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# Comparison of Experimental and Calculated Geometries of Sesquibicyclic Hydrazines

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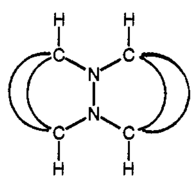
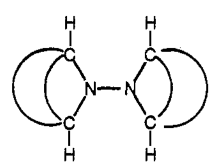
**Abstract:** X-ray crystal structures are reported for bis(N,N′-bicyclic) hydrazines **2–4** and **7–9**. In contrast to **1–8**, which are cis fused at the nitrogens, **9** is trans fused. Molecular mechanics (MM2), semiempirical MO (AM1), and *ab initio* (6-31G*, on **1–3**, **5**, and **6**, and MP2/6-31G* on **6**) calculations are compared with the experimental geometries. MM2 calculations seriously underestimate the NN bond length but do an excellent job of predicting pyramidality at nitrogen and correctly get the trans fused geometry for **9** as the more stable one. AM1 calculations also underestimate the NN bond length and do not estimate enough torsion at CNNC ring bonds, causing cis fused **9** to be calculated as more stable than the trans form. The 6-31G* calculations make about half as large an error in the NN bond lengths as do MM2 and AM1 but are significantly poorer at obtaining the proper pyramidality at nitrogen. The MP2/6-31G* calculation on **6** predicts the X-ray NN bond length and nitrogen pyramidality $\alpha$(av) to within experimental error. Errors in calculated structures and relative energies of conformations for less constrained hydrazines are discussed.

Bis-N,N′-bicyclic ("sesquibicyclic") hydrazines of structure **A** and bis-N,N-bicyclic ones of structure **B** have been of special interest to our group in our efforts to understand the influence



**A**



**B**

of the large geometry changes which accompany electron loss in hydrazines on their electron transfer reactions.[1] Neutral hydrazines with both **A** and **B** substitution patterns have lone pair, lone pair twist angles $\theta$ far from the electronically preferred value of 90°. Assuming that the lone pair orbital axes bisect the CNC angles in a Newman projection down the NN bond, $\theta$ is the average of either interring or intraring CNNC angles for *syn* hydrazines, and the average of these angles for *anti* hydrazines is $\theta$ and 180-$\theta$. Published examples of **A** hydrazines are *syn* with $\theta < 15°$ and **B** hydrazines *anti*, with $\theta \sim 180°$.[1]

The presence of bicycloheptyl to bicyclononyl rings in bis-bicyclic hydrazines requires the bridgehead CH bonds $\alpha$ to N to lie near the nodal plane of the p-rich orbitals at N in oxidized forms. This inhibits the usual decomposition reactions of oxidized hydrazines, which result in breakage of a $C_\alpha$–H bond. This "Bredt's rule kinetic protection" [2] allows isolation of the radical cations of both sorts of bis-bicyclic hydrazines in several examples. For electron-transfer considerations it is important to establish how well calculations handle the geometry changes which accompany bicyclic ring size changes. In this paper we examine the geometries determined by X-ray for several neutral hydrazines of type **A** and consider how well both molecular mechanics and molecular orbital calculations perform for these and other tetraalkylhydrazines. An important goal of this work was to establish the structural features necessary for AM1 calculations (which can model electron transfer reactions) to work well and what sort of failures occur when these structural features are not present.

## Results: X-ray Structures

Sesquibicyclic hydrazines are prepared by "proton driven" Diels–Alder addition of cyclic dienes to protonated bicyclic azo compounds, followed by deprotonation and hydrogenation.[3] The principal compounds discussed here are **1–9**, for which preparations have been reported previously[3–7] except for **7**, which is described in the Experimental Section. X-ray structures were reported previously for **5** and **6**,[8] although crystals of **5** are disordered in position of the double bond, precluding detailed comparisons of the calculated geometry and experiment. We have been unable to obtain a structure for **1** which refines to R below 15 despite several attempts; unresolved domain twinning problems are present. Structures for **2–4** and **7–9** are reported here. Diagrams of **2–4** and **7–9** showing the heavy atom bond lengths and bond angles appear in the supplementary material. The thermal ellipsoid drawing of **7** (Figure 1) shows that the benzene ring attached to C(1) is nearly eclipsed with the inner dimethylene bridge; the C(16)C(11), C(1)C(2) torsion angle is 11.5°. The thermal ellipsoid drawing of **9** (Figure 2) shows it to be trans fused at the nitrogens. Enlarging one of the bridging rings from three to four methylenes results in the alkyl substituents of the *N,N′*-bicyclo[4.2.2]decyl ring (for convenience we shall designate this ring as **42** {the nitrogen containing bridge of a sesquibicyclic hydrazine is two atoms by definition} and use analogous abbreviations for other compounds) being substituted trans on the **22** ring, making the nitrogen lone pairs *anti*, instead

(1) For reviews of tetraalkylhydrazine oxidation chemistry, see: (a) Nelsen, S. F. Hydrazine, Hydrazine Cation Radical Electron Transfer Reactions. In *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, p 1. (b) Nelsen, S. F. Internal Geometry Relaxation Effects on Electron Tranfer Rates of Amino Centered System. In *Advances in Electron Transfer Chemistry, Vol. 3*; Mariano, P. S., Ed.; JAI: Greeenwich, CT, in press.

(2) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

(3) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366.

(4) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* **1986**, *42*, 1769.

(5) Nelsen, S. F.; Frigo, T. B.; Kim, Y.; Thompson-Colon, J. A.; Blackstock, S. C. *J. Am. Chem. Soc.* **1986**, *108*, 7926.

(6) Nelsen, S. F.; Frigo, T. B.; Kim, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5387.

(7) Nelsen, S. F.; Wang, Y. *J. Am. Chem. Soc.* **1992**, *114*, 7923–4.

(8) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. *Tetrahedron* **1986**, *42*, 6101.

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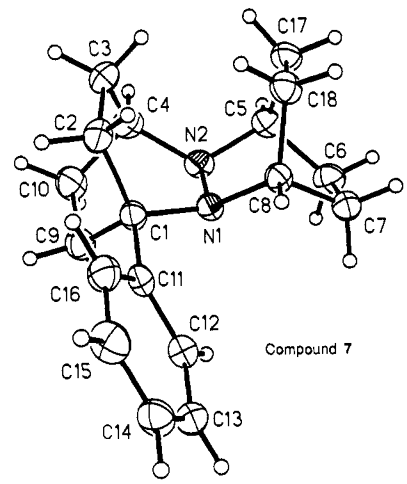
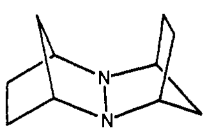
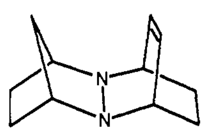


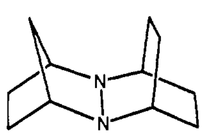

**Figure 1.** Thermal ellipsoid plot (50% probability) drawing of the X-ray structure for **7**.



**1**



**2**



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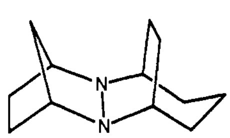
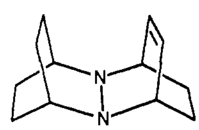
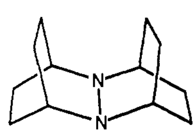


