(5) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(6) J. R. Van Wazer, "Determination of Organic Structures by Physical Methods", Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N.Y., 1971, p 393.
(7) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
(8) T. D. Brown, Ph.D. Thesis, University of Utah, 1966.
(9) Reference 5, p 160.
(10) Estimated from the data of ref 8, p 62.
(11) Reference 5, p 104.
(12) For a theoretical study of the mechanism of electron delocalization in vinyl groups, see L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
(13) D. Rosenberg and W. Drenth, *Tetrahedron*, **27**, 3893 (1971).
(14) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).
(15) See, for example, the discussion in ref 5, p 375.
(16) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1965).
(17) It must be noted that several approximations were made in the Letcher–Van Wazer study; namely, $\langle r^{-3} \rangle$ for the p and d orbital contributions were held constant and terms resulting from interactions of the groups around phosphorus mixing into certain excited electronic states on the phosphorus atom through multiple bond interactions were neglected.
(18) R. K. Howe, *J. Am. Chem. Soc.*, **93**, 3549 (1971).
(19) A. I. Razumov et al., *J. Gen. Chem. USSR (Engl. Transl.)*, **40**, 1704 (1970).
(20) W. P. Murray, M.S. Thesis, University of Delaware, 1973.

Homoallyl Interaction between the Nitrogen Lone Pair and the Nonadjacent π Bond. ^{1}H and ^{13}C Nuclear Magnetic Resonance Contact Shifts and the Orientation of the Lone Pair Electrons in 2-Azabicyclo[2.2.2]oct-5-enes[1,2]

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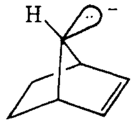
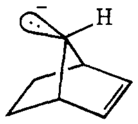
Abstract: The orientation of the nitrogen lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene and its *N*-methyl derivative has been studied with the aid of Ni(AA)$_2$ (nickel acetylacetonate) induced ^{1}H and ^{13}C NMR contact shifts and molecular orbital calculations in view of elucidation of nonbonded n,π interaction (n–π transannular interaction) in azabicyclic molecules. Ni(AA)$_2$-induced ^{1}H and ^{13}C contact shifts for these molecules were plausibly explained by the spin density distributions obtained by INDO-UHF-MO calculation for the corresponding hydrocarbon σ radical, bicyclo[2.2.2]oct-5-en-2-yl, in which the radical lobe occupies exo and endo positions. This allowed us to conclude that the nitrogen lone pair for *N*-methyl derivative is preferentially oriented at the exo position while the exo and endo positions are equally favored for the N-H derivative. This was further confirmed by other NMR evidence. CNDO/2-MO calculations were also performed for above azabicyclic molecules to illuminate the factors that determine the nitrogen lone pair orientation. It is concluded that steric repulsion and n–π transannular electronic stabilization energies are essentially important to determine the lone pair orientation in the title molecule.

Neighboring group participation in the reaction intermediate or in the electronic and geometrical structures of ground or excited state of molecules constitutes an essential concept in the organic chemistry. As a part of our continuing investigations[2,3] toward understanding neighboring group participation in the electronic structures of rigid σ-bonded molecules, we have studied here the stereospecific orientation of lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene derivatives. Much attention has been paid to the transannular interaction between nonbonded π electrons.[4] However, quite limited studies have been available concerning the neighboring group effect on the stereospecific orientation of lone pair electrons which appears to be one of the interesting problems in the stereochemistry of organic molecules.

The specific orientation of the lone pair electrons on the C$_7$ carbon in 7-norbornenyl anion has been studied[5] 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 bishomoantiaromatic character of this anion. Quantum chemical studies of this anion have also been performed. However, semiempirical MO calculations failed to determine definitely the orientation of lone pair electrons in 7-norbornenyl anion.[6,7] It may be readily accessible from this example that the problem on the transannular effect between lone pair electrons and the neighboring π bond in bicyclic molecule is still open to further experimental and theoretical studies.

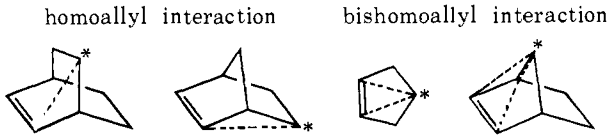


1-s (syn)



1-a (anti)

We have recently carried out a photoelectron spectroscopic study of nonbonded n,π interaction involved in several cyclic and bicyclic amines containing nonadjacent π bonds.[2] It was revealed that the feature of the nonadjacent n,π interaction is quite different between homoallyl and bishomoallyl n,π interacting systems; for the homoallyl interaction, both n,π and n,π* interactions contribute competitively to the relative stability of the interacting system. It is, therefore, of interest to study the orientation of lone pair electrons in homoallyl n,π interacting molecules in relation to the bishomoconjugative system.[8]



In these circumstances, we have studied here the orientation of nitrogen lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene (**2**), its *N*-methyl derivative (**3**), and their saturated homologs (**4**, **5**) with the aid of

