Homoallylic Interaction between a Nitrogen Lone Pair and a Non-adjacent π-Bond. Part 6.[1] Nature of the Lone-pair Electrons in *n*,π-Homoconjugated Aliphatic Amines

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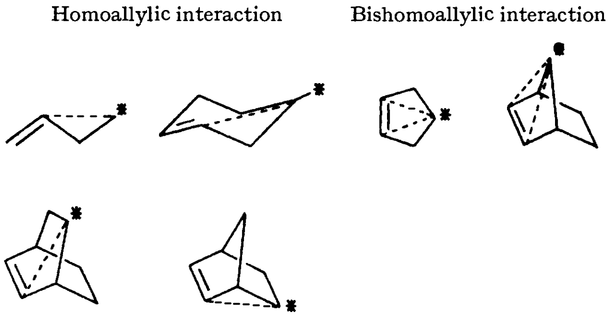
In order to elucidate the nature of the lone-pair electrons involved in the *n*,π-homoconjugative system, u.v. absorption spectra have been obtained for several cyclic and bicyclic amines containing a non-adjacent benzene ring. The spectra of bishomobenzylic *n*,π-interacting systems (1,2,3,4-tetrahydro-1,4-iminonaphthalene derivatives) are different from those of homobenzylic systems (1,2,3,4-tetrahydroisoquinoline derivatives). We have also studied the charge-transfer complexes of iodine with various cyclic and bicyclic amines containing non-adjacent π-groups and shown that iodine–amine charge-transfer absorption is a useful means of assigning the *n*-orbital ionizations in the photoelectron spectra of amines. Differences in the nature of the lone-pair electrons between bishomoallylic and homoallylic *n*,π-interacting systems and between bishomobenzylic and homobenzylic *n*,π-interacting systems are discussed in relation to homoconjugation.

THE consequence of homoconjugation between π-electrons and a non-adjacent cationic, radical, or anionic centre has been a subject of continuing controversy. Such interactions also have a bearing on the nature of aromaticity and antiaromaticity.[2] In particular, the interaction between a cationic centre and a non-adjacent π-bond has been studied extensively.[3] π-Electron participation resulting in a greatly increased rate of solvolysis in homoconjugated and bishomoconjugated systems is well established.[3] However, studies on the non-bonded interaction between doubly occupied *n* orbitals and non-adjacent π-groups are few.[4,5]



*Active centre (cation, radical, or anion).

We are currently interested in the orientation of nitrogen lone-pair electrons in cyclic and bicyclic amines.[1,6-8] We have reported structural effects on homoconjugative [7,8] and bishomoconjugative [1] interactions between a nitrogen lone pair and π-electrons with the aid of ^{1}H and ^{13}C n.m.r. measurements. These studies revealed that *n*- and π-electrons are 'repulsive' in 7-azanorbornene derivatives, which constitute a bishomoallylic or bishomobenzylic interacting system, whereas these electrons are rather 'attractive' in a homoallylic or homobenzylic interacting system.[7,8]

Recently we have also carried out a photoelectron spectroscopic study [9] of non-bonded *n*,π-interactions in several cyclic and bicyclic amines containing non-adjacent π-bonds. The results showed that the non-adjacent *n*,π-interaction in a homoallylic system is of a different type from that in a bishomoallylic system. In the latter case, direct interaction between *n* and π*

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[1] Part 5, K. Yoshikawa, K. Bekki, M. Karatsu, K. Toyoda, T. Kamio, and I. Morishima, *J. Amer. Chem. Soc.*, 1976, **28**, 3272,

[2] See *e.g.* M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, 1971, **93**, 6193.

[3] See *e.g.* S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, 1960, **82**, 2085; S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 1955, **77**, 4183.

[4] J. K. Stille and K. N. Sannes, *J. Amer. Chem. Soc.*, 1972, **94**, 7489.

[5] C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J.C.S. Perkin II*, 1973, 210.

[6] T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, 1970, **92**, 1267; I. Morishima, K. Okada, and T. Yonezawa, *Chem. Comm.*, 1971, 33; I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 1971, **93**, 3922; K. Yoshikawa, M. Hashimoto, H. Masuda, and I. Morishima, *J.C.S. Perkin II*, in the press.

[7] I. Morishima and K. Yoshikawa, *J. Amer. Chem. Soc.*, 1975, **97**, 2950; I. Morishima, K. Yoshikawa, and K. Okada, *ibid.*, 1976, **98**, 3787.