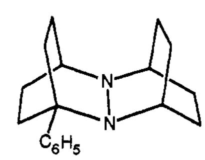
**4**



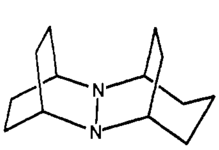
**5**



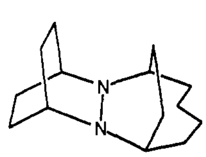
**6**



**7**



**8**



**9**

of *syn*, as they are in the other **A** compounds. We examined the $^{13}C$ NMR spectrum of **9** to determine whether it is also in the *anti* form in solution. A single set of 14 carbons is observed at 190 K (see Experimental Section), so only one form is detectably occupied. The downfield $CH_2$ pair (33.8 and 36.2 $\delta$ at 190 K, $\Delta\delta$ 2.6) is assigned to the $CH_2$'s which are adjacent to the bridgehead carbons in the $(CH_2)_4$ bridge; the corresponding carbons of the $(CH_2)_3$ bridge of **8** occur at 36.3 $\delta$ at 190 K (see Experimental Section). The 250 K spectrum of **9** shows that one of the four remaining $CH_2$ pairs averages to 27.2 $\delta$ and has a significantly smaller $\Delta\delta$ than 1.6 (we assign it as the 27.14 and 25.87 $\delta$ signals in the 190 K spectrum), while the other three have $\delta_{av}$ smaller than 27 and significantly larger $\Delta\delta$ than 1.6. Because *syn* **9** should not have such large $\Delta\delta$ values at both $CH_2$ pairs of

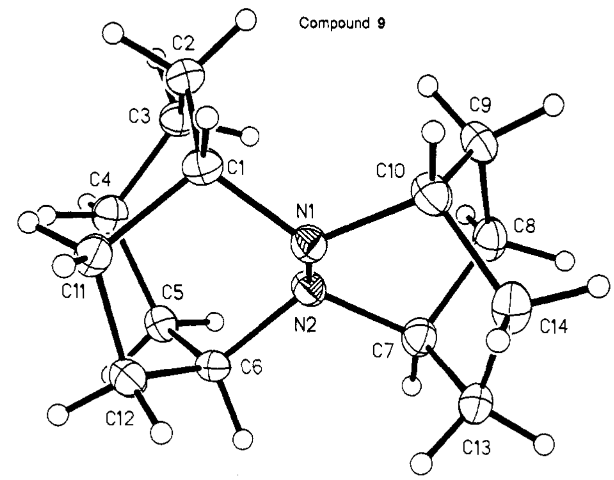



**Figure 2.** Thermal ellipsoid plot (50% probability) drawing of the X-ray structure for **9**.

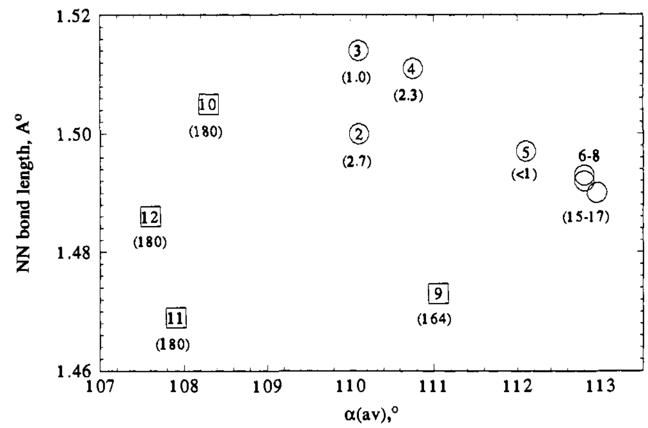


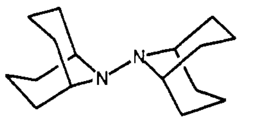

**Figure 3.** Plot of NN bond distance versus $\alpha_{av}$ for **2–12**. *Syn* lone pair compounds are shown as circles, and *anti* ones as squares, and $\theta$ values are given in parentheses.

its **22** ring, we argue that these spectra demonstrate that **9** is *anti* in solution as well as in the crystal.

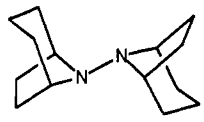
Parameters describing the geometry at nitrogen for these compounds appear in Tables I–III. The geometries at nitrogen for the **22/22** compounds **6** and **7** are quite similar. The other compounds show fairly regular changes in geometry about the nitrogens as bicyclic ring size is changed except for the *anti* lone pair compound **9**. The $\theta$ values are 2.7° or less for the two unsaturated compounds (**2** and **5**) and the compounds containing a **21** ring (**3** and **4**), but $\theta$ increases to 15.0–16.7° for the saturated compounds containing only **22** and **32** rings (**6–8**). The *anti* lone pair compound **9** has $\theta$ = 164.4°.

Figure 3 illustrates the dependence of NN bond length upon structure as a plot versus the average of the bond angles at N, $\alpha_{av}$. There is a fairly linear correlation between shorter NN bond length and higher $\alpha_{av}$ as the nitrogens flatten with larger bicyclic ring size for six of the seven *syn* lone pair compounds. The unsaturated **21/u22** compound **2** has an anomalously short NN bond length in this plot, for unknown reasons. The *anti* lone pair compound **9** has a significantly shorter NN bond length than any of the *syn* **A** compounds. Also included in Figure 3 are data for the two published examples of compounds of substitution pattern **B**, **10**[9] and **11**,[10] both of which crystallize in $\theta$ = 180° conformations with both $R_2N$- substituents axial to a piperidine ring and the $C_\alpha$-unbranched mono-N,N-cyclic diazadecalin **12**, which has $\theta$

(9) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7876.
(10) Nelsen, S. F.; Cunkle, G. T.; Evans, D. H.; Haller, K. J.; Kaftory, M.; Kirste, B.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 3829.



**10**



**11**

**12**

of 179.9°.[11] The NN bond length for **9** is 0.013 Å longer than that for the more pyramidal N compound with unbranched $\alpha$ substituents **12**, but 0.004 Å shorter than that for **11**, which has the same tetra-$\alpha$-branched alkyl substitution pattern and also has substantially more pyramidal nitrogens than **9** and lacks N,N′ rings. There is not a simple relationship between NN bond length and the geometry parameters we have considered, especially for the *anti* compounds.

**Results and Discussion: Calculations on Sesquibicyclic Hydrazines**

Saunders's stochastic search program[12] was used to find minima using Allinger's MM2 molecular mechanics program[13] for these hydrazines (employing Allinger's hydrazine parameters supplied with this program), and Clark's VAMP program package[14] for carrying out Dewar AM1[15] molecular orbital calculations. The use of structures generated by MM2 has been especially valuable in finding AM1 energy minima which lie far above the more stable one, as well as for less constrained compounds. We carried out *ab initio* calculations at the 6-31G* level for **1**, **2**, **3**, **5**, and **6** using Pople's Gaussian 90 and 92 programs.[16] Compounds **1**, **2**, **3**, and **5** were constrained to $C_s$ symmetry because of the small amount of bicyclic ring twist known to be present. Allowing bicyclic torsion from the $C_{2v}$ untwisted structure of **6** to twisted $C_2$ symmetry lowered the energy 0.89 kcal/mol and resulted in 13.6° of bicyclic torsion, accompanied by an NN bond length increase of 0.012 Å and an $\alpha_{av}$ decrease of 0.3°. Substantial amounts of computer time are required for geometry optimizations at 6-31G*: 14 h of IBM RS-6000 CPU time for **3** constrained to $C_s$ symmetry starting from the AM1 structure and 36.5 h for **6** starting from the minimum obtained at $C_{2v}$ symmetry. An MP2/6-31G* geometry optimization of **6** from the 6-31G* structure required 300 h of CPU time, making such calculations impractical to carry out for all the compounds considered here.

