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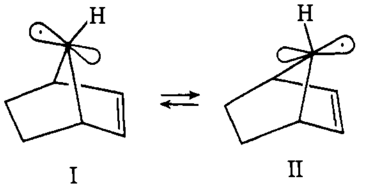
Homoallyl Interaction between the Nitrogen Lone Pair and the Nonadjacent π-Bond in Cyclic and Bicyclic Amines. V.[1] The Stereospecific Orientation of the Lone Pair Electrons in 7-Azanorbornene Derivatives

Kenichi Yoshikawa,[2] Katsutoshi Bekki,[3] Masanori Karatsu,[2] Koji Toyoda,[2] Tetsuki Kamio,[2] and Isao Morishima*[2]

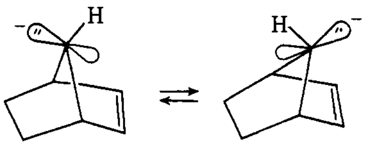
Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, and the Department of Chemistry, Kyoto Institute of Technology, Kyoto, Japan. *Received April 1, 1975*

Abstract: In order to gain insight into the effect of n,π bishomoallyl interaction on the orientation of the lone pair electrons, we have carried out ^1H and ^{13}C NMR spectroscopic studies of 7-azanorbornene and 7-azanorbornadiene derivatives. Based on the stereospecific shifts and the line broadening effects of ^1H NMR signals induced by Eu^{3+} and Gd^{3+}, it was concluded that the lone pair electrons preferentially occupy an anti position with respect to the electron rich π-bond in *N*-methyl-7-azanorbornadiene-2,3-dicarboxylic acid. This preferential orientation of the nitrogen lone pair in 7-azanorbornene derivatives was also confirmed by the stereospecific ^{13}C chemical shift changes induced by *N*-methyl substitution and by the Eu(fod)$_3$-induced ^1H shifts. A similar trend of the specific lone pair orientation is also encountered for N-H 7-azanorbornene derivatives. From these experimental results it is concluded that n and π electrons are "repulsive" in bishomoallyl and bishomobenzyl interacting systems involved in the five- and six-membered cyclic and bicyclic amines and that the nitrogen lone pair electrons prefer an anti position with respect to the π bond or π electron rich group so as to avoid the "repulsive" interaction.

The 7-norbornenyl system offers a structural framework from which long-range nonbonded interactions may be examined. The 7-norbornenyl cation has been shown to exhibit such bonding to an unusual degree.[4] This has been attributed to the nonclassical nature of the 7-norbornenyl cation resulting from the overlapping of the unoccupied and the nonadjacent orbitals. Similarly, the nonclassical nature of the 7-norbornenyl radical has been proposed by Kochi et al.[5] based on its electron spin resonance spectrum. They claimed that I is more stable than II and that the interaction between the π orbital on C-2,3 and the half-occupied orbital on C-7 has a destabilizing effect. However, the studies on the nonbonded interaction between the doubly occupied n orbital (anion center) and the nonadjacent π group have been quite limited. Recently, the specific orientation of the lone pair electrons on C-7 in 7-norbornenyl anion has been studied[6] by stereospecific deuteron capture of anti and syn anion intermediates. The preference for *anti*-7-norbornenyl anion has been suggested and interpreted as resulting from possible bishomoantiaromatic character of this anion. Quantum chemical studies of 7-norbornenyl anion have also been performed.[7,8] The semiempirical molecular orbital calculations, however, failed to predict definitely the orientation of the lone pair electrons. It may be, therefore, readily seen from these examples that the problem on the transannular effect between the lone pair electrons and the neighboring π bond in bicyclic molecules is still open to further experimental and theoretical studies.

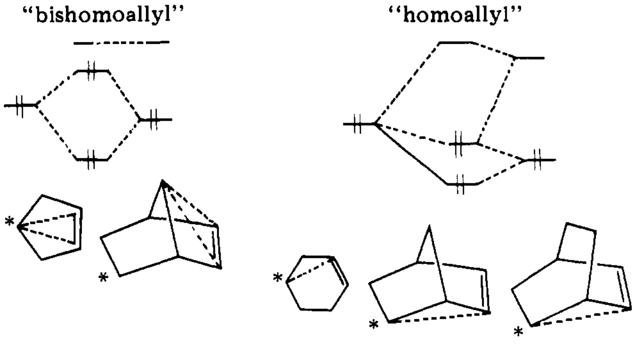


I II



anti syn

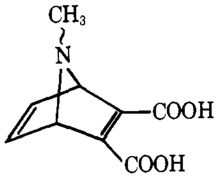
In our recent photoelectron spectroscopic studies[1,9,10] on the nonbonded n,π interaction involved in several cyclic and bicyclic amines containing a nonadjacent π bond, it has been shown that the feature of the nonbonded n,π interaction is quite different between homoallyl and bishomoallyl n,π interacting systems. In the homoallyl interacting system, both n,π and n,π* interactions contribute competitively to the relative stability of the interacting system and, therefore, the system is elec-



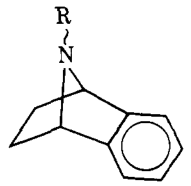
* = N-H, N-CH$_3$

tronically stabilized.[9,10,13] On the contrary, bishomoallyl n,π interaction makes the interacting system less stable, because the n,π^* interaction is forbidden from the orbital symmetry. In other words, n and π electrons in the bishomoallyl interacting system[9] are "repulsive", while, these electrons are rather "attractive" in the homoallyl system.[9,10,13] It is therefore of interest to study the specific orientation of the lone pair electrons in bicyclic amines in which homoallyl and bishomoallyl n,π interactions may be involved and to elucidate the intrinsic nature of these homoconjugative interactions.

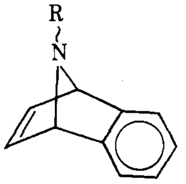
We have previously reported the stereospecific orientation of the lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene derivatives[13] and *N*-methyl-2-aza-5-norbornene derivatives,[10] the homoallyl n,π interacting systems. It has been shown that the direct interaction between n and π electrons plays an important role in the specific lone pair orientation and that these electrons are "electronically attractive", as is expected from the molecular symmetry. In these circumstances, we have studied here the orientation of the nitrogen lone pair electrons and electronic structures in 7-azanorbornene derivatives, the bishomoallyl interacting system. The following compounds were studied: *N*-methyl-7-azanorbornadiene-2,3-dicarboxylic acid (**1**), *N*-methyl-7-azabenzonorbornene (**2**), *N*-methyl-7-azabenzonorbornadiene (**3**), 7-azabenzonorbornene (**4**), and 7-azabenzonorbornadiene (**5**). The aim of this study is to delineate the following problems, intrinsic in these molecules. (1) Is the n,π bishomoconjugation interaction "attractive" or "repulsive"? (2) How is the effect of this n,π nonbonded interaction on the stereospecific orientation of the lone pair electrons?



1



2, R = CH3
4, R = H



3, R = CH3
5, R = H

Experimental Section

Materials. *N*-Methyl-7-azanorbornadiene-2,3-dicarboxylic acid (**1**) was synthesized by referring to Kitzing et al.[14] 7-Azabenzonorbornene (**4**) and 7-azabenzonorbornadiene (**5**) were prepared by the method of Carpino.[15] *N*-Methyl-7-azabenzonorbornene (**2**) and *N*-methyl-7-azabenzonorbornadiene (**3**) were prepared by N-methylation of the parent amines (**4** and **5**). $Eu(NO_3)_3$, $Gd(NO_3)_3$, $Eu(fod)_3$ (tris(heptafluorobutanoylpivaloylmethanato)europium), and $Ni(AA)_2$ (nickel bisacetyl acetonate) are commercially available. $Eu(fod)_3$ and $Ni(AA)_2$ were dried in vacuo over 3 days at 60° and at room temperature, respectively, before use.