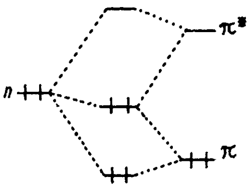
[8] I. Morishima, K. Yoshikawa, K. Toyoda, M. Karatsu, T. Yonezawa, S. Sakata, and S. Igegami, submitted for publication.

[9] I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, *J. Amer. Chem. Soc.*, 1975, **97**, 4283.

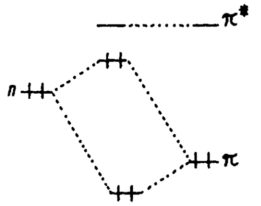
orbitals is forbidden on the basis of the molecular symmetry; therefore only direct n,π-interaction is significant. Such bishomoallylic n,π-interaction between the doubly occupied orbitals destabilizes the system. In the case of homoallylic interaction, however, the n orbital is allowed to interact with both π and π^* orbitals because of the molecular dissymmetry. As a result, this interacting system is electronically stabilized. The results from the photoelectron spectroscopic study were also discussed in relation to lone-pair orientation in bicyclic and cyclic amines.[1,7,8]

In order to gain further insight into the nature of homoconjugation between lone-pair and π-electrons, we have performed a u.v. absorption spectroscopic study of non-adjacent n,π-interactions in various cyclic and bicyclic amines. We have also observed the charge-transfer absorption bands of iodine–amine complexes. These results are discussed in relation to lone-pair ionization potentials obtained from the photoelectron spectroscopic study[9] and to the amine basicities. Marked differences in the nature of the lone pair electrons between bishomoallylic (or bishomobenzylic) and homoallylic (or homobenzylic) interacting systems were found. Together with our previous results[1,7-9] these experimental trends are discussed in relation to homoconjugation and homoaromaticity.

Homoallylic interaction



Bishomoallylic interaction



EXPERIMENTAL

Cyclic and bicyclic amines and the related carbocyclic compounds examined are listed in Tables 1 and 2. 1,2,3,4-Tetrahydro-1,4-iminonaphthalene (14) and 1,4-dihydro-1,4-iminonaphthalene (15) were prepared by the method of Carpino *et al.*[10] The synthesis of 2,3-*exo*-dimethyl-2-azanorbornane (12) and 2,3-*exo*-dimethyl-2-azanorborn-5-ene (13) is reported elsewhere.[8] 1,2,3,6-Tetrahydro-*N*-methylpyridine (11) and 1,2,3,4-tetrahydro-*N*-methylisoquinoline (17) were synthesized by *N*-methylation of the parent amines.[11] All samples were purified by distillation or sublimation. Commercial iodine was sublimed and kept in a desiccator. In the measurement of charge-transfer absorption of iodine–amine complexes, concentrations were *ca.* 10^{-5} and 10^{-3}—10^{-4} mol l^{-1} for iodine and amine, respectively. U.v. spectra were recorded with a Hitachi ERS-3T spectrometer at ambient temperature.

RESULTS AND DISCUSSION

U.v. Spectra.—We obtained the u.v. spectra of cyclic and bicyclic amines containing a benzene ring non-adjacent to the nitrogen atom. The spectra of 1,2,3,4-tetrahydro-1,4-iminonaphthalene (14), 1,4-dihydro-1,4-iminonaphthalene (15), 1,2,3,4-tetrahydro-1,4-methanonaphthalene, and 1,4-dihydro-1,4-methanonaphthalene are shown as examples in Figure 1. Table 1 summarizes the results. The compounds studied (Table 1) exhibit a $\pi^*\leftarrow\pi$ absorption band with the vibrational fine structure of the benzene ring with maxima in the region 270—280 nm. It is noteworthy that the $\pi^*\leftarrow\pi$ band in the spectra of (14) and (15) is at longer wavelength than in the hydrocarbon analogues [$\Delta\lambda$ 4—5.5 nm for (14) and 7.5 nm for (15)] and that $\varepsilon_{max.}$ are increased. In contrast, in the spectra of 1,2,3,4-tetrahydroisoquinoline (16) and its *N*-methyl derivative (17) the $\pi^*\leftarrow\pi$ absorption is at slightly shorter wavelength than in the spectra of tetralin (Table 1). These differences may be attributed to differences in effect of the non-adjacent nitrogen atom on the π-electrons in the bishomobenzylic and homobenzylic n,π-interacting systems. It is also to be noted that the $\pi^*\leftarrow\pi$ band is shifted to shorter wavelength in protic solvents (methanol and water), and that these solvent-induced shifts in the bishomobenzylic n,π-interacting systems [(14) and (15)] are greater than those in the homobenzylic system [(16) and (17)]. This is attributable to differences in the nature of n and π or π^* orbital interactions in the two systems.