Calculated and X-ray geometries about nitrogen are compared in Tables I–III. The most poorly fit parameter in all these calculations is the NN bond length, calculated for **2**, **3**, and **6**, respectively, as 5.0, 6.0, and 5.8% too short by AM1 and 5.6, 6.9, and 5.6% too short by MM2. The 6-31G* calculations roughly halve this error to 2.5, 3.1, and 2.4% too short. The rather poor geometries (especially NN bond length) for 6-31G* calculations of hydrazines are not caused by using too small a basis set size but by not including proper electron correlation. Calculations on hydrazine itself have shown that methods which correlate four electrons simultaneously are necessary to obtain the proper NN bond length; MP4/6-31G* optimizations suffice.[17] The MP2/6-31G* structure of **6** obtains the X-ray NN bond length to within experimental error.

The major structural change besides that of NN bond length which accompanies bicyclic ring size change is the amount of pyramidalization at nitrogen. These parameters are interdependent (see Figure 3). We employ $\alpha_{av}$ as a quantitative measure of nitrogen pyramidality because it is about linear with hybridization at N and hence with lone pair orbital energy, while other measures of pyramidality are quite nonlinear.[1] Despite the better NN bond length in 6-31G* calculations, they do a significantly poorer job of obtaining the proper pyramidality at nitrogen than either AM1 or MM2 calculations. The 6-31G* calculations overestimate $\alpha_{av}$ at N by 1.3, 1.7, and 1.4° for **2**, **3**, and **6**, respectively, corresponding to 12, 16, and 13% of the change in $\alpha_{av}$ between a tetrahedral and a planar atom. The MP2/6-31G* calculation obtained the X-ray $\alpha_{av}$ to within experimental error. A summary comparing the experimental average $\alpha_{av}$ and $\theta$ values at the hydrazine unit with the values calculated by MM2 and by AM1 for sesquibicyclic hydrazines appears as Table IV, and

**Table I.** Comparison of X-ray with Calculated Geometries about Nitrogen for Smaller Saturated Sesquibicyclic Hydrazines

| | compound numbers | | |
|---|---|---|---|
| rings present | **1** (21/21) | **3** (21/22) | **6** (22/22) |
| *d*(NN), Å X-ray | | 1.514(2) | 1.492(2) |
| MM2 | 1.403 | 1.410 | 1.409 |
| AM1 | 1.442 | 1.423 | 1.406 |
| 6-31G*[MP2/] | 1.473 | 1.467 | 1.456 [1.490] |
| *d*(CN), Å | | 1.482, 1.486[a] | 1.478, 1.469 |
| MM2 | 1.470[n] | 1.472[a] | 1.471, 1.473 |
| AM1 | 1.499[n] | 1.508[a] | 1.486 |
| 6-31G*[MP2/] | 1.464[n] | 1.467[a] | 1.463, 1.456, [1.478, 1.468] |
| *d*(CN), Å | | 1.481, 1.482[b] | 1.478, 1.469 |
| MM2 | 1.468[x] | 1.471[b] | 1.471, 1.473 |
| AM1 | 1.501[x] | 1.486[b] | 1.486 |
| 6-31G*[MP2/] | 1.465[x] | 1.462[b] | 1.463, 1.456 [1.478, 1.468] |
| ∠(NNC), deg | | 103.1, 103.7[a] | 108.7, 111.0 |
| MM2 | 105.1[n] | 104.8[a] | 108.8, 111.7 |
| AM1 | 105.7[n] | 105.9[a] | 111.9 |
| 6-31G*[MP2/] | 104.6[n] | 104.5[a] | 110.1, 111.7, [108.3, 111.3] |
| ∠(NNC),[big], deg | | 109.4, 110.3[b] | 108.7, 111.0 |
| MM2 | 105.2[x] | 111.6[b] | 108.8, 111.7 |
| AM1 | 105.7[x] | 111.6[b] | 111.9 |
| 6-31G*[MP2/] | 104.5[x] | 111.1[b] | 110.1, 111.7 [108.3, 111.3] |
| ∠(CNC), deg | | 116.9, 117.1 | 118.6(1) |
| MM2 | 118.6 | 115.3 | 116.5 |
| AM1 | 119.0 | 115.4 | 116.8 |
| 6-31G*[MP2/] | 123.2 | 119.7 | 120.9 [119.1] |
| $\alpha$(av), deg | | 110.0, 110.2 | 112.8 |
| MM2 | 109.6 | 110.6 | 113.0 |
| AM1 | 110.1 | 110.9 | 113.6 |
| 6-31G*[MP2/] | 110.8 | 111.8 | 114.2 [112.9] |
| dih∠(CNNC), deg | | 1.2(1)[a] | 15.0(2) |
| MM2 | 0.0 | 0.0 | 14.6 |
| AM1 | 0.0 | 0.0 | 0.0 |
| 6-31G*[MP2/] | [0.0] | [0.0] | 13.6[16.7] |
| dih∠(CNNC), deg | | 0.8(2)[b] | 15.0(2) |
| MM2 | 0.0 | 0.0 | 14.6 |
| AM1 | 0.0 | 0.0 | 0.0 |
| 6-31G*[MP2/] | [0.0] | [0.0] | 13.6 [16.7] |
| dih∠(CNNC'), deg | | –124.6(1) | 147.2 |
| MM2 | 125.9 | –125.4 | 146.3 |
| AM1 | 127.0 | –126.3 | 133.3 |
| 6-31G*[MP2/] | 130.7 | –130.3 | 150.8 [149.4] |
| dih∠(CNNC"), deg | | 126.7(1) | –117.2 |
| MM2 | –125.9 | 125.4 | –117.0 |
| AM1 | –127.0 | 126.3 | –133.3 |
| 6-31G*[MP2/] | –130.7 | 130.3 | –127.7 [–116.0] |

[a] In **21** ring. [b] In **22** ring: x, for *exo* dialkylated ring; n, for *endo* dialkylated ring.

(11) Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461.

(12) Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150. We have used VAXMOLE5, most kindly supplied by its author.

(13) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. *QCPE* **1980**, *12*, 395.

(14) Clark, T.; Rauhut, G., unpublished. These calculations were carried out using VAMP Versions 4.3 or 4.4. We thank Timothy Clark for supplying this program modified for use on a Stardent computer.

(15) Dewar, M. J. S.; Zoebisch, E. GF.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(16) *Gaussian 90*: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc.; Pittsburgh PA, 1990. *Gaussian 92*: Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc.; Pittsburgh PA, 1992.

(17) Petillo, P. A., Ph.D. Thesis, University of Wisconsin, 1991, submitted for publication.

