Eclipsed Isopropyl Conformations of Two Dimeric Hydrazines

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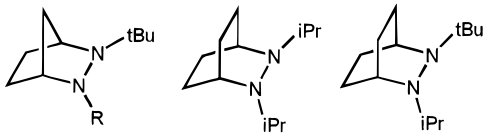
The X-ray structures of 4,10-di-*tert*-butyl-5,9-diisopropyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}]-tetradecane (**s4iPr**) and its 4,9-di-*tert*-butyl-5,10-diisopropyl isomer (**a4iPr**) are reported. Both compounds are in conformations having their *in*-*N*-alkyl groups (directed toward the central CH−CH bond of the molecule) *anti* to each other, as expected from previous work. The principal feature of interest is that one *in*-isopropyl group in each compound is in an eclipsed conformation, NN,C$_\alpha$Me twist angle −0.5(5)° for **s4iPr** and −6.4(4)° for **a4iPr**. Low energy (somewhat less) eclipsed *in*-isopropyl conformations are predicted by both molecular mechanics (MM2) and semiempirical quantum mechanical (AM1) calculations. The asymmetry of the potentially C_2 symmetric **a4iPr** because the two *in*-isopropyl groups are in different rotamers is apparently not a result of crystal packing forces, because a conformation with different isopropyl rotamers is the more stable one by at least 1.0 kcal/mol in solution, determined by ^{13}C-NMR spectroscopy. This result is not predicted by either calculation method. The "monomer", 2-*tert*-butyl-3-isopropyl-2,3-diazabicyclo[2.2.2]octane (**3**), proves to be a poor model for the conformations of **4iPr**.

Introduction

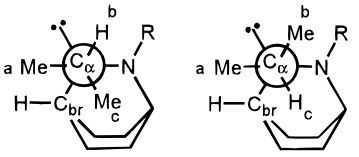
We have extensively used N,N′-bicyclic hydrazines as positive charge-bearing units for electron transfer studies.[1] The barrier to electron transfer is very sensitive to the geometry change between the neutral and positively charged oxidation states, so it is important to know the geometry of the neutral compounds studied. The geometry about the nitrogen atoms, the NN distance, nitrogen pyramidality (best considered using α_{av}, the average of the heavy atom bond angles at nitrogen), and the lone pair, lone pair dihedral angle, θ, are all sensitive to the alkyl groups attached to nitrogen.[2] Only the *trans* conformations ($\theta \sim 120°$) of 2,3-dialkyl-2,3-diazabicyclo-[2.2.*n*]hydrazines **1R**, **2**, and **3** are observed because the *cis* conformations are destabilized both sterically and



1 **2** **3**

electronically, as first pointed out by Lehn and Anderson in 1967.[3] A *cis* form has never been detected for an N,N′-bicyclic hydrazine with singly attached alkyl groups. In contrast, only *cis* conformations are observed when a five-membered monocyclic ring or a second bicyclic ring containing only five- to seven-membered rings are present.[4]

Unusual conformational effects arise for N,N'-bicyclic hydrazines when the size of R is increased. The tBu-*endo* conformation of **1R** is barely detectable when R is Me (the tBu *exo*:*endo* ratio is 93:7 at 25 °C, $\Delta G° = 1.5$ kcal/mol), but is almost as stable as the tBu-*exo* conformation when R is iPr (ratio 54:46 at −27 °C, $\Delta G° = 0.1$ kcal/mol).[5] The reason that iPr appears to be about as large as tBu in these systems may be understood considering Newman projections down the isopropyl group C$_\alpha$−N bond, as indicated below (for the bicyclooctyl compounds **2** or **3**). In these idealized views, a staggered iPr group might have three orientations for the C$_\alpha$−H



bH **cH**

bond: (a) H anti to the NN bond (very destabilized and not shown), (b) H anti to the C$_{br}$N bond, shown as **bH**, and (c) H anti to the N lone pair, shown as **cH**. The diisopropyl compound **2** shows a single symmetrical isopropyl rotamer by ^{13}C-NMR at low temperature, argued to be bis-**cH** on the basis of calculations and unusual cyclic voltammetry behavior rationalized by invoking "gearing" effects as the electron is removed.[6] The **cH** conformation being more stable implies that steric interactions with the bicyclic ring are smaller than with the NiPr′ group. For **3** the most stable conformation was argued to be **bH**, principally on the basis of calculations. A second isopropyl rotamer, assigned as **cH**, lies about 0.8 kcal/mol higher in free energy, although its contribution becomes so small at low temperature that the only evidence for its presence was ^{13}C NMR line broadening at intermediate temperatures.[6] It is reasonable that increasing the size of the NR′ substituent would destabilize **cH** with respect to **bH**.

