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A QUANTITATIVE ANALYSIS OF THE THROUGH-SPACE AND THE THROUGH-BOND INTERACTIONS BETWEEN LONE-PAIRS AND σ-FRAMES: S-TRIAZINE AND S-TETRAZINE

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Abstract—The CNDO/2 and INDO calculations were performed on s-triazine and s-tetrazine. The s-triazine has three lone-pairs in a molecule, and these can be combined into three combinations, A, n_S and n_A. Among the three, n_S and n_A are degenerated when the whole interaction conserves its molecular point symmetry, D_{3h}. The s-tetrazine has four lone-pairs, which can be transformed into four combinations, SS, SA, AS and AA. The energies of these orbitals show interesting behavior. The results were subjected to an analysis from the standpoint of the through-space and through-bond interactions using the localized molecular orbitals. As a result of these analyses, the interactions were expressed by several interaction terms.

The absorption and photoelectron spectra of s-triazine and s-tetrazine have been studied extensively from experimental theoretical standpoints.[1-4] While the assignments of the spectra, are not always coincident with each other, they and the orbital interactions are closely related.

The long-range interactions between remote orbitals have been reported by Hoffmann *et al.* using the terminologies "through-space" and "through-bond" interactions.[5,6] Previously, the procedure to estimate the effect of a particular through-bond/through-space interaction between remote orbitals was proposed[7,8] and successfully applied to explain the long-range hyperfine spin coupling constants in alkyl radicals,[9,10] to explain lone-pair orbital (LPO) interaction in azines,[8,11] and to explain the long-range effect of the LPO to optical rotatory strength.[12] In the present paper, the method is applied to s-triazine and s-tetrazine to analyse the orbital interactions between LPOs, and between LPOs and σ-frames.

The s-triazine has three lone-pairs in a molecule as shown in Fig. 1. The symmetry-adapted linear combination of the lone-pair orbitals, n_1, n_2 and n_3, is shown below,

$$A = (n_1 + n_2 + n_3)/\sqrt{3}$$

$$E\begin{cases} n_S = (2n_1 - n_2 - n_3)/\sqrt{6} \\ n_A = (n_2 - n_3)/\sqrt{2}. \end{cases} \qquad (1)$$

Doubly degenerate combination E is separated into two components, n_S and n_A, when the interaction as a whole does not conserve the D_{3h} symmetry.

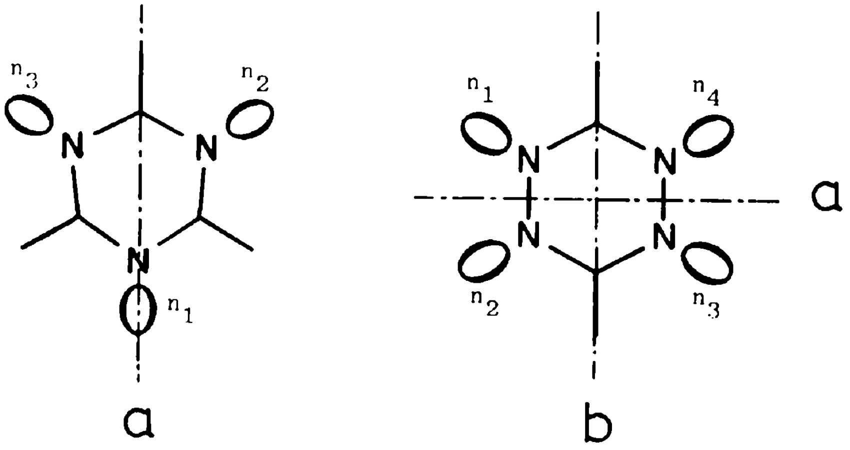


Fig. 1. Schematic structure, LPO numbering, and symmetry axis in s-triazine and s-tetrazine.

