restrained to be equal (±0.05 Å), C−C−H angles were restrained to be equal (±2°), and isotropic displacement parameters were restrained to be equal to the component of the C atom displacement parameter in the C−H bond direction (±0.01 Å^2). Drawings were produced using the Oxford University program CAMERON.[8] Full reports on both structures are available as CIF files.

Theoretical Calculations. Molecular mechanics, AM1, and PM3 theoretical calculations were performed using the PC Spartan Plus suite of programs, version 1.5.[9]

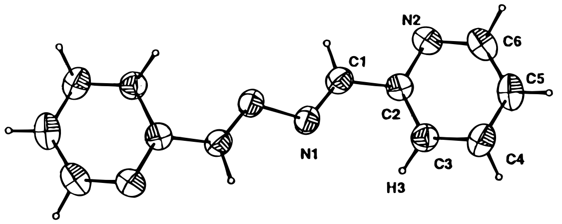

Figure 1. The molecular structure of 2-pyridinecarboxaldehydeazine, **1**, showing the labeling scheme and atoms refined using anisotropic displacement parameters (50% probability ellipsoids).

Table 2. Atomic Coordinates

atom	x	y	z	U (Å^2)
		1, $C_{12}H_{10}N_4$[a,b]		
N(1)	0.47587(8)	0.0989(2)	0.45862(7)	0.0476
N(2)	0.18328(9)	0.5216(2)	0.46238(8)	0.0556
C(1)	0.3683(1)	0.2157(2)	0.48900(8)	0.0470
C(2)	0.29706(9)	0.4272(2)	0.41765(8)	0.0427
C(3)	0.3439(1)	0.5195(2)	0.31239(8)	0.0481
C(4)	0.2691(1)	0.7168(2)	0.25064(9)	0.0571
C(5)	0.1515(1)	0.8142(3)	0.2953(1)	0.0617
C(6)	0.1128(1)	0.7121(3)	0.4000(1)	0.0635
		2, $C_8H_{12}O_2N_2$[a,b]		
C(1)	0.8101(4)	0.0385(4)	0.5088(6)	0.1058
C(2)	0.7076(4)	0.1170(4)	0.5512(5)	0.0787
C(3)	0.5728(4)	0.1261(3)	0.4373(5)	0.0659
C(4)	0.4670(5)	0.1980(3)	0.4848(5)	0.0917
N(1)	0.5619(3)	0.0694(3)	0.3025(4)	0.0706
O(1)	0.7301(3)	0.1756(3)	0.6732(4)	0.0991

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as: $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$. [b] Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

Table 3. Bond Lengths (Å) and Angles (deg)

	1, $C_{12}H_{10}N_4$		
N(1)−N(1)	1.413(1)	C(2)−C(3)	1.391(1)
N(1)−C(1)	1.266(1)	C(3)−C(4)	1.380(1)
N(2)−C(2)	1.339(1)	C(4)−C(5)	1.376(2)
N(2)−C(6)	1.340(1)	C(5)−C(6)	1.374(2)
C(1)−C(2)	1.466(1)		
N(1)−N(1)−C(1)	111.83(9)	C(1)−C(2)−C(3)	122.57(9)
C(2)−N(2)−C(6)	116.8(1)	C(2)−C(3)−C(4)	118.4(1)
N(1)−C(1)−C(2)	122.60(9)	C(3)−C(4)−C(5)	118.9(1)
N(2)−C(2)−C(1)	114.17(8)	C(4)−C(5)−C(6)	118.9(1)
N(2)−C(2)−C(3)	123.26(9)	N(2)−C(6)−C(5)	123.7(1)
	2, $C_8H_{12}O_2N_2$		
C(1)−C(2)	1.479(6)	C(3)−C(4)	1.465(5)
C(2)−C(3)	1.500(5)	C(3)−N(1)	1.274(4)
C(2)−O(1)	1.207(4)	N(1)−N(1)	1.376(6)
C(1)−C(2)−C(3)	119.2(4)	C(2)−C(3)−N(1)	115.1(4)
C(1)−C(2)−O(1)	121.9(4)	C(4)−C(3)−N(1)	125.3(3)
C(3)−C(2)−O(1)	118.8(4)	C(3)−N(1)−N(1)	117.9(3)
C(2)−C(3)−C(4)	119.6(4)		