**Table II.** Comparison of X-ray and Calculated Geometries about Nitrogen for Unsaturated Sesquibicyclic Hydrazines

| | compound numbers | |
|---|---|---|
| rings present | **2** (21/u22) | **5** (22/u22) |
| d(NN), Å X-ray | 1.500(2) | 1.497(4) |
| MM2 | 1.416 | 1.418 |
| AM1 | 1.425 | 1.409 |
| 6-31G* | 1.462 | 1.461 |
| d(CN), Å[a] | 1.490, 1.494 | "1.483(5)"[c] |
| MM2 | 1.473 | 1.473 |
| AM1 | 1.510 | 1.491 |
| 6-31G* | 1.470 | 1.469 |
| d(CN), Å[b] | 1.494, 1.494 | "1.498(4)"[c] |
| MM2 | 1.473 | 1.476 |
| AM1 | 1.498 | 1.502 |
| 6-31G* | 1.471 | |
| ∠(NNC), deg[a] | 103.1, 104.2 | "110.1(1)"[c] |
| MM2 | 104.6 | 111.4 |
| AM1 | 105.9 | 111.7 |
| 6-31G* | 104.5 | 110.5 |
| ∠(NNC), deg[b] | 109.3, 109.7 | "110.1(6)"[c] |
| MM2 | 111.6 | 111.6 |
| AM1 | 111.5 | 111.6 |
| 6-31G* | 110.6 | 111.0 |
| ∠(CNC), deg | 116.7, 117.2 | 116.2(1) |
| MM2 | 113.6 | 113.4 |
| AM1 | 114.0 | 113.5 |
| 6-31G* | 119.2 | 118.1 |
| α(av), deg | 110.0, 110.2 | 112.1 |
| MM2 | 110.0 | 112.1 |
| AM1 | 110.4 | 112.3 |
| 6-31G* | 111.4 | 113.2 |
| dih∠(CNNC), deg[a] | −2.6(2) | "0.4(3)"[c] |
| MM2 | −0.6 | 0.1 |
| AM1 | 0.0 | 0.0 |
| 6-31G* | [0.0] | [0.0] |
| dih∠(CNNC), deg[b] | −2.8(2) | "0.0(4)"[c] |
| MM2 | −0.7 | 0.1 |
| AM1 | 0.0 | 0.0 |
| 6-31G* | [0.0] | [0.0] |
| dih∠(CNNC′), deg | 122.8(2) | "129.5"[c] |
| MM2 | 122.6 | 127.9 |
| AM1 | 124.4 | 128.3 |
| 6-31G* | 129.4 | 133.1 |
| dih∠(CNNC″), deg | −128.2(2) | "−129.1"[c] |
| MM2 | −124.0 | −127.8 |
| AM1 | −124.4 | −128.3 |
| 6-31G* | −129.4 | −133.1 |

[a] In **21** or **u22** ring. [b] In **22** ring. [c] Structure disordered at the HC=CH and $CH_2CH_2$ groups, so these are weighted averages.

Figure 4 shows the correlation of calculated $\alpha_{av}$ with experiment. If the calculations agreed perfectly with experiment, the points would fall upon the line drawn. The $\alpha_{av}$ values calculated by MM2 for the *syn* compounds show rather good agreement with the X-ray values. The **21/22** compound **3** shows the poorest correlation, calculated to have a 0.6° larger $\alpha_{av}$ than **21/u22** but experimentally only showing a 0.1° larger value. We note that the correlation of experimental NN bond length with $\alpha_{av}$ of Figure 3 also shows an anomaly between these two compounds, but here it is **2** that lies off the line given by the other *syn* compounds. Although the $\alpha_{av}$ values calculated by AM1 are slightly larger than those obtained from MM2, the correlation with the experimental values is about as good: a linear regression for the MM2 values predicts $\alpha_{av}$ over the X-ray range 110–113° at 110.3–113.2°, $r = 0.988$, while that for the AM1 values gives 110.5–113.7°, $r = 0.985$. The AM1 calculations estimate the change in $\alpha_{av}$ with bicyclic ring size basically correctly, which is presumably why the correlation of both experimental formal potential for oxidation and AM1-calculated [$\Delta H_f$(cation) − $\Delta H_f$(neutral)] with AM1-calculated $\alpha_{av}$ for sesquibicyclic hydrazines is linear.[9] Points for the *anti* **42/22** compound **9** are also included in Figure 4. The AM1 point shown is for the AM1 optimized structure, which is incorrectly obtained to be *syn*; the point for the *anti* AM1 structure falls even further from the X-ray value.

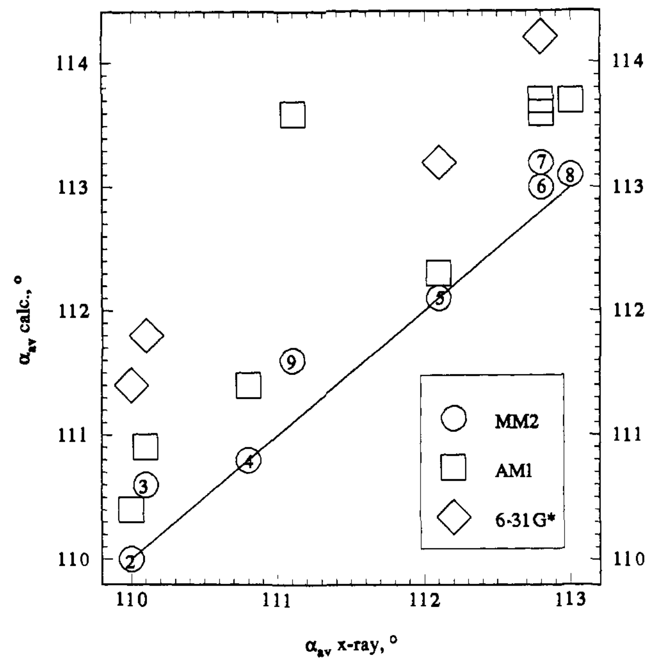



**Figure 4.** Comparison of calculated and experimental $\alpha_{av}$ values for sesquibicyclic hydrazines.

Both MM2 and AM1 calculate similar near eclipsing of the phenyl group with the inner dimethylene bridge of **7**, which is found in the X-ray structure (Figure 1), making it seem unlikely that this alignment is a result of crystal packing forces. AM1 calculations predict a >11 kcal/mol barrier for rotating the phenyl group past the nitrogen and its attached **22** ring, unusually high for a *tertiary* alkyl benzene.[18] The ortho and meta phenyl carbons remain isochronous down to −50 °C in the $^{13}C$ NMR spectrum of **7**, as expected from the low calculated energy for C–Ph rotation which does not pass the nitrogens. The $^{13}C$ NMR coalescence temperature for **7** is close to the −65 °C of **6**,[5] showing that bridgehead phenyl substitution does not significantly raise the double nitrogen inversion barrier. Both ortho and meta carbons are interconverted by double N inversion which interconverts the dimethylene bridges and an "easy" C–Ph rotation which does not require passing the nitrogens.

As shown in Table IV, AM1 calculations get the amount of torsion in **22** and **32** hydrazines **6–8** far too small, and, from the data for **9**, they also do a very poor job of estimating the energy difference between the *syn*- and *anti*-fused conformations. MM2 does a much better job, estimating the NN twist for all these compounds well and also correctly calculating *anti* **9** to be more stable than *syn* **9**. We suggest that the comparison of calculated energy differences between *anti* and *syn* substituted sesquibicyclic hydrazines which appears in Table V is useful in rationalizing the large observed difference in double nitrogen inversion barriers between **21/21** (**1**), $\Delta G^‡$ 27.0 kcal/mol (at 80 °C), and **22/22** (**6**), $\Delta G^‡$ 10.3 kcal/mol (at −55 °C).[5] The 16.7 kcal/mol increase in barrier for **2** compared to **6** would appear more reasonable if **6** were inverting one nitrogen at a time, going through an *anti* intermediate, while **1** was not, being required to undergo simultaneous double nitrogen inversion. AM1 greatly overestimates double nitrogen inversion barriers for sesquibicyclic hydrazines, including **6**, and were unable to locate an *anti* energy minimum by AM1 for **6** which would allow reasonable rationalization of the 2.6-fold increase in barrier in going from **6** to **1**.[5] Use of the Saunders search program reliably generates all energy minima for MM2 calculations, allowing estimation of the *anti,syn* energy difference even for **1** (Table V). By using these structures as input for AM1 calculations, the major features of AM1 energy surface could be examined as well. Although AM1 appears not to have an *anti*-fused energy minimum structure for

(18) Berg, U.; Sandström, J. *Prog. Phys. Org. Chem.* **1989**, *25*, 74.