Results and Discussion

NMR Spectra. This work concerns dimeric hydrazines derived formally by merging the CH_2CH_2 bridges

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(1) For reviews, see (a) Nelsen, S. F. *Molecular Structures and Energetics*; Liebman, J. F.; Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Ch. 1, p 1. (b) Nelsen, S. F. *Advances in Electron Transfer Chemistry;* Mariano, P. S., Ed., JAI: Greeenwich, CT, 1993; Vol. 3, p 167.

(2) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hiyashi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(3) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 81.

(4) Nelsen, S. F. In *Acyclic Organonitrogen Stereodynamics,* Lambert, J. B., Takeuchi, Y., Eds., VCH: New York, 1992; Chapter 3, p 89.

(5) Nelsen, S. F.; Chen, L.-J. *J. Org. Chem.* **1995**, *60*, 3263.

(6) Nelsen, S. F.; Chen, L.-J.; Petillo, P. A.; Evans, D. H.; Neugebauer, F. A. *J. Am. Chem. Soc.* **1993**, *115*, 10611.

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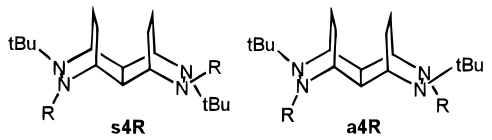
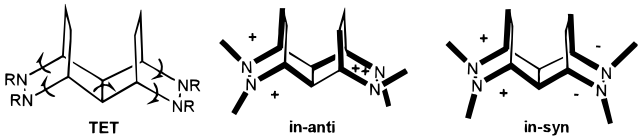
of two bicyclooctyl "monomers", that is, derivatives of 4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}]-tetradecane, **s4R** and **a4R**. These compounds are prepared by *tert*-butylation of the bis-azo compound, which produces an equal mix-



ture of *syn* and *anti* bis(diazenium) salt diastereomers which were separated by crystallization, followed by double addition of Grignard reagents, producing **s4R** or **a4R**.[7] These dimeric compounds could have two relative orientations of their *trans* hydrazine units. If *out* and *in* (outer and inner, respectively) are used to abbreviate whether an *N*-alkyl group is directed away from or toward the central CH−CH bond of the molecule, the in alkyl groups can either be *anti* to each other or *syn*. Both **4Me** isomers exist exclusively in the *in-anti* nitrogen inversion forms, both in crystals and in solution.[7] Despite the large difference in size between tBu and Me,



the important thing is not whether the tBu is directed *in* or *out* (sterics are quite similar for the two) but that substituents on opposite corners have the same orientation (i.e. *in-anti*). Calculations showed that this occurs principally because the tetracyclic core is torsionally twisted. This twist only relieves $RNC_{br}CH_2$ and $R'N'C_{br}'CH$ nonbonded steric interactions at both hydrazine units for the *in-anti* alkyl group arrangement,[7] as indicated on the structures above, where + signs indicate increased gauche CCNR twist angles (which is stabilizing), and − signs decreased ones (destabilizing), upon twisting the tetracyclic framework as shown.

