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A QUANTITATIVE ANALYSIS OF THE THROUGH-SPACE AND THE THROUGH-BOND INTERACTIONS BETWEEN LONE-PAIRS IN AZINES: PYRIDAZINE, PYRIMIDINE AND PYRAZINE

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Abstract—The INDO calculations were performed on the three azines: pyridazine, pyrimidine, and pyrazine. The canonical molecular orbitals obtained by these calculations were then transformed into the localized molecular orbitals. With the use of the localized molecular orbitals, the variation in the lone-pair orbital energies of these molecules were pursued in the light of the through-space and/or the through-bond interactions between the specified localized molecular orbitals in a molecule selectively. The interactions were expressed by the summation of several terms: through-space, through-bond, through-virtuals and coupling terms.

The long-range interactions between remote orbitals have firstly been reported by Hoffmann *et al.* using the terminologies "through-space" and "through-bond" interactions.[1,2] In the preceding paper,[3] the procedure to estimate the effect of a particular through-bond or a through-space interaction between remote orbitals is proposed. In that paper, the through-bond or the through-space interactions have been treated in several cases in azines with the CNDO/2 method.[4] However, the role of interaction terms have not been estimated quantitatively.

In the present paper, developing the procedure described above, the interaction energy between two lone-pair orbitals (LPO) in azines is decomposed into the contributions of the through-space, the through-bond, the through-virtual, and their coupling terms. Accordingly, we can see the contributions of various types of the interactions to the separation in energy between the LPO, that is the S and A combinations which will be mentioned later. Moreover, in the present paper, the INDO method[5] was used instead of the CNDO/2 method since the interaction energy between the LPO in azines calculated by the INDO method is in excellent agreement with that by the *ab initio* method[6] as was shown in the previous work.[3]

In the molecules under study, there are two lone-pair orbitals as mentioned above. These two LPO can be classified into symmetric (S) or antisymmetric (A) combination. In connection with this, the order of the lone-pair orbital energies (LPOE) is different from molecule to molecule. In the present article, the through-bond interaction (or the through-space interaction) was attempted to evaluate quantitatively by using the localized molecular orbitals (LMO) transformed from the canonical molecular orbitals (CMO).

Method of calculations

Twelve occupied σ-orbitals obtained from the INDO calculation[5] were localized by the procedure of Edmiston and Ruedenberg.[7] The occupied π and all of the virtual orbitals were not transformed into the LMO. The geometries used for the azines in the present calculations were assumed identical with those summarized in the previous paper.[3]

The detailed analysis procedure used is described in the previous paper.[3] Now the essential features of the method are reviewed briefly as follows.

A core resonance integral, I^0_{rs}, between atomic orbitals, χ_r and χ_s, can be expressed by the summation of the core resonance integrals, I_{ij}, between the LMO, ϕ_i and ϕ_j,

$$I^0_{rs} = \sum_i \sum_j c_{ir} c_{js} I_{ij}. \qquad (1)$$

By modifying eqn (1), we can obtain the value of the core resonance integral, I_{rs}, between the atomic orbitals which gives zero for the core resonance integrals between the specified LMO, and gives the core resonance integrals between the other LMO correctly,

$$I_{rs} = I^0_{rs} - \sum_{(i_1-j_1)} (c_{i_1r}c_{j_1s} + c_{i_1s}c_{j_1r}) I_{i_1j_1} \qquad (2)$$

where the summation should cover only definite pairs of the specified LMO.

When the LMO, ϕ_i and ϕ_j, which specified the bonds i and j, were picked up in eqn (2), the core resonance integral between ϕ_i and ϕ_j should be cut off, that is the through-bond (or through-space) interaction between the bonds i and j can be considered to be cut off. Therefore the SCF calculations by using the core resonance integrals in eqn (2) gives us the energy without the appropriate through-bond or the through-space interaction.

RESULTS AND DISCUSSION

The calculated results are summarized in Figs. 1–3 and Tables 1–3.