Proton NMR Measurement. All the proton spectra were measured with a Varian Associates HR-220 high-resolution spectrometer (Kyoto University) operating at 220 MHz. Assignments of well-separated proton signals were made by referencing the spectral patterns, $Eu(fod)_3$-induced shifts, and the spectra of the related carbocyclic compounds. Me_4Si or DSS was used as an internal standard. The perturbed spectra were taken at room temperature (24°) in the presence of varying amounts of the paramagnetic reagents.

Carbon NMR Measurement. All the ^{13}C spectra were obtained at 25.1 MHz on a Jeolco ^{13}C Fourier transform NMR system, JNM-PFT-100, and were recorded after 100–10 000 pulses with intervals of 2 or 3 s. An internal ^2D lock was employed. The assignments of ^{13}C NMR spectra were made by comparing each other (**1–5**) and by referring to the spectra of their carbocyclic derivatives. The half-decoupled technique was also used to help the signal assignment of the ^{13}C NMR spectra.

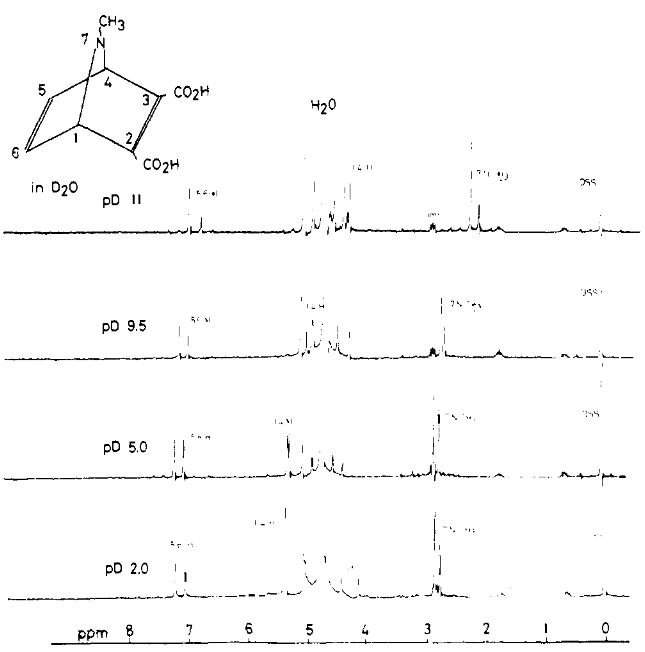
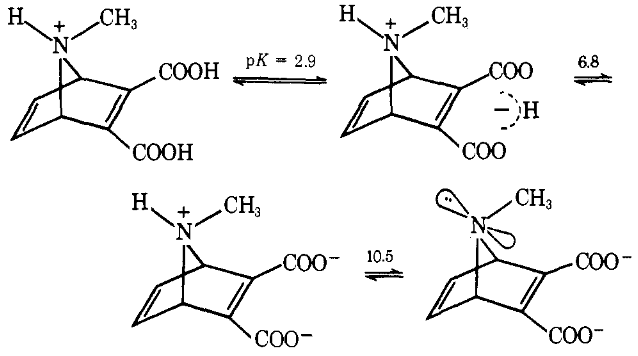


Figure 1. The 220-MHz ^1H NMR spectra of **1** in acidic, neutral, and basic D_2O solutions.

Results and Discussion

A. The Specific Orientation of the *N*-Methyl Group in 7-Azanorbornadiene-2,3-dicarboxylic Acid. The p*K* values of 2.9, 6.8, and 10.5 for **1** were obtained from the pH measurement of its hydrochloride solution by titration with aqueous NaOH. The values of pK = 2.9 and 6.8 are attributable to the dissociation of two carboxyl groups and pK = 10.5 represents the dissociation of a proton from the ammonium group. Therefore, four steps of ionization are deduced as shown below.[17] Figure 1 shows the 220-MHz ^1H NMR spectra of **1** in acidic, neutral, and basic D_2O solutions. As the pD is raised, the shieldings of all the protons (*N*-methyl, bridgehead (1,4-H) and vinylidene (5,6-H) protons) increase. This is because dissociation of the proton at the carboxyl or the ammonium group enhances electron densities on the neighboring hydrogen atoms. A remarkable feature to be noted in Figure 1 is that the ^1H NMR spectra of **1** exhibit two separate absorptions for each proton,[18] which is most possibly resulting from the presence of two *N*-methyl invertomers, *N*-methyl syn and anti ones. The invertomer ratio obtained by integration of each proton absorption (most accurately the *N*-methyl proton signals) was seriously affected by the variation of the pD values as is shown in Figure 1 and Table I. At high pD values (greater than pD 10.5), where the nitrogen atom is free from protonation, one invertomer is strongly favored over the other (80:20). In the acidic media, however, the invertomer ratio becomes close to 1:1. This experimental trend may allow us to expect that n,π bishomo-



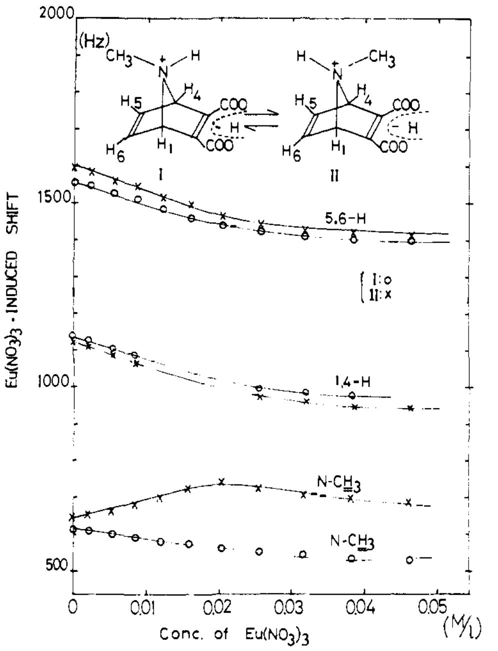


Figure 2. Plots of Eu^{3+}-induced pseudo-contact shifts vs. the metal concentration for **1**.

Table I. Relative Populations of the Two Invertomers

Compounds	Solvents (pD)	Relative populations[a]
1	D_2O (1.4)	58:42
	(4.6)	55:45
	(9)	74:26[b]
	(11)	80:20
	Me_2SO	24:76
2	$CDCl_3$	80:20
	CF_3COOD	70:30
3	$CDCl_3$	94:6
	CF_3COOD	76:24

[a] Obtained from the integration of the *N*-methyl proton signals of the two invertomers. [b] Obtained from the integration of 1,4-H signals.

conjugative interaction is responsible for the specfic orientation of the nitrogen lone pair electrons and that the steric effect of the *N*-methyl group on the lone pair orientation is less important.

