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THE GAS-PHASE CONFORMATION OF 3,7-DIMETHYL-3,7-DIAZABICYCLO[3.3.1]NONANE

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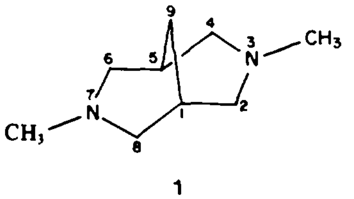
Abstract—The gas-phase conformation of the title compound (1) is discussed in reference to its photoelectron spectrum. The experimental lone-pair/lone-pair splitting (0.51 eV), when compared with that of similar diamines and with the results of three sets of MO calculations (MINDO/3, MNDO and STO-3G), leads to the conclusion that 1 exists in the chair-chair conformation. A remarkable sensitivity of the calculations to slight changes in the geometry is noted, and it is suggested that calculations of this type must include geometry-optimization. The question of through-space vs through-bond inteaction of the nitrogen lone pairs was explored by performing MNDO calculations in which the N-N resonance integrals were set to zero. These calculations indicate that in the chair-chair conformation the N-N interaction is mainly through-space. The ^{13}C NMR and Ni(acac)$_2$-induced ^{13}C shifts of 1 are discussed.

The bicyclo[3.3.1]nonane skeleton may be viewed as two cyclohexane rings fused with three ring carbons in common. Considered in this manner, it seems reasonable to expect the so-called chair–chair conformation to be preferred to either the boat–chair or boat–boat (Fig. 1). For the parent and several substituted systems this expectation is borne out.[1] The 3,7-dialkyl-3,7-diaza analogues offer additional facets to consider, namely (i) the possibility of *exo* and *endo* disposition of the N-alkyl substituents (ii) possible dipole–dipole repulsion of the heteroatoms in the chair–chair conformation, and (iii) possible direct overlap of the nitrogen lone-pair orbitals (the "hockey stick" effect), also in the chair–chair conformation. We have utilized photoelectron spectroscopy (PES) to provide information about the gas-phase conformational preference of 3,7 - dimethyl - 3,7 - diazabicyclo[3.3.1]nonane, 1, (N,N' - dimethylbispidine). Aside from the fascinating basic conformational questions posed by 1, it is of interest as a model of the B and C rings of sparteine.[2–4]



1

EXPERIMENTAL

Of the several synthetic routes to N,N'-dimethylbispidine,[3,5,6] the method of Douglass and Ratliff[6] was used. The sample used for PES was distilled twice under vacuum through a 12-in. Vigreux column, b.p. 58°/15 mm. A mass spectrum revealed no ions above the molecular weight of 1, and the H-decoupled ^{13}C NMR showed four singlets only.

The photoelectron spectra were obtained by a Perkin–Elmer model PS-18 spectrometer. Xenon and argon were employed as calibrants in all runs. The final data quoted in this paper represent an average of several spectra. Proton NMR spectra were obtained on a Varian EM-390 spectrometer, and ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer. All chemical shifts are referenced to internal TMS.

N,N,N',N'-tetramethylpropane-1,3-diamine was distilled from sodium under N_2.

RESULTS

The PES spectrum of 1 is shown in Fig. 2. The bands at 7.84 and 8.35 eV correspond to ionization processes in which electrons are removed from the so-called "lone-pair" orbitals on the nitrogens. The two bands split by 0.51 eV (i) could be the result of the presence in the sample of a mixture of conformers, with each conformer characterized by a single PES band corresponding to ionization from the degenerate or nearly degenerate nitrogen lone-pair orbitals, or (ii) the splitting might represent the spectrum of a single conformer having non-equivalent nitrogen lone-pair ionization potentials. To assess these possibilities molecular orbital calculations were carried out on conformers of 1.

Duplicate calculations, employing two semi-empirical schemes, MINDO/3[7] and MNDO,[8] were performed in hopes that any result reproducible by the two approximate methods would be more credible. In addition *ab initio* calculations at the STO-3G level[9] were performed as a further basis for comparison.