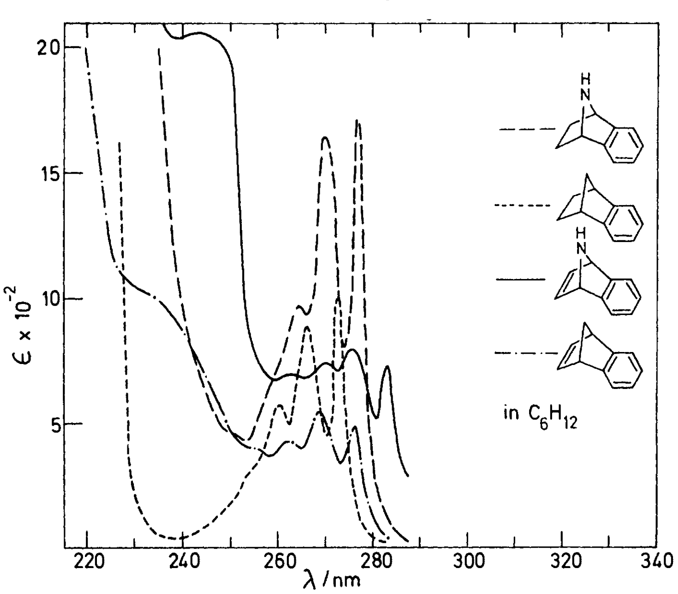
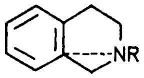
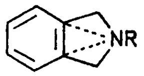


FIGURE 1 U.v. spectra (solvent cyclohexane)

Homobenzylic interaction



Bishomobenzylic interaction



Iodine–Amine Charge-transfer Absorptions.—We have performed a study of the u.v. charge-transfer (CT) transitions of various iodine–amine complexes. An example of the absorption spectra is given in Figure 2.

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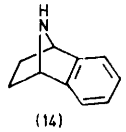
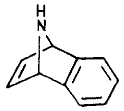
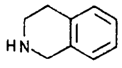
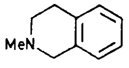
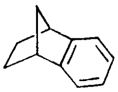
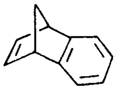
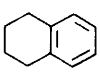
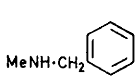
[10] L. A. Carpino and D. E. Barr, *J. Org. Chem.*, 1966, **31**, 764.

[11] H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Amer. Chem. Soc.*, 1933, **55**, 4571.

The wavelengths (λ_{CT}) of the CT absorption maxima are given in Table 2 together with the vertical ionization potentials (IP) of the *n* and π electrons in various cyclic and bicyclic amines. Comparison with some other iodine–amine complexes [12] suggests that the absorption in the 230—290 nm region is due to the CT band. We obtained the equilibrium constant for formation of the iodine–tetrahydroiminonaphthalene (14) complex from measurements of the absorbance variation with concentration of the amine (14), by the method of Benesi and Hildebrand.[13,14] The value obtained ($K = 2\,200$ at 60 °C) appears to be in the usual range for iodine–amine complexes.[12] This implies that the amines examined in this study form σ-type complexes with iodine. In Figure 3, the transition energies ($h\nu_{CT}$) of the CT bands are plotted against the IPs of *n*-electrons in the donor amines. This Figure and Table 2 show that the lower the ionization potential of the electron donor, the smaller is the transition energy of the CT band, as expected from Mulliken's theory.[14] The relation in Figure 3 appears to confirm the assignments of the *n* orbital IPs in the amines (1)—(23). In our previous photoelectron spectroscopic studies the first IPs (8.44 and 8.25 eV) of compounds (14) and (15) were attributed to ionization from the *n* orbital and the second IPs (9.10 and 9.05 eV) to ionization from the π orbital, on the basis of orbital correlation with related compounds. If this is not true, the points for (14) and (15) should deviate from the linear relation. For compounds (22) and (23), the photoelectron spectral assignments of the *n* orbital IPs were difficult, owing to overlap of the bands. Heilbronner *et al.* estimated the *n* electron IP of quinoline (22) to be 9.2—9.3 eV and that of isoquinoline (23) to be 9.3 eV, on the basis of an orbital correlation diagram.[15] These *n* electron bands are small, and appear merely as shoulders on the π bands. Figure 3 also confirms these assignments. The above results and discussion show that the measurement of iodine–amine CT absorption is a useful tool for assignment of the *n* orbital ionization in photoelectron spectra of amines.