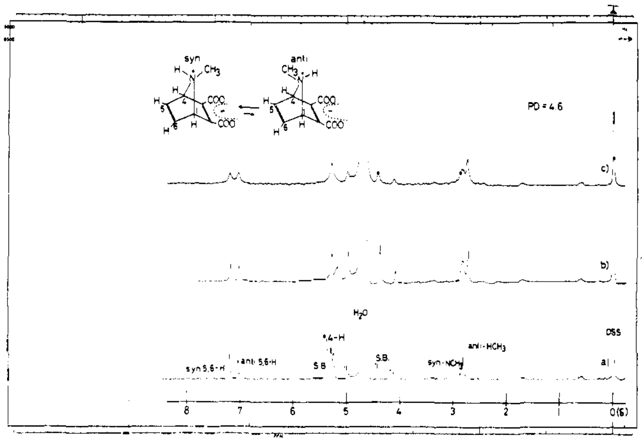
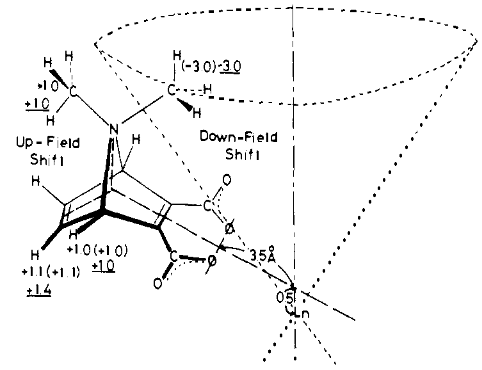


Figure 3. The 220-MHz ^1H NMR spectra of 1 (pD 4.6): (a) in D_2O (3×10^{-1} M); (b, c) in the presence of 1×10^{-1} and 3×10^{-1} mM $Gd(NO_3)_3$ in solution, respectively.

Table II. ^1H Chemical Shifts, Eu^{3+}-Induced Shifts, and Calculated Pseudo-Contact Shifts for 1 (pD 4.6)



Conformer	Position	^1H chemical shift, δ[a]	Eu^{3+}-induced ^1H shift (rel)[b]	Calcd values (rel)[c]
N-Methyl-syn[e]	*N*-Methyl	2.95	−3.0	−3.0
	1,4-H[d]	5.09	+1.0	+1.0
	5,6-H	7.25	+1.1	+1.4
N-Methyl-anti	*N*-Methyl	2.76	+1.0	+1.0
	1,4-H	5.19	+1.0	+1.0
	5,6-H	7.09	+1.1	+1.4

[a] Diamagnetic reference positions from DSS observed at 220 MHz at room temperature (24 °C) in D_2O solution. [b] Obtained from the relative values of linear plots in the low concentration of Eu^{3+} (see Figure 2). The plus and minus signs denote upfield and downfield pseudo-contact shifts, respectively. [c] Calculated following the equation of McCornell and Robertson.[20] The optimized values are shown. The location of the Eu^{3+} used for the calculation is shown. [d] The shifts of this proton was normalized to unity. [e] The major conformer.

In order to assign these two sets to separate signals, we studied Eu^{3+}-induced pseudo-contact shifts for **1**. Figure 2 shows the plots of Eu^{3+}-induced paramagnetic shifts vs. the concentration of added $Eu(NO_3)_3$ for the 0.05 M D_2O solution of **1**. Here pD was adjusted to 4.6 which is most suitable for the observation of Eu^{3+}-induced shifts. The relative intensity of each set of the proton signals did not vary with the addition of the paramagnetic shift reagent. The spectra are time averaged between complexed and uncomplexed species. When the concentration of Eu^{3+} is lower than 0.017–0.018 M, the addition of $Eu(NO_3)_3$ caused upfield shifts for each of the proton signals except for the *N*-methyl signal of the predominant invertomer. It is well known[19] that carboxyl anions or carboxyl groups associate perpendicularly to the principal magnetic axis of a lanthanide ion and form a 3:1 complex of ligands and metal ion. Axial symmetry around the metal ion is also expected in the 3:1 complex of **1** and Eu^{3+}. It is, therefore, likely that the relative values of the Eu^{3+}-induced shifts at low ion concentration are significant in the present study. The relative values of Eu^{3+}-induced shifts of the 3:1 complex of the ligands and the Eu^{3+} ion, with the value for the bridgehead proton normalized to unity, are shown in Table II. In order to substantiate these paramagnetic shifts, we calculated the geometric factor,[20] $(1 - 3\cos^2\theta)/r^3$, with the assumption that the dicarboxyl group of **1** associates perpendicularly to the principal axis of Eu^{3+}. The relative values of the calculated geometric factors which give the best agreement with the observed paramagnetic shifts are also given in Table II. Correspondence between the relative values of the observed shifts and those of the calculated geometric factors may allow us to assign the major conformer to the one having the *N*-methyl group on the same side as the dicarboxyl group (*N*-methyl-syn conformer). To verify further the preferential orientation of the *N*-methyl group to the syn position, we have also studied the specific line broadening of the proton resonances induced by the addition of $Gd(NO_3)_3$ to the aqueous solution of **1** (Figure 3). The lower field *N*-methyl resonance (δ 2.83) with

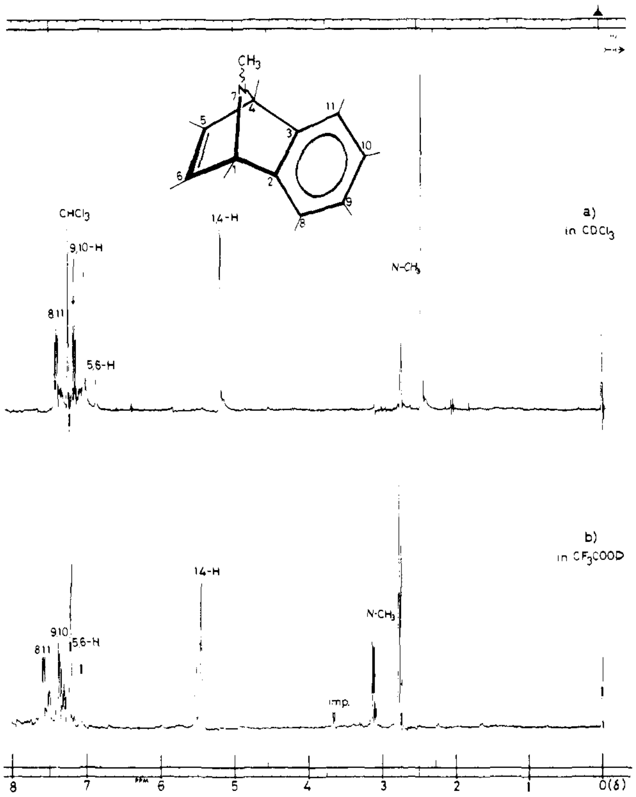


Figure 4. The 220-MHz ^1H NMR spectra of **3**: (a) in $CDCl_3$ and (b) in CF_3COOD solutions.

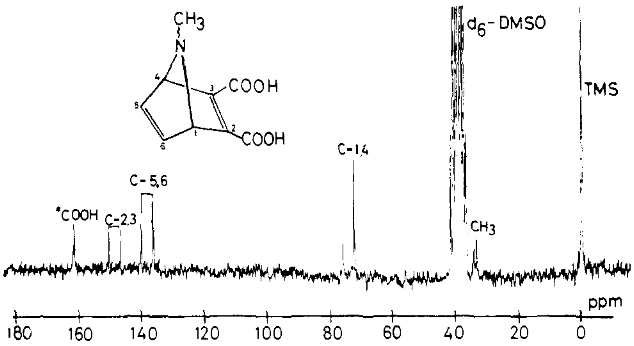


Figure 5. ^{13}C NMR spectrum of **1** in Me_2SO-d_6 solution (at 25.1 MHz).