The semi-empirical calculations were carried out on the three conformers shown in Fig. 3, where the *exo* and *endo* notation refers to the disposition of the N-Me groups. Each semi-empirical calculation included


chair - chair
boat - chair
boat - boat

Fig. 1. Conformations of the bicyclo[3.3.1]nonane skeleton.

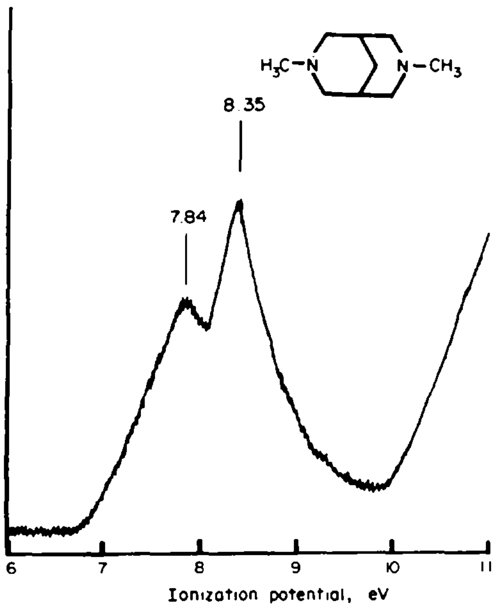
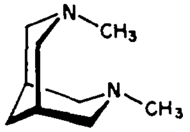


Fig. 2. The photoelectron spectrum of N,N'-dimethylbispidine. The excitation source was the HeI resonance line.

geometry-optimization; in the case of **1a** 44 bond lengths, angles and dihedral angles were varied. In the case of **1b**, 56 were varied, and for **1c**, 38. The *ab initio* calculations did not include geometry optimization. Here the optimum geometry of each conformer generated by the MNDO calculations was used. Further, because of core limitations, the *ab initio* calculations were performed for the bispidine parent system, i.e. in **1** N-Me's were replaced with N-H's, with the N-H bond length fixed at 1.009 Å.[10] The results of these calculations are presented in Table 1.

The possibility that one N-Me group might be placed *endo* in the chair–chair form, as shown below, was explored. An MNDO calculation predicted the heat of formation for this invertomer to be +9.04 kcal/mole, which was surprisingly close to the ΔH_f of +7.00 kcal/mole of **1a**. However, the geometry about the nitrogen bearing the *endo* Me had become essentially



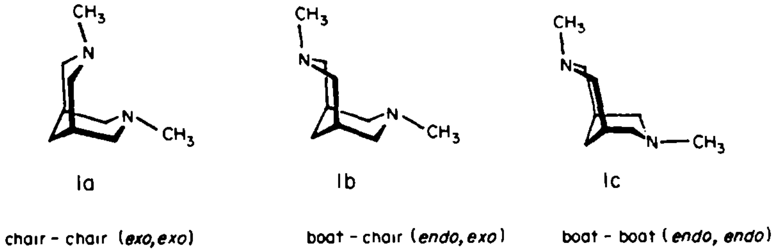


Fig. 3. Conformations of N,N'-dimethylbispidine. *Exo*/*endo* notation refers to disposition of N-methyl groups.

Table 1. Results of molecular orbital calculations on conformers of 1

Conformer[a]	MINDO/3	MNDO	STO-3G[b]
1a	ΔH_f = +48.9 kcal/mole	ΔH_f = +7.00 kcal/mole	E ≡ 0 kcal/mole[c]
	IP_1 = 8.37 eV	IP_1 = 9.21 eV	IP_1 = 6.84 eV
	IP_2 = 8.83 eV	IP_2 = 9.38 eV	IP_2 = 7.50 eV
	ΔIP = 0.46 eV	ΔIP = 0.17 eV	ΔIP = 0.66 eV
1b	ΔH_f = +52.6 kcal/mole	ΔH_f = +12.3 kcal/mole	E = +0.84 kcal/mole[c]
	IP_1 = 8.42 eV	IP_1 = 9.45 eV	IP_1 = 7.27 eV
	IP_2 = 8.61 eV	IP_2 = 9.58 eV	IP_2 = 7.58 eV
	ΔIP = 0.19 eV	ΔIP = 0.14 eV	ΔIP = 0.31 eV
1c	ΔH_f = +57.2 kcal/mole	ΔH_f = +18.3 kcal/mole[d]	E = +9.04 kcal/mole[c]
	IP_1 = 8.36 eV	IP_1 = 9.52 eV	IP_1 = 7.29 eV
	IP_2 = 8.54 eV	IP_2 = 9.58 eV	IP_2 = 7.54 eV
	ΔIP = 0.18 eV	ΔIP = 0.064 eV	ΔIP = 0.25 eV

