(E) for the polarized benzene, consistent with localization of the unpaired electron at the site at which bond rupture occurred.
(32) FOCUS Library Program E2-VAND-FIT.
(33) R. Hiatt in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, Chapter 8.
(34) W. B. Moniz and S. A. Sojka, Abstracts of the 14th Experimental NMR Conference, University of Colorado, Boulder, April 15–18, 1973, Session 8.
(35) O. A. Gansow and W. Schittenhelm, *J. Am. Chem. Soc.*, **93**, 4294 (1971).
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(37) We thank E. Tucker for a copy of this computer program.

Homoallylic Interaction between the Nitrogen Lone Pair and the Nonadjacent π Bond in Cyclic and Bicyclic Amines. I. Photoelectron Spectroscopic Study[1]

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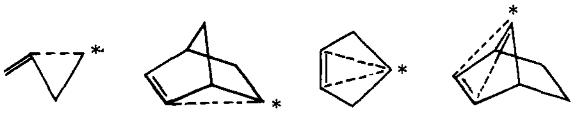
Received September 16, 1974

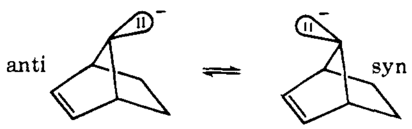
Abstract: In order to study the nonadjacent n,π electronic interaction, photoelectron spectra have been obtained for saturated and unsaturated derivatives of five- and six-membered cyclic and bicyclic amines. It was found that perturbation of nitrogen lone pair ionization potentials (IP's) induced by the interaction with nonadjacent carbon–carbon double bond is quite different in β,γ-unsaturated five-membered cyclic amines and β,γ-unsaturated six-membered amines. The bishomoallyl homoconjugation in five-membered amines favors n,π through-space interaction with destabilization of lone pair orbital, and homoallyl conjugation in six-membered amines involves n,π and n,π* interactions with a little stabilization or destabilization of the lone pair orbital. Different features of lone pair IP's were also encountered for *N*-H and *N*-methyl derivatives of six-membered amines. These were discussed in terms of relative importance of n,π and n,π* interactions which depend on molecular symmetry (bishomoallyl or homoallyl interaction), orbital energy level, and orientation of lone pair in cyclic and bicyclic amines.

During the last decade, the consequences of homoconjugation between an unsaturated group and an active center in cations, radicals and anions have been a subject of controversy. Particularly, studies on the interaction between the cation center and the nonadjacent π bond have been extensively performed[3] in connection with the debate on "the nonclassical carbonium ion". The great π electron participation in the acceleration of the rate of solvolysis in norbornene derivatives has been well established. Concerning the interaction between the half-occupied orbital and the nonadjacent π bond, Kochi et al.[4] have reported the ESR studies of 7-norbornenyl radical, and claimed that the configuration with the sp hybrid orbital directed toward the anti side is the most stable form, and that the interaction between the orbitals of carbon 2,3 and the half-occupied orbital on carbon 7 would have a destabilizing effect.



* = cation, radical, anion

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 Stille et al.[5] have speculated, based on the experimental results of the 7-norbornenyl anion system, that bishomoallyl type interaction makes the n–π interacting system less stable due to the antiaromatic character. The conformation of 7-norbornenyl anion has also been examined quantum chemically using CNDO/2 and MINDO/2 MO calculations by Santry[6] and Dewar,[7] respectively. However, these semiempirical MO calculations failed to predict definitely the orientation of lone pair electrons affected by the neighboring double bond in the 7-norbornenyl anion.[8] Consequently, the interaction between the lone pair electrons and the nonadjacent π electrons (homoallyl type interaction) is still open to further experimental and theoretical studies.



Recently photoelectron spectroscopy (PES) has proved to be extremely useful in evaluating the electronic interaction between nonadjacent groups[9] in the ground state molecules. The usefulness of PES in studying π,π interactions in dienes and n,n interactions in various nitrogen and oxygen containing molecules has been demonstrated.[10] The PES studies concerning n,π interactions in unsaturated ketones and ethers have also been reported.[11] However, there have been no systematic studies[12] on the n,π interaction between nitrogen lone pair and nonadjacent olefin or benzene π electrons.