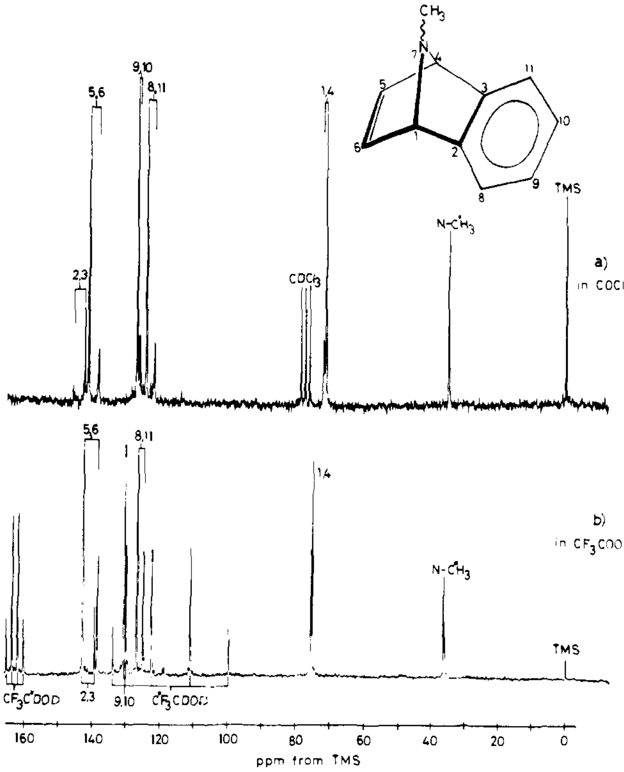
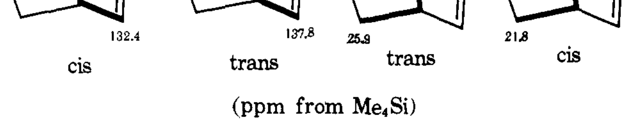


Figure 6. ^{13}C NMR spectra of **3**: (a) in $CDCl_3$ and (b) in CF_3COOD solutions (at 25.1 MHz).

the greater signal intensity exhibits preferential line broadening, compared with the upfield one. While, the other sets of proton signals (the bridgehead (1,4-H) and the vinylidene (5,6-H) protons) of the two invertomers show the line broadening to an equal extent. It has been well established[21] that the long electron relaxation time and highly isotropic magnetic moment of Gd^{3+} make it the ideal lanthanide "relaxation reagent" with the desired $\langle r^{-6} \rangle$ line width dependence. Accordingly, the above differential line broadening effect appears to confirm our assignment of the major invertomer to the *N*-methyl-syn conformer.

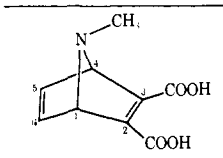
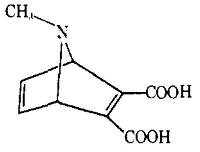
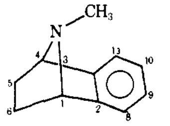
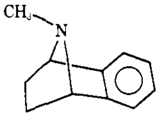
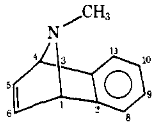
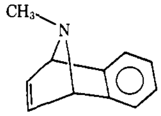
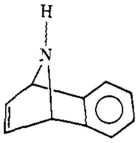
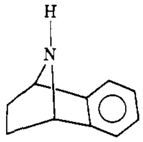
B. The Orientation of the Lone Pair Electrons in *N*-Methyl-7-azanorbornene Derivatives. Figure 4 exemplifies the 220-MHz ^1H NMR spectra for **3**. As is evidently shown in this figure, the ^1H NMR spectra of **2** and **3** in $CDCl_3$ or in CF_3COOD solution also exhibit two separate absorptions for each proton, resulting from the presence of the two *N*-methyl invertomers. The invertomer ratio of these compounds obtained from the integration of the proton absorptions are given in Table I together with the result for **1**. In order to delineate the stereospecific orientation of the nitrogen lone pair electrons, the ^{13}C NMR chemical shifts for **1–5** were measured in various solvents. The ^{13}C NMR spectrum of **1** in Me_2SO-d_6 is shown in Figure 5. The two invertomers give rise to two distinct sets of ^{13}C chemical shifts for each carbon, as is the case for ^1H NMR spectra. In Me_2SO solution, as has been discussed in section A, the *N*-methyl-anti conformer is the major one. Figure 6 shows the ^{13}C NMR spectra of **3** in $CDCl_3$ and in CF_3COOD. As is the case for **1**, inspection of Figure 6 shows the presence of the two *N*-methyl invertomers for **3**. The ^{13}C NMR shifts of 7-azanorbornene derivatives are summarized in Table III. Unfortunately, the ^{13}C NMR signals of the minor conformer of **2** in $CDCl_3$ solution were not detected because of the considerably small population (6:94, see Table I). On the other hand, the ^1H and ^{13}C NMR spectra of **4** and **5** showed a single set of time-averaged signals. In the Me_2SO solution of **1**, the 2,3 carbon resonance of the *N*-methyl-syn conformer is 3.3 ppm upfield with respect to that in *N*-methyl-anti. However, the 5,6 carbons of the former resonate at 3.2 ppm downfield from those of the latter. A similar trend of the ^{13}C chemical shifts of 2,3 and 5,6 carbons is also encountered in the D_2O solution of **1** (Table III). It is well established[21] that the effect of methyl substitution on the ^{13}C chemical shift is quite sensitive to the structural changes of the carbon skeleton in organic compounds. In the 7-methyl syn and anti conformers of 7-methylnorbornene, the γ-carbon that lies on the cis skeleton resonates at higher field than that on the trans one. Such an experimental trend of ^{13}C chemical shifts



(ppm from Me_4Si)

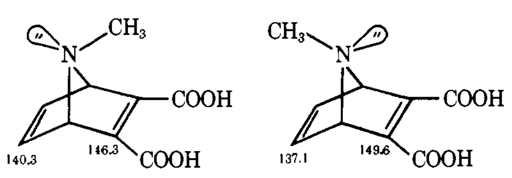
in carbocyclic compounds is well known[22,23] as the "γ-effect" of methyl substitution. It is worth noting that this "γ-effect"

Table III. ^{13}C Chemical Shifts of 7-Azanorbornene Derivatives (ppm from Me$_4$Si)

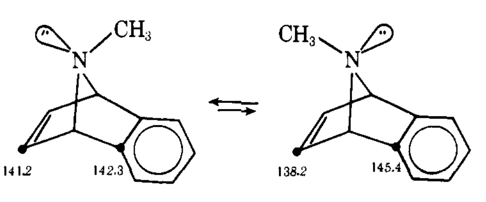
Compounds	Solvent (pD)	1,4	2,3	5,6	N–C*H$_3$	C*OOH	8,11	9,10
 1 (*N*-methyl-syn)[a]	DMSO	77.2	146.3	140.3	35.1	160.4		
	D$_2$O (2.0)	74.4	149.1	141.4	35.7	166.4		
	(4.5)	74.3	147.4	141.2	34.8	166.7		
	(8.0)	74.9	146.0	142.9	36.4	167.4[c]		
	(12.0)	75.4	148.4	144.5	36.1	174.9		
 1 (*N*-methyl-anti)	DMSO	74.9	149.6	137.1	34.2	160.4		
	D$_2$O (2.0)	74.4	153.3	137.4	35.7	166.4		
	(4.5)	74.3	151.8	137.4	34.8	166.7		
	(8.0)	74.9	149.8	138.0	36.4	167.4[c]		
	(12.0)	75.4	153.8	139.5	36.1	174.9		
 2 (*N*-methyl-syn)[b]	CDCl$_3$	67.7	140.1	25.4	33.3		122.1	128.2
	CF$_3$COOD	73.1	138.4	27.2	34.2		124.5	132.2
 2 (*N*-methyl-anti)	CF$_3$COOD	71.9	—[d]	24.1	34.2		123.0	131.9
 3 (*N*-methyl-syn)[a]	CDCl$_3$	71.3	142.3	141.2	34.9		124.3	127.0
	CF$_3$COOD	75.0	139.0	142.4	36.3		126.6	130.3
 3 (*N*-methyl-anti)	CDCl$_3$	71.9	145.4	138.2	34.9		121.8	126.2
	CF$_3$COOD	75.4	142.5	138.2	36.0		124.7	129.8
 4	CDCl$_3$	61.1	148.5	26.5			119.1	125.9
	CF$_3$COOD	65.8	139.4	25.4			124.7	129.5
 5	CDCl$_3$	66.2	151.2	144.4			120.6	124.4
	CF$_3$COOD	68.4	141.4	141.0			126.2	128.8