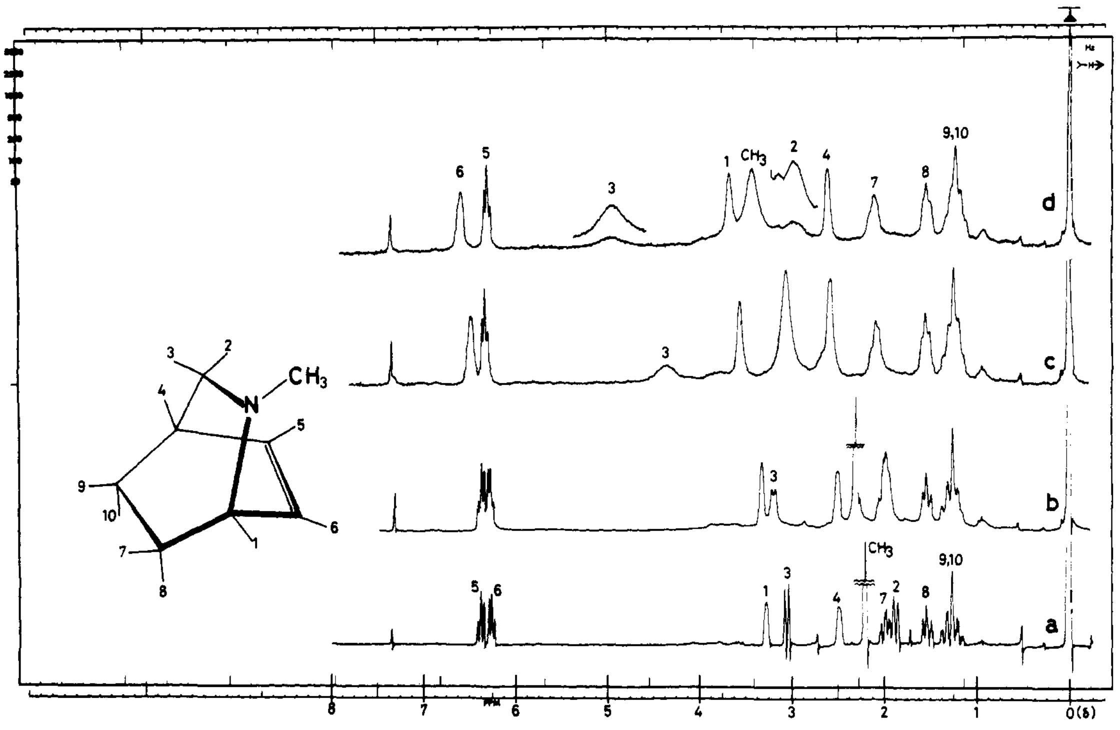
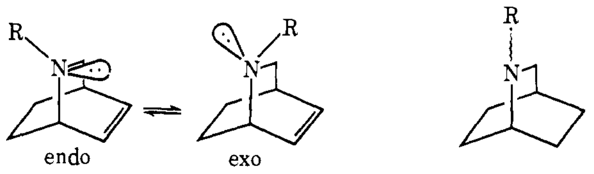


Figure 1. ${}^1H$ NMR spectra of 3 (a) in $CDCl_3$ and (b-d) in $CDCl_3$ containing varying amounts of $Ni(AA)_2$ (at 220 MHz).



2, R = H
3, R = CH_3

4, R = H
5, R = CH_3

$Ni(AA)_2$ (nickel acetylacetonate) induced ${}^1H$ and ${}^{13}C$ NMR contact shifts and molecular orbital calculations.[9] **2** and **3** have two possible orientations of nitrogen lone pair electrons, endo (syn) and exo (anti) with respect to the double bond. In order to determine the lone pair orientation, we have examined conformational dependence of $Ni(AA)_2$-induced ${}^1H$ and ${}^{13}C$ contact shifts for these molecules together with other subsidiary methods. Stereospecific intramolecular electron spin transmission was also studied with the aid of MO calculation in relation to the lone pair orientation. The factor that determines the specific lone pair orientation in **2** and **3** was illuminated with the aid of CNDO/2-MO calculations of these molecules and the results were also discussed in relation to the electronic structure of the corresponding hydrocarbon carbanions in which the nitrogen lone pair is replaced by the carbon anion.

Experimental Section

Materials. 2-Azabicyclo[2.2.2]oct-5-ene (**2**), 2-methyl-2-azabicyclo[2.2.2]oct-5-ene (**3**), 2-azabicyclo[2.2.2]octane (**4**), and 2-methyl-2-azabicyclo[2.2.2]octane (**5**) were prepared by the method of Cava et al.[10] Commercially available $Ni(AA)_2$ (nickel bisacetylacetonate) was dried in vacuo over 30 hr at 60° before use.

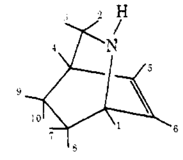
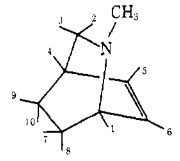
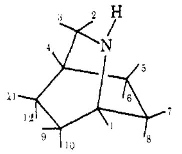
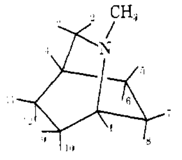
Proton NMR Measurements. All samples were made in $CDCl_3$ solution, ca. 150 mmol/l. for **2** and **4**, and ca. 300 mmol/l. for **3** and **5**. NMR samples were prepared by the addition of a given amount of $Ni(AA)_2$ to the $CDCl_3$ solution of these cyclic amines. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer from our department. TMS was used as an internal standard. Assignment of well separated proton signals was easily made by referencing the spectral patterns. Assignment of rather complicated signals was assisted by the use of a benzene solvent induced shift. The spectra were taken at room temperature (24°) in the presence of a varying amount of $Ni(AA)_2$. The observed paramagnetic shift is relative to the free ligand. For **2** and **3**, $Eu(DPM)_3$ (europium dipivaloylmalonate) induced shifts were also obtained.