In order to elucidate the structural effect on the homoconjugative interaction between lone pair and π electrons, we have performed here a PES study of nonadjacent n,π interaction in various cyclic and bicyclic amines (**1–18**). Here we are concerned with difference in the intrinsic nature of homoallyl and bishomoallyl n,π interactions. Amines containing the nonadjacent unsaturated group seem to be quite relevant for the study of the intramolecular n,π interactions. The PES study on this n,π homoconjugative interac-

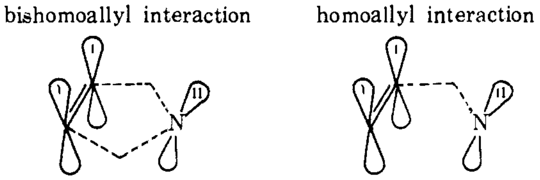
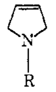
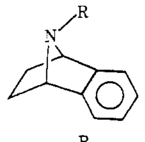
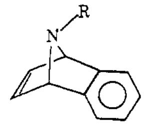
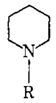
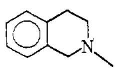
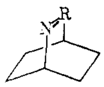
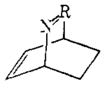


Table I. Ionization Potentials (eV) of Cyclic Amines

	Ionization potential[a]			
Compd	Compd no.	R = H	Compd no.	R = CH_3
	**1**	8.7_7(n), 11.4_9	2	8.4_1 (n), 11.1_6
	**3**	8.6_1 (n), 9.7_7 (π)	**4**	8.2_1 (n), 9.6_6 (π)
	**5**	8.4_4 (n), 9.1_0 (π)	**6**	8.3_3 (n), 8.9_6 (π)
	7	8.2_5 (n), 9.0_5 (π), 9.9_7 (π)	8	8.1_8 (n), 8.7_8 (π), 9.0_6 (π), 9.6_6 (π)
	**9**	8.6_4 (n), 10.7_5	10	8.2_9 (n), 10.5_9
	**11**	8.6_4 (n), 9.3_3 (π)	**12**	8.6_7 (n), 9.3_7 (π)
	**13**	8.5_7 (n, π),[b] 9.3_3 (π)	**14**	8.6_0 (n, π),[b] 9.3_0 (π)
	**15**	8.2_2 (n), 10.2_9	**16**	7.7_8 (n), 10.0_9
	**17**	8.3_5 (n), 9.3_6 (π)	**18**	7.9_7 (n), 9.2_8 (π)

[a] Vertical ionization potentials (±0.05 eV). [b] This band seems to contain two ionizations.

tion is expected to serve as an aid in studying neighboring group participations of π electrons associated with carbon lone pair in carbanion, the significant reaction intermediate.

Experimental Section

Measurement of Ionization Potential. Helium 504 Å photoelectron spectra were obtained on a JASCO PE-1 photoelectron spectrometer. Calibration of the spectra as effected by using the $^2P_{3/2,1/2}$ doublet of xenon (12.12, 13.44 eV). The estimated uncertainty is about ±0.05 eV.

Materials. Cyclic and bicyclic amines examined in the present study are listed in Table I. 7-Azabenzonorbornene (**5**) and 7-azabenzonorbornadiene (**7**) were prepared following the method of Carpino et al.[13] 2-Azabicyclo[2.2.2]octane (**15**), *N*-methyl-2-azabicyclo[2.2.2]octane (**16**), 2-azabicyclo[2.2.2]oct-5-ene (**17**), and *N*-methyl-2-azabicyclo[2.2.2]oct-5-ene (**18**) were synthesized by referring to Cava et al.[14] *N*-Methylpyrrolidine (**2**), *N*-methylpyroline (**4**), *N*-methyl-7-azabenzonorbornene (**6**), *N*-methyl-7-azabenzonorbornadiene (**8**), *N*-methyl-1,2,3,6-tetrahydropyridine (**12**), and *N*-methyl-1,2,3,4-tetrahydroisoquinoline (**14**) were prepared by *N*-methylation[15] of the parent N-H derivatives. Benzonorbornene (**21**) and benzonorbornadiene (**22**) were the gift from Dr. H. Tanida of Shionogi Research Laboratory and were used to aid the PE spectral analysis of **5-8**. The other compounds (**1**, **3**, **9**, **10**, **11**, **13**) were commercially available. The purity of all the samples was checked under the ^1H NMR measurement using a Varian HR-220 NMR spectrometer.