[a] The major invertomer. [b] The major invertomer. The ^{13}C signals of the minor one were not observed in CDCl$_3$ due to its rather small relative ratio. [c] The chemical shift was somewhat uncertain. [d] This signal was not obtained.

is also encountered in our *N*-methyl-7-azanorbornadiene system and therefore affords further support of the above assignment.[24] It is, therefore, now possible to assign two invertomers of 3 with the aid of the ^{13}C chemical shift difference between the 2,3 and 5,6 carbons. The 2,3 carbon of the major conformer of 3 resonates at the higher field than that of the minor one. On the contrary, the 5,6 carbon resonance of the former is 3.0 ppm downfield from that of the latter. Thus, use of the "γ-effect" established for 1 may suggest that the *N*-methyl-syn conformer is the major one in 3. For 2 we cannot directly determine the orientation of the lone pair by comparing



(ppm from Me$_4$Si, in Me$_2$SO)



(ppm from Me$_4$Si, in CDCl$_3$)

the 2,3 and 5,6 carbon chemical shifts of the two invertomers, because only one set (the major invertomer) of the ^{13}C NMR signals was detected. However, the difference of the ^{13}C chemical shifts between the two conformers of **4** in CF_3COOD corresponds well to that of **5** (Table III). For example, the 5,6 carbon resonance of the minor conformer is 3.1 ppm higher than that of the major one. It is also to be noted that the 5,6 carbon resonance moves by 7.4 ppm to the higher field on going from the N-H 7-azabenzonorbornene (**4**) to the *N*-methyl derivative (**2**), while the 2,3 carbon resonance remains almost unchanged. Referring to the "γ-effect" of the ^{13}C chemical shift leads us to expect that the *N*-methyl group occupies preferentially a syn position in **2**, similar to the case for **1** and **3**.

In order to obtain further confirmation of this stereospecific orientation of the *N*-methyl group, we obtained $Eu(fod)_3$-induced ^1H NMR shifts for **2** and **3**. The relative values of the $Eu(fod)_3$-induced shifts obtained from the relative values of the linear plots of the observed ^1H paramagnetic shift vs. the concentration of added $Eu(fod)_3$ are listed in Table IV. Here, the larger shift of the vinylidene proton (5,6-H) and the smaller shifts of the benzene-ring protons (8,9,10,11-H) in the major conformer are more noticeable than those of the corresponding protons of the minor one. Taking into account the $1/r^3$ dependence of pseudo-contact shifts,[20] this trend support the assumption that the lone pair anti conformer is the major one. It is also apparent that the relative $Eu(fod)_3$-induced shifts of the predominant invertomer of **2** correspond well to those of the major one (the *N*-methyl-syn conformer) in **3**. This experimental trend confirms that the *N*-methyl group preferentially occupies a syn position in **2**. Based on the above discussion, the specific orientation of the lone pair electrons in **2** and **3** is now determined as below.[25]

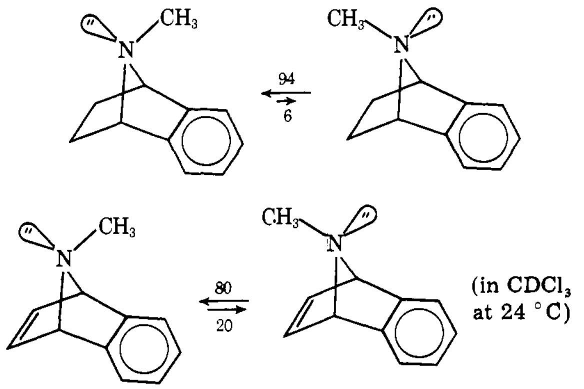
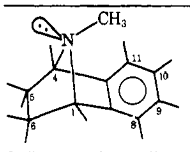
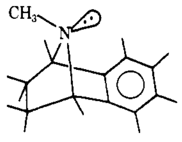
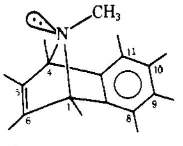
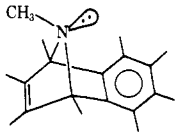
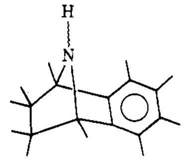
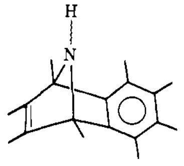


Table IV. $Eu(fod)_3$- and $Ni(AA)_2$-Induced Proton Shifts

Compounds	Position	^1H chemical shift, δ[a]	$Eu(fod)_3$-induced ^1H shift (rel)[b]	$Ni(AA)_2$-induced ^1H shift (rel)[b]
 **2** (lone pair anti)	1,4	4.73	−1.00	
	5,6-exo	2.58	−0.83	
	5,6-endo	1.45	−0.37	
	8,11	7.37	−0.19	
	9,10	7.35	−0.10	
	N−CH_3	2.39	−0.87	
 **2** (lone pair syn)	5,6-endo	1.17		
	N−CH_3	2.31		
 **3** (lone pair anti)	1,4	5.00	−1.00	
	5,6	6.74	−0.56	
	8,11	7.18	−0.17	
	9,10	6.91	−0.10	
	N−CH_3	2.60	−0.96	
 **3** (lone pair syn)	1,4	5.00	−1.00	
	5,6	6.91	−0.22	
	8,11	7.30	−0.34	
	9,10	7.02	−0.20	
	N−CH_3	2.36	−0.70	
 **4**	1,4	4.53	−1.00	1.00
	5,6-exo	2.05	−0.91	−0.34
	5,6-endo	1.24	−0.59	0.44
	8,11	7.18	−0.26	−0.11
	9,10	7.07	−0.14	0.14
 **5**	1,4	4.53	−1.00	1.00
	5,6	6.99	−0.56	0.74
	8,11	7.24	−0.22	−0.06
	9,10	6.92	−0.12	0.07

[a] Diamagnetic reference positions from Me_4Si are observed at 220 MHz at room temperature in $CDCl_3$ solution. [b] Obtained from the relative values of the slopes of linear plots of observed ^1H contact shifts vs. concentration of added $Eu(fod)_3$ or $Ni(AA)_2$.

C. The Orientation of the Lone Pair Electrons in N-H 7-Azanorbornene Derivatives. Here we wish to extend our study to the N-H 7-azanorbornene derivatives. The stereospecific ^{13}C shifts induced by the *N*-methyl groups, which has been discussed in section B, could not serve as a tool for the determination of the nitrogen lone pair orientation. We have to be very careful when we want to determine the steric structure of organic compounds based only on the lanthanide-induced NMR shifts, because these paramagnetic shifts have considerable contact contribution beside the pseudo-contact effect.[26] Thus, in order to examine the lone pair orientation of the N-H derivatives, we have measured $Ni(AA)_2$-induced ^1H and ^{13}C NMR contact shifts. As is well-documented,[27-29] $Ni(AA)_2$-induced ^1H and ^{13}C NMR contact shifts are substantially sensitive to the conformational changes and, therefore, are quite useful in the studies of the molecular conformation associated with the orientation of the lone pair electrons. In order to study the specific orientation of the nitrogen lone pair and the manner of the intramolecular electron spin transmission in N-H 7-azanorbornene derivatives, $Ni(AA)_2$-induced ^1H and ^{13}C NMR contact shifts were observed for **4** and **5**. The signal changes of each proton and carbon, as $Ni(AA)_2$ is successively added to the solution of **5** in $CDCl_3$, are exemplified in Figures 7 and 9. Figures 8 and 10 show the linear plots of $Ni(AA)_2$-induced ^1H and ^{13}C contact shifts vs. the concentration of added $Ni(AA)_2$ for **5**. The spectra are time averaged between complexed and uncomplexed species, and the proton and carbon resonances of the ligand shift toward the resonance position of the paramagnetic adduct. Therefore, only the relative values of these shifts are significant in the present study. Relative values of $Ni(AA)_2$-induced shifts for various protons of **4** and **5** are shown in Table IV. The relative ^{13}C contact shifts of **4** and **5** are given in Figure 11 and Table V. Here, the positive and negative signs correspond to upfield and downfield shifts, respectively. It is to be noted in Figure 11 that the relative ^{13}C contact shifts of the β-carbons are remarkably different between 2,3 and 5,6 carbons in **4**. It is well established[13,28] that electron spin reaches the β carbon to a greater extent by a zigzag path than a folded one. Therefore, the large difference in the β carbon contact shifts of **4** may suggest that