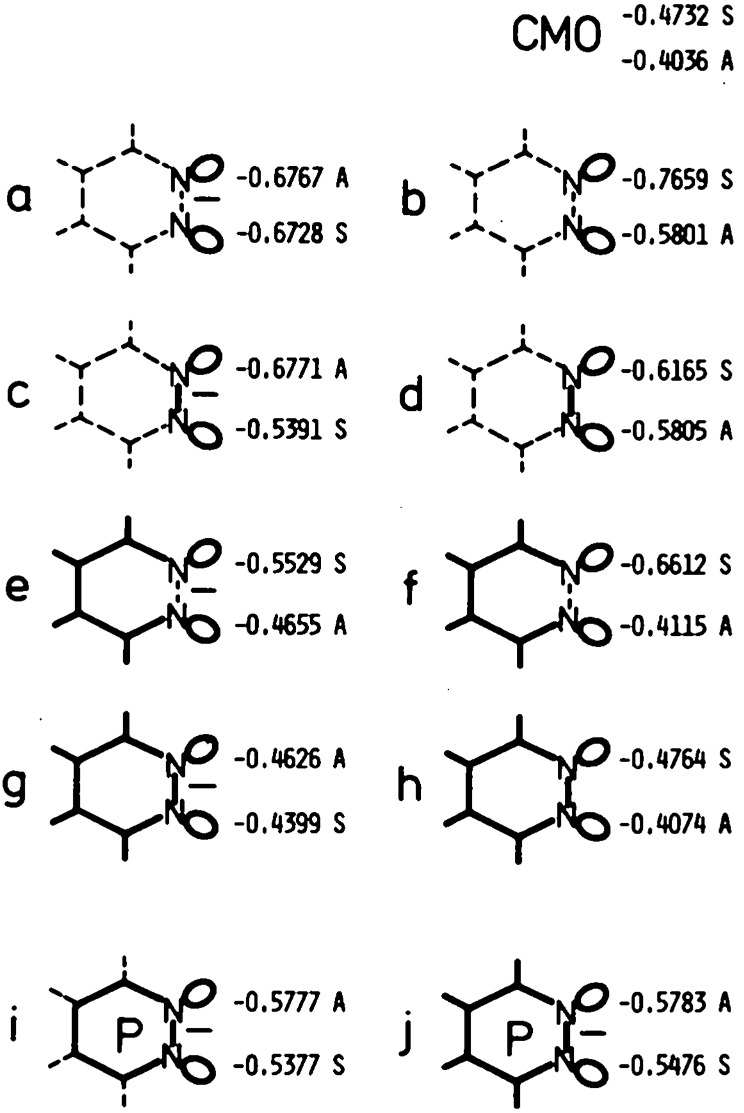

Fig. 1. LPO interaction diagram for pyridazine. Orbital energy: in au. CMO: full interaction case. Broad line part shows the interaction allowed part. In the case with — sign between the LPO, the direct through-space interaction between the LPO is forbidden, and in the case without the sign it is allowed. P (Pure through-bond interaction); only the through bond interaction between the neighbouring orbitals is allowed. In all cases except CMO, all of the occupied π and the virtual orbitals in relation to the interaction are cut off from the interactions.

The through-space interaction. It is well known that there is an intimate relation between the magnitude of the direct through-space interaction and the distance between the LPO.[1-3] The distance between N–N or N···N and the role of the direct through-space interaction in azines under study are shown below.

	Pyridazine	Pyrimidine	Pyrazine
Distance between N–N or N···N (Å)	1.33	2.37	2.81
Through-space (%) S	−46.6	−2.3	−0.7
A	35.4	1.9	1.4

The magnitude of the direct through-space interaction decreases from pyridazine to pyrimidine drastically, and a little from pyrimidine to pyrazine. Therefore we can easily recognize that in pyrimidine and pyrazine, the direct through-space interaction is not large enough to govern the interactions. This is already seen in the pre-