Results and Discussion

The photoelectron spectra of pyrroline (**3**), 1,2,3,6-tetrahydropyridine (**11**), 7-azabenzonorbornene (**5**), and 7-azabenzonorbornadiene (**7**) are exemplified in Figures 1 and 2. Table I lists vertical ionization potentials (IP's) in eV unit for the cyclic and bicyclic amines studied here. Due to the rather large band width, the uncertainty of the IP values is estimated to be ca. ±0.05 eV. The first IP's (in Table I) can be readily assigned to the ionization from the nitrogen lone pair electrons and the second ones in unsaturated amines to the ionization from the π electrons. For comparison, the IP's of several five- and six-membered cyclic hydrocarbons are listed in Table II.

At first we will discuss IP's of five-membered cyclic and bicyclic amines in terms of the bishomoallyl type n,π interaction and then of six-membered cyclic and bicyclic compounds in terms of the homoallyl type interaction.

(A) Bishomoallyl Type n,π Interaction. In five-membered *N*-H and *N*-methyl cyclic amines, introduction of the double bond increases the first IP's by 0.1-0.2 eV (compare **3** to **1**, and **4** to **2**). The π IP of **3** or **4** is 0.5-0.6 eV larger than that of cyclopentene (9.18 eV).[16] The correlation between the n and π orbitals in pyrrolidine (**1**), pyrroline (**3**), and cyclopentene is schematically shown in Figure 3.

For the interaction between nitrogen lone pair and neighboring π electrons, the π and π* orbitals are considered to

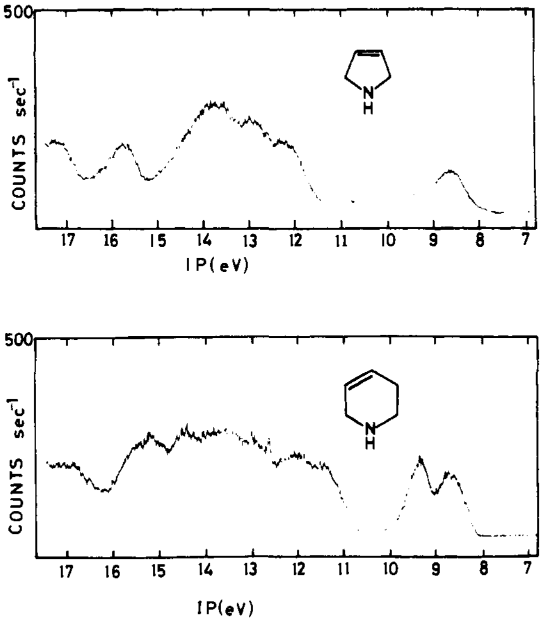
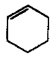
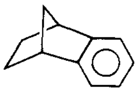
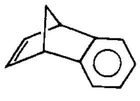
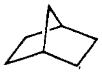
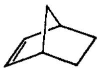
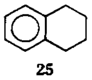
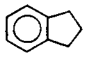


Figure 1. The photoelectron spectra of pyrroline and 1,2,3,6-tetrahydropyridine.

Table II. Ionization Potentials (eV) of Cyclic Hydrocarbons

Compd no.	Ionization potential	Ref
 19	9.1_8	16
 20	9.1_2	16
 21	8.4_2, 8.9_3, 10.1_5	This study[a]
 22	8.3_0, 8.9_1, 9.2_7, 10.8_8	This study[a]
 23	9.2_0	18
 24	8.9_5, 9.7_8	18
 25	8.4_4, 8.9_6	19
 26	8.4_6, 9.0_4	19

[a] Vertical ionization potentials (±0.05 eV).