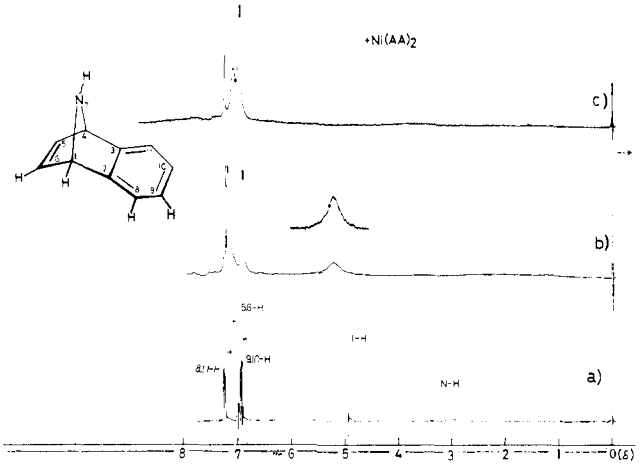


Figure 7. ^1H NMR spectra of **5**: (a) in $CDCl_3$ and (b, c) in $CDCl_3$ containing varying amounts of $Ni(AA)_2$ (at 220 MHz).

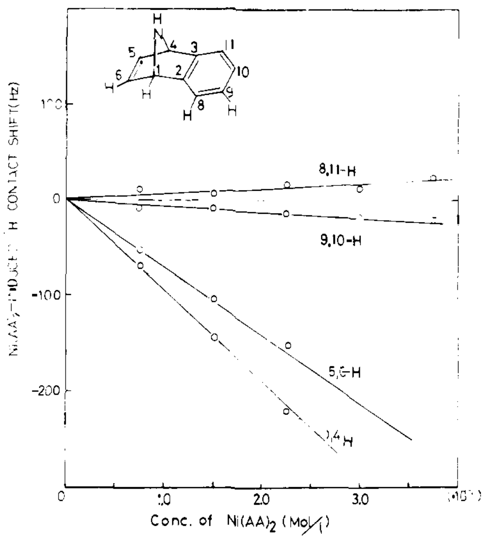
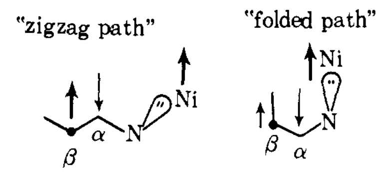


Figure 8. Plots of isotropic paramagnetic ^1H shifts vs. concentration of $Ni(AA)_2$ for **5**.



the lone pair electrons occupy preferentially an anti position with respect to the benzene ring. In **5**, the relative value (−1.62) of the contact shift for the 2,3 carbon is not so different from that for the 5,6 carbon (−1.00), indicating that the relative ratio of the invertomers are nearly equal or the lone pair anti conformer is a little favored. In order to gain further insight into the relative stability of lone pair anti and syn conformers in **4** and **5**, comparison was made between relative values of observed contact shifts and calculated spin densities by the INDO method[30] for the corresponding hydrocarbon σ-radical, 7-norbornenyl (**6**) and 7-norbornadienyl (**7**), in which the radical lobe occupies an anti or syn position (Table V). In our previous investigations, we demonstrated[26,27] that $Ni(AA)_2$-induced ^1H and ^{13}C contact shifts for the nitrogen containing molecules are plausibly reproduced theoretically by the INDO-UHF MO[30] calculations of electron spin densities for the corresponding hydrocarbon σ-radicals. For the proton 1s spin densities (Table VI), the large positive spin densities on the vinyl and methylene protons lying on the zigzag path are noticeable in **6**-*anti*, **6**-*syn*, and **7**. The spin density on these protons (+0.006 in **6**-*anti*, +0.008 in **6**-*syn*, and +0.005 in **7**) is two-three times larger than that of the bridgehead proton. Contrary to this, relatively small negative spin density is induced on the other protons (2,3 or 5,6 protons)

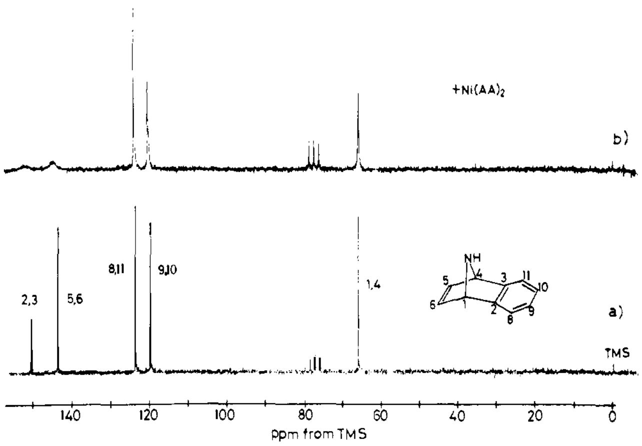


Figure 9. ^{13}C NMR spectra of **5**: (a) in $CDCl_3$ and (b) in $CDCl_3$ containing $Ni(AA)_2$ (at 25.1 MHz).

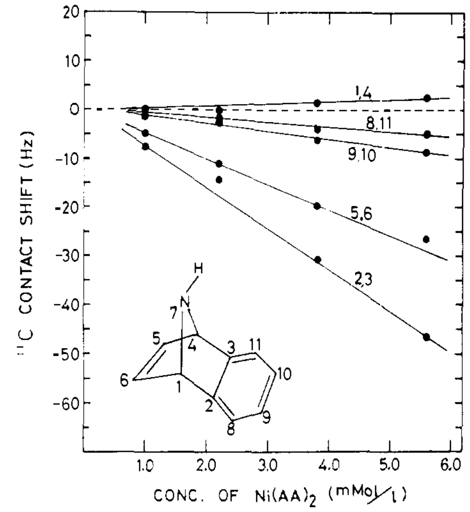


Figure 10. Plots of isotropic paramagnetic ^{13}C shifts vs. concentration of $Ni(AA)_2$ for **5**.

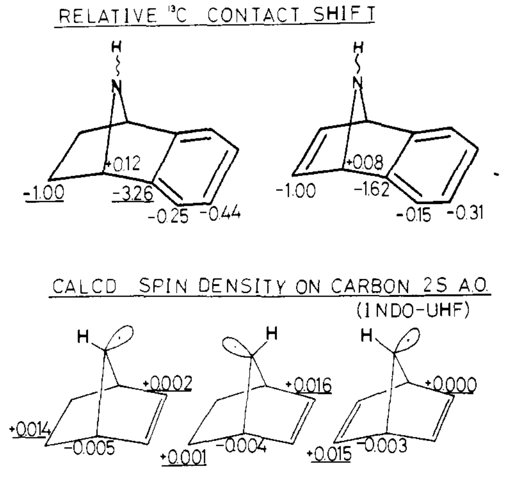


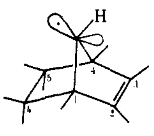
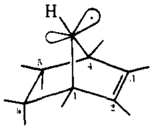
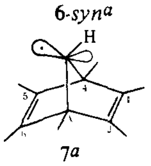
Figure 11. Comparison between the relative $Ni(AA)_2$-induced ^{13}C contact shifts in **4** and **5** and the INDO MO calculated spin densities on carbon 2s AO's in **6**-*anti*, **6**-*syn*, and **7**.