In this work we examined the **4iPr** analogues of **4Me**, which we expected to be a routine (although complex) exercise. We fully expected these compounds to exist as nearly equal mixtures of tBu-*in* and tBu-*out* conformations because of the similar effective size of tBu and iPr in the **1iPr** monomer, and to have the iPr groups very predominately in **bH** conformations like the monomer **3**. Neither prediction proved correct, despite the apparently good models available.

s4iPr is asymmetric because it is in *in-anti* conformations and will show 20 ^{13}C lines for each double nitrogen inversion conformation present (at room temperature, where isopropyl rotation is fast on the NMR time scale). Although one 20 line spectrum clearly predominates at room temperature, speculation about what might be the predominant conformation appears fruitless. The ^{13}C NMR of **a4iPr** shows a major set of 10 lines at room temperature and a minor set (of which 8 lines were resolved from those of the major isomer) which corresponds to under 15% of the material. Because double nitrogen inversions are slow on the NMR time scale for these compounds,[5−7] these sets of lines can only reasonably correspond to the room temperature effectively C_2 symmetric *in-anti* conformations. The major conformation was shown to be tBu-*out* by NOE studies which established that the isopropyl methyl groups are close to the central CHCH bond of the molecule; tBu-*out* is therefore ≥1.0 kcal/mol more stable than tBu-*in*. This demonstrates that "monomer" **3** is a poor model for the conformations of **a4iPr**. Despite its bicyclooctyl partstructures, the faces of **a4iPr** in fact differ more than do the *exo* and *endo* faces of **1iPr**, and the two isopropyl groups have a distinct preference for occupying different rotamers, despite the fact that a single rotamer predominates for **3**.

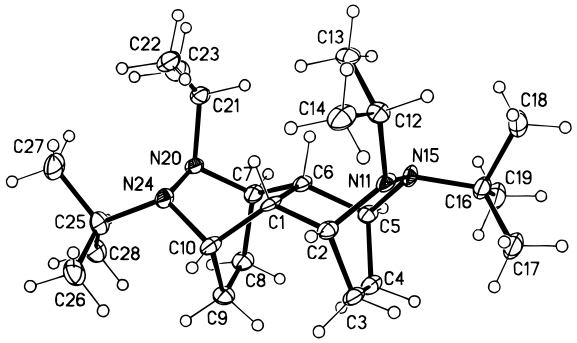


Figure 1. Thermal ellipsoid drawing (50% probability level) of **a4iPr**.

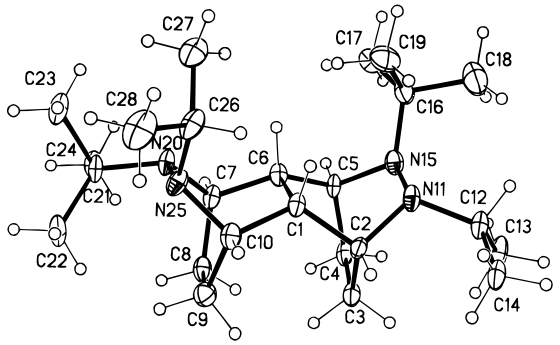


Figure 2. Thermal ellipsoid drawing (50% probability level) of **s4iPr**.

X-ray Structures. The X-ray crystal structures show that both isomers are in the expected *in-anti* conformations, and that **a4iPr** is in the same tBu-*out* conformation as it is in solution (See Figures 1 and 2 for thermal ellipsoid drawings). The **4Me** and **4iPr** structures are quantitatively compared in Tables 1 and 2. Replacing methyl by isopropyl significantly flattens the nitrogens, increasing α_{av} by 2.3°, 22% of the change from a tetrahedral to a planar nitrogen for **s4R**, and by 1.6° (16%) and 2.6° (25%) for **a4R**. It slightly decreases twist at the central CHCH bond of **s4R** (average value 13.2° → 11.5°, a −1.7° change), but increases it more in **a4R** (12.7° → 17.4°, a +4.7° change). Changes in torsional angles of the dimethylene and the dinitrogen bridges are irregular, complicated to consider, and unrevealing to us. The increase in nonbonded interactions caused by changing methyl to isopropyl in these systems is substantial, and is accommodated in a complex manner by rather small changes in most of the torsional angles.

The **4iPr** X-ray structures reveal one quite unanticipated feature. The isopropyl groups of the two hydrazine units of each are in different rotamers, and one isopropyl

(7) Nelsen, S. F.; Wolff, J. J.; Chang, H.; Powell, D, R. *J. Am. Chem. Soc.* **1991**, *113*, 7882.

(8) (a) Seiler, P.; Weisman, G. R.; Glendening, E. D.; Weinhold, F.; Johnson, V. B.; Dunitz, J. D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1175. (b) Seiler, P.; Dunitz, J. D. *Helv. Chim. Acta* **1989**, *72*, 1125.