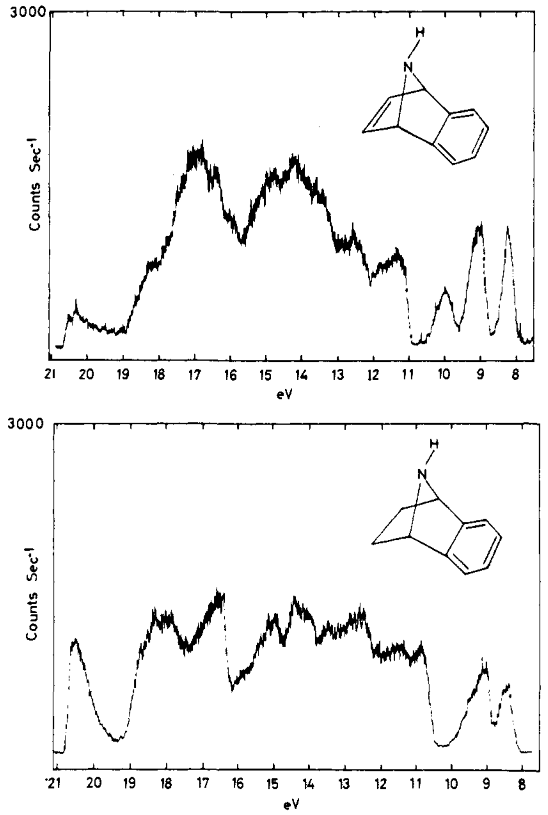


Figure 2. The photoelectron spectra of 7-azabenzonorbornene and 7-azabenzonorbornadiene.

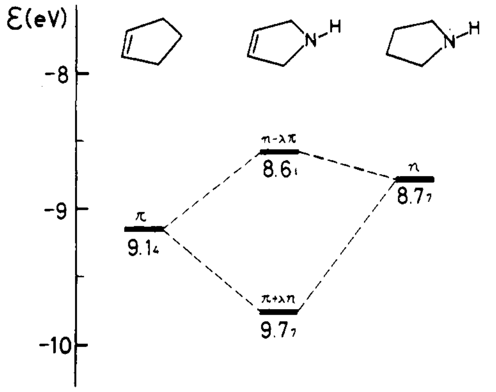


Figure 3. Orbital correlation diagram of the bishomoallyl interacting system.

play a significant role. The n,π and n,π* through-space interactions lead to destabilization and stabilization of the n level, respectively.[9] The stabilization of the n level in **3** and **4** indicates that the through-space interaction between n and π orbitals is significantly important. This is because the molecular symmetry forbids the n,π* interaction in the five-membered compounds. Besides this n,π through-space interaction, the "inductive effect" of the olefinic bond upon the n orbital or the "inductive effect" of the nitrogen atom on the π orbital should be taken into account, which causes the unsymmetrical n,π splitting. The midpoint (9.19 eV) of the n and π IP's for **3** is about 0.2 eV larger than that of the n IP for **1** and the π IP for **19**. However, the contribution of the inductive effect seems to be less important in this case, as the orbital correlation diagram in Figure 3 shows a typical feature of through-space interaction between n and π orbitals.[9] The similar n,π interaction is also encountered for 7-azabenzonorbornene (**5**) and 7-azabenzonorbornadiene (**7**).