Table V. Ni(AA)$_2$-Induced ^{13}C Contact Shifts

Compounds	Position	^{13}C contact shift (rel)^a
7-Azabenzonorbornene (**4**)	1,4	+0.12
	2,3	−3.26
	5,6	−1.00^b
	8,11	−0.25
	9,10	−0.44
7-Azabenzonorbornadiene (**5**)	1,4	+0.08
	2,3	−1.62
	5,6	−1.00^c
	8,11	−0.15
	9,10	−0.31

^{a} Obtained from the relative values of the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of added Ni(AA)$_2$. The plus and minus signs denote upfield and downfield contact shifts, respectively. ^{b} The actual shift is 1.0 ppm (25 Hz) per 5 mM Ni(AA)$_2$ in 1.7 M CDCl$_3$ solution. ^{c} The actual shift is 1.6 ppm per 5 mM Ni(AA)$_2$ in 1.6 M CDCl$_3$ solution.

Table VI. Calculated Spin Densities on the H 1s and C 2s AO's for Hydrocarbon σ-Radicals (INDO–UHF–MO)

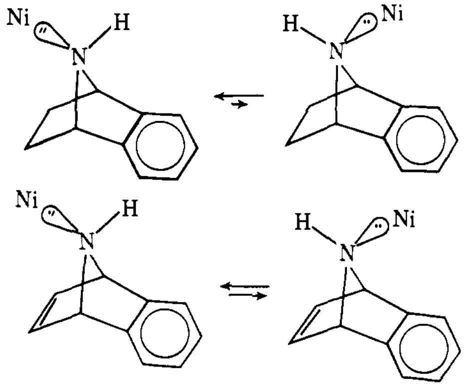
Radical	Position	Calcd value of spin density
 **6**-*anti*^{a}	1,4-C	−0.004
	2,3-C	+0.016
	5,6-C	+0.001
	1,4-H	+0.003
	2,3-H	+0.006
	5,6-exo H	−0.001
	5,6-endo H	−0.002
 **6**-*syn*^{a}	1,4-C	−0.005
	2,3-C	+0.002
	5,6-C	+0.014
	1,4-H	+0.003
	2,3-H	−0.001
	5,6-exo H	−0.001
	5,6-endo H	+0.008
 **7**^{a}	1,4-C	−0.003
	2,3-C	+0.015
	5,6-C	+0.000
	1,4-H	+0.003
	2,3-H	+0.005
	5,6-H	−0.001

^{a}The bond angles and lengths are selected referring to the structures of norbornane and norbornene reported by A. Yokoyagi and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 44, 2356 (1971).

which lie on the folded path. It is apparent from these features that the relative ^{1}H contact shifts for **4** cannot be reproduced only by the calculated spin densities for **6**-*anti* or **6**-*syn*. However, if one supposes that both the lone pair anti and syn conformers are present and that the former is more favored, it is easily recognized that the relative ^{1}H contact shifts can be well reproduced by the weighted average of the spin densities for **6**-*anti* and **6**-*syn* conformers. A similar trend is encountered between **5** and the corresponding σ-radical, **7**. The relative ^{1}H contact shift (+0.62) of the β-proton for **5** does not simply correspond to the large positive spin density (+0.005) nor to the small negative spin density on the vinylidene protons of either side in **7**. The relative ^{1}H contact shifts of the β-protons in **5** are reproduced by the average of the spin densities of these vinylidene protons in **7**. This may suggest that the lone pair electrons occupy the anti and syn positions to an equal extent.

As to the carbon contact shifts, the calculated results for **6**-*anti* and **6**-*syn* radical conformers and for **7** show that relatively large positive spin densities are induced on the carbons that lie on the zigzag path. On the other hand, small positive spin densities are induced on the carbons that lie on the zigzag path. On the other hand small positive densities are induced on the carbons lying on the folded path (Figure 11). Similar to the case of the ^{1}H contact shifts, the relative ^{13}C contact shifts of **4** are again reproduced by the weighted average of the carbon 2s spin densities in **6**-*anti* and **6**-*syn* conformers in which the former is predominant. Comparing with the calculated results for **7**, the larger shift of the 2,3 carbons than the 5,6 carbons in **4** suggests that the lone pair anti conformer is also preferred.

From the above discussion concerning the feature of the ^{1}H and ^{13}C contact shifts, it is concluded that, at least in the presence of Ni(AA)$_2$, the population of the lone pair anti conformer is larger than that of the syn and that this trend is more pronounced in **4** than in **5**.[31,32] The experimental trend of the Eu(fod)$_3$-induced shifts in **4** and **5** supports this conclusion (Table IV). It is apparent that the relative ^{1}H pseudo-contact shifts of **4** and **5** correspond well to those of the major conformers (the lone pair anti ones) of **2** and **3**, respectively. This shows that the lone pair electrons of **4** and **5** preferentially occupy the anti position with respect to the benzene ring at least in the form of complexes.



D. Bishomoallyl and Bishomobenzyl n,π Interactions. In our recent photoelectron, uv, and fluorescence spectroscopic studies[1,9,10] of the cyclic and bicyclic amines containing nonadjacent π group, we have shown that bishomoallyl or bishomobenzyl n,π interaction destabilizes the interacting system. This may allow us to expect that n and π electrons are "repulsive" in 7-azanorbornene derivatives. For **1**, in the aqueous basic solution (pD 11), where the dicarboxyl group is ionized and electron densities are rather large on the C-2,3 π bond, as is evidenced by the ^{13}C chemical shifts (see Table III), the lone pair electrons favor the anti position with respect to the monoanionic dicarboxyl group (see section A). In Me$_2$SO solution, however, the lone pair electrons preferentially occupy a syn position. This may be explained as follows; in Me$_2$SO solution, where dissociation of the carboxyl proton is prohibited, the dicarboxyl group serves as electron withdrawing from the C-2,3 π bond (see ^{13}C shifts in Table III). Thus, the bishomoallyl "repulsive" interaction between the nitrogen lone pair and the C-5,6 π electrons becomes more important than that between n and the C-2,3 π electrons. This may be responsible for the preferential lone pair orientation at the syn position. In **3** and **5**, the lone pair electrons predominantly occupy the anti position with respect to benzene.[6b] The lone pair in **2** and **4** also prefers the anti position to the benzene ring in which the highest occupied π orbital energy is higher than that of the C-5,6 π bond. Consequently, these experimental trends suggest that the lone pair electrons preferentially occupy the anti position with respect to the π bond associated with the higher orbital energy or with the "electron rich" π group, so as to avoid the "repulsive" n,π bishomoallyl interaction. This interpretation is consistent with Stille's suggestion[6] that the lone pair electrons prefers the anti position in 7-norbornenyl anion from its possible bishomoantiaromatic character. In order to gain

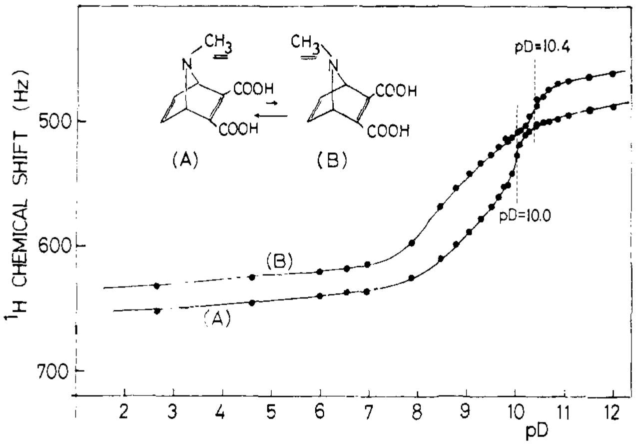


Figure 12. The ^{1}H chemical shifts of the N-methyl protons of **1** vs. pD (Hz from Me_4Si, at 220 MHz).