Results and Discussion

Final coordinates for **1** and **2** are given in Table 2 and bond lengths and bond angles are given in Table 3. The molecular structure of **1** is shown in Figure 1; the molecule is planar with the azine linkages in the *E*,*E* conformation, suggesting conjugation throughout the π systems. The pyridine groups in **1** are coplanar with the azine unit to within 0.02 Å, in contrast to the solution state, where the NMR spectrum of **1** indicates that the pyridine groups are freely rotating.[1g] The planarity in **1** may arise due to two effects. First, the N(2)−H(1) distance is 2.44 Å, substantially less than the sum of the van der Waals radii for H and N (2.75 Å), suggesting a possible interaction between these two atoms. The stereochemical influence of the nitrogen lone pairs is reflected in the bond angles. The C1−N1−N1′ angle

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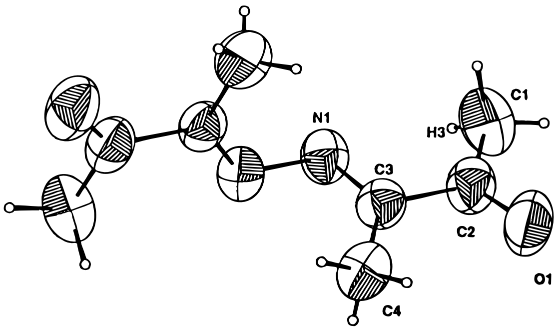

Figure 2. The molecular structure of biacetylazine, **2**, showing the labeling scheme and atoms refined using anisotropic displacement parameters (40% probability ellipsoids).

Table 4. Comparison of Metrical Parameters

compound	r(C═N) (Å)	r(N−N) (Å)	∠C═N−N (deg)	type
GDH[a]	1.2777(15)	1.3827(32)	117.10(25)	diimine
2-nitrophenyl[b]	1.282(12)	1.368(15)	117.4(10)	diimine
BDDH[c]	1.291(1)	1.387(1)	117.29(8)	dimine
GAG[d]	1.300(2)	1.381(2)	117.11(13)	diimine
4-nitrophenyl[e]	1.306(10)	1.371(8)	117.4(6)	diimine
1	1.266(1)	1.413(1)	111.83(9)	azine
2	1.274(4)	1.376(6)	117.9(3)	azine
formaldazine[f]	1.277(2)	1.418(3)	111.4(2)	azine
tolylazine[g]	1.279(4)	1.405(5)	114.1(3)	azine

[a] Glyoxaldihydrazone, ref 1c. [b] *E*,*E*-2,3-butanedione bis(2′-nitrophenylhydrazone), ref 11. [c] Butanedionedihydrazone, ref 1a. [d] Dimethylglyoxal bisguanylhydrazone, ref 12. [e] *E*,*E*-2,3-butanedione bis(4′-nitrophenylhydrazone), ref 13. [f] Gas phase, ref 14. [g] Methyl(*p*-tolyl)ketone azine, ref 15.

(111.83°) is significantly below the ideal sp^2 value of 120°, a consequence of the repulsion between the nitrogen lone pair and the adjacent bonds. Second, the planarity may be due to packing effects, but this is difficult to quantify. The structure of **2** is shown in Figure 2. The C(3)−N(1)−N(1)′−C(3)′ torsion angle is 102.6°. This large deviation from planarity has two consequences. First, there is a loss of conjugation between the imine bonds across the azine bond, reflected in the shorter imine bond length. The torsion also leads to a shorter N(1)−N(1) bond length (1.376(6) Å) compared to that observed for **1** (1.413(1) Å). In this conformation the lone pair of N(1) can interact with the π orbital of the N(1)′−C(3)′ double bond. Finally, a short intramolecular contact between N(1) and H(3), 2.66(3) Å, may add a favorable electrostatic contribution to the stability of this conformation.