In order to interpret the n,π interaction in these compounds, let us first take a look at the feature of the π,π interaction realized in the PES of benzonorbornene (**21**) and benzonorbornadiene (**22**), the related hydrocarbon homologues. The π orbital levels of benzene,[17] **21**, **22**, norbornene (**23**), and norbornadiene (**24**) are schematically shown in Figure 4. These levels may be correlated with each other in

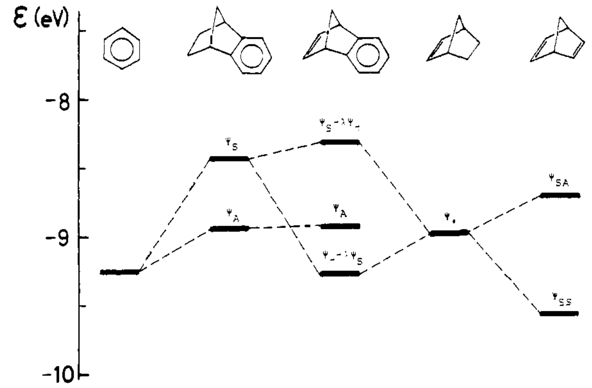


Figure 4. Orbital correlation diagram of benzene, benzonorbornene, benzonorbornadiene, norbornene, and norbornadiene.

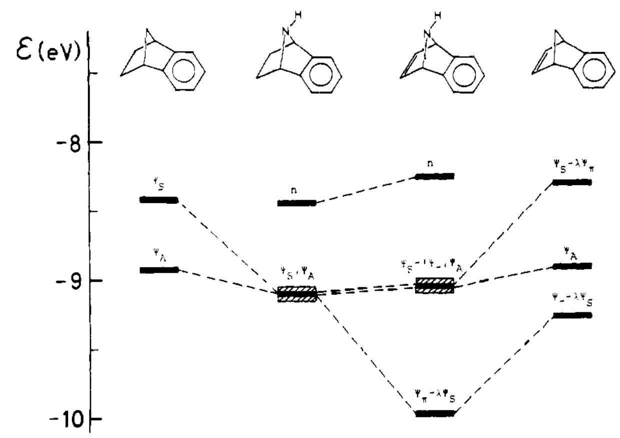
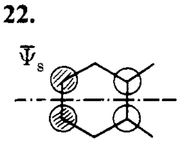
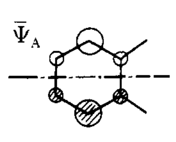


Figure 5. Orbital correlation diagram of 7-azabenzonorbornene and 7-azabenzonorbornadiene.

the manners that are depicted with the dotted lines in this figure. It has already been pointed out[17] that the degeneracy of the highest occupied orbitals ($^2e_{1g}$) in benzene is removed by the presence of two ortho disubstituents, and that the $\Psi_S(b_1)$ orbital lies above the $\Psi_A(a_2)$ orbital in benzocycloalkene derivatives. Further the combination of Ψ_S in the benzene ring of **21** and the π orbital (Ψ_π) in norbornene may produce the new levels in **22**, which appear to correspond to the first band ($\Psi_S - \lambda\Psi_\pi$, 8.30 eV) and to the third band ($\Psi_\pi + \lambda\Psi_S$, 9.27 eV). Contrary to this, Ψ_A in **21** remains essentially constant and corresponds to the second band in **22**.





Keeping the above discussions in mind, we then discuss the n,π interaction in **5**, **6**, **7**, and **8**. The first ionization of these compounds is assigned to the removal of an n electron. The n level in **7** and **8** is destabilized by 0.15-0.2 eV relative to that in **5** and **6**, respectively. This value appears to be comparable with that of pyrrolidine (**3** and **4**) and is attributed to the direct (or through space) n,π interaction. As to the π orbitals only the symmetrical orbitals may be stabilized by the interaction with the n orbital from the symmetry allowance. However, the antisymmetric π orbitals may remain constant. Accordingly, we can assign the observed spectra of **5** and **7** as shown in Figure 5 by referring to the energy diagram in Figure 4 and the above symmetry rule. In **5** the second band (9.10 eV) consists of Ψ_S and Ψ_A orbitals and in **7** the second band (9.05 eV) is attributed to $\Psi_S - \lambda\Psi_\pi$ and Ψ_A orbitals and the third band (9.97 eV) to $\Psi_\pi + \lambda\Psi_S$ orbital. In this energy diagram, the symmetrical orbitals (Ψ_S, $\Psi_S - \lambda\Psi_\pi$, $\Psi_\pi + \lambda\Psi_S$) are stabilized by about 0.7 eV when the bridging carbon is replaced by the nitrogen atom in Figure 6. All the n and π orbitals can be assigned similarly to the case of *N*-H derivatives (**5** and **7**). There is no apparent difference in the lone pair destabilization energy produced by n,π interaction between *N*-H and *N*-methyl derivatives of pyrroline and 7-azabenzonorbornene derivatives. This is in contrast with the case of six-membered cyclic amines which follows.