Table 1. Comparison of Methyl and Isopropyl s4R X-ray Structures

	R = methyl[a]		R = isopropyl	
	Me-*out* unit	Me-*in* unit	iPr-*out*, **bH** unit	iPr-*in*, **Ecl** unit
		NN Bond Parameters		
d(NN), Å	1.489(5)	1.486(5)	1.482(4)	1.483(4)
α(BNC$_b$)	119.4(3)	118.7(3)	118.7(3)	115.9(3)
α(BNN)	111.5(3)	111.0(3)	111.8(3)	111.1(3)
α(C$_b$NN)	109.6(3)	109.9(3)	109.9(3)	109.5(3)
α$_{av}$(NtBu)	113.5(Bi)	113.2(Bo)	113.5(Bi)	112.2(Bo)
α(RNC$_b$)	111.4(4)	111.7(3)	116.0(3)	110.6(3)
α(RNN)	108.4(3)	108.9(3)	111.2(3)	116.2(3)
α(C$_b$NN)	110.7(3)	110.1(3)	110.4(3)	110.5(3)
α$_{av}$(NR)	110.2(Mo)	110.2(Mi)	112.5(Po)	112.4(Pi)
C$_b$NNC$_b$	−3.8(4)	−2.3(4)	−0.9(4)	−3.0(4)
BNNR twist	−106.9(4)	−106.2(4)	−96.8(3)	−106.6(3)
BNNC$_b$	+130.6(3)	+120.5(3)	+133.0(3)	126.3(3)
RNNC$_b$	+118.6(4)	+131.1(4)	+129.3(3)	124.2(3)
θ [b]	+124.6	+125.8	+131.2	+125.2
		Bicyclic Ring Torsion		
C$_b$CHCHC$_b$	−13.3(4)	−13.1(5)	−11.5(4)	−11.5(4)
C$_b$CH$_2$CH$_2$C$_b$	−12.3(4)	−10.7(4)	−12.1(4)	−11.2(4)
		N-tBu and *N*-iPr Alignment		
tBu twist[c]	−172.6(3)	−170.2(4)	−164.5 (3)	−166.3(3)
iPr NNC$_\alpha$Me			−171.1(3),−42.1(5)	127.3(3),−0.5(5)
iPr C$_b$NC$_\alpha$Me			−43.84(5),+85.12(3)	−105.6(4),125.5(4)
HC$_\alpha$NN twist[d]			+73.4	−116.6
HC$_\alpha$NC$_b$ twist[d]			−159.4	+10.5
		N,N Distance (Å), Across Nitrogens Linked by 4 σ-Bonds		
d(NB,NB)	4.843		4.871	
d(NR,NR)	4.681		4.851	
ave NN, NN dist.	4.762		4.862	

[a] From ref 7. [b] Assuming the lone pairs bisect the CNC angle in a Newman projection down the NN bond. [c] Largest MeCNN twist angle. [d] Assuming the iPr C$_\alpha$H bond bisects the MeC$_\alpha$C angle in a Newman projection down the NC$_\alpha$ bond.

Table 2. Comparison of Methyl and Isopropyl a4R X-ray Structures[e]