TABLE 1

U.v. absorption data

		$\lambda_{max.}$/nm(ε)	
Solvent:	Cyclohexane	Methanol	Water
 (14)	264.5 (970) 270 (1 650) 277 (1 720)	262.5 (620) 267 (770) 274 (730)	261.5 (600) 266.5 (730) 273 (640)
 (15)	244 (2 100) 272.5 (740) 275.5 (800) 283 (730)	243 (2 330) 265 (690) 272.5 (720) 280 (630)	265 (600) 271.5 (620) 279.5 (530)
 (16)	259 (580) 266 (620) 273.5 (600)	257.5 (630) 265 (660) 272.5 (580)	257 (660) 263.5 (680) 271.5 (540)
 (17)	260 (330) 267 (430) 274 (460)	259 (380) 266 (460) 273 (490)	257 (320) 265 (430) 272.5 (400)
	260 (570) 266 (880) 272.5 (1 000)		
	261.5 (430) 268 (550) 275.5 (490)		
	261 (390) 267.5 (550) 274.5 (640) 288 (16)		
 (18)	248.5 (450) 253.5 (430) 259.5 (440) 265.5 (320) 269.5 (160)	248.5 (200) 253.5 (230) 259 (250) 264.5 (200) 268.5 (150)	248 (210) 252.5 (240) 258 (270) 263 (230) 267.5 (170)

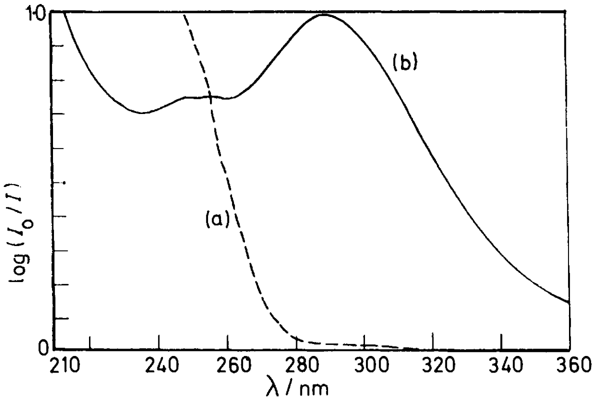


FIGURE 2 Charge-transfer absorption spectrum of the iodine–2,3-*exo*-dimethyl-2-azanorborn-5-ene (13) complex at room temperature in cyclohexane: (a) spectrum in the absence of iodine (7.76×10^{-4} mol l^{-1}); (b) in the presence of iodine (3.88×10^{-4} mol l^{-1})

Nagakura *et al.* derived a general equation (i) to reproduce observed transition energies of CT absorptions, and fitted separate curves to the data for primary, secondary, and tertiary amines.[12] They used different parameters [overlap integral (S), exchange integral (β), and effective electron density (A)] for the three kinds of

$$h\nu_{CT} = [(\mathrm{IP} - A)^2 - 4S\beta(\mathrm{IP} - A) + 4\beta^2]^{\frac{1}{2}}/(1 - S^2) \quad \text{(i)}$$

amines. The values of S, $|\beta|$, and A decrease in the order of primary > secondary > tertiary amine. This

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[12] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1660.

[13] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[14] R. S. Mulliken and W. B. Person, ' Molecular Complexes,' Wiley, New York, 1969.