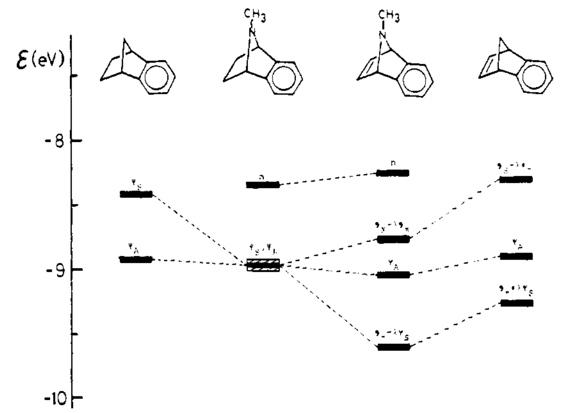


Figure 6. Orbital correlation diagram of *N*-methyl-7-azabenzonorbornene and *N*-methyl-7-azabenzonorbornadiene.

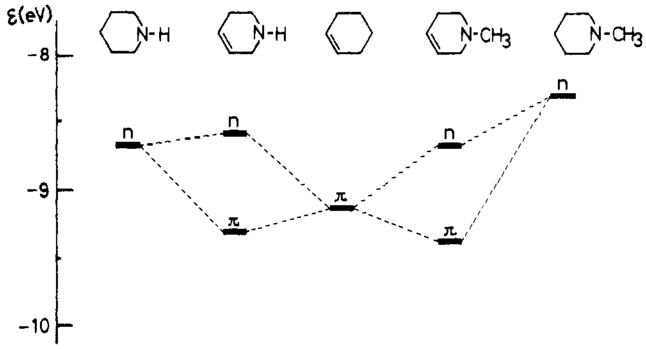


Figure 7. Orbital correlation diagram of the homoallyl interacting system.

(B) Homoallyl Type n,π Interaction. Inspection of Table I shows that in the six-membered cyclic amines the lone pair IP's (the first IP's) are affected in a different manner by the interaction with the double bond compared to the case of the five-membered amines already discussed above. For the five-membered *N*-H and *N*-methyl cyclic amines, introduction of a double bond makes the first IP's decrease. In the six-membered ring compounds, on the other hand, the n level remains essentially constant or is rather a little destabilized for the *N*-H derivatives (compare **11** and **13** to **9**), while for the *N*-methyl derivatives the lone pair IP is increased by about 0.3-0.4 eV by introduction of the π bond (compare **12** and **14** to **10**). In the six-membered bicyclic molecules (**17** and **18**), nitrogen lone pair electrons gain stabilization for both *N*-H and *N*-methyl derivatives. The π levels in **11** and **12** are lowered by 0.2-0.25 eV compared with that in cyclohexene (9.12 eV).[16] Those in **13** and **14** are also stabilized by 0.1-0.4 eV compared to those in benzocyclohexene (8.44 (b_1) and 8.96 (a_2) eV).[19] Similar observations were also encountered for bicyclic amines (**17**, **18**).[20] These features of the perturbation of the lone pair and the π levels are schematically exemplified for *N*-H and *N*-methyl derivatives of 1,2,3,6-tetrahydropyridine in Fig-

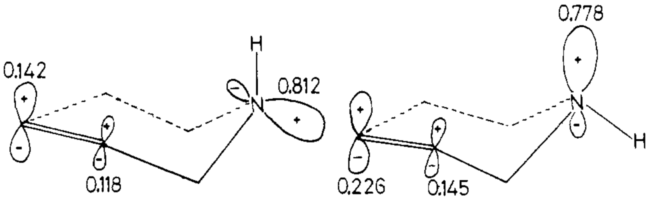
Table III. Calculated Total Energies and Orbital Energies for the Two Conformers of 3-Propenylamine[a] (INDO–MO)