[a] see Figure 3 [b] N-CH_3 replaced by N-H [c] total energy relative to 1a ≡ 0 kcal/mole

[d] C_{2v} symmetry, see text

planar during geometry optimization (sum of angles = 357°). Hehre[11] has pointed out the tendency of MINDO/3 to flatten the geometry about nitrogen. While we are not prepared to state that MNDO suffers the same affliction, we suggest that the potential well corresponding to the planar nitrogen is shallow and, moreover, artificial; it probably occurs along a potential surface otherwise smoothly decreasing from (*exo*/*endo*) invertometer to (*exo*/*exo*) invertomer. Another calculation in which the *endo* Me was fixed in the *endo* position while other parameters were optimized gave $\Delta H_f = 32.0$ kcal/mole (sum of angles about nitrogen = 346°). Clearly, the chair-chair (*exo*/*endo*) form is quite high in energy relative to the chair–chair (*exo*/*exo*) form, and the possibility that Fig. 2 represents the spectrum of two invertomers may be ruled out.

DISCUSSION

Regardless of method of calculation, we find the chair-chair conformation of 1 more stable than the boat–chair or the boat-boat (Table 1). Translating the energy differences in Table 1 into Boltzmann populations at 25°, according to MINDO/3 the chair–chair (*exo*/*exo*) is present to the extent of 99.8%; MNDO predicts it to be present to the extent of 96.9%. The energy differences for 1 (N-H instead of N-Me) found by the *ab initio* procedure correspond to a chair–chair population of 80.4% (however, *vide infra*). All these calculations suggest that in the gas phase one conformer, namely, **1a**, the chair–chair (*exo*/*exo*) exists.

Furthermore, it is for the chair–chair conformer that we find the largest ΔIP (difference in energy between the highest and penultimate occupied MO's).[12] These results lend credence to the simplest interpretation of Fig. 2 which is that it represents the photoelectron spectrum of the chair–chair (*exo*/*exo*) conformer of 1, and that this conformer alone is responsible for the splitting of 0.51 eV.

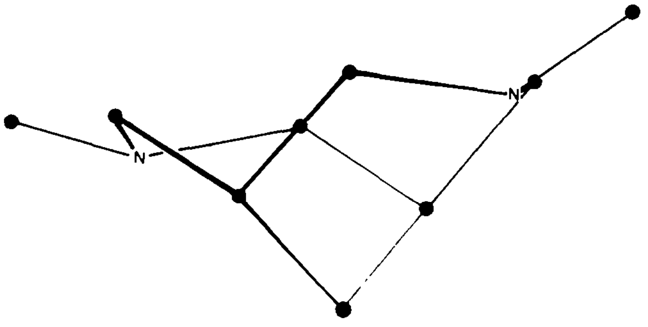
Chakrabarty *et al.*[13] obtained results in qualitative agreement with those in Table 1 using extended Huckel and CNDO/2 approximations; both calculations indicated that the chair–chair is the most stable conformer. The ordering of energies (chair–chair, boat–chair, boat-boat, in kcal/mole) was: EH; 0,+20.6,+45.4; CNDO/2; 0,+18.0,+24.9. However, these authors assumed C-N distances equal to C–C distances and used tetrahedral angles throughout. We have found in our calculations a sensitivity to slight changes in geometry which would render any non-geometry-optimized calculation suspect.