Carbon-13 NMR Measurement. For **4**, completely proton decoupled ${}^{13}C$ NMR spectra were obtained at 15.1 MHz on a Jeolco-C-60HL spectrometer equipped with an IS-60 field/frequency synchronous sweep system of the proton irradiation frequency and an SD-HC heteronuclear spin decoupler. The spectra were accumulated in 32-128 scans using the Jeolco S/N booster. These spectra were measured with the external field locking mode and were calibrated with the internal cyclohexane (ca. 5 vol %, 27.3 ppm from TMS). The ${}^{13}C$ spectra of **2**, **3**, and **5** were obtained at 25.1 MHz on a Jeolco ${}^{13}C$ fourier transform NMR system, JNM-PFT-100, and were recorded after 100-1000 pulses with intervals of 2 or 3 sec. An internal ${}^2D$ lock was employed. The ${}^{13}C$ chemical shifts of these three compounds were measured with respect to the internal $CDCl_3$ (77.1 ppm). All samples were made in $CDCl_3$ solution, ca. 1 *M*, in 8 mm sample tubes. All the spectra were taken at room temperature (24°) in the presence of varying amounts of $Ni(AA)_2$. The assignments of ${}^{13}C$ NMR spectra were made by comparing unsaturated and saturated bicycles, by referring the methyl substitution effect to the ${}^{13}C$ chemical shift,[11] and by the use of the stereospecific ${}^{13}C$ contact shift induced by $Ni(AA)_2$.[12] The half-decoupled technique was used to help the signal assignment of the ${}^{13}C$ NMR spectra.

Results

${}^1H$ Contact Shifts. The signal changes of each proton as $Ni(AA)_2$ is successively added to the solution of **3** in $CDCl_3$ are exemplified in Figure 1. Figure 2 shows the linear plots of $Ni(AA)_2$ induced contact shifts vs. the concentration of added $Ni(AA)_2$ for **3**. The spectra are time averaged between complexed and uncomplexed species, and the proton 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 work. The proton chemical shifts and the relative values of $Ni(AA)_2$-induced ${}^1H$ contact shifts for **2** to **5** are summarized in Table I. The $Eu(DPM)_3$-induced shifts and benzene solvent shifts, which are defined as the shift on going

Table I. $Ni(AA)_2$- and $Eu(DPM)_3$-Induced Proton Shifts and Benzene-Induced Solvent Shifts

Molecule	Position	^{1}H chemical shift, δ[a]	$Ni(AA)_2$-induced ^{1}H shift (rel)[b]	$Eu(DPM)_3$-induced ^{1}H shift (rel)[b]	Benzene-induced ^{1}H shift, ppm[c]
 **2**	1	3.53	−1.00[d]	−1.00	+0.28
	2 (endo)	2.46	−3.0[h]	−0.85	+0.26
	3 (exo)	2.92	−3.0[h]	−1.07	+0.12
	4	2.58	−0.13	−0.38	+0.38
	5	6.38	+0.21	−0.36	
	6	6.43	−0.44	−0.37	
	7	1.93	−0.07	−0.69	+0.01
	8	1.63	−0.11	−0.42	+0.18
	9, 10[i]	~1.3	~+0.03	−0.33, −0.40	
 **3**	1	3.30	−1.00[e]	−1.00	+0.22
	2 (endo)	1.87	−2.90	−0.88	+0,14
	3 (exo)	3.06	−4.94	−0.91	+0.04
	4	2.50	−0.29	−0.42	+0.33
	5	6.39	+0.22	−0.43	
	6	6.26	−0.90	−0.47	
	7	1.99	−0.35	−0.67	−0.03
	8	1.53	−0.07	−0.41	+0.14
	9, 10[i]	1.25	0.00	−0.35, −0.46	
	N-CH_3	2.22	−3.24	−1.05	
 **4**	1	2.86	−1.0[f]		+0.19
	2, 3	3.01	−4.2[h]		+0.15
	4	1.73	0.0[h]		
	5,6,8,10,11,12[i]	1.60−1.65			
	7, 9	1.87	~+0.0		
 **5**	1	2.44	−1.00[g]		+0.18
	2, 3	2.70	−2.63		+0.08
	4	1.48	−0.05		
	5, 6, 11, 12[i]	1.52	~0.0		
	7, 9	1.97	+0.12		+0.04
	8, 10	1.62	−0.15		+0.08
	N-CH_3	2.35	−2.18		+0.12

[a] Diamagnetic reference positions 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 ^{1}H contact shifts vs. concentration of added $Ni(AA)_2$ or $Eu(DPM)_3$. The plus and minus signs denote upfield and downfield contact shifts, respectively. [c] The plus sign means the upfield benzene-induced solvent shifts. [d] The actual shift is 0.45 ppm per 0.01 mol of $Ni(AA)_2$ in the 0.15 *M* $CDCl_3$ solution. [e] The actual shift is 0.6 ppm per 0.1 mol of $Ni(AA)_2$ in the 0.3 *M* $CDCl_3$ solution. [f] The actual shift is 0.34 ppm per 0.01 mol of $Ni(AA)_2$ in the 0.15 *M* $CDCl_3$ solution. [g] The actual shift is 0.4 ppm per 0.1 mol of $Ni(AA)_2$ in the 0.3 *M* $CDCl_3$ solution. [h] Precise values of the relative contact shift could not be obtained due to the rapid broadening. [i] Proton signals could not be distinguished due to the superposition.

from the $CDCl_3$ solution to the benzene solution, are also included in Table I. As Figure 1 shows, the proton signals of **3** are well separated in a diamagnetic solution (in the absence of $Ni(AA)_2$) in the 220 MHz NMR spectra except for those of β- and γ-methylene protons. Similar spectra were also obtained for **2**, **4**, and **5**. The two α-methylene protons (adjacent to the nitrogen atom) are magnetically equivalent for **4** and **5** due to the rapid inversion of nitrogen lone pair.

Inspection of Table I shows that all the protons except for H_5 in **2** and **3** exhibit downfield shifts in the $Ni(AA)_2$ system. As is well documented,[13,14] the isotropic shift induced by complexation with $Ni(AA)_2$ is predominantly caused by the Fermi contact shift which is related to electron spin density, ρ_H, induced on the proton. The downfield and upfield contact shifts correspond to the positive and negative spin densities on the proton, respectively. Therefore, the relative contact shifts in Table I mean the relative spin densities with the opposite sign.