Lone pair →		Conformer[a] I equatorial	Conformer[a] II axial
Total energy, eV		−1004.97	−1005.11
	LU (π^*)	5.50	5.47
Orbital energy, eV	HO (n)	−12.26	−12.54
	NHO (π)	−13.98	−14.25

[a] These geometries (I and II) are taken as the simplified models (half-chair conformation) of 1,2,3,6-tetrahydropyridine with the equatorial and axial lone pair electrons, respectively (see Figure 8). The dihedral angle between the lone pair lobe and the C_2–C_3 bond is 180° for conformer I and 60° for II. The dihedral angle between the N_1–C_2 and C_3=C_4 bonds is taken as 120° and tetrahedral bond angles were employed at unsaturated and saturated carbons. Bond lengths are taken as follows: N_1–C_2, 1.47; C_2–C_3, 1.53; C_3=C_4, 1.33; N_1–H, 1.01; C_2–H, 1.09; C_3–H and C_4–H, 1.07 Å.

ure 7. The destabilization energy of lone pair for the six-membered amines is much less than the corresponding value for the five-membered ones. For the six-membered molecules, both the n,π and n,π^* interactions are allowed by symmetry. This may be responsible for the different manner of perturbation of the n and π levels in the homallyl system associated with six-membered amines and in the bishomoallyl system with five-membered amines. It is also worth noting that in the six-membered amines the manner of the perturbation of the n level is different between *N*-H and *N*-methyl derivatives. In addition to the "through-space" n,π interaction, we should also take into account the "inductive effect" which enhances[11] the IP's of both the n and π levels in going from the separated system (saturated cyclic amine + cycloalkene) to the combined one (β,γ-unsaturated cyclic amines). In the six-membered ring compounds, "through-space" n,π interaction may be diminished due to the molecular nonsymmetry compared with five-membered ring compounds. Hence, the n,π^* interaction and the "inductive effect" may become relatively important, resulting in a small stabilization or no apparent variation of the n level. However, the inductive effect on the n IP induced by replacing the two sp^3 hybridized carbons by the sp^2 ones in *N*-H derivatives of the six-membered cyclic amines is considered to be not so different from that of the *N*-methyl homologues. Accordingly, the different features of the perturbation of the lone pair ionization potential between the *N*-H (**11**, **13**) and *N*-methyl derivatives (**12, 14**) of six-membered compounds could be attributable to some other contributions.[22]

It is tempting to suggest that the different features of the lone pair orientation are also responsible for the different manner of n,π interaction between *N*-H and *N*-methyl derivatives in the six-membered ring system. It has been well documented[23] that the nitrogen lone pair electrons have a greater preference for the equatorial position in *N*-H piperidines[24] while those in *N*-methylpiperidines preferentially occupy an axial position. In order to gain further insight into the effect of the lone pair orientation, we have carried out here INDO[28] MO calculations of 3-propenylamine, a simple model of the homoallyl n,π interacting system. The calculated results are presented in Table III. This table indicates that the conformer II with axial lone pair is more stable than I with equatorial lone pair by ca. 0.14 eV and that both the highest and the next highest occupied orbitals (HOMO, NHOMO) in II are more stable than those in I. The greater IP of lone pair resides preferentially at an axial position and appears to correspond to the lower HOMO energy level for II. This implies that the difference in the lone pair orientation seems to be responsible for different features of the n,π interactions.[29]



I

II

Figure 8. The diagram of the highest occupied molecular orbital (HOMO). (The geometries are the same as is shown in Table III. The atomic orbital coefficients of π and n orbitals are also shown.)