**Table III.** Comparison of X-ray with Calculated Geometries about Nitrogen for Larger Saturated Sesquibicyclic Hydrazines

| | compound numbers | | | |
|---|---|---|---|---|
| rings present | 7 1Ph-(22/22) | 4 (21/32) | 8 (22/32) | 9 (22/42)[a] |
| d(NN), Å X-ray | 1.493(2) | 1.511(2) | 1.490(3) | 1.473(2) |
| MM2 | 1.408 | 1.412 | 1.408 | 1.392 |
| AM1 | 1.403 | 1.414 | 1.399 | 1.403 |
| d(CN), [sm], Å[b] | 1.481, 1.469○ | 1.487, 1.476 | 1.471, 1.481 | 1.473, 1.476 |
| MM2 | 1.474, 1.472○ | 1.475, 1.475 | 1.474, 1.475 | 1.466, 1.476 |
| AM1 | 1.488, 1.487○ | 1.514, 1.514 | 1.493, 1.493 | 1.479, 1.484 |
| d(CN), [big], Å | ♦1.487, 1.475 | 1.478, 1.481 | 1.464, 1.492 | 1.466, 1.485 |
| MM2 | ♦1.479, 1.471 | 1.471, 1.470 | 1.467, 1.476 | 1.468, 1.469 |
| AM1 | ♦1.505, 1.484 | 1.481, 1.481 | 1.482, 1.483 | 1.469, 1.470 |
| ∠(NNC), [sm], deg | ○108.3, 110.8 | 103.6, 102.9 | 108.0, 111.0 | 106.8, 107.5 |
| MM2 | ○110.6, 111.7 | 104.6, 104.4 | 109.5, 112.0 | 106.1, 109.8 |
| AM1 | ○112.1, 111.7 | 105.9, 105.9 | 111.7, 111.8 | 109.5, 110.4 |
| ∠(NNC), [big], deg | ♦109.5, 111.1 | 112.9, 113.6 | 111.5, 116.1 | 106.6, 109.6 |
| MM2 | ♦111.6, 111.9 | 114.7, 114.6 | 112.8, 115.0 | 109.6, 110.8 |
| AM1 | ♦112.3, 112.6 | 115.2, 115.2 | 115.3, 115.4 | 111.3, 113.9 |
| ∠(CNC), deg | ♦118.7, 118.5○ | 115.5, 115.8 | 115.1, 117.5 | 120.0, 115.7 |
| MM2 | ♦117.1, 116.1○ | 113.4, 113.4 | 113.5, 115.7 | 117.7, 115.3 |
| AM1 | ♦117.1, 116.5○ | 113.1, 113.1 | 113.8, 113.9 | 120.0, 119.9 |
| α(av), deg | ○112.6, 113.0♦ | 110.7, 110.8 | 113.3, 112.6 | 111.2, 110.9 |
| MM2 | ○112.9, 113.5♦ | 110.8, 110.9 | 113.5, 112.7 | 112.0, 111.2 |
| AM1 | ○113.7, 113.7♦ | 111.4, 111.4 | 113.7, 113.6 | 114.7, 113.6 |
| dih∠(CNNC), [sm] | ○15.9 | −2.2(2) | 15.1 | 36.4 |
| MM2 | ○15.6 | −0.9 | 18.5 | 30.5 |
| AM1 | ○1.6 | 0.0 | 1.1 | 30.1 |
| dih∠(CNNC), [big] | ♦16.9 | −2.5(2) | 18.2 | −67.6 |
| MM2 | ♦17.7 | −1.1 | 22.0 | −72.8 |
| AM1 | ♦1.9 | 0.0 | 1.2 | −56.5 |
| dih∠(CNNC'), deg | ♦148.8○ | 123.4(2) | 148.1 | 162.9 |
| MM2 | ♦148.9○ | 123.8 | 151.1 | 158.6 |
| AM1 | ♦135.3○ | 125.7 | 133.3 | 165.1 |
| dih∠(CNNC") deg | −115.9 | −128.2(2) | −114.8 | 165.9 |
| MM2 | −115.5 | −125.7 | −110.7 | 159.0 |
| AM1 | −132.0 | −125.7 | −131.0 | 168.4 |
| dih∠(Ar,CC), deg[c] | 11.5 | | | |
| MM2 | 9.2 | | | |
| AM1 | 0.9 | | | |

[a] *Anti* by X-ray. MM2 gets *anti* 4.2 kcal/mol more stable than *syn*. AM1 gets *syn* 9.1 kcal/mol more stable than *anti*, but the *anti* structure is that listed. [b] [sm] and [big] in the first column refer to the smaller and the larger bicyclic ring respectively. ♦ and ○ for **7** refer to the PhC–N unit and the N'–CH unit in the opposite bicyclic ring, respectively. [c] The smaller dihedral angle between the phenyl ring and the *inner* bridgehead, $CH_2$ bond for compound **7**.

**Table IV.** Comparison of Experimental and Calculated Pyramidalities at N and NN Bond Twist Angles for Sesquibicyclic Hydrazines

| rings present | compd no. | exper. (X-Ray) α(av) | exper. (X-Ray) θ | MM2 calc α(av) | MM2 calc θ | AM1 calc α(av) | AM1 calc θ |
|---|---|---|---|---|---|---|---|
| 21/21 | **1** | | | 109.6 | 0.1 | 110.1 | 0.0 |
| 21/u22 | **2** | 110.0 | 2.7 | 110.0 | 0.7 | 110.4 | 0.0 |
| 21/22 | **3** | 110.1 | 1.1 | 110.6 | 0.0 | 110.9 | 0.0 |
| 21/32 | **4** | 110.8 | 2.4 | 110.8 | 2.4 | 111.4 | 0.0 |
| 22/u22 | **5** | 112.1 | 0.2 | 112.1 | 0.1 | 112.3 | 0.0 |
| 22/u22 | **6** | 112.8 | 15.0 | 113.0 | 14.6 | 113.6 | 0.5 |
| 1-Ph-22/22 | **7** | 112.8 | 16.4 | 113.2 | 16.7 | 113.7 | 1.7 |
| 22/32 | **8** | 113.0 | 16.7 | 113.1 | 20.2 | 113.7 | 1.2 |
| 22/42(*syn*) | **9** | (is anti) | | 113.2 | 22.6 | 113.6 | 9.3 |
| 22/42(*anti*) | **9** | 111.1 | 164.4 | 111.6 | 158.8 | 114.2 | 167.8 |

**1**, **3**, or **6**, the energy surface is flat enough near the MM2 *anti* fused structures for **3** and **6** (but not for **1**) that use of AMPAC 1.0[19] using the default optimization protocol produced partially optimized *anti* fused structures (gradient normal >8) at 24.9 kcal/mol higher energy than the fully optimized *syn* structure for **3** and 18.2 for **6**. Optimization with VAMP 4.4 or adding the "PRECISE" keyword to the control line in AMPAC 1.0 optimizations leads to the *syn* form. It appears from Table V that AM1 incorrectly calculates *anti* forms of sesquibicyclic hydrazines to lie on the order of 10 kcal/mol higher in energy relative to *syn* forms than it should. MM2 calculations predict that the *anti* energy minimum for **6** lies low enough that it can invert its nitrogens sequentially, while **1** does not have such an

(19) AMPAC 1.0: *QCPE Bull* **1986**, *506*, 24a.