	R = methyl[a]		R = isopropyl	
	N(11)N(16) unit	N(18)N(23) unit	iPr **bH**	iPr **Ecl**
		NN Bond Parameters		
d(NN),Å	1.479(7)	1.482(7)	1.478(4)	1.472(4)
α(BNC$_b$)	118.4(4)	118.6(4)	117.2(2)	117.1(3)
α(BNN)	111.2(4)	111.5(4)	111.6(2)	111.5(2)
α(C$_b$NN)	109.4(4)	108.7(4)	108.8(2)	109.0(2)
α$_{av}$(NtBu)	113.0(Bo)	112.9(Bo)	112.5(Bo)	112.5(Bo)
α(RNC$_b$)	113.3(4)	112.8(5)	117.0(2)	111.3(2)
α(RNN)	108.9(4)	108.2(4)	111.8(2)	115.0(2)
α(C$_b$NN)	110.2(4)	111.2(4)	111.5(2)	110.9(2)
α$_{av}$(NR)	110.8(Mi)	110.7(Mi)	113.4(Pi)	112.4(Pi)
C$_b$NNC$_b$	−4.6(6)	−3.9(6)	+2.9(4)	+7.4(3)
BNNR twist	−106.3(5)	−107.0(5)	+99.1(3)	+109.3(3)
BNNC$_b$	+128.9(5)	+128.6(5)	−128.0(3)	−123.5(3)
RNNC$_b$	+120.6(5)	+120.5(5)	−130.1(3)	−119.9(3)
θ [b]	+124.8	+124.6	−129.0	−121.7
		Bicyclic Ring Torsion		
C$_b$CHCHC$_b$	−12.5(6)	−12.8(6)	+17.1(3)	+17.7(3)
C$_b$CH$_2$CH$_2$C$_b$	−10.5(6)	−11.0(6)	+9.3(3)	+9.8(3)
		N-tBu and *N*-iPr Alignment		
tBu twist[c]	−170.8(5)	−171.8(5)	+166.7(3)	+166.4(3)
iPr NNC$_\alpha$Me			+42.2(4)	−6.4(4)
iPr NNC$_\alpha$Me′			+172.6(2)	−132.1(3)
iPr C$_b$NC$_\alpha$Me			+42.4(4)	−138.8(3)
iPr C$_b$NC$_\alpha$Me′			−88.0(4)	+100.4(4)
HC$_\alpha$NN twist[d]			+72.6	−110.7
HC$_\alpha$NC$_b$ twist[d]			−157.2	+16.5
		N,N Distance (Å), Across Nitrogens Linked by 4 σ-Bonds		
d(NB,NR)	4.803		4.844	
d(NB,NR)	4.818		4.875	
ave NN, NN dist	4.811		4.859	

[a–d] As for Table 1. [e] Both hydrazine units are **tBu**-*out*, **R**-*in*.

group of each is in an ∠NNC$_\alpha$Me near 0° (almost eclipsed) conformation. Views down the C$_\alpha$N bonds are shown for each hydrazine unit of **s4iPr** and **a4iPr** in Figure 3. The eclipsing of the C$_\alpha$Me bond with the NN bond is within experimental error of being complete for **s4iPr** (∠NNC$_\alpha$Me = −0.5(5)°, ∠C$_b$NC$_\alpha$Me = +10.5°). **a4iPr** could have C_2 symmetry if both its *in*-isopropyl groups were in the same rotamer, but instead, one is **bH**, while the other is

Table 3. Comparison of MM2 and AM1 Calculations of Isopropyl Rotamers of a4iPr, tBu-*out* Conformations

	rel energy (kcal/mol)		∠NNC$_\alpha$Me in the two hydrazine units, deg	
iPr rotamers	MM2	AM1	MM2 calculations	AM1 calculations
bH,**bH**	0.0	0.0	−175.6,−42.7;−42.8,−175.7	−164.5,−35.7;−35.9,−164.6
bH,**Ecl**	0.5	0.0	+17.2,+143.9;−40.7,−174.1	−10.5,+115.3;−33.2,−162.3
bH,**cH**	0.1	3.9	+54.1,+177.6;−41.1,−174.5	+63.3,−175.3;−34.9,−164.0
cH,**cH**	1.8	7.2	+51.6,+175.2;+50.4,+174.3	+62.4,−176.2;+62.6,−176.0
Ecl,**Ecl**	4.2	0.2	+11.7,+138.3;+11.7,−113.8	−12.8,+113.3;−12.7,+13.5

Table 4. MM2 Calculations of Isopropyl Rotamers of s4iPr in *in-anti* Conformations [a]

iPr rotamers	rel energy (kcal/mol)	∠NNC$_\alpha$Me in the two hydrazine units, deg	
		iPr inner	iPr outer
ibH,**obH**	0.0	+42.9,+175.7	+172.1,+38.4
ibH,**ocH**	0.1	−172.7,−38.8	+53.2,+176.8
iEcl,**obH**	0.5	+20.8,+147.9	−173.1,−39.4
iEcl,**ocH**	2.8	−141.5,−14.7	−177.7,−54.4

[a] Lowest energy iPr-*in*-**syn** conformation has **bH**,**bH** isopropyl rotamers and lies 2.65 kcal/mol higher in steric energy.