Table 4 shows a comparison of the C═N and N−N bond lengths and the angles about the C and N atoms in a number of diimine and azine compounds. The imine bond length in the diimine compounds range from 1.278 to 1.306 Å (an average of 1.291 Å), while the imine bond length in the azines range from 1.266 to 1.279 Å (an average of 1.273 Å). The longest C═N bond length in the azines (1.279 Å, tolylazine) is the same length as the shortest C═N bond length of the diimines (1.278 Å, glyoxal dihydrazone). This shows that the conjugation of adjacent imine bonds can be better than through a carbon−carbon linkage than through a nitrogen−nitrogen linkage. In these cases this is caused by repulsion originating from the lone pairs on the nitrogens. However, nitrogen lone pairs also can be used to conjugate into the π system. This is shown by the N−N bond length data given in Table 4. All of the diimine compounds are dihydrazones, so the terminal imines have NH_2 groups appended to the nitrogen atoms and the amine lone pairs can conjugate into the imine π bonds. The N−N bond lengths in the dihydrazones average 1.378 Å (range 1.368−1.387 Å), about the same as the N−N bond length in **2**. In contrast, in the azine compounds (eliminating the nonplanar **2**), the average N−N bond length is 1.412 Å (range 1.405−1.418 Å). For comparison purposes, the N−N single bond length in hydrazine, NH_2NH_2, is 1.449 Å.[10] Thus, there is some double bond character in the azine N−N bonds but significantly more in the hydrazone N−N bonds. These conclusions are supported by the data for the C═N−N bond angles. In the dihydrazones, the average angle is 117.26°. In **2**, the angle is about the same, 117.7°, while in the other azines the C═N−N angle is much less, ranging from 111.4° to 114.1°. Again, the nonplanar **2** looks like a well-conjugated dihydrazone rather than a poorly conjugated azine.

Table 5. Comparison of the Calculated and Observed Structures for 2-Pyridinecarboxaldehydeazine, 1

	observed	SYBYL	AM1	PM3
	Bond Distance (Å)			
N1−N1	1.413	1.4201	1.3497	1.3915
C1−N1	1.266	1.2725	1.3044	1.3012
C1−C2	1.466	1.5119	1.4853	1.4734
C2−C3	1.391	1.3991	1.4103	1.3988
C3−C4	1.380	1.3973	1.3983	1.3938
C4−C5	1.376	1.3969	1.3922	1.3885
C5−C6	1.374	1.3975	1.4101	1.3985
C6−N2	1.340	1.3492	1.3405	1.3463
N2−C2	1.339	1.3500	1.3625	1.3665
	Bond Angle (deg)			
N1−C1−C2	122.60	120.14	120.25	119.10
C1−C2−C3	122.57	121.06	120.93	123.95
C1−C2−N2	114.17	118.98	116.60	115.21
N1−N1−C1	111.83	113.48	118.18	117.45
	Dihedral Angle (deg)			
C1−N1−N1−C1	180.00	180.00	180.00	180.00
N1−C1−C2−N2	180.00	180.00	156.68	180.00
ΔH_f (kcal/mol)			134.35	118.09

The structures of **1** and **2** were calculated using molecular mechanics (with the SYBYL force field[16]), AM1,[17] and PM3[18] methods in order to better understand the role of packing on the crystal structures, particularly to see if packing forces are responsible for the twisted structure of **2**. The results are given in Tables 5 and 6. While these are all empirical methods, they can give reasonable qualitative insight into the structures that might be expected for gas-phase molecules. For **1**, the SYBYL molecular mechanics and PM3 calculations converged to planar structures, even when the minimizations started with a variety of twisted

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Table 6. Comparison of the Calculated and Observed Structures for Biacetylazine, 2