^{13}C Contact Shifts. Peturbation of the ^{13}C NMR spectrum caused by the addition of $Ni(AA)_2$ is shown in Figure 3 for **3**, as an example. Relative values of ^{13}C contact shifts were obtained from the slopes of the linear plot for various carbons, with the value for α-methyne carbon (C_1) normalized to unity. The results are summarized in Table II. The feature of relative ^{13}C contact shifts for **3** is close to that for **5**, but somewhat different from **2**.

Molecular Orbital Calculations. In order to substantiate theoretically the observed trend of ^{1}H and ^{13}C contact shifts, we calculated electron spin densities on the proton 1s and carbon 2s AO's for the corresponding hydrocarbon σ radicals which are expected to have isoelectronic structure with these bicyclic amines complexed with $Ni(AA)_2$ (see Tables III and IV). Previously we demonstrated[14] that the relative values of the $Ni(AA)_2$-induced contact shifts are most plausibly reproduced by the INDO-UHF-MO[15] calculations of spin densities for the corresponding hydrocarbon σ radicals. For example, relative values of spin densities calculated for cyclohexyl and phenyl radicals correspond well to the relative contact shifts for piperidine and pyridine complexed with $Ni(AA)_2$, respectively. We have carried out INDO-MO calculations for the two conformers of 2-bicyclo[2.2.2]oct-5-enyl σ radical with the orientation of the radical lobe in the endo and exo positions and for 2-bicyclo[2.2.2]octyl σ radical. Bond lengths used for the MO calculations are taken as C-H, 1.09, C-C, 1.54, and C=C, 1.35 Å. We also assumed that there is no strain in geometries for these compounds, that is, all the bond angles except for the sp^2 carbons (120°) are taken as 109°28′. The calculated spin densities on the proton 1s and carbon 2s AO's for

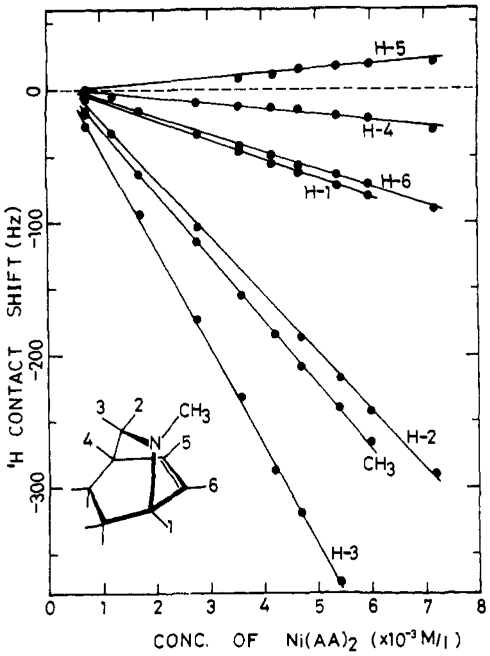


Figure 2. Plots of isotropic paramagnetic shifts vs. concentration of $Ni(AA)_2$ for **3**.

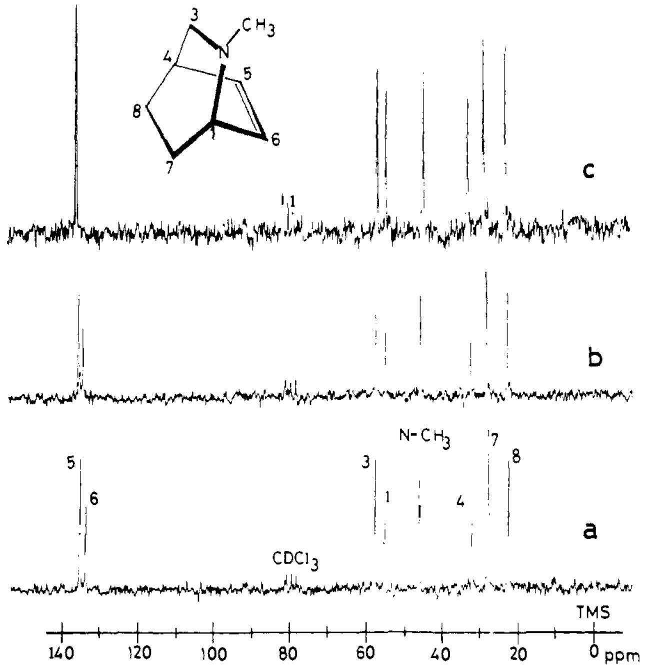
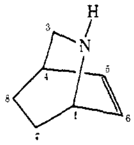
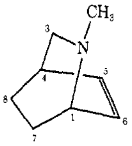
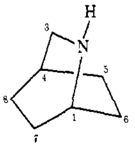
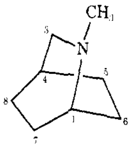


Figure 3. ^{13}C NMR spectra of **3** (a) in $CDCl_3$ (b and c) and in $CDCl_3$ containing varying amounts of $Ni(AA)_2$ (at 220 MHz).

these σ radicals are summarized in Tables III and IV, respectively. Spin densities on H_2, C_5, and C_6 in 2-bicyclo[2.2.2]octyl radical were obtained by taking an average between those associated with the atoms located symmetrically to the $C_1NC_3C_4$ plane. It is readily seen that the calculated results for 2-bicyclo[2.2.2]octyl radical plausibly account for the relative values of $Ni(AA)_2$-induced ^{1}H and ^{13}C contact shifts in **4** and **5**.