**Table V.** Comparison of *Syn* and *Anti* Conformation Energies for Sesquibicyclic Hydrazines

| compd | most stable conform | MM2 calculations type | MM2 calculations *anti–syn*[a] | AM1 Calculations type | AM1 Calculations *anti–syn*[b] | AM1–MM2[c] |
|---|---|---|---|---|---|---|
| **21/21 (1)** | *syn* | *syn* | +32.9 | *syn* | *anti* not min | |
| **21/22 (3)** | *syn* | *syn* | +22.9 | *syn* | *anti* not min | (∼6.6)[d] |
| **22/22 (6)** | *syn* | *syn* | +9.9 | *syn* | *anti* not min | (∼8.3)[d] |
| **22/32 (8)** | *syn* | *syn* | +4.2 | *syn* | +13.9 | 9.6 |
| **22/42 (9)** | *anti* | *anti* | −4.7 | *syn* | +9.1 | 13.8 |

[a] Difference in steric energies, kcal/mol for MM2-optimized structures. [b] Difference in $\Delta H_f$, kcal/mol, for AM1-optimized structures. [c] (*Anti–syn*) entry for AM1 minus that for MM2 calculations. [d] See text for the source of this estimated number.

*anti* minimum low enough in energy and ought to undergo the simultaneous double N inversion implied by the large $\Delta G^{\ddagger}$ observed.

## Discussion: Less Constrained Hydrazines

Another hydrazine conformational problem to which we recently applied AM1 calculations was rationalization of the fact that the *anti*-di-*tert*-butyl-dimethyl hydrazine **13** exists both in solution and in crystalline form only in the conformation shown, that with both *tert*-butyls directed away from the center of the molecule (Outer), but the *syn* isomer **14** has one *tert*-butyl directed Inner, as shown.[20] Although AM1 calculations made the correct prediction of most stable conformation, they failed to obtain a large enough energy difference between the outer and inner *tert*-butyl conformations of **13** to be consistent with experiment, where

**Table VI.** Comparison of Energy Differences Calculated for Fused *bis*(*N-tert*-butyl-*N*-methylbicyclo[2.2.2]octyl) Species

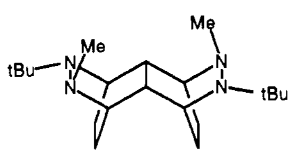
| | | experimental | | MM2 calculations | | AM1 calculations | |
|---|---|---|---|---|---|---|---|
| compd | conf | rel *E* | dih∠[a] | ΔSE | dih∠[a] | $\Delta\Delta H_f$ | dih∠[a] |
| (**13**)*anti*-Bu | Oi,Oi | [0][b] | 12.5, 12.8 | [0] | 11.9, 11.9 | [0] | 9.8, 9.8 |
| | Io,Io | | | 1.6 | 9.0, 9.0 | 0.4 | 9.9, 9.9 |
| | Oi,Io | | | 4.3 | 3.5, 9.5 | 1.4 | 8.8, 8.8 |
| (**14**)*syn*-*t*Bu | Oi,oI | [0][b] | 13.1, 13.3 | [0] | 10.8, 11.2 | [0] | 10.4, 10.5 |
| | Oi,iO | | | 4.9 | 10.0, 4.8 | 1.5 | 10.4, 10.5 |
| | Io,oI | | | 6.2 | 8.1, 11.6 | 2.1 | 10.4, 10.5 |

[a] Dihedral angles about the central CH–CH bond of the molecule. [b] Other conformations were not observed in solution by $^{13}$C NMR and are estimated to lie at least 1.0 kcal/mol higher in energy.

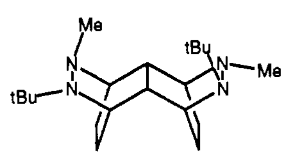
**Table VII.** Comparison of Relative Energies of Conformations for Some Less Constrained Hydrazines

| compd | conformation | experiment[a] | MM2 | AM1 |
|---|---|---|---|---|
| **15** | (*anti*) | [0] (NMR)[22] | [0] | [0] |
| | (*syn*) | unobs (NMR) | 11.9 | 1.6 |
| **16** | (*anti*) | [0] (NMR)[22] | [0] | [0] |
| | (*syn*) | unobs (NMR) | 14.6 | 2.6 |
| **17** | twist (*syn*) | [0] (ED, $\theta$ = 38°)[23] | [0] ($\theta$ = 44°) | *b* |
| | eclipsed (*syn*) | | 3.2 ($\theta$ = 0°) | [0] |
| | (*ani*) | | 4.2 | 18.3 |
| **18** | $T_{ee}$ (*anti*) | [0] (PE)[24] | 4.5 | 2.3 |
| | $T_{aa}$ (*gauche*) | <1 (PE) | [0] | [0] |
| **19** | 19ee (*anti*) | [0] (PE, NMR)[25] | 5.3 | 3.6 |
| | 19ae (*gauche*) | 1.2 (PE) 0.4 (NMR) | 2.0 | 1.7 |
| | 19aa (*anti*) | unobs (PE, NMR) | [0] | [0] |
| **20** | 20ee (*anti*) | [0] (NMR, X-ray)[25] | 1.1 | 2.6 |
| | 20ae (*gauche*) | >2.5 (NMR) | [0] | [0] |
| **11** | 11ee (*anti*) | [0] (NMR)[10] | 0.8 | 0.12 |
| | 11ae (*anti*) | 0.3 (NMR) | 2.0 | 0.08 |
| | 11aa (*anti*) | 0.5 (NMR) | [0] | [0] |
| | 11 (*gauche*) | unobs (PE) | *b* | −2.2 |

[a] Numbers in brackets are relative conformational energies in kcal/mol as indicated by the type of experiment shown in parentheses. Superscripts are reference numbers. ED is electron diffraction, and PE is photoelectron spectroscopy. [b] Not calculated to be an energy minimum.



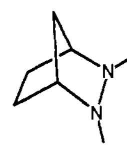

13 (Oi,Oi)



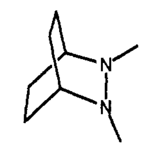

14 (Oi,oI)

only the **Oi,Oi** conformation was observed.[20] As shown in Table VI, MM2 treats this question better, both in terms of obtaining torsional twists slightly closer to the X-ray values and in predicting larger differences between different nitrogen inversion isomers.

We do not want to leave the impression that either the current MM2 parameters or AM1 calculations lead to correct predictions of relative conformational energies for most hydrazines;[21] they do not. When fewer conformational constraints are built into the compounds, serious errors in relative energies result, as is demonstrated in Table VII. Both MM2 and AM1 correctly predict the *anti* conformations of the bicyclic *N,N′*-dimethylhydrazines **15** and **16** to be significantly more stable than *syn* ones, consistent with Anderson and Lehn's demonstration at the beginning of conformational work on hydrazines by NMR that only *anti* conformations could be detected.[22] Anderson and Lehn pointed out that the undetected *syn* compounds must be intermediates in the inversion process, but how high these intermediates might lie in energy remains unknown. Although AM1 calculations predict this energy difference to be under 3