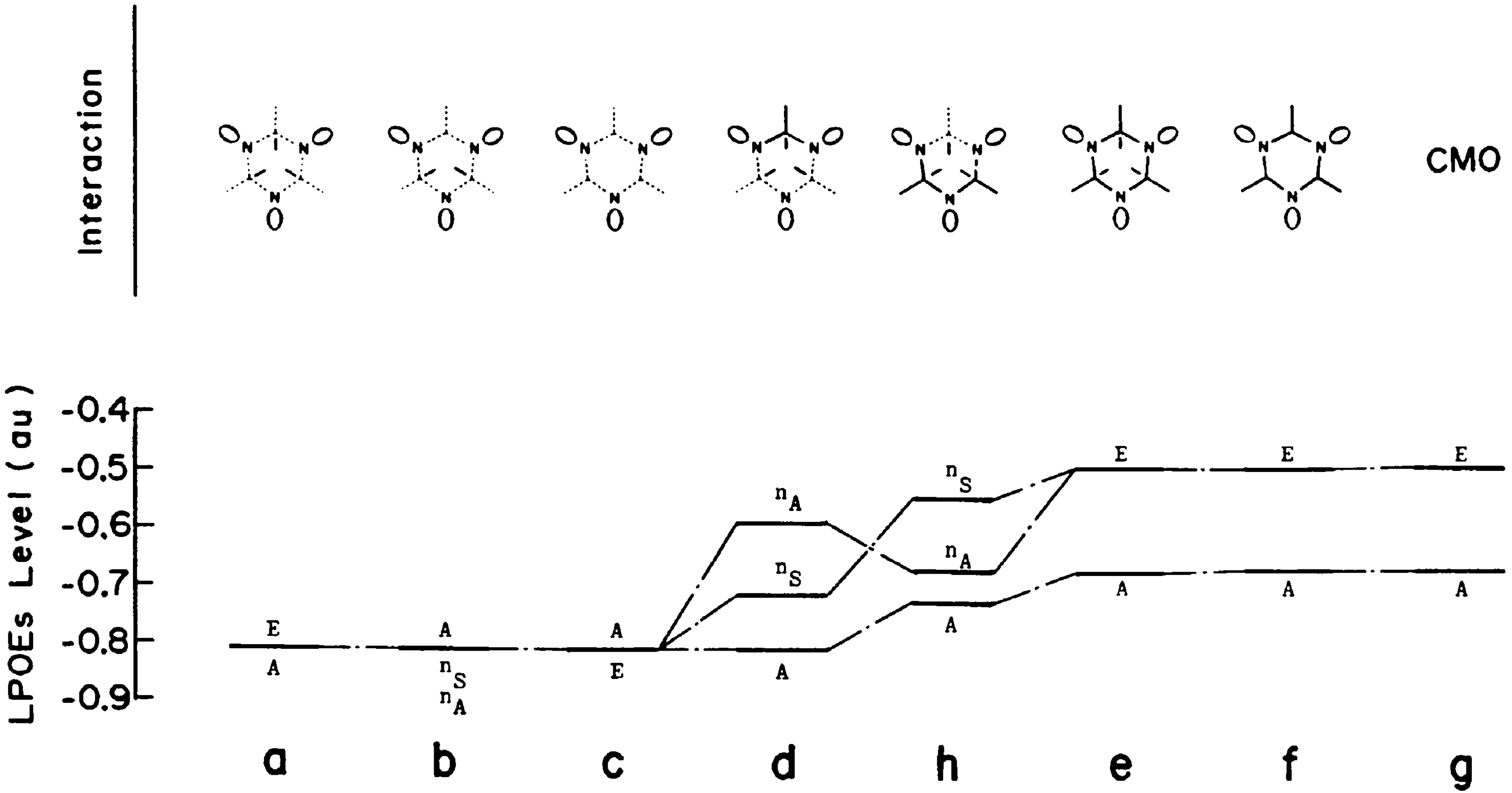


Fig. 2 LPO interaction diagram for s-triazine by the CNDO/2 calculations. Orbital energy in au. CMO full interaction case. Broad line part shows the interaction allowed part In the case with sign between the LPOs, the direct through-space interaction between them is forbidden, and in the case without the sign it is allowed In all cases except the CMO, all of the occupied π and the virtual orbitals in relation to the interaction are cut off from the interactions

The s-tetrazine has four lone-pairs and we can take up the following symmetry-adapted linear combinations of the lone-pair orbitals, n_1, n_2, n_3 and n_4,

$$\begin{aligned} SS &= (n_1 + n_2 + n_3 + n_4)/2 \\ SA &= (n_1 + n_2 - n_3 - n_4)/2 \\ AS &= (n_1 - n_2 - n_3 + n_4)/2 \\ AA &= (n_1 - n_2 + n_3 - n_4)/2. \end{aligned} \tag{2}$$

Here, the first letter reflects the symmetry property in relation to the a axis and the second the b axis as shown in Fig. 1.

In connection with these, the lone-pair orbital energies (LPOEs) vary with different interactions. In the present article, the through-bond interaction or through-space interaction was attempted to evaluate quantitatively by using the localized molecular orbitals (LMOs) transformed from the canonical molecular orbitals (CMOs).