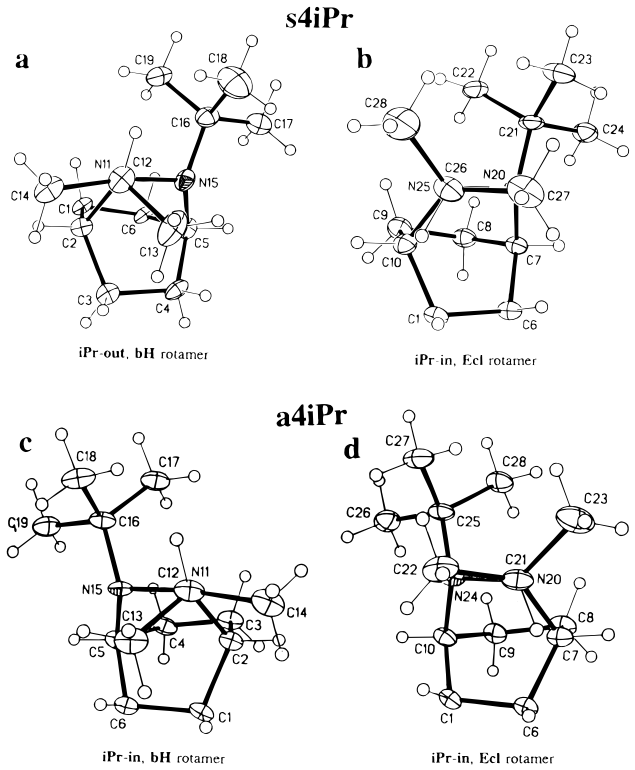


Figure 3. Newman projections down the isopropyl group C$_\alpha$N bonds from the X-ray structures of **s4iPr** (a and b) and **a4iPr** (c and d). **bH** isopropyl rotamers are shown at the left and **Ecl** rotamers at the right.

closest to **Ecl** (∠NNC$_\alpha$Me = −6.4(4)°, ∠C$_b$NC$_\alpha$Me = +16.5°). The rotational angles for occupied rotamers about the C$_\alpha$N bond differing in phase by about 180° instead of the expected 120° appears unusual. The only precedent of which we are aware for an eclipsed conformation at a single bond between two formally sp^3 hybridized atoms which is not included in a ring is for an eclipsed H$_3$C−C(NR2)$_3$ bond in a crystalline trihydrate (but not in the unhydrated crystal);[6] the reason for eclipsing here was identified as CH hydrogen bonding, and this case obviously has nothing to do with the present ones. Eclipsing in **4iPr** presumably is a result of the severe steric interactions of the NiPr groups with both the NtBu and the bicyclic rings. We note that the lone pairs both as the third substituent at the nitrogen to which the isopropyl group is attached and at the NtBu nitrogen being directed toward a C$_\alpha$ methyl group will make **Ecl** conformations of **4iPr** less sterically destabilized than those of C−C σ bonds. It is possible that the presence of **Ecl** rotamers is a result of crystal packing forces, but this seems unlikely to us because it occurs in the X-ray structures of both compounds and because calculations also get **Ecl** conformations as being low-lying energy minima.