First, changes in geometry affect the total energy significantly. With MINDO/3 bond lengths and angles for the boat–boat conformer were optimized, and these values were used as a basis for constructing the starting geometry for the MNDO boat–boat optimization. Even beginning with the MINDO/3-optimized geometry, the MNDO boat–boat geometry optimization procedure decreased the ΔH_f by approximately 4 kcal/mole. When any optimization using idealized tetrahedral geometry and "reasonable" bond lengths (based on model compounds) was begun, ΔH_f was reduced by *ca* 45 kcal/mole. We encountered a particularly striking example of the effect of geometry optimization on ΔH_f in pursuing the question of twist–boat–twist–boat conformers. In our MNDO calculation on the boat–boat conformer a C_{2v} geometry was specified and thus forms of lower symmetry, such as the (twist-boat)^2 form (C_2) were precluded. In order to calculate the (twist–boat)^2 form, the appropriate symmetry restrictions were removed, and the geometry optimization was renewed. We felt that the boat-boat form would be a saddle point connecting the two (twist-boat)^2 forms, if, indeed they were lower in energy than the boat–boat. (If they were higher in energy that the boat-boat, they could by ignored.) The change of geometry was minor (Fig. 4). However, this minor adjustment in geometry brought ΔH_f from 18.3 kcal/mole to 14.9 kcal/mole, a substantial change. The price paid for the 3.4 kcal/mole improvement in energy was double the calculation time spent for boat–boat (C_{2v}).

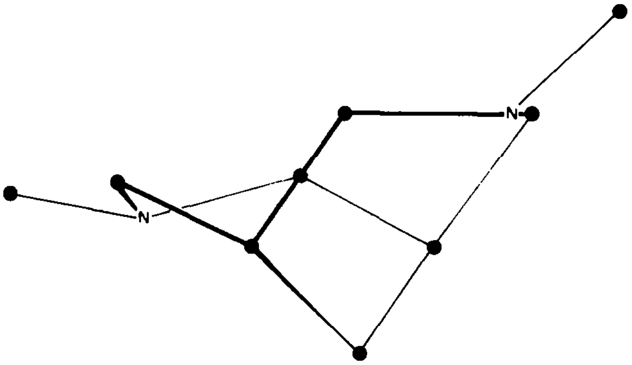
Therefore, the *ab initio* calculations, which were done on fixed geometries (the MNDO-generated geometries) must be viewed with some skepticism. Probably the difference in energy between the boat–chair and the chair–chair conformers would be changed significantly on geometry optimization. However, this task is gargantuan. In any event, the main conclusion is only a semi-quantitative one, namely that by any method of calculation the chair–chair conformer is the most stable one, and that it is predicted to be stable enough relative to the other conformers to dominate any gas-phase sample of N,N′-dimethylbispidine. Since PES represents a Franck–Condon electronic transition, a sample containing over 90% of a conformer will give rise to the PE spectrum of only that conformer.

The ΔIP values also were sensitive to changes in geometry. We were concerned that the ΔIP calculated by MNDO for the chair–chair case (0.17 eV) was quite small relative to the experimental value of 0.51 eV, and, more importantly, not much larger than ΔIP calculated for the boat–chair (0.14 eV). For reasons to be discussed, we felt that ΔIP arose mainly from a "through-space" N-N interaction in the chair–chair conformer, and this should depend quite sensitively on the distance between and relative orientation of the nitrogens. A series of calculations in which the frame of the chair–chair molecule was deformed so as to bring the nitrogens successively closer was undertaken. The C8–C1-C2 angle (=C6–C5–C4), θ, was compressed, and all other bond lengths and angles were preserved. The original ΔIP of 0.168 eV at a N–N distance of 3.12 Å became 0.242 eV at a N–N distance of 2.91 Å which is a 44% change in the value of ΔIP brought about by a change in d_{NN} of only −7%. (Of course the relative orientation of the nitrogen lone-pairs is changing as well as d_{NN}.) When an MNDO calculation was performed using the chair–chair geometry generated by the MINDO/3 optimization, having $d_{NN} = 2.86$ Å, ΔIP was 0.332 eV. Thus, it appeared that ΔIP may depend markedly on the geometry optimization procedure.