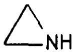
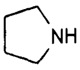
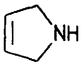
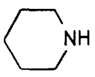
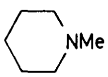
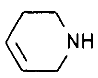
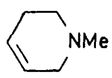
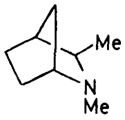
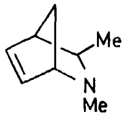
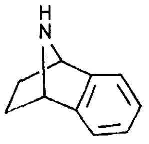
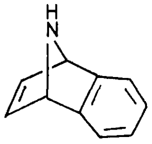
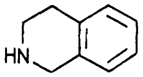
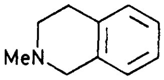
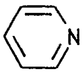
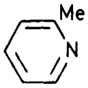
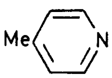
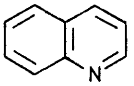
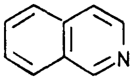
[15] F. Brogli, E. Heilbronner, and T. Kobayashi, *Helv. Chim. Acta*, 1972, **55**, 274.

may imply that other physical factors besides the IP values should be taken into account to interpret the nature of the lone-pair electrons. In other words, the ' size ' of the lone-pair electrons, or penetration of the *n* orbital into the π and σ orbitals, or some other steric effect might be important. These factors may influence the mode of CT interaction of iodine with primary, secondary, and tertiary amines. The deviation of the solid line in Figure 3 from linearity may be due to such effects.

It is also noteworthy in Figure 3 that the amines having homoallylic [(11) and (13)] or homobenzylic [(16)—(18)] *n*,π-interactions deviate negatively from the linear relation. In contrast, the bishomoallylic (7) and bishomobenzylic [(14) and (15)] *n*,π-interacting amines show no significant deviation from the solid line. It has been indicated that in homoallylic and homobenzylic interacting systems the *n* orbital can mix with π and π* orbitals, whereas in bishomoallylic and bishomobenzylic systems the *n* orbital interacts only with π orbitals.[1,7-9] This suggests that the *n* orbital contributes to the π and π* orbitals effectively in the former systems, which may result in a decrease in ' size ' of the front side of the lone-pair orbital. This may be responsible for the decrease in the overlap integral (*S*) and exchange integral (|β|) in the iodine-amine complexes, leading to a decrease in $h\nu_{CT}$. A similar trend is observed in the case of a ' conjugated ' lone pair. For

TABLE 2

Charge-transfer absorption maxima (λ_{CT}) and ionization potentials (IP) of amines

Compound		λ_{CT}/nm	IP/ev
NH_3	(1)	229 [a]	10.85 (*n*) [b]
$MeNH_2$	(2)	245 [a]	9.64 (*n*) [b]
$EtNH_2$	(3)	246 [a]	9.50 (*n*) [b]
Bu^nNH_2	(4)	247 [a]	9.40 (*n*) [b]
	(5)	240	9.85 (*n*) [c]
	(6)	258	8.77 (*n*) [c]
	(7)	261	8.61 (*n*) 9.77 (π) [c]
	(8)	261	8.64 (*n*)
	(9)	273	8.29 (*n*) [c]
	(10)	259	8.64 (*n*) 9.33 (π) [c]
	(11)	275	8.67 (*n*) 9.37 (π) [c]
	(12)	291	7.81 (*n*) [d]
	(13)	291	8.01 (*n*) 9.14 (π) [d]
	(14)	275—280	8.44 (*n*) 9.10 (π) [c]
	(15)	275—280	8.25 (*n*) 9.05 (π) 9.97 (π) [c]
	(16)	283	8.57 (*n*, π) 9.33 (π) [c]
	(17)	282	8.60 (*n*, π) 9.30 (π) [c]
$PhCH_2NHMe$	(18)	272	8.78 (*n*) 9.12 (π) [e]
	(19)	235	9.60 (π) 9.75 (*n*) [g]
	(20)	239 [j]	9.20 (π) 9.50 (*n*) [g]
	(21)	239	9.50 (*n*) 9.60 (π) [g]
	(22)	238 [h]	8.62 (π) 9.16 (π) 9.2—9.31 (*n*) [i]
	(23)	240.5 [h]	8.50 (π) 9.3 (*n*) 9.41 (π) [i]
PhNHMe	(24)	359 [j]	7.73 (π) 9.03 (π) 10.24 (*n*) [k]

[a] Ref. 13. [b] D. W. Turner, ' Molecular Photoelectron Spectroscopy,' Wiley, New York, 1970. [c] Ref. 9. [d] Ref. 8. [e] K. Yoshikawa and I. Morishima, unpublished result. [f] K. R. Bhaskar and S. Singh, *Spectrochim. Acta*, 1967, **23A**, 1155. [g] E. Heilbronner, V. Hornung, P. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, 1972, **55**, 289. [h] V. G. Krishna and B. B. Bhowmik, *J. Amer. Chem. Soc.*, 1968, **90**, 1700. [i] Ref. 14. [j] A. K. Chandra and D. C. Mukherjee, *Trans. Faraday Soc.*, 1964, **60**, 62. [k] A. D. Bekcer, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

example, *N*-methylaniline (24) [$h\nu_{CT}$ 3.45 eV; IP(n) 10.24 eV] deviates negatively from the linear relation. Though the magnitude of this deviation is different, this is the same direction of deviation as with the homoallylic and homobenzylic n,π-interacting systems. Such a trend indicates, therefore, the presence of homoconjugation in homoallylic and homobenzylic n,π-interacting systems.