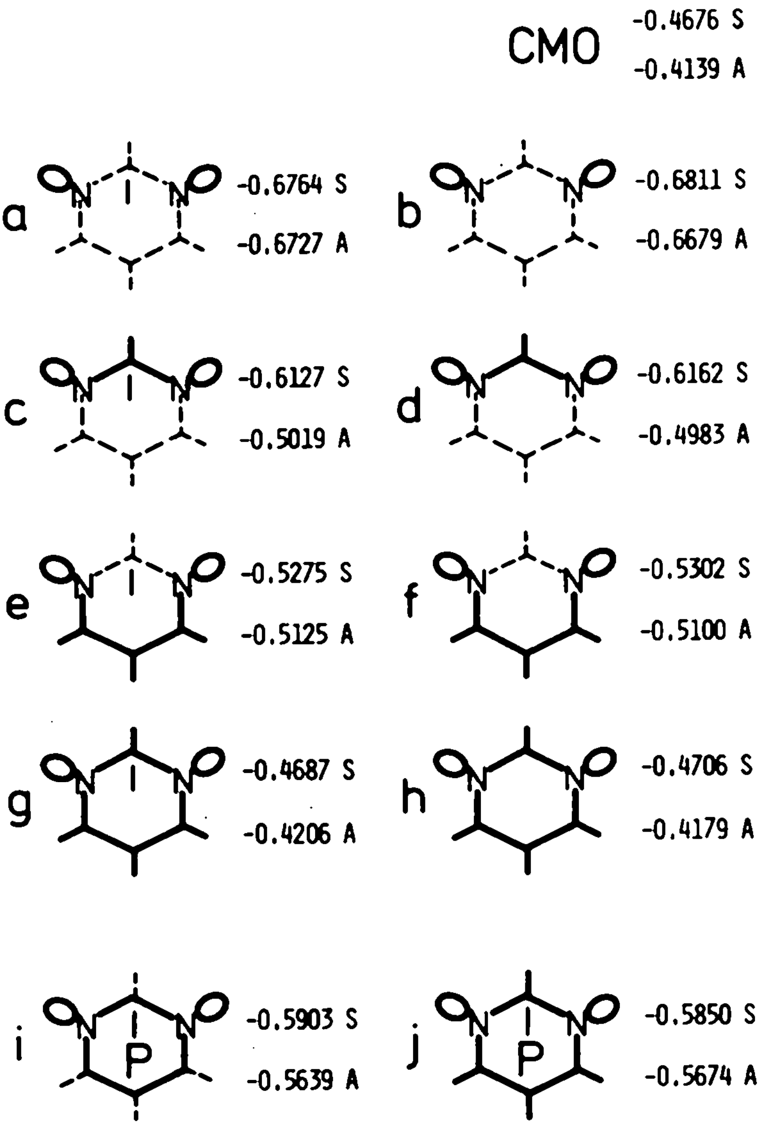

Fig. 2. LPO interaction diagram for pyrimidine. Notations: see Fig. 1.

vious papers.[1-3] In the cases of pyrimidine and pyrazine, a very small contribution is, however, seen in the present INDO calculation differ from the result of the CNDO/2 calculation.[3]

The through-bond interaction. With pyridazine, S is destabilized by the long path as well as the short path, and destabilization occurs with nearly the same percentage both by the long and the short paths, while A is destabilized almost only by the long path. With pyrimidine, S interacts via the long path rather than the short path. On the other hand A interacts through the short path as well as the long path with nearly equal quantity. As for pyrazine, both S and A interact with almost the same percentage through the path.

The pure through-bond interactions are shown in digrams i and j in Figs. 1 and 2, and g and h in Fig. 3, respectively. The LPOE with the pure through-bond interactions are fairly different from those of the states including indirect through-space interactions, e.g. between i and g, or between j and g of Fig. 1. From these it can be concluded that the through-bond interaction including indirect through-space—through-bond after through-space or through-space after through-bond—interaction is one of the important interaction courses between the LPO in these molecules.

The coupling terms. In the present article, we dealt with the coupling terms in two types: (i) "through-bond through-bond coupling" and (ii) "through-bond through-space coupling". Now we discuss at first from the through-bond through-bond coupling. With pyridazine, the coupling of S is fairly large, but A is very small. In the case of pyrimidine, the coupling term is large in A, but it is indeed very small in S. With pyrazine, the coupling term is large both in A and S. This type of coupling term in general plays an important role in the cases of pyrimidine and pyrazine in which the through-space interaction is negligibly small.

The coupling term between the through-bond and the through-space interactions is very small in pyrimidine and pyrazine. In these molecules the direct through-