As a control, it was necessary to show that in the conformers exhibiting low ΔIP's, an analogous deformation of the carbon skeleton to bring the nitrogens closer together would result in little change in ΔIP. In the boat–chair system, bringing the nitrogens from 3.61 to 3.53 Å apart resulted in essentially no change in ΔIP (ΔIP = 0.136 eV became ΔIP = 0.135 eV). Surprisingly, when the system was deformed still further, ΔIP increased substantially (ΔIP = 0.176 eV at $d_{NN} = 3.44$ Å). The cause for this behavior is that the ring deformation brings the "lone-pair orbital" on N-7 close to the *endo* hydrogens on C-2 and C-4 ($d_{NH} = 2.62$ Å) each of which contributes significantly to the two highest MO's as shown. It can be seen that bringing N-7 closer to the C-2 and C-4 *endo* hydrogens by compression of the C8–C1-C2(=C6–C5–C4) bond angle (θ) would serve to des-

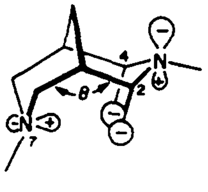


Original

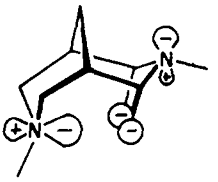


Allowed to twist

Fig. 4. Change in geometry on relaxation of symmetry restrictions from C_{2v} to C_2. (MNDO) Drawings were plotted on isometric projection paper using x, y and z coordinates from the calculations.



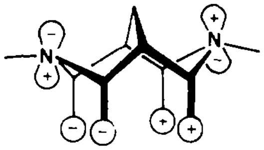
HOMO



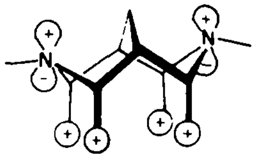
Second Highest MO

tabilize the HOMO and stabilize the next orbital by virtue of the antibonding (in the HOMO) and bonding (in the second highest orbital) relationship of the N7 "lone-pair orbital" with the C2 and C4 *endo* hydrogens. Note that considering *only* the N-centered orbitals, compressing θ would tend to stabilize the HOMO and destabilize the second orbital and result in a smaller ΔIP—just the reverse of the prediction including the hydrogens. In fact, ΔIP increases. It should be noted that orbitals centered on the ring carbons contribute only in a minor way to the two highest occupied MO's, ruling out through-bond coupling in the usual sense. Thus, geometry optimization may be slightly inaccurate in the case of the boat–chair, and ΔIP will increase only slightly, and, further, will remain small compared to the experimental value.

In the boat–boat case, direct through-space N–N interaction may be ruled out owing to the distance involved (d_{NN}=4.11 Å). Even so, compression of the bicyclic frame caused ΔIP to increase. Again, the ring carbons were not playing a role here. Rather the skeletal deformation forced the *endo* hydrogens on C2 and C4 toward the *endo* hydrogens on C6 and C8, producing the interactions shown.



HOMO



Second Highest MO

Again, the HOMO should move up in energy, and the second highest MO down, resulting in a larger ΔIP on the compression of the bridgehead angle. Although the H–H distances are shorter than the N–H distances in the boat–chair system (here d_{HH}=1.79 Å), the overlap is s-σ, as opposed to p-σ, which would tend to weaken the effect. The net result is that the sensitivity of ΔIP to skeletal deformation in the boat–boat system is about the same as that exhibited by the chair–chair system, and somewhat greater than that of the boat–chair system. Most important, though, is the observation that in the boat–boat system ΔIP never becomes comparable in magnitude to the experimental ΔIP.

In summary, the effect of an inaccurate geometry optimization is, on a percent basis, large in the value of ΔIP for all three conformers (MNDO). However, on an absolute basis, only the chair–chair ΔIP created by a modest geometry inaccuracy is comparable to the experimental value.