METHOD OF CALCULATION

Twelve occupied σ-orbitals obtained from the CNDO/2[13] and the INDO[14] calculations were localized by the procedure of Edmiston and Ruedenberg.[15] The occupied π and all of the virtual orbitals were not transformed into the LMO. The geometries for the calculations were identical with those reported previously.[1]

The detailed analysis procedure used has been described in the previous paper.[8]

RESULTS AND DISCUSSION

The calculated results are summarized in Figs 2–6 and Tables 1 and 4.

s-Triazine. As for the order of the LPOE levels calculated for the full interaction case, A is lower than E. This corresponds well to the experimental result and SCF MO calculations.[2–4] Here the levels of n_S and n_A have completely degenerated.

CNDO/2 calculations. Three LPOs are cut off from the interactions, the LPOEs levels are overlapped with each other (**a**). Even when the through-space interactions are allowed (**b** and **c**), LPOEs do not vary very much from the initial diagram (**a**). A similar situation is seen in pyrimidine.[8–11] The through-bond interaction is allowed, n_A and n_S are destabilized (**d**). With the diagrams **d** and **h**, since the interaction path as a whole does not conserve the point symmetry of the molecule D_{3h}, E level splits into two components, n_A and n_S. The order of n_A and n_S in the diagram **d** is reserved in the diagram **h**. We can easily recognize that the interaction between lone-pairs depends largely on the kind of σ-frames included in the interactions. When the interaction path does not conserve the D_{3h} symmetry, n_A, n_S and A cannot be simply expressed by the eqn (1). Therefore in the diagrams **d** and **h**, for example, these are mixed with each other. When the interactions of **d** and **h** are combined (**e**), n_S and n_A become one component, E.

In the comparison of diagrams **d** and **e**, A is considerably destabilized when the whole interaction conserves the D_{3h} symmetry. In the diagram **d**, A is not greatly destabilized but in the diagram **e**, A is more destabilized. This can be explained as follows: in the diagram **d** the n_1 LPO is almost localized on N atom. As a result, three LPOs cannot be mixed together, and therefore A is not sufficiently destabilized.

In addition to the diagram **e**, the through-space interactions are added (**f**), energy levels of A and E do not vary much from the diagram **e**. Full interaction state, the CMO calculations are shown by **g**.

INDO calculation. Figure 3 shows the interaction diagram calculated by the INDO method. Energy levels obtained by the INDO calculations are very similar to those obtained by the CNDO/2 calculations. The energy levels calculated by the INDO method in general shifted upward, and minor difference appeared in the diagrams **b**, **c**, and **h**. That is, in the diagrams **b** and **c**, the through-space interaction by the INDO calculations affects the energy levels from the diagram **a**, although the effects are very small. In the diagram **h**, the separation between n_S and n_A is smaller in the INDO calculations than in the CNDO/2 calculations.

s-Tetrazine. The order of the LPOE level is calculated both by the CNDO/2 and INDO methods as AA, SS, AS and SA in the order from unstable to stable. This corresponds with that of the *ab initio* calculations and the assignments of the observed photoelectron spectra,[2–4] although the agreement is not complete. As there are four LPOs in this molecule, the order of the LPOEs show a slightly complicated behavior.

CNDO calculations. All of the LPOs are cut off from the interactions (**a**), four LPOE levels are overlapped with each other. The through-space interaction between n_1 and n_2, and between n_3 and n_4 are allowed, AS and AA go up while SA and SS lower (**b**). The direct through-space interactions between the long paths are allowed (**c**), these four levels do not vary very much from the **a** state as expected, that is, in pyrimidine[8–11] and in s-triazine as we have already seen. The through-space interactions among the LPOs are fully allowed

Table 1. LPOEs (au) under different interaction states[a] in s-triazine

	a	**b**	**c**	**d**	**e**	**f**	**g**[b]	**h**
CNDO								
E [n_S	-0.8122	-0.8122	-0.8138	-0.7151	-0.4935	-0.4937	-0.4906	-0.5343
n_A	-0.8123	-0.8137	-0.8126	-0.5894	-0.4930	-0.4937	-0.4906	-0.6616
A	-0.8115	-0.8100	-0.8096	-0.8113	-0.6743	-0.6728	-0.6700	-0.7177
INDO								
E [n_S	-0.6840	-0.6854	-0.6775	-0.6340	-0.4431	-0.4395	-0.4367	-0.4736
n_A	-0.6843	-0.6783	-0.6797	-0.5179	-0.4421.	-0.4395	-0.4367	-0.5360
A	-0.6918	-0.6964	-0.7030	-0.6876	-0.6026	-0.6114	-0.6069	-0.6307

[a] See also Figs. 2 and 3. [b] Full interaction state (CMO).