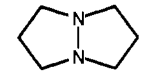



15

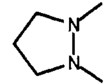



16

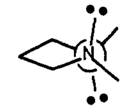
kcal/mol (and hence that relatively modest nonbonded steric interactions introduced by properly placed substituents might allow preparation of analogues with *syn* conformations detectably occupied), as shown in Table V, AM1 predicts *syn* conformations of sesquibicyclic hydrazines to be far too stable relative to *anti* ones. On the other hand, the consideration of N,N′-monocyclic hydrazines below suggests that the MM2 prediction that *syn* conformations for **15** and **16** are above 10 kcal/mol higher in energy than *anti* ones is likely to be too high, because MM2 significantly overestimates the difference between *syn* and *anti* conformations of five- and six-membered ring hydrazines. MM2 does predict proper torsion in 1,5-diazabicyclo[3.3.0]octane **17**,[23] for which AM1 fails miserably. However, even MM2 does not handle relative energies of *gauche* and *anti* lone pair conformations either in pyrazolidine **18**[24] or hexahydropyridazine derivatives



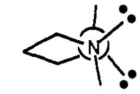

17




18

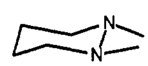


$T_{ee}$

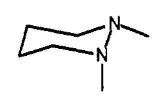


$T_{aa}$

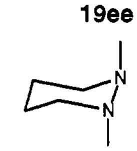
**19** and **20**.[25] We find it rather discouraging that MM2 and AM1 show such substantial agreement in obtaining the wrong ordering



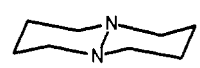

19ee




19ae

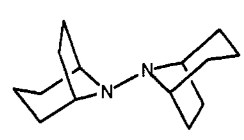



19aa

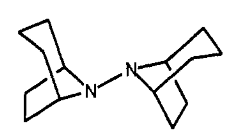



20ee

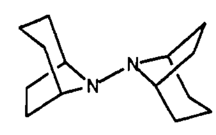
of the chair conformations of **19**; when two such different methods of calculation give the same answer, one's tendency would be to believe the answer. This clearly would be unwise for unconstrained hydrazines. Even for the relatively constrained bis-N,N-bicyclic **11**, both AM1 and MM2 get the relative order of the $\theta \sim 180°$ solution conformations wrong, and **11** crystallizes as **11aa** which NMR studies have demonstrated is the least stable of the three forms in solution.[10]




11ee




11ea




11aa

## Conclusion

MM2 calculations give rather good agreement with experimental pyramidalities at N for sesquibicyclic hydrazines and do

(20) Nelsen, S. F.; Wolff, J. J.; Chang, H.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 7882.
(21) For a recent review of hydrazine conformations, see: Nelsen, S. F. In *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B., Takeuchi, Y., Eds.; VCH: New York, 1992; p 88.
(22) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 91.
(23) Rademacher, P. *J. Mol. Struct.* **1975**, *28*, 97.
(24) (a) Rademacher, P.; Koopman, H. *Chem. Ber.* **1975**, *108*, 1557. (b) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6982, 6987.
(25) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.

Table VIII. Summary of Crystal Data and Refinement Parameters

| compd no. | 2 | 3 | 4 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|
| empirical formula | $C_{11}H_{16}N_2$ | $C_{11}H_{18}N_2$ | $C_{12}H_{20}N_2$ | $C_{18}N_{24}N_2$ | $C_{13}H_{22}N_2$ | $C_{14}H_{24}N_2$ |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 8.288(2) | 8.318(2) | 12.234(6) | 6.1733(12) | 6.343(4) | 10.909(5) |
| $b$, Å | 9.886(2) | 9.999(3) | 8.085(4) | 19.794(5) | 17.284(10) | 7.169(3) |
| $c$, Å | 11.520(2) | 11.718(3) | 11.400(5) | 11.697(3) | 10.198(6) | 15.669(6) |
| $\beta$,° | 103.80(2)° | 105.70(3) | 112.37(4) | 99.76(2) | 91.75(5) | 99.46(3) |
| volume, Å$^3$ | 916.1(3) | 938.9(5) | 1042.6(8) | 1408.6(6) | 1117.5(11) | 1208.7(9) |
| density(calc), g/cm$^3$ | 1.278 | 1.262 | 1.225 | 1.266 | 1.226 | 1.211 |
| $F$(000) | 384 | 392 | 424 | 584 | 456 | 488 |
| speed, deg min in $\omega$ | 2.0–12.0 | 2.0–30.0 | 3.0–30.0 | 2.0–20.0 | 2.0–20.0 | 3.0–30.0 |
| $\omega$ range, deg | 0.5 | 0.5 | 0.9 | 0.5 | 1.2 | 0.5 |
| reflcns collected | 2460 | 2693 | 1461 | 3191 | 1672 | 1885 |
| independent reflcns$^a$ | 1149(2.60) | 1259(3.08) | 1277(6.86) | 1904(5.78) | 1457(3.53) | 1623(2.04) |
| obsd reflcns$^b$ | 1039 | 1154 | 1167 | 1596 | 1190 | 1451 |
| parameters refined | 119 | 119 | 128 | 182 | 137 | 146 |
| $R/R_w$ (obs/data), % | 4.14/6.02 | 3.95/5.78 | 5.16/7.17 | 4.24/5.39 | 5.24/6.36 | 3.74/5.47 |
| $R/R_w$ (all data), % | 4.65/6.21 | 4.35/5.93 | 5.53/8.11 | 5.20/5.81 | 6.34/6.63 | 4.21/5.62 |
| goodness of fit | 1.75 | 1.90 | 2.36 | 1.35 | 1.80 | 1.76 |
| data/parameter ratio | 8.7/1 | 9.7/1 | 9.1/1 | 8.8/1 | 8.7/1 | 9.9/1 |
| largest differences$^c$ | 0.20/–0.18 | 0.17/–0.18 | 0.22/–0.19 | 0.17/–0.22 | 0.19/–0.31 | 0.17/–0.18 |

$^a$ In parentheses: $R_{int}$, %. $^b$ ($F > 4.0\sigma(F)$). $^c$ In eÅ$^{-3}$.

a qualitatively good job at handling twisting about the NN bond in several geometry-constrained cases, although the deficiencies in NN bond length (severely underestimated) and *anti, gauche* energy difference for less constrained hydrazines such as hexahydropyridazine make MM2 calculations inadequate to reliably estimate energy differences between conformations of very different $\theta$. The errors 6-31G* calculations make for hydrazine[17] appear to be a significant part of what is wrong with present MM2 hydrazine parameters, which were apparently calibrated with the 6-31G* structure of hydrazine, but another difficulty is the fact that the "strain free" NN bond length depends on both $\theta$ and pyramidality of N, and these effects are not built into the MM2 parameter system. It would clearly be desirable to reparameterize molecular mechanics so that it would make the proper predictions for hydrazines, but this task has not yet been started.[26,27] It is unfortunate that even 6-31G* *ab initio* calculations do a rather poor job of calculating hydrazine geometries, as these calculations are so time-consuming that it is still impractical to do geometry optimizations at higher levels for molecules of this size. The single MP2/6-31G* calculation done in this series gave essentially the experimental geometry for **6**, but whether such calculations would be as successful for less constrained hydrazines remains unknown.

This work documents some serious deficiencies in the structures of neutral hydrazines calculated by AM1: the NN bonds are calculated to be far too short and too little twist is calculated for both N,N′-bicyclic and monocyclic rings. These errors result for example in AM1 predicting **22/42 (9)** to be more stable in the *syn* conformation and incorrectly predicting **17** to be untwisted. However, AM1 calculations do a significantly better job at predicting $\alpha_{av}$ for sesquibicyclic hydrazines than do the far more computationally demanding 6-31G* *ab initio* calculations. As has been discussed elsewhere,[1] AM1 calculations are remarkably successful in estimating the geometry and energy changes which occur upon electron removal from hydrazines and, in fact, appear to be superior to 6-31G* calculations for the consideration of this problem. This success of AM1 calculations obviously involves fortunate cancellation of errors in the energy changes.