We feel that it is not a coincidence that all three calculation schemes found ΔIP for the chair–chair larger than ΔIP for the other forms, and that each calculation places the ΔIP's in the same order. The fact that the margin by which ΔIP for the chair–chair exceeds that for the boat–chair is small may result from a slightly erroneous geometry.

Further support for the conclusion that Fig. 2 is the PE spectrum of chair–chair N,N'-dimethylbispidine is provided by comparison with the spectra of similar diamines. The values of ΔIP for a few diamines structurally similar to 1 are shown in Fig. 5. It is reasonable that ΔIP for 1 is smaller than those of 2–4, since 1 lacks a one-carbon bridge fixing the two nitrogens relative to each other.

Through-space vs *through-bond interaction*

It is of interest to inquire whether the interaction of the nitrogen lone-pairs occurs "through-space" via direct orbital overlap or "through-bond".[16–19]

One way to approach this problem is to examine model compounds. Since in 1 the shortest sigma bond path connecting the nitrogens is a three-carbon path, we obtained the PE spectrum of N,N,N',N'-tetramethyl-1,3-diaminopropane, 5 (Fig. 6). One would expect the extended chain form of 5 to be the predominant contributor to the total conformational population and, indeed, of the conformations treated (Table 2) it is found that the extended form is most stable. In this conformation direct through-space interaction would be vanishingly small since the N–N distance is so large (on the order of 5 Å). The lone-pair ionizations were not resolved in the PE spectrum of 5 indicating that (i) the through-bond interaction is small and/or (ii) the radical cation formed by ionization form the lone-pair MO's is of significantly different geometry than the neutral precursor (i.e. broad vibrational envelopes for two bands). This latter explanation vitiates the drawing of conclusions from model compounds. One may speculate that the preferred geometry for $5^{+\cdot}$ is cyclic, as shown below. Halpern[20] has deduced from UV spectroscopic studies that 5 forms intramolecular excimers presumably of gross geometry similar to $5^{+\cdot}$. If $5^{+\cdot}$ is of the geometry

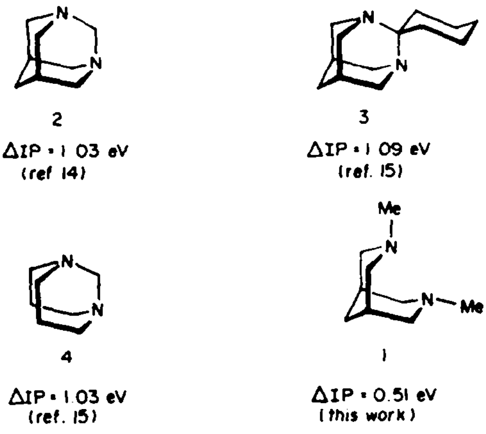


Fig. 5. ΔIP's of model compounds.

Table 2. Results of NMDO calculations on N,N,N'N,'-tetramethylpropane-1,3-diamine, 5

N-C-C-C Dihedral Angle (°)	ΔH_f(kcal/mole)	ΔIP (eV)
180	2.71	0.32
150	3.22	0.30
120	3.91	0.27
90	3.98	0.24
60	4.22	0.23
30	4.16	0.38
0	5.30	0.37

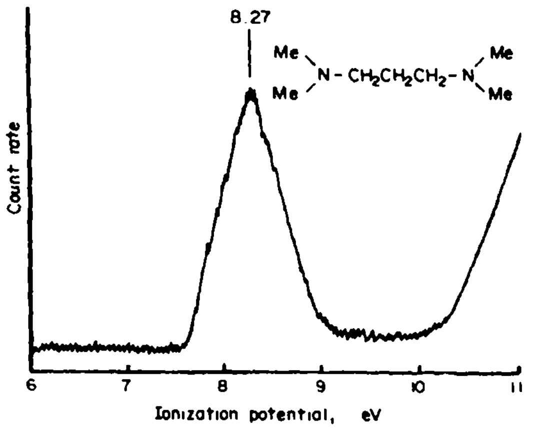
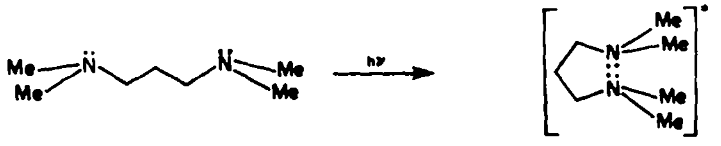
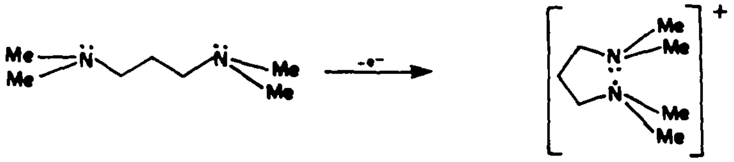