In order to get insight into the stereospecific orientation of the nitrogen lone pair electrons and relative stability of the two conformers, CNDO/2-MO[16] calculations were performed for **2**, **3**, **4**, and **5** with the nitrogen lone pair orientation at endo and exo positions. Here bond lengths are: C-N, 1.54; N-H, 1.01 Å. Other bond lengths and bond angles are taken similary to the case of the hydrocarbon σ radicals described above. Similar calculations were also carried out for the corresponding carbanions in which the nitrogen lone pair in **2**–**5** is replaced by the carbon anion C^-.

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

Molecule	Position	δ ^{13}C[a]	$Ni(AA)_2$-induced ^{13}C shift (rel)[b]
 **2**	1	46,6	+1.00[c]
	3	46.6	+1.33
	4	30.6	−1,25
	5	133.1	−0.09
	6	134.8	−2.38
	7	27.1	−1.15
	8	23.9	−0.28
 **3**	1	55.2	+1.00[d]
	3	57.7	+1.15
	4	32.3	−0.23
	5	134.3	+0.02
	6	132.9	−1.18
	7	28.1	−0.32
	8	22.8	+0.05
	$N-CH_3$	46.2	+1.68
 **4**	1	43.6	+1.00[e]
	3	47.1	+1.30
	4	24.7	−0.26
	5, 8	25.0	+0,00
	6, 7	27.1	−1.31
 **5**	1	51.9	+1.00[f]
	3	58.6	+1.31
	4	26.9	−0.29
	5, 8	25.7	+0,07
	6, 7	24.8	−0.80
	$N-CH_3$	43.9	+1.53

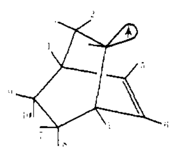
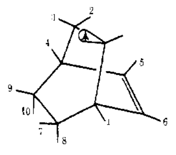
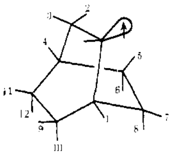
[a] In parts per million from TMS. [b] Obtained from the relative values of the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of added $Ni(AA)_2$. The plus and minus signs denote upfield and downfield contact shifts, respectively. [c] The actual shift is 1.9 ppm per 0.02 mol of $Ni(AA)_2$ in the 1 *M* $CDCl_3$ solution. [d] The actual shift is 0.6 ppm per 0.02 mol of $Ni(AA)_2$ in the 1 *M* $CDCl_3$ solution. [e] The actual shift is 3.4 ppm per 0.02 mol of $Ni(AA)_2$ in the 1 *M* $CDCl_3$ solution. [f] The actual shift is 0.5 ppm per 0.02 mol of $Ni(AA)_2$ in the 1 *M* $CDCl_3$ solution.

Discussion

A. The Orientation of the Lone Pair Electrons. Inspection of Table I shows that the difference in the α-methylene proton chemical shifts between endo (H_2) and exo (H_3) protons is quite different for **2** and **3**. The shift difference for **2** (Δ = 0.46 ppm) is small and rather close to that for bicyclo[2.2.2]oct-2-ene (Δ = 0.23 ppm).[17] It is well documented[18,19] that the chemical shift of the proton adjacent to the nitrogen lone pair is affected by the long range shielding effect of the oriented lone pair. Therefore, one may expect that the two α-methylene protons (H_2, H_3) sense to the same extent the long range shielding effect of the adjacent nitrogen lone pair electrons, probably because equilibrium orientation of the lone pair occurs in almost equal population for the exo and endo conformers. The large shift difference (Δ = 1.19 ppm) for **3**, however, allows us to expect preferential orientation of the lone pair at the exo or endo position.

The $Ni(AA)_2$-induced ^{1}H contact shifts for these two α-methylene protons also reflect different modes of lone pair orientation in **2** and **3**; for **3**, the α-exo proton (H_3) experiences greater downfield contact shift than the α-endo proton (H_2), while these contact shifts for **2** are almost equal. The large difference in the $Ni(AA)_2$-induced contact shifts

Table III. Calculated Spin Densities on the H 1s AO's for Hydrocarbon σ Radicals (INDO–UHF–MO)

Radical	Position	Relative value of spin density	Calcd value of spin density
 **6**-endo	1	+1.00	+0.0107
	2 (endo)	+5.38	+0.0575
	3 (exo)	+2.58	+0.0275
	4	+0.16	+0.0017
	5	+0.05	+0.0006
	6	+0.00	+0.0000
	7	−0.18	−0.0019
	8	+0.93	+0.0099
	9	+0.04	+0.0004
	10	+0.12	+0.0013
 **6**-exo	1	+1.00	+0.0090
	2 (endo)	+3.06	+0.0275
	3 (exo)	+5.84	+0.0524
	4	+0.25	+0.0023
	5	+0.32	+0.0029
	6	+0.84	+0.0076
	7	−0.04	−0.0003
	8	−0.19	−0.0017
	9	+0.14	+0.0013
	10	+0.03	+0.0003
 **7**	1	+1.00	+0.0102
	2, 3[a]	+4.15	+0.0422
	4	+0.18	+0.0018
	5, 11[a]	+0.06	+0.0006
	6, 12[a]	+0.09	+0.0009
	7, 9[a]	−0.14	−0.0014
	8, 10[a]	+0.42	+0.0042

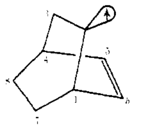
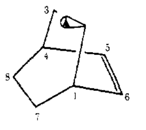
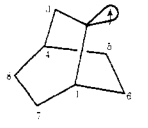
[a] Averaged values of these two protons.

for H_2 and H_3 in **3** is again attributable to preferential orientation of the nitrogen lone pair.