In order to delineate further these different behaviors of the n,π interaction due to the different lone pair orientation, the orbital scheme and the atomic orbital coefficients of the nitrogen lone pair sp^3 orbital and the π orbitals in the HOMO are given in Figure 8. This leads us to see that the π and π^* orbitals mix with the n orbital by the n,π interaction and the mode of this orbital mixing is apparently different between I and II. The atomic orbital coefficient of the nitrogen sp^3 orbital in II is smaller than that in I, which implies that the lone pair electrons in II are delocalized to a greater extent than in I. It is also to be noted that the difference between C_3 and C_4 π orbital coefficients for conformer II (0.081) is larger than that for I (0.024), suggesting that n,π^* interaction in II is greater than that in I. Since the n,π^* interaction stabilizes the n level, this greater contribution of the n,π^* interaction in II would result in the greater stability of the n level in II (Table III). It is conceivable from the above results and discussions that in the homoallyl interacting system the orientation of the lone pair electrons plays an important role in the n,π and n,π^* interactions which determine the stability of the n,π interacting system.[31]

It is also to be noted that the homoallyl system is rather stabilized by the interaction between n and π electrons, which is quite different from the bishomoallyl system. In other words, in the bishomoallyl interacting system n and π electrons are "repulsive". On the contrary, n and π electrons are rather "attractive" in the homoallyl interacting system.

It seems, therefore, reasonable to conclude that PES is very useful for the study of homoconjugative interaction between the nitrogen lone pair and the π bond, and that an intrinsic nature of homoallyl and bishomoallyl n,π interactions in cyclic and bicyclic amines is quite sensitive to the molecular symmetry, the orbital level, and the orientation of the lone pair electrons.

Acknowledgment. The authors are grateful to Dr. T. Kobayashi and Professor S. Nagakura of the University of Tokyo for making their PE-1 PE spectrometer available to us. They also wish to thank Professor T. Yonezawa for support and encouragement of this work. This work is also partially supported by a research grant donated to I.M. from Kawakami Memorial Foundation.

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Metal Assisted Ring Expansions. The Stereospecific Expansion of Pinene Induced by $Fe(CO)_5$

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Abstract: Iron pentacarbonyl induced carbonyl insertions into the cyclobutane rings of α- and β-pinene are described and are the first metal induced ring expansions of monovinylcyclobutane derivatives. Under experimental conditions employed, the location of cyclobutane ring opening is governed by the entering iron species and not by the simple thermally controlled ring opening process generally observed. Expansion is thought to proceed via σ–π-allyl metal and acyl–π-allyl intermediates. The two ketonic products formed in synthetically useful quantities are skeletally enantiomeric and are formed stereospecifically.

Since the observation that metals frequently induce formal symmetry-forbidden molecular rearrangements,[2] the interest in the versatility and pathways available to such systems has blossomed. Much elegant work has been described of the opening of cyclopropyl rings as in bicyclo[1.1.0]butanes,[3] quadricyclene,[4] unsaturated bicyclic systems such as hexamethyl(Dewar benzene),[5] and four-membered rings as in cubane.[6] Both stoichiometric and catalytic reactions have been considered, and product sensitivity to the electronic properties of the metal has been noted.[6,7] Controversy still rages[8] as to whether these systems are best described as concerted, symmetry-allowed processes taking advantage of the metal orbital structure to become allowed, or as sequential processes which take advantage of formal radical or ionic pathways made low in energy by the metal system.

Metal induced ring opening with metal retention has been demonstrated for numerous polycyclic three-membered rings,[2] the four-membered ring system of cubane,[6a] and a divinylcyclobutane system[6b] reported by Cotton. Reports have appeared describing ring opening of vinylcyclopropyl systems which retain the metal simultaneously bound to the resultant π-allyl function and the linkage deficient carbon. Semibullvalene,[9a] bullvalene,[9b] and bicyclo[3.1.0]hexene[10] undergo such reactions with $Fe_2(CO)_9$ forming the chelated $Fe(CO)_3$ product. Related ring openings of polycyclic ketones containing three-membered rings have also been reported; barbaralone[11] may be opened with $Fe_2(CO)_9$.

Expansion of carbon skeletons via introduction of the highly versatile carbonyl function is frequently difficult but is of major synthetic importance. Metal catalyzed or as-