Fig. 6. The photoelectron spectrum of N,N,N',N'-tetramethyl-1,3-diaminopropane. The excitation source was the HeI resonance line.



5 5*



5 $5^{+\cdot}$

shown, the minimum in the $5^{+\cdot}$ potential energy-geometry hypersurface would be offset from the minimum in the potential energy-geometry hypersurface of 5, making the vertical IP and the adiabatic IP more disparate, and resulting in a broadened PES band. Thus, the unresolved lone-pair splitting in the PE spectrum of 5 may be two "narrow" bands too close to resolve, (small through-bond coupling) or two "broad" bands widely spaced (large through-bond coupling) unresovable due to their breadth. Thus, it is unwarranted to make even a qualitative statement that the through-bond interaction in 5 is "small". Further, since the magnitude of through-bond coupling should be a sensitive function of the orientation of the lone-pair orbitals relative to the σ-bond bridge orbitals and a function of the actual conformation of the bridge, it might be argued that no compound is a good model for the through-bond coupling in **1a** since a good model for **1a** would need to approximate **1a**'s geometry, and any such compound would have a sizable through-space coupling component.

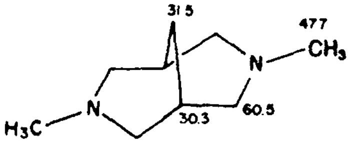
Another approach to the problem is to perform calculations in which the through-space N-N interaction is artifically "turned off". This was done by setting the N-N core resonance integrals equal to zero.[21] The results are given in Table 3. Qualitatively, the effect on ΔIP of removing the through-space interaction was an order of magnitude larger for the chair-chair case than for the other conformers. Thus, the qualitative conclusion is that in the chair-chair case the calculated ΔIP derives in large part from direct through-space N-N interaction. This supports the notion that conformers of 1 ought to be distinguishable by PES. The small *increase* in ΔIP on setting N-N core resonance integrals to zero in the boat-chair case is rationalized by noting that in the HOMO the direct N3-N7 interaction is bonding (in-phase) and in the second highest orbital it is anti-bonding (out-of-phase), so removal of this interaction should destabilize the HOMO and stabilize the next highest orbital leading to a larger ΔIP, as found. The effect is not large since the N3-N7 direct interaction is not large.

Gas phase conformation vs *liquid phase conformation*

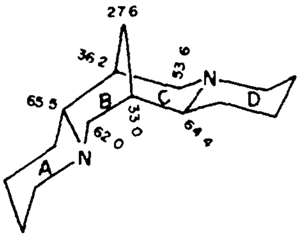
The liquid-phase conformation of 1 was discussed by Douglass and Ratliff.[6] They measured the dipole moment of 1 and compared this with dipole moments calculated for each of the three conformers of 1. On this basis the boat-boat conformer provided the best agreement between calculation and experiment. The authors amended this conclusion by stating that either the boat-boat conformation or a chair-chair conformation having flattened wings would accomodate their results; however, no calculated dipole moment for a chair-chair conformation having flattened wings was reported. Support for the chair-chair conformation was provided by the close similarity of the chemical shift of the C9 protons of 1 to that of the C4 protons of N-methylpiperidine, which was believed to prefer the chair conformation, with methyl equatorial. The effect of flattening of the wings on the chemical shift of the C9 protons of 1 was not discussed.