On the Nature of the Nitrogen Lone-pair Electrons.—On the basis of the above results and discussion, we will discuss the nature of the nitrogen lone-pair electrons in relation to the structure of the amine. As a result of the recent development of ion cyclotron resonance spectroscopy, gas-phase basicities of alkylamines have been reported.[16,17] It has been established[16,17] that gas-phase basicities follow the order, NH_3 < primary < secondary < tertiary amine, which corresponds well to the decreasing order of IP values of the lone-pair electrons. This order of gas-phase basicities was attributed mainly to a polarization effect.*

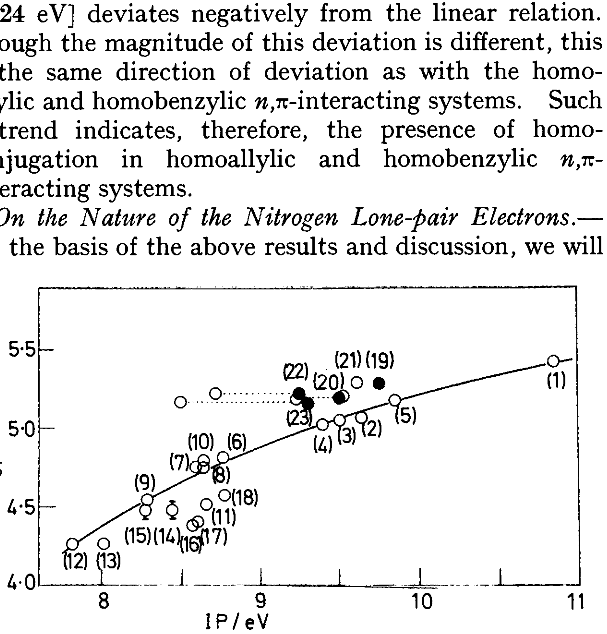
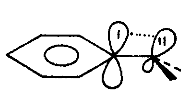
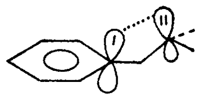


FIGURE 3 Dependence of the CT transition energy, $h\nu_{CT}$, of iodine complexes upon the ionization potential, IP, of the lone pair in the donor amines; values of IP and $h\nu_{CT}$ are given in Table 2; an open circle shows the first ionization potential; a filled circle shows the ionization potential of n electrons in amines where the first IP involves a π orbital

Benzylic interaction

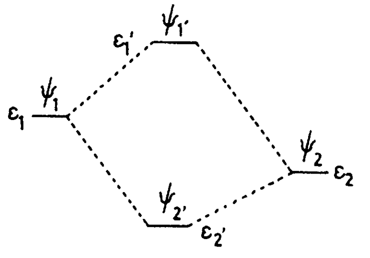


Homobenzylic interaction



Since the polarizability of a molecule or a bond is connected with both the energy and the coefficients of the molecular orbital, polarization effects are expected to be related to the extent of delocalization (or penetration) of the lone pair orbital into the skeleton. It is likely that the extent of the n orbital delocalization (or penetration) increases in the order primary < secondary < tertiary amine. The differences in $h\nu_{CT}$ for the iodine complexes of primary, secondary, and tertiary amines are probably attributable to these effects. The negative deviation in Figure 3 may also be due to such effects, *i.e.* the n orbital may mix substantially with the π and π^* orbitals in these dissymmetric systems.