## Experimental Section

Preparations of **1**,[4] **2**,[3] **3**,[3] **4**,[4] **8**,[5] and **9**[7] have been reported elsewhere.

**1-Phenyl-2,7-diazatetracyclo[6.2.2.2$^{3,6}$.0$^{2,7}$]tetradecane (7).** A solution of 1-phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene[28] (550 mg, 2.96 mmol) in 25 mL ether was treated with a solution of $HBF_4{\cdot}Et_2O$ (85%, 0.6 mL, 3.46 mmol) in 10 mL of ether, leading to immediate precipitation of the protonated azo compound as a white solid. After stirring 20 min at room temperature, filtration, washing with 3 × 20 mL of ether, and drying under a stream of nitrogen for 2 h, this material was dissolved in 20 mL of acetonitrile, 1,3-cyclohexadiene (0.3 mL) was added, and the mixture was stirred under nitrogen at 50 °C for 20 h. The red solution was concentrated to 10 mL, and ether was added slowly to precipitate the product, giving crude protonated 1-phenyl-2,7-diazatetracyclo-[6.2.2.2$^{3,6}$.0$^{2,7}$]tetradeca-4-ene tetrafluoroborate, which was obtained as a red solid (0.86 g, 82% yield) after solvent removal [$^1$H NMR (200 MHz, $CD_3CN$) $\delta$ 1.20-2.40 (m, 12H), 3.42 (br s, 1H), 3.67 (br s, 1H), 4.40 (br s, 1H), 6.55 (m, 2H), 7.10–7.60 (m, 5H)]. Deprotonation of this material led to retro-Diels–Alder cleavage with a half-life of under 3 h at room temperature, so it was hydrogenated before deprotonation. A mixture of the above material (300 mg, 0.847 mmol) and 5% Rh/$Al_2O_3$ (50 mg) in 100 mL of acetic acid was hydrogenated at atmospheric pressure until hydrogen uptake ceased, the catalyst was separated by filtration through Celite, and the solution was concentrated to give 350 mg of yellow oil (solvent residue remaining). This oil was stirred with powdered potassium hydroxide (85%, 2.5 g) in 100 mL of ether in an ice bath under an argon atmosphere for 15 h. Filtration, concentration, and sublimation (0.02 mmHg, 65 °C bath temperature) gave **7** as a white solid (168.1 mg, 74.0% yield): mp 115–116 °C; $^1$H NMR (500.13 MHz, $CDCl_3$) $\delta$ 1.45–1.55 (m, 2H), 1.58–1.63 (m, 2H), 1.76–1.80 (m, 2H), 1.92–1.96 (m, 2H), 2.11–2.16 (m, 2H), 2.27–2.31 (m, 2H), 2.41–2.43 (m, 5H), 2.84 (br s, 2H), 7.19 (br t, $J$ = 7.3 Hz, 2H), 7.28 (br t, $J$ = 7.4 Hz, 1H), 7.49 (br d, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (125.56 MHz, $CDCl_3$) $\delta$ 24.55 (br), 27.60 (br), 28.11 (br), 33.00 (br), 45.12, 51.02, 52.07, 56.92, 126.18, 126.29, 127.89, 146.45; HRMS calcd for $C_{18}H_{24}N_2$ 268.1940, found 268.1973.

**2,8-Diazatetracyclo[8.2.2.2$^{3,7}$.0$^{2,8}$]pentadecane (8):** $^{13}$C NMR ($CD_2Cl_2$) $\delta$ at 298 K 54.61, 53.52, 37.84, 29.64, 23.90, 21.24, 19.86 (half intensity); at 190 K 52.99, 52.02, 36.36, 28.17, 22.41, 19.50, 18.76 (half intensity).

**2,9-Diazatetracyclo[8.2.2.2$^{3,8}$.0$^{2,9}$]hexadecane (9):** $^{13}$C NMR ($CD_2Cl_2$) $\delta$ at 298 K 59.24, 55.54, 36.35, 27.70, 26.92, 26.58, 25.96; at 190 K 58.46, 57.17, 54.93, 53.16, 36.42, 33.83, 28.16, 27.96, 27.14 (assigned as two overlapping carbons), 25.87, 23.82, 22.83, 22.02; 250 K broadened signals at 58.68, 54.90, 35.87, 27.22, and a very broadened signal centered upfield of 27.

**Crystal Structures.** Crystal sizes, mm **2**, 0.15 × 0.40 × 0.45; **3**, 0.1 × 0.4 × 0.4; **4**, 0.4 × 0.5 × 0.5; **7**, 0.2 × 0.2 × 0.3; **8**, 0.2 × 0.2 × 0.2;

(26) The hydrazine parameters in MM3[27] are similar to those in MM2 and make the same types of errors. Provision is made in MM3 to allow stretch–bend and stretch–twist corrections so that it should prove feasible to obtain a parameter set which is far more successful than that used in this work.

(27) Allinger, N. L.; Yuh, Y. H.; Lii, H.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(28) (a) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102. (b) In our hands the 10% Pd/C hydrogenation catalyst used by Engel and co-workers for reduction of the *N*-methyltriazolenedione adduct of 1-phenylcyclohexa-1,3-diene led to a significant amount of N–C bond cleavage. We carried out the reduction in 1:1 ethyl acetate/ethanol using 5% $Rh/Al_2O_3$ without detecting N–C bond cleavage.

(29) Sheldrick, G. M. *SHELXTL PLUS*; Version 4.2, Siemans Analytical Instruments, Inc.: Madison, WI, 1990.

(30) Complex neutral atom scattering factors from *International Tables for X-ray Crystallography*; Kynoch: Birmingham, Vol. IV, Tables 2.2b and 2.3.1 (present distributor Kluwer).

**9**, 0.6 × 0.3 × 0.2. All these molecules crystallized in monoclinic space groups with $Z = 4$. Intensity data were measured with a Siemens P3f diffractometer using graphite monochromated Cu K$\alpha$ radiation ($\lambda$ = 1.54178 Å), Wyckoff scan type. Data were collected over a $2\theta$ range of 4–114°, except for **2**, for which the $2\theta$ range was 3.5–110.0°. Data were collected at −160(2) °C, except for **2**, at −165(2) °C, and **7**, −100(2) °C. The solution of the structures with direct methods in full-matrix least-squares refinement of $\sum w(F_o - F_c)^2$used Siemens SHELXTL PLUS (VMS).[29,30] Hydrogen atoms were located in a difference map and treated by the riding model using isotropic $U$ and weighting scheme $w^{-1} = \sigma^2(F) + CF^2$, with C = 0.0007 for **2** and **7**, 0.0006 for **4**, **8**, and **9**, and 0.0005 for **3**. A summary of crystallographic results appears in Table VIII.

**Calculations.** Saunders's MM2 search program VAXMOL5[15] was by modified Peter A. Petillo to allow use of a VAX 8650 to run the calculations employing initial structures generated from molecular orbital calculations, using program NEWSEL, written by PAP. Molecular orbital calculations[14,16,19] were carried out on VAX 8650, IBM-RS6000, or Stardent 3000 computers.

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**Supplementary Material Available:** Thermal ellipsoid plots (50% probability) for **2–4** and **8**, diagrams of heavy atom bond lengths and bond angles for **2–4** and **7–9**, tables of atomic coordinates and isotropic displacements, bond lengths, bond angles, anisostropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients for **2–4** and **7–9** (23 pages). Ordering information is given on any current masthead page.