MM2 molecular mechanics[9] and AM1 semiempirical[10] calculations have been carried out on **a4iPr** and MM2 calculations on **s4iPr**; similar calculations on both **4Me** isomers have been published previously.[11] Energy minima were found using Saunders's random search program,[12] and AM1 calculations were carried out starting from the MM2 energy minima (and in all cases gave the same conformational type). The calculations successfully get *in-anti* conformations as the more stable ones (the lowest-lying *in-syn* conformation found by MM2 for **a4iPr** lies 4.9 kcal/mol above the minimum steric energy one, and that for **s4iPr** lies 2.6 kcal/mol higher). AM1 calculations get tBu-*out* **a4iPr** 0.6 kcal/mol lower in heat of formation than tBu-*in* (the ^{13}C-NMR experiment shows that the free energy difference is ≥1.0 kcal/mol at room temperature), but the MM2 calculations get the same steric energy for these conformations (a difference of only 0.02 kcal/mol). The relative energies of various iPr rotamers of tBu-*out* **a4iPr** are listed in Table 3, and those of **s4iPr** in Table 4. Low steric energy **Ecl** rotamers were only found for the isopropyl-*in* groups. Neither calculation method gets the isopropyl rotamers as different in energy as required by the NMR spectrum. Having different rotamer conformations should be favored by an entropy of mixing corresponding to Rln2 (1.4 cal/mol-deg, 0.3 kcal/mol at −85 °C), and **Ecl** and **cH** rotamers may still be interconverting rapidly on the NMR time scale at −85 °C, but neither calculation predicts the experimental result that it is principally different isopropyl rotamers that are present, or gets an isopropyl methyl quite as eclipsed with the NN bond in **Ecl** as do the X-ray structures of **4iPr**.

Because d(NN) and α_{av} are so close for the **4iPr** isomers, the most important difference between the hydrazine units for electron transfer considerations is θ; changes in θ have the largest effect the electron transfer

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

(10) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Our AM1 calculations were carried out using various versions program VAMP: versions 4.40 or 5.0 (on a Stardent 3000 computer), 5.6 (on an IBM RS-6000). Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. *VAMP 5.0*, Oxford Molecular, Oxford, 1994.

(11) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hayshi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(12) (a) Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150. (b) We thank Prof. Saunders for providing program VAXMOL5,[7a] and Peter A. Petillo for modifying it to run in our computer environment (VAX 8650 computer) and providing program NEWSEL for preparation and manipulation of its input and output files.

barrier.[13] The RNNB angle of **s4iPr** is about 10° smaller for the iPr-*out* (**bH**) hydrazine unit than for the iPr-*in* unit or for either **s4Me** hydrazine unit. This results in a 6° larger θ value for this hydrazine than for the iPr-*in* unit in the same compound, while the latter is the average of those for the two **4Me** isomers, which only differ in θ by 1.2°. **a4iPr** has both hydrazine units in tBu-*out* invertomers, and the iPr staggered one has a 7.3° larger θ value than the iPr eclipsed one. Although the radical cation conformations and not those of the neutral compound is what is important for intermolecular ET within the radical cations, these X-ray results suggest that the reorganization energy might be significantly smaller for **4iPr** than for **4Me**, because both θ and α_{av} values should cause lower reorganization energy relative to the R = Me compound. This proves to be the case for the radical cations, as will be documented in due course.

Experimental Section

4,9-Di-*tert*-butyl-5,10-diisopropyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}]tetradecane (**a4iPr**). Commercial isopropylmagnesium chloride (2.50 mL, 2.0 M in THF, 5 mmol, 10 equiv) was added dropwise to a suspension of the *anti*-bis-*tert*-butyl bis(diazenium) $(BF_4^-)_2$ salt (0.241 g, 0.50 mmol) in THF (5 mL) under nitrogen. After stirring for 14 h, water (20 mL total) was added, initially dropwise until vigorous bubbling subsided. Extraction with ether (4 × 50 mL), washing with brine, drying with magnesium sulfate, and concentration gave a blue oil which solidified upon standing. Flash chromatography on 34 g of silica gel with ether eluant gave crude **a4iPr** (0.20 g) as a white solid which turned blue upon standing. Passing this sample through basic alumina with $CHCl_3$ as eluant and concentration gave white solid (0.16 g, 81.9%), mp 100.5−102 °C. ^{1}H NMR ($CDCl_3$) δ 3.27 (sept, J = 6.5 Hz, 2H); 3.02 (bs, 2H); 2.89 (bs, 2H); 2.55 (bs, 2H); 1.80 (complex, 8H); 1.17 (s, 18H); 1.15 (d, J = 7 Hz, 6H); 1.12 (d, J = 7 Hz, 6H). Small peaks for a second conformation (approximately 12−15%) were resolved at δ 3.32 (bs); 2.92 (bs); 1.21 (s, tBu). ^{13}C NMR($CDCl_3$) δ 57.7 (q); 53.5; 51.7; 49.5; 36.7; 30.0; 25.0 (CH_2); 22.1; 19.8; 19.5 (CH_2) (assignments in parentheses from DEPT-135). Also saw a second tBu Me signal at 30.3 δ). MS: exper 390.3140 (47.7% intensity) calcd for $C_{24}H_{46}N_4$ 390.3726 (3.1 ppm error).