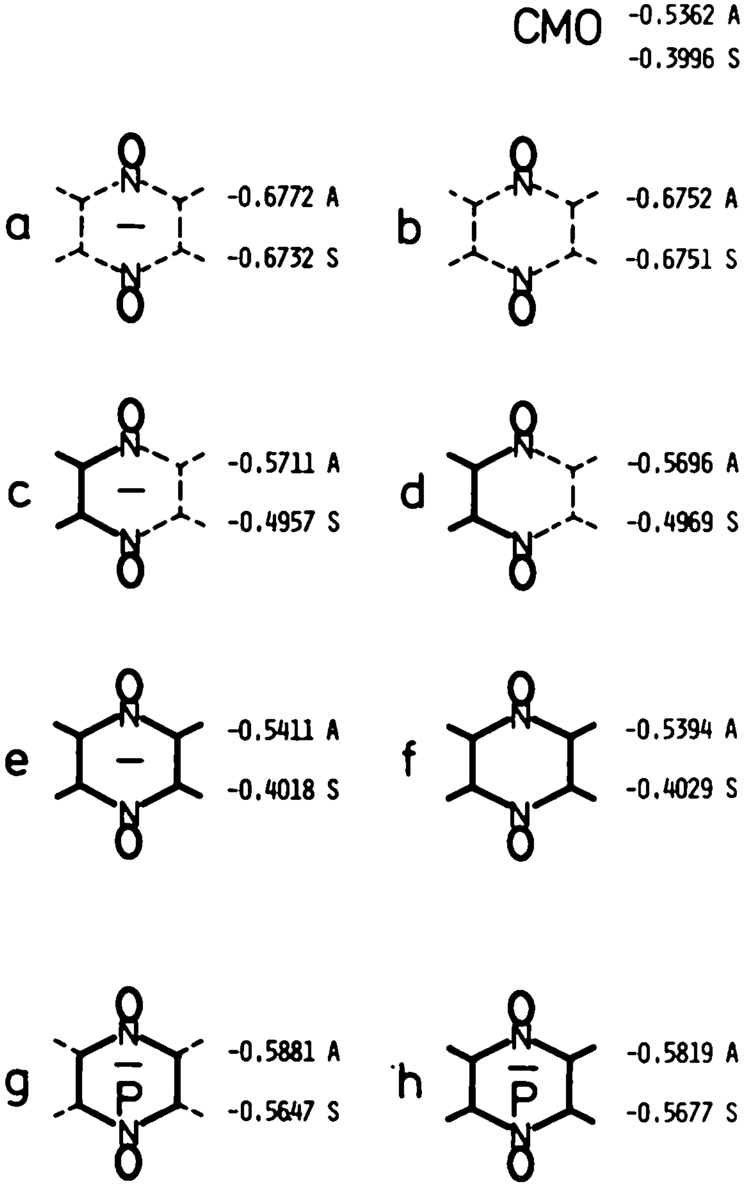

Fig. 3. LPO interaction diagram for pyrazine. Notations: see Fig. 1.

space interactions in origin are very small at all. With pyridazine, this type of the coupling term took a role to govern the interactions between the LPO, where S is the positive coupling and on the other hand A is negative.

The role of virtual orbitals. We have previously shown that in the bridgehead radicals the spin delocalization via the virtual orbitals plays an important role.[8] On the other hand in these azines now concerned, the interactions between the LPO via the virtual orbitals are very small. This should be due to the fact that the LPOE levels of these azines are located fairly far from the virtual orbital energy levels.

CONCLUSIONS

With the use of the localized molecular orbitals, the variation in the lone-pair orbital energies of three azines, pyridazine, pyrimidine, and pyrazine, were pursued in the light of the through-space and/or the through-bond interactions, and these interaction terms were estimated quantitatively. The method used in the present article is a newly developed one, and this analysis method will be very useful in the identification or assignment of ionization potentials and/or absorption spectra of the molecules.

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Table 1. Analysis of LPOE in pyridazine

		Δ[a]	%	Descriptions[b]
Through-space	S	-931	-46.6	b - a
	A	966	35.4	
Through-bond by a short path	S	1337	67.0	c - a
	A	-4	-0.1	
Through-bond by a long path	S	1199	60.1	e - a
	A	2112	77.3	
A short and a long paths coupling	S	-207	-10.4	(g - a) - [(c - a) + (e - a)]
	A	33	1.2	
Through-space and through-bond coupling	S	566	28.4	(h - a) - [(b - a) + (g - a)]
	A	-414	-15.2	
Through-virtuals	S	32	1.6	CMO - h
	A	38	1.4	
Total	S	1996	100.	CMO - a
	A	2731	100.	

[a] Δ: energy difference in × 10^{-4} au.

[b] See Fig. 1; CMO: full interaction case.

Table 2. Analysis of LPOE in pyrimidine

		Δ[a]	%	Descriptions[b]
Through-space	S	-47	-2.3	b - a
	A	48	1.9	
Through-bond by a short path	S	637	30.5	c - a
	A	1708	66.0	
Through-bond by a long path	S	1489	71.3	e - a
	A	1602	61.9	
A short and a long paths coupling	S	-49	-2.3	(g - a) - [(c - a) + (e - a)]
	A	-789	-30.5	
Through-space and through-bond coupling	S	28	1.3	(h - a) - [(b - a) + (g - a)]
	A	-21	-0.8	
Through-virtuals	S	30	1.4	CMO - h
	A	40	1.5	
Total	S	2088	100.	CMO - a
	A	2588	100.	

[a] Δ: energy difference in × 10^{-4} au.

[b] See Fig. 2; CMO: full interaction case.

Table 3. Analysis of LPOE in pyrazine

		Δ[a]	%	Descriptions[b]
Through-space	A	20	1.4	b - a
	S	-19	-0.7	
Through-bond by single path	A	1061	75.2	c - a
	S	1775	64.9	
Two paths coupling	A	-761	-54.0	(e - a) - 2(c - a)
	S	-836	-30.6	
Through-space and through-bond coupling	A	-3	-0.2	(f - a) - [(b - a) + (e - a)]
	S	8	0.3	
Through-virtuals	A	32	2.3	CMO - f
	S	33	1.2	
Total	A	1410	100.	CMO - a
	S	2736	100.	

[a] Δ: energy difference in × 10^{-4} au.

[b] See Fig. 3; CMO: full interaction case.

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