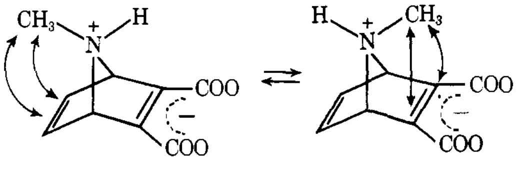
Table VII. pK Values Obtained from the 220-MHz NMR Measurement[a] (in D_2O, 24 °C)

Compounds	Orientation of lone pair electrons	pK[d]
1	anti[b]	10.0
	syn	10.4
2	anti[c]	9.4
	syn	9.7
3	anti[c]	9.4
	syn	9.6

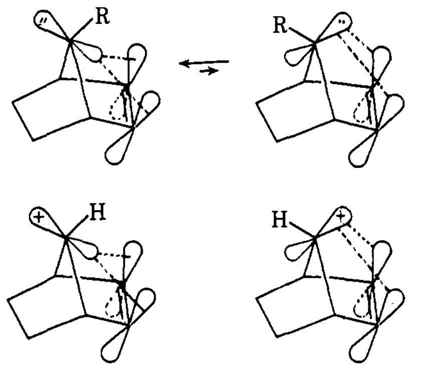
[a] Obtained from the inflection point of the titration curve in which the ^{1}H NMR chemical shifts are plotted vs. pD values. [b] Anti with respect to the dicarboxyl group. [c] Anti to the benzene ring. [d] The estimated uncertainty is ±0.2.

further insight into the intrinsic nature of the lone pair electrons in the bishomoallyl and the bishomobenzyl n,π interacting systems, pK values of **1–3** were obtained from the 220-MHz NMR measurements. The variation of the ^{1}H NMR chemical shifts of the N-methyl protons vs. pD is exemplified in Figure 12. The pK's of the amino groups of the two invertomers were determined directly from the pD values of the inflection points of the NMR titration curves for two separate N-methyl signals. The pK values of **1**, **2**, and **3** are summarized in Table VII. It is of particular interest to note that the pK value of the lone pair anti conformer is smaller than that of the syn. From the specific orientation of the lone pair electrons in **1–5**, it has been suggested that the larger repulsive n,π interaction in the lone pair syn conformer destabilize its nonbonded orbital more than in the anti conformer. It is, therefore, apparent that the bishomoallyl "repulsive" n,π interaction affects the electronic structure of 7-azanorbornenyl derivatives substantially and makes the basicity of the amino group stronger.

Strictly speaking, in N-methyl-7-azanorbornene derivatives (**1**, **2**, **3**), "steric" repulsion[33] should be taken into account besides the bishomoallyl or bishomobenzyl n,π "electronic" effect. In **1**, however, when the nitrogen lone pair electrons are "completely" protonated (at pD 1.4 or 4.6, see Table I), the invertomer ratio becomes close to 1:1. This indicates that the steric repulsion energy between the N-methyl group and the 2,3-carbons or the dicarboxyl group in the N-methyl-syn invertomer is nearly equal to that between the methyl group and the 5,6-carbons in the anti invertomer, and that the steric effect of the N-methyl group on stereochemistry seems to become minimal in the 7-azanorbornadiene skeleton. While, in **2** and **3** the N-methyl-syn conformer is still preferred (70:30) on N-protonation, although the difference in the invertomer ratio is reduced in going from CF_3COOD solution to the $CDCl_3$ solution. In this case, the "steric" repulsion may be also responsible for the orientation of the N-methyl group toward the anti position which is the same direction caused by the n,π repulsive "electronic" interaction and this "steric effect" seems to be comparable with the repulsive bishomoallyl or bishomobenzyl n,π electronic interaction. The cancelling effect of the "steric" and the "electronic" repulsive interactions may cause only a slight difference in the relative stability of the two invertomers of **3**. However, for **2**, the lone pair anti conformer is much preferred (94:6) in $CDCl_3$ solution compared with that in CF_3COOD. This may suggest that bishomobenzyl "electronic" n,π interaction contributes mainly to the specific lone pair orientation in **2**.



Summarizing the above discussion, it is concluded that n and π electrons in the 7-azanorbornenyl system are "repulsive" by the bishomoallyl n,π interaction and that the nitrogen lone pair electrons preferentially occupy an anti position with respect to the π bond or π electron rich group to avoid this "repulsive" interaction. The specific orientation of nitrogen lon pair electrons in the 7-azanorbornenyl system may lead us to expect that the overlap between the nonbonded orbital and the π orbital in the lone pair anti conformer is smaller than that in the syn.[34] This is in marked contrast with well-established π-participation in the solvolysis of 7-norbornenyl tosylate or 7-benzonorbornenyl tosylate.[35] Based on the great difference in the solvolysis rate constants for these compounds, the π-participation (stabilization) in **8**-*anti* is considered to be larger than in **8**-*syn*. This suggests that the overlap between the empty orbital and the π orbital in **8**-*anti* is larger than in **8**-*syn*, inversely to the case of n,π overlap in 7-azanorbornene derivatives or 7-norbornenyl anion. These features reflect that the magnitude of the overlap between the n orbital at C-7 and the C-2,3 π orbital is quite responsible for the structural fluctuation in the 7-norbornenyl system. The unusual temperature dependence of the ESR spectra of the 7-norbornenyl radical reported by Kochi et al.[5] also may be due to the similar structural flexibility of this radical. The present results also appear to be quite interesting in relation to the specific orientation of the radical lobe in the related free radicals, 7-azabenzonorbornene-7-oxyl,[36] 7-azabenzonorbornadiene-7-oxyl,[36] 7-benzonorbornenyl,[37] and 7-benzonorbornadienyl.[37] Details in the MO theoretical analysis of relative stability of 7-norbornenyl system are now under way.[38]



8-*anti* **8**-*syn*

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Conformational Interconversions in Hexahydropyridazine Derivatives

S. F. Nelsen* and G. R. Weisman

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received October 14, 1975*

Abstract: Variable-temperature ^{13}C NMR data for 1,2-dimethylhexahydropyridazine (**1**), its *cis*- and *trans*-3,6-dimethyl derivatives, and 3,4-dimethyl-3,4-diaza-*trans*-bicyclo[4.4.0]decane are reported. These data show that the equatorial, equatorial *N*-methyl conformation of 1 is about 0.3 kcal/mol lower in enthalpy than the equatorial,axial conformation, and that $\Delta G^{\ddagger}$ for the two different nitrogen inversions possible for 1 differ by about 4.8 kcal/mol, which is interpreted to be principally caused by lone-pair–lone-pair repulsion.

Although the conformations of six-membered rings have been by far the most important and best studied, an understanding of the conformational equilibria involved in azacyclohexanes has been slow to develop, largely because of the difficulty in separating nitrogen inversion from ring inversion, and the lack of experimental techniques which can directly observe and identify different conformations. A capsulation of published conformational work on 1,2-dimethylhexahydropyridazine (**1**) illustrates this point. Anderson[1] concluded that **1** exists solely in the diequatorial methyl conformation **1ee** because the ^{1}H NMR *N*-methyl signal remained a singlet, even at temperatures where two *N*-methyl signals were observed