4,10-Di-*tert*-butyl-5,9-diisopropyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}]tetradecane (**s4iPr**) was prepared and purified by the same method as the anti compound, starting with the *syn*-bis(diazenium) salt (0.226 g, 0.47 mmol), giving **4siPr** a white solid (0.18 g, 97.8%), mp 129−130 °C. ^{1}H NMR ($CDCl_3$) δ 3.34 (sept, J = 6.9 Hz, 1H); 3.22 (sept, J = 6.7 Hz, 1H); 3.14 (m, 1H); 2.98 (bs, 1H); 2.89 (bs, 1H); 2.82 (m, 1H); 2.66 (br d, J = 12.1 Hz, 1H); 2.39 (br d, J = 12.7 Hz, 1H); 1.85 (m, 8H); 1.26 (d, J = 6.9 Hz, 3H); 1.20 (s, 9H); 1.15 (s, 9H); 1.14−1.09 (3 overlapping d, 9H). ^{13}C NMR ($CDCl_3$) δ 57.43 (q); 57.28 (q); 54.70; 52.74; 52.10; 49.86; 49.43; 49.26; 38.36; 35.65; 30.13; 30.05; 26.29 (CH_2); 25.07 (CH_2); 22.94; 20.43; 20.07; 19.75; 19.69; 19.48 (CH_2) (assignments in parentheses from DEPT-135). MS: exper 390.3725 (36.1% intensity) calcd for $C_{24}H_{46}N_4$ 390.3726 (0.2 ppm error).

Table 5. Crystallographic Data and Refinement Parameters

	a4iPr	s4iPr
crystal size, mm	0.30 × 0.20 × 0.05	0.40 × 0.20 × 0.10
temperature, K	113(2)	113(2)
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	6.4103(5)	10.3624(10)
b, Å	11.1213(5)	24.585(2)
c, Å	16.3061(10)	9.1463(10)
α, deg	79.674(5)	90
β, deg	85.875(6)	97.051(8)
γ, deg	81.369(5)	90
V, Å^3	1129.48(12)	2312.5(4)
Z	2	4
D_{calcd}, mg/m^3	1.149	1.122
F(000)	436	872
reflections collected	3340	3320
independent reflections	3016	3097
parameters refined	254	254
R/R_w (obsd data), %	6.26/15.45	6.55/13.94
R/R_w (all data), %	8.8/17.56	11.75/16.76
goodness of fit on F^2	1.032	1.017
largest differences eÅ^{-3}	0.264/−0.263	0.442/−0.260

X-ray Structure Analysis of a4iPr and s4iPr.[15] Intensity data were measured on a Siemens P4 diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å), ω scan type, θ 2−57° for **a4iPr** and 1.5−57° for **s4iPr**, variable scan speed 2−40°/min, and ω range 0.7° for **a4iPr** and 0.8° for **s4iPr**. The solution of the structures with direct methods in full-matrix least-squares on F^2 used Siemens SHELX86.[14] Hydrogen atoms were treated by the riding model and weighting scheme $w^{-1} = \sigma^2(F_o)^2 + (0.0941P)^2 + 0.8362P$ for **a4iPr** and $w^{-1} = \sigma^2(F_o)^2 + (0.665P)^2 + 1.0078P$ for **siPr4**, where $P = [F_o2+2F_c2]/3$ for both. The crystallographic data and the parameters of structure refinement are given in Table 5.

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Supporting Information Available: ^{1}H and ^{13}C-NMR spectra for **s4iPr** and **a4iPr**. Atomic coordinates, bond length/bond angle, and anisotropic displacement tables for both compounds (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Nelsen, S. F.; Ismagilov, R. F.; Chen, L. J.; Brandt, J. L.; Chen, X.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 1555.

(14) Sheldrick, G. M. SHELEXS86. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; 1985, pp 175−189.

(15) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.