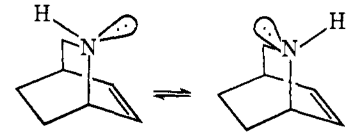
In order to gain further insight into the relative importance of lone pair endo or exo conformer in **2** and **3**, comparison was made between relative values of observed contact shifts and those of calculated spin densities by the INDO method for the corresponding hydrocarbon σ radical, 2-bicyclo[2.2.2]oct-5-enyl, in which the radical lobe occupies an endo (**6**-endo) or an exo (**6**-exo) position. In our previous investigations we demonstrated[12,14] that ^1H and ^{13}C contact shifts for the nitrogen-containing molecules induced by the coordination with $Ni(AA)_2$ depend on the orientation of the nitrogen lone pair and are plausibly reproduced theoretically by the INDO-MO calculations of electron spin densities for the corresponding hydrocarbon σ radicals. The observed trend of the ^1H and ^{13}C contact shifts for **3** appears to be fairly well reproduced[20] by the calculated spin densities for the corresponding hydrocarbon σ radical **6**-exo (Tables III and IV) where the radical lobe is oriented at an exo position. However, the contact shifts for **2** correspond to neither **6**-endo nor **6**-exo. They are rather explained reasonably by the calculated spin densities averaged between two radical conformers **6**-endo and **6**-exo (see Tables III and IV). It is therefore likely that the exo and endo orientations of the nitrogen lone pair of **2** are equally favored.

The $Eu(DPM)_3$-induced ^1H pseudocontact shifts for **2** and **3** (Table I) show that the shift difference between two α-methylene protons in **2** is greater than that in **3**, quite different from the $Ni(AA)_2$-induced shifts. It is especially worth noting that the exo proton (H_3) experienced greater $Eu(DPM)_3$-induced shift than the endo one (H_2) for **2**. This observation implies that the presence of $Eu(DPM)_3$ causes different populations of lone pair exo and endo conformers for **2**.[22]

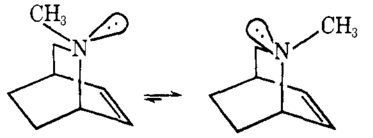
Table IV. Calculated Spin Densities on the C 2s AO's for Hydrocarbon σ Radicals (INDO–UHF–MO)

Radical	Position	Relative value of spin density	Calcd value of spin density
 **6**-endo	1	−1.00	−0.0063
	3	−1.36	−0.0085
	4	+0.51	+0.0032
	5	−0.16	−0.0010
	6	+0.55	+0.0034
	7	+1.81	+0.0113
	8	−0.19	−0.0012
 **6**-exo	1	−1.00	−0.0061
	3	−1.13	−0.0069
	4	+0.48	+0.0029
	5	−0.07	−0.0004
	6	+2.39	+0.0145
	7	+0.52	+0.0032
	8	−0.04	−0.0003
 **7**	1	−1.00	−0.0064
	3	−1.34	−0.0085
	4	+0.51	+0.0032
	5, 8[a]	−0.13	−0.0008
	6, 7[b]	+1.18	+0.0075

[a] Averaged value between C_5 and C_8. [b] Averaged value between C_6 and C_7.



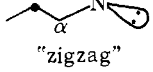
2-endo **2**-exo



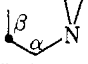
3-endo **3**-exo

Another evidence for different modes of nitrogen lone pair orientation in **2** and **3** resulted from benzene solvent induced shift for H_2 and H_3. It is established[23] that the upfield benzene solvent shift is more pronounced for the proton that is more distant from the nitrogen lone pair electrons; for example, the proton trans to the nitrogen lone pair in ketimines, aziridines, and oximes senses greater upfield solvent shift than the cis one.[22] As Table I shows, H_3 in **3** experiences less upfield benzene-induced solvent shift than H_3 in **2** or H_2 in **5**. This may also be due to the preferential orientation of the nitrogen lone pair electrons at the exo position in **3**.

B. ^1H and ^{13}C Contact Shifts and Mechanism of Electron Spin Transmission in Relation to Nonbonded n,π Interaction. Here we will examine the different feature of the relative ^1H and ^{13}C contact shifts for **2** and **3** in view of elucidation of neighboring group participation in the intramolecular electron spin transmission. It is to be noted in Table II that the relative ^{13}C contact shifts of β carbons (C_4, C_6, and C_7) are remarkably different between **2** and **3**. Quite rapid attenuation of the contact shift of C_4 in **3** is to be compared with the one in **2**. This different feature of the ^{13}C contact shifts is attributable to different nitrogen lone pair orientations as discussed above. It is well established that electron spin reaches the β carbon to a greater extent by a *zigzag*



"zigzag"



"folded"

Table V. Calculated Total Energies for 2-Azabicyclo[2.2.2]oct-5-enes, eV (CNDO/2)[a]

Molecule	Total electronic energy (*A*)	Core repulsion energy (*B*)	Total energy (*A* + *B*)
2-endo	−7634.47	5727.00	−1907.47
2-exo	−7632.34	5724.88	−1907.46
3-endo	−9260.66	7116.74	−2143.92
3-exo	−9241.37	7097.35	−2144.02

[a] Any minimization of energy with respect to geometry is not performed in the present calculation.

path than a *folded* one.[12] The above features of β-carbon contact shifts correspond to this general trend. For **3** in which the lone pair occupies preferentially an exo position, C_7 lying on a *folded* path shows a rather small downfield contact shift. On the other hand, C_7 of **2** exhibits a greater magnitude of the ^{13}C contact shift than C_1. The relative value (−1.15) of the contact shift for this C_7 carbon is comparable with that for C_6 (−1.31) of **4**, indicating that the effect of the lone pair orientation on the contact shift of C_7 in **2** is averaged out due to the rapid nitrogen inversion, i.e., equal orientation of the lone pair, as is the case for **4**. This is reasonably confirmed by the spin density calculation when we compare these contact shift values (−1.15, −1.31) with the averaged value of the spin densities for the two conformers (**6**-endo and **6**-exo) $((+0.52 + 1.81)/2 = +1.16)$. A similar discussion appears to be valid for the ^1H contact shifts.