			AM1		PM3	
	observed	SYBYL	planar[a]	twisted[b]	planar[a]	twisted[b]
			Bond Distance (Å)			
N1−N1	1.376	1.4201	1.3447	1.3195	1.3860	1.3714
C3−N1	1.274	1.2743	1.3096	1.3040	1.3044	1.2990
C3−C4	1.465	1.5129	1.4947	1.4943	1.4915	1.4885
C2−C3	1.500	1.4792	1.5149	1.5099	1.5189	1.5117
C2−C1	1.479	1.5084	1.4929	1.4899	1.5056	1.5023
C2−O1	1.207	1.2208	1.2362	1.2330	1.2173	1.2125
			Bond Angle (deg)			
N1−N1−C3	117.1	114.93	119.56	125.54	119.92	122.39
N1−C3−C2	115.1	117.93	118.04	117.93	116.39	116.28
C3−C2−C1	119.2	122.43	118.04	116.68	119.75	115.04
C3−C2−O1	118.8	119.56	118.87	119.95	119.75	121.46
			Dihedral Angle (deg)			
C3−N1−N1−C3	102.6	180.00	180.00	97.60	180.00	129.45
N1−C3−C2−O1	180.0	180.00	180.00	39.14	180.00	81.41
ΔH_f (kcal/mol)			−23.93	−29.75	−37.43	−44.08

[a] The initial structure before minimization was planar. [b] The initial structure before minimization was the experimentally observed structure.

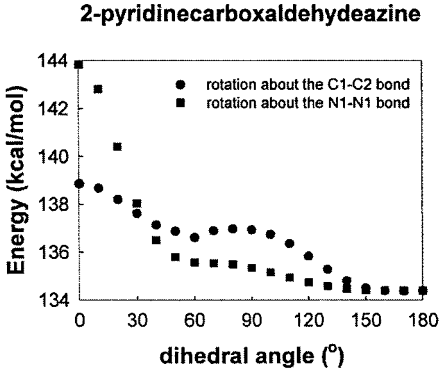

Figure 3. AM1 calculations for 2-pyridinecarboxaldehydeazine, **1**. The circles show the rotation about the C1−C2 bond; the inversion symmetry and azine planarity was maintained at each angle. The squares show the rotation of the N1−N1 bond; the planarity between the imine and the pyridine ring was maintained at each angle.

structures. In all cases, the dihedral angle about the azine linkage in **1** was 180° (a value greater than 90° indicates that the N1−N1 bond is in the anti conformation), consistent with the experimental observations. The AM1 calculation minimized with the pyridine ring at a dihedral angle of about 156° from the azine linkage. An AM1 calculation on **1** as a function of the rotation angle between the azine linkage and the pyridine ring, shown in Figure 3, found a rotational barrier between the minimum and maximum energy structures of 4.5 kcal/mol, consistent with the suggestion of free rotation in solution. The rotational energy curve is broad around the minimum, and the difference between the minimized structure and the planar structure is well below the confidence level of the theory. The maximum energy structure is also planar, but with the nitrogen atoms syn to each other, which is likely due to repulsions between the lone pairs on these atoms. An AM1 calculation of the energies as a function of rotation about the N−N bond was also performed. The minimum is at a C−N−N−C dihedral angle of 180°, and the rotational barrier is quite high between the maximum and minimum energy structures, 9.4 kcal/mol. However, the minimum is very broad; even a 90° dihedral angle is only 1 kcal/mol higher in energy than the 180° structure. This indicates that the azine linkage is probably susceptible to a wide variety of geometries depending on subtle effects not probed by the AM1 calculations, such as crystal packing or solvation. While none of the methods give especially good quantitative agreement with experiment, all of them indicate that **1** should be planar, or nearly so, through the azine linkage and the pyridine ring. At most, the crystal packing energies contribute a small amount toward stabilizing the observed planar structure. In **1**, then, it appears that the geometry is primarily determined by conjugation through the nitrogen π orbitals of the azine and that the conjugation extends into the pyridine ring.

The situation for **2** is quite different, as shown in Table 6. As with **1**, the molecular mechanics calculation minimizes to the all-planar structure, independent of the initial conformation. In contrast, the AM1 and PM3 methods lead to different results, depending upon the initial geometry. When starting with the planar structure found using the SYBYL force field, both the AM1 and PM3 calculations minimize to the planar geometry. However, when the initial geometry is chosen so that the C3−N1−N1−C3 dihedral angle is 90°, then the minimized structure is significantly twisted at both the N1−N1 bond and the chain C2−C3 bond. For both semiempirical methods the twisted geometry is about 6 kcal/mol more stable than the planar structure. Further, the planarity is lost across both the C3−N1−N1−C3 and N1−C3−C2−O1 linkages and the molecule has C_2 symmetry (i.e., there is no inversion symmetry). The nonplanar azine linkage is in accord with experiment for **2**, but the significantly twisted imine−ketone (39° by AM1, 81° by PM3) is not. To explore this, AM1 calculations were done to estimate the relative rotational barriers for the N1−N1 bond and the C2−C3 bond, and these results are shown in Figure 4. Rotation of the carbon−carbon bond while the azine is kept planar, shown as the squares in Figure 4, leads to a shallow, broad minimum at a dihedral angle of about 130°, a low barrier through the anti structure (dihedral angle of 180°), and a high barrier through the syn structure (dihedral angle of 0°, not shown). Between dihedral angles of 60° and 180°, there is less than 2 kcal/