Homoconjugation.—There has been much recent discussion over the concepts of homoconjugation and homoaromaticity.[19-21] Homoconjugation has been discussed in relation to molecular symmetry, topology, and numbers of π electrons [$4n$ or $4n + 2$]. However, reports on the nature of homoconjugation and homoaromaticity seem to be speculative as yet. In this section, we discuss homoconjugation in connection with our experimental results. In our recent papers on photoelectron and n.m.r. spectroscopic studies,[1,7-9] we reported that homoallylic systems tend to be stabilized by interaction between n- and π-electrons, whereas bishomoallylic systems are destabilized. Similarly it has been suggested that homobenzylic and bishomobenzylic interactions lead to stabilization and destabilization, respectively.[9]



Let us consider a simple interacting system, an orbital ψ_1 of energy ε_1 interacting with ψ_2, an orbital of lower energy ε_2.[22] When two levels are both doubly occupied, the energy change in the system after interaction is given by equation (ii), where ε_1' and ε_2' are the energies

$$\begin{aligned}\Delta E &= 2(\varepsilon_1' - \varepsilon_1) + 2(\varepsilon_2' - \varepsilon_2)\\ &= -4SH_{12}' + 2S^2(\varepsilon_1 + \varepsilon_2) > 0 \qquad \text{(ii)}\end{aligned}$$

after interaction, S is the overlap integral, and H_{12}' is the matrix element of the perturbation. Usually, H_{12}' has the opposite sign to S. As $|H_{12}'|$ is a little larger than $|S(\varepsilon_1 + \varepsilon_2)/2|$,[23,24] ΔE is positive and relatively small. This implies that the interaction between doubly occupied orbitals causes a small destabilization. On the other hand, when ψ_1 is unoccupied and ψ_2 is doubly occupied, the stabilization energy is given by

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* For strained cyclic amines, the importance of the effect of lone-pair hybridization on IP values and basicities has been indicated.[16,18]

[16] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 4314; D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, 1972, **94**, 2726; 1975, **97**, 4136; 1976, **98**, 311.

[17] E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4726; W. G. Henderson, M. Taggepera, D. Holtz, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *ibid.*, p. 4728; R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *ibid.*, 1973, **95**, 3811.

[18] K. Yoshikawa, M. Hashimoto, and I. Morishima, *J. Amer. Chem. Soc.*, 1974, **96**, 288.

[19] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1969, **52**, 1745.

[20] S. Winstein, *Quart. Rev.*, 1969, **23**, 141.

[21] M. Goldstein, *J. Amer. Chem. Soc.*, 1967, **89**, 6357.

[22] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543.

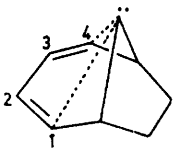
[23] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[24] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

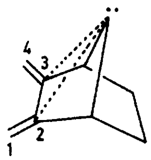
equation (iii), which implies that stabilization due to the interaction between doubly occupied and unoccupied orbitals is often much larger than destabilization due to the interaction between two doubly occupied orbitals.*

$$\Delta E = 2\Delta\varepsilon_2 = -2(H_{21}' - S\varepsilon_2)/(\varepsilon_1 - \varepsilon_2) < 0 \quad \text{(iii)}$$

Therefore, when an n orbital can interact with both π and π^* orbitals, the stabilization due to n–π^* orbital interaction is more important than the destabilization due to n–π interaction. From the above discussion, it is clear that n,π-homoconjugation is closely connected with the concept of how effectively π^* orbitals are involved in occupied orbitals, resulting in stabilization of the interacting systems. The ideas of bicycloaromaticity and bicycloantiaromaticity,[21] based on molecular symmetry, may also be associated with such stabilization and destabilization of π-electron systems. For example, let us consider the anionic n,π-interacting systems (I) and (II). Both include the π-conjugative system of buta-1,3-diene. In these systems, the nonbonded orbital interacts mainly with the lowest unoccupied orbital, because the interaction with the highest occupied orbital is symmetry-forbidden. However, the π atomic orbital coefficients of the 1- and 4-carbon atoms in the butadiene skeleton are smaller than those of the 2- and 3-carbon atoms. Consequently, we expect greater stabilization in (II) than in (I) due to n,π-'homoconjugation.' From the above discussion, we suggest that the concept of how effectively π^* orbitals are involved in occupied orbitals, is quite important, when we are dealing with the problems concerning homoconjugation or homoaromaticity. Such an idea may be related to n orbital delocalization (or penetration) into the skeleton, discussed in the previous section.



(I)



(II)

We thank Professor T. Yonezawa for encouragement, and Dr. S. Ikegami for a gift of compounds (12) and (13) and for suggestions.

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* In general, the n–π and n–π^* energy gaps which appear in the denominator of the ΔE equation cannot be ignored, and their relative sizes are also important.