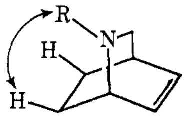
It is of particular interest to note that the ^{13}C contact shift of C_6 in **2** is much greater than that in **3**. The C_6 β carbon in **3**, lying on a zigzag arrangement with respect to the lone pair orientation, shows unexpectedly smaller downfield shift than the corresponding carbon in **2** where the lone pair $N-C_1-C_6$ arrangement has more folded nature resulting from equal contributions of two lone pair orientations. This unusually large downfield ^{13}C contact shift, characteristic of large positive spin density on the carbon, could be attributable to the direct delocalization of spin density from the lone pair coordinated with $Ni(AA)_2$ onto the C_6 carbon. The lone pair orbital facilitates delocalization of positive spin density onto C_6 by the "through-space" spin transmission. It is also to be noted that C_5 and C_8 carbons in **2** experienced downfield contact shift while those in **3** showed upfield shift. The general trend of the alternating ^{13}C contact shifts established for piperidine derivatives is also encountered for **3**, **4**, and **5**, but not for **2**. These unusual downfield contact shifts for C_5 and C_8 in **2** could also be attributed to the direct spin transmission which is facilitated by the substantial contribution of the lone pair endo conformation.

C. The Relative Stability of an n,π Homoallyl Interacting System. In order to illuminate the factor that determines the nitrogen lone pair orientation in **2** and **3**, we have carried out CNDO/2 MO calculations for the two conformers of those molecules. The results are given in Table V. The endo conformer (**2**-endo) is more stable than the exo one (**2**-exo) by about 48 kcal/mol (2.13 eV) in terms of total electronic energy. However, the greater value of the core repulsion energy for **2**-endo compared to **2**-exo cancels above electronic stabilization energy and results in nearly equal total energy of two conformers. This may correspond to the experimental finding for **2** that exo and endo positions of lone pair are nearly equally favored (see section A). As to the *N*-methyl derivative (**3**), the exo conformer is more stable than the endo one by 0.1 eV (2.2 kcal/mol), corresponding to the experimental trend. This is attributable to the repulsive interaction between $N-CH_3$ and β,γ exo protons, as is revealed in Table VI. It is, therefore, likely that the endo conformer of **2** or **3** is electronically more stable than the exo one; however, the steric repulsion between N–R and β,γ exo protons plays an important role in this system.

Table VI. Calculated Total Energies for Bicyclo[2.2.2]oct-5-en-2-yl Anion, eV (CNDO/2)[a]

Conformer	Total electronic energy (*A*)	Core repulsion energy (*B*)	Total energy (*A* + *B*)
Lone pair = endo	−7195.29	5415.91	−1779.38
Lone pair = exo	−7193.24	5413.83	−1779.41

[a] Any minimization of energy with respect to geometry is not performed in the present calculation.



R = H, CH_3

In our recent photoelectron spectroscopic study[2] of **2**–**5** together with several other related cyclic and bicyclic amines, we have shown that in the homoallyl interacting system the stereospecific orientation of the lone pair electrons plays an important role in the n,π and n,π* homoconjugative interactions. Therefore, this different feature of electronic stability between the two conformers is attributable to relative contributions of n,π and n,π* orbital interactions (or mixings) which lead to stabilization and destabilization of the system, respectively. The endo conformer may be more stabilized by the greater contribution of n,π* interaction than the exo one. This trend seems to suggest that the interaction between n and π electrons is rather *attractive*.

In order to discuss the relative stability of the conformers of the corresponding hydrocarbon anion, CNDO/2-MO calculated total energy of 2-bicyclo[2.2.2]oct-5-enyl anion is represented in Table VI. Similarly to the case of the bicyclo amine (**2**), the difference in the total electronic energies of the two conformers is canceled out by the difference in the nuclear repulsion energies. Accordingly it follows that there is no difference in the stability of these two conformers. This corresponds to the result for **2**, the *N*-azahomolog of this carbon anion.

It seems, therefore, reasonable to conclude that the $Ni(AA)_2$-induced ^1H and ^{13}C contact shift serves as a useful probe for the study of homoconjugation between the nitrogen lone pair and the π bond, and that in the homoallyl interacting system both the n,π electronic interaction and the steric repulsive interactions between H–H and $H-CH_3$ are important for the determination of the orientation of lone pair electrons and the relative stability of the molecule.[24]

Acknowledgment. The authors are grateful to Professor T. Yonezawa for support and encouragement of this work. They wish to express their appreciation to the Data Processing Center of Kyoto University for the use of the FACOM 230-60 computer.

References and Notes

(1) Presented partly at XIth European Congress on Molecular Spectroscopy, Tallin, USSR, May, 1973. This paper is referred to as part II of a series on homoallyl n,π interaction in cyclic and bicyclic amines.
(2) Part I: I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, submitted for publication.
(3) I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, *J. Am. Chem. Soc.*, **95**, 5815 (1973).
(4) See, e.g., S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 141 (1969); P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).
(5) J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972).
(6) H. O. Ohorodynyk and D. P. Santry, *J. Am. Chem. Soc.*, **91**, 4711 (1969).
(7) M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971).

(8) As to the bishomoallyl interacting system, the lone pair orientations in 7-azanorbornene derivatives have also been studied: I. Morishima, K. Yoshikawa, K. Toyoda, K. Bekki, to be submitted for publication.