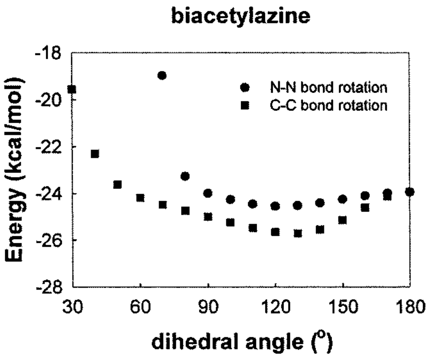

Figure 4. AM1 calculations for biacetylazine, **2**. The circles show the rotation about the N1−N1 bond; the inversion symmetry and ketone−imine planarity was maintained at each angle. The squares show the rotation of the C2−C3 bond; C_2 symmetry and the planarity of the azine linkage were maintained at each angle.

mol difference in energies for any given structure. A similar result is found when the N−N bond is rotated while the rest of the molecule is kept planar, shown as the circles in Figure 4. A shallow minimum near a dihedral angle of 120°, a low barrier at a dihedral angle of 180° (<1 kcal/mol), and a very high barrier at low angles (energies were not calculated below dihedral angles of 60°, since hydrogen atoms on the methyl groups overlap) are found. For **2**, then, the structure arises from a compromise of steric factors and conjugation of the ketone and imine π bonds with the adjacent nitrogen lone pair. Again, solid-state packing forces probably contribute only minimally to the observed structure.

Conclusion

This analysis implies that the structure of azines are influenced by subtle effects. **1** is structurally similar to most other reported azines. The C═N−N═C linkage is planar, the imine bonds are slightly longer than in isolated imines, and the N−N bond is shorter than in hydrazines. All of these observations imply a small degree of delocalization through the azine π system. In contrast, **2** is nonplanar and the C═N and N−N bond lengths suggest that delocalization must occur through the nitrogen lone pairs, perhaps a consequence of the presence of the electronegative oxygen atom. The rotational energy curves calculated for **1** and **2** are in agreement with that found in formaldazine using ab initio methods,[2e] indicating that, in general, azines can be expected to be rotationally floppy.

Polyazines can be thought of as having either a diimine, $-(\mathrm{N{=}C(R)-C(R){=}N})_x-$, or an azine, $-(\mathrm{C(R){=}N-N{=}C(R)})_x-$ repeat unit. Experimental observations indicate that the polyazines have relatively short conjugation lengths and do not dope by oxidation of the π system. The work presented here implies that this is accounted for by the poor conjugation through the N−N linkage. Further, the N−N linkage is susceptible to twisting, as in **2**, so even if the polyazines are planar in the ground state, low-energy twisting motions are available that further reduce the electronic communication along the polymer backbone. Thus, these materials are probably better thought of as fairly localized poly(diimines) rather than poly(azines). Finally, reaction of polyazines with iodine leads to disproportionation of the iodine into iodonium and triiodide ions, with complexation of the iodonium ion to the azine.[1h] On the basis of the findings reported here, it seems likely that the complexation of the iodonium ion to the azine causes a sufficiently large electronic perturbation to the polyazine π system to induce the N−N bond in the polymer to twist, analogous to the role of the ketone in **2**. If this happens, then the delocalization along the polymer chain is disrupted, preventing oxidation and the formation of charge carriers.

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Supporting Information Available: View of the unit cell, H atom parameters, anisotropic displacement parameters, bond lengths and angles, and observed and calculated structure factors for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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