Zefirov and Rogozina[22] compared the proton NMR spectrum of 1 and N,N'diphenylbispidine with the proton spectrum of a number of heteroatom-substituted bicyclo[3.3.1]nonanes. Their discussion implied that in 1 and in the N,N'-diphenyl derivative the flattened-wing chair-chair conformation is adopted.

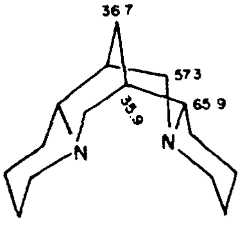
We have examined the ^{13}C NMR spectrum of 1. The chemical shifts in ppm relative to internal TMS ($CDCl_3$) are shown below.



These values may be compared with the chemical shift data for sparteine and α-isosparteine[23] shown below.



sparteine



α-isosparteine

As pointed out by Bohlmann and Zeisberg the chemical shift of the carbon of the one-carbon bridge in the bicyclo[3.3.1] moiety is a sensitive monitor of ring conformation (27.6 ppm vs 36.7 ppm for sparteine and α-isosparteine and similar differences in a large series of sparteine-like alkoloids). The value of 31.5 ppm for N,N'-dimethylbispidine places it midway between the chair-chair conformation of the B and C rings of α-isosparteine and the boat-chair conformation of the B and C rings of sparteine. One possible explanation is that 1

Table 3. MNDO calculations on 1 with and without N-N core resonance integrals (β_{NN})

	ΔH_f (kcal/mole)		ΔIP (eV)		
	Normal	$\beta_{NN}=0$	Normal	$\beta_{NN} = 0$	%Change
1a	7.00	7.00	0.168	0.076	-55%
1b	12.31	12.31	0.136	0.141	+3%
1c	18.27	18.27	0.064	0.063	- 0.5%

adopts a chair–chair conformation with "flattened wings". Also, the CH_2 alpha to nitrogen in **1** (60.5 ppm) absorbs more like the analogous CH_2 in the B ring of sparteine (62.0 ppm) and the CH_2 in the B and C rings of α-isosparteine (57.3 ppm) both of which are in chair conformations, than the CH_2 in the C ring of sparteine (53.6 ppm) which is in a boat conformation. Therefore these two points of evidence lead to the conclusion that N,N'-dimethylbispidine, in the liquid phase, adopts the chair–chair conformation, perhaps with flattened wings.

The N–Me ^{13}C chemical shifts of a number of substituted piperidines and decahydroquinolines reported by Eliel and Vierhapper[24] shed some light on the disposition of the Me groups of **1**. In cases of equatorial N–Me groups, in the decahydroquinoline series, δ^c was about 43 ppm, whereas for axial N–Me δ^c was about 33 ppm. For several substituted piperidines, equatorial N–Me appeared at about 47 ppm. The δ^c of 47.7 ppm for the N–Me of **1** is therefore consistent with each Me group occupying an equatorial position of a chair piperidine ring.

Finally, it was hoped that nickel-induced ^{13}C NMR shifts might help assign conformation in **1**.[25] The slopes of plots of $\Delta\delta^c$ vs added $\mathrm{Ni(acac)_2}$ for the four different carbons of **1** may be expressed relative to that of the α-carbon: α,+1.00; β,+1.27; γ,+0.82; N–Me,+0.40. The positive sign denotes an upfield shift. Alternation of sign is not observed, indicating the shift mechanism may not be purely contact. Stetter and Merten[26] have found that the parent bispidine (N–H instead of N–Me) forms a complex with nickel of general formula $(\mathrm{NiBisp_2})^{2+}2\mathrm{Cl}^-$, having a dissociation constant of 1.66×10^{-17}. If the N,N'-dimethylbispidine under consideration here were also to bind Ni strongly, one would expect a sizable pseudocontact contribution. The interaction of the diamine with Ni may *induce* conformational changes in the bicyclic ligand.[27] Therefore the Ni induced ^{13}C shift data do not admit of a simple interpretation. A more rigorous calculation than we were able to undertake would be required to support any conclusions about the liquid phase conformation of **1** drawn solely from Ni-induced shifts.

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