(9) The π participation effect on the rate of carbonium ion reaction in 2-bicyclo[2.2.2]oct-5-enyl structure has been appreciated: A. Lebel, J. E. Huber, Abstract of the 144th National Meeting of the American Chemical Society, March–April 1963, Los Angeles, Calif., 52M.

(10) M. P. Cava, C. K. Wilkins, Jr., D. R. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965).

(11) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) J. B. Grutaner, M. Jautelet, J. B. Dence, R. A. Smith, and J. D. Roberts, *Ibid.*, **92**, 7107 (1970).

(12) (a) I. Morishima, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **92**, 6651 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **93**, 3922 (1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972).

(13) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1311 (1963); R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).

(14) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, and T. Yonezawa, *Chem. Commun.*, 33 (1971); (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, **54**, 3238 (1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **43**, 379 (1970).

(15) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1967).

(16) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(17) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

(18) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).

(19) S. F. Nelsen, P. J. Hintz, and R. T. Landis, II, *J. Am. Chem. Soc.*, **94**, 7105 (1972).

(20) The ESR hyperfine coupling constant of 2-bicyclo[2.2.2]oct-5-enyl radical has been reported.[21] However, due to the planar structure around the radical center in this radical, these splitting constants do not correspond to the feature of the $Ni(AA)_2$-induced ^1H contact shifts of 2-azabicyclo[2.2.2]oct-5-enes.

(21) L. Bonazzola and R. Max, *Mol. Phys.*, **19**, 405, 899 (1970).

(22) The sizable contribution of contact shift to the $Eu(DPM)_3$-induced paramagnetic shift could also lead to misleading conclusions concerning the lone pair orientation.

(23) T. Yonezawa, I. Morishima, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **41**, 2297 (1968).

(24) The detailed study concerning the geometries of various bicyclic amines with minimization of calculated total energies will appear in a separate paper.

Raman Spectra of Alkali Metal–Iodine Matrix Reaction Products. Resonance Raman Spectrum of the Iodine Molecular Anion, I_2^-

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Abstract: Argon matrix reactions of iodine ($Ar:I_2 = 500:1$) and alkali metal atoms have been examined by Raman spectroscopy. Excitation with the red line from a krypton ion laser has yielded a resonance Raman progression for each of the five alkali metal $M^+I_2^-$ species. Each series consisted of five or six members which decreased regularly in intensity and increased steadily in half-width. Statistical analysis gave the harmonic and first-order anharmonic frequencies and an estimate of the dissociation energy of I_2^-.

This study, the third in a series involving alkali metal–halogen reaction intermediates, was prompted by our earlier successes with $M^+F_2^-$ and $M^+Cl_2^-$.[1,2] Person estimated properties of I_2^- in 1963,[3] and the anion has been prepared by several routes and identified by electron spin resonance spectroscopy since then. For example, Zvi et al.[4] detected I_2^- in the ESR spectrum of 2537 Å photolyzed LiI glass at 77°K. Porret and Rossel[5] studied γ-irradiated CsI held at 100°K or less, and from the ESR spectrum of the crystal assigned a stability limit of 87°K to I_2^-. Lastly, Symons and Marov[6] bombarded 77°K aqueous solutions of alkali iodides with γ-rays and attributed subsequent ESR signals to the iodine molecular anion. Since the low-temperature matrix lends stability to otherwise elusive molecules, the study of I_2 matrix reactions with alkali metals was undertaken in search of the $M^+I_2^-$ species.

Experimental Section

The experimental technique, spectroscopic equipment, and cryogenic assembly have been previously described.[7,8] Iodine crystals (Mallinckrodt, Analytical Reagent) were held in a glass finger, and the vapor was allowed to reach equilibrium pressure (0.25 Torr)[9] in a 2-l. stainless steel sample can, after which sufficient Ar diluent was added to attain an $Ar:I_2$ ratio of 500:1. The gaseous sample was condensed on a tilted copper wedge maintained at 12°K at a spray-on rate of 2–3 mmol/hr. An atomic beam of alkali metal was simultaneously directed at the substrate, with metal vapor pressures of approximately 1 μ.[10] Raman spectra were recorded at 20 cm^{-1}/min from 50 to 800 cm^{-1} on a Spex Ramalog, using 500 μ slits and 6471, 5682, and 5309 Å excitation from a Coherent Radiation krypton plasma laser. Dielectric filters were employed to eliminate unwanted plasma emission lines; laser power was 200 mW at the sample with 6471 Å light, 100 mW with 5682 Å, and 150 mW with 5309 Å.

Calibration of the 6471 Å Raman spectra was done relative to the laser line. In order to provide a check, band separation in the progressions was plotted versus quantum number. The intercept gave the fundamental and the overtone wavenumbers were obtained by addition of the observed spacings. Wavenumber accuracy is ±1 cm^{-1}.

Results

Laser Raman spectra of matrix-isolated iodine species have been studied extensively.[11] Two resonance Raman progressions were observed using 5145 Å excitation, one originating at 212 cm^{-1} which was attributed to matrix-isolated I_2 monomer and another starting at 180 cm^{-1} which was assigned to aggregated I_2. The latter series was favored at higher iodine concentrations. Several of the resonance Raman bands of $(I_2)_n$ were observed here; however, the I_2 monomer species, which was much weaker with red excitation, was not detected in the present study.

A typical 6471 Å excited Raman spectrum following the addition of alkali metal atoms to the I_2 matrix sample is shown in Figure 1 for the K + I_2 reaction. The intense fundamental shifted near 114 cm^{-1} and four or five overtones with rapidly decreasing intensities were observed for all of the alkali metal reactions; Table I lists the wavenumber