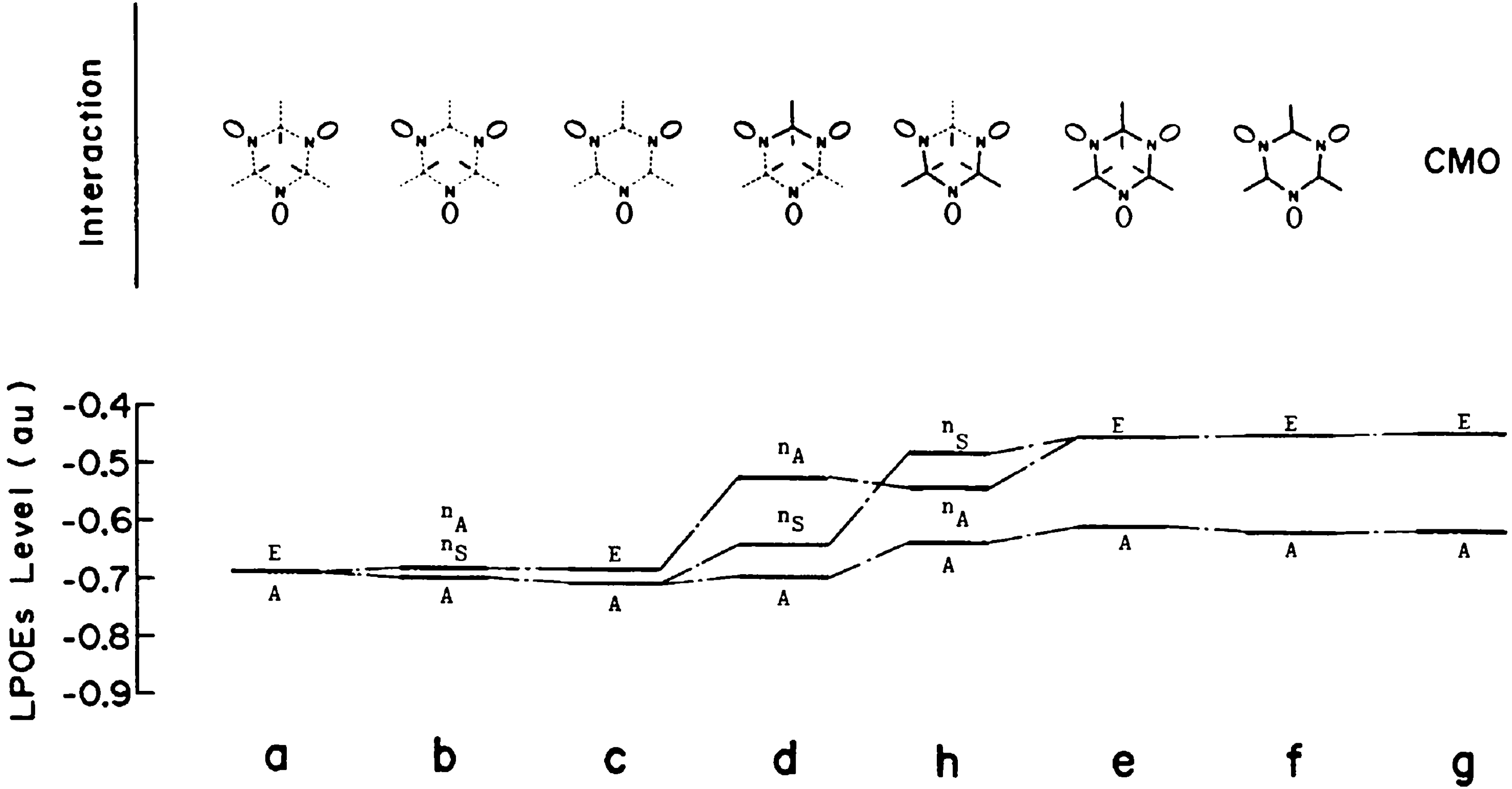


Fig. 3 LPO interaction diagram for s-triazine by the INDO calculations. Notations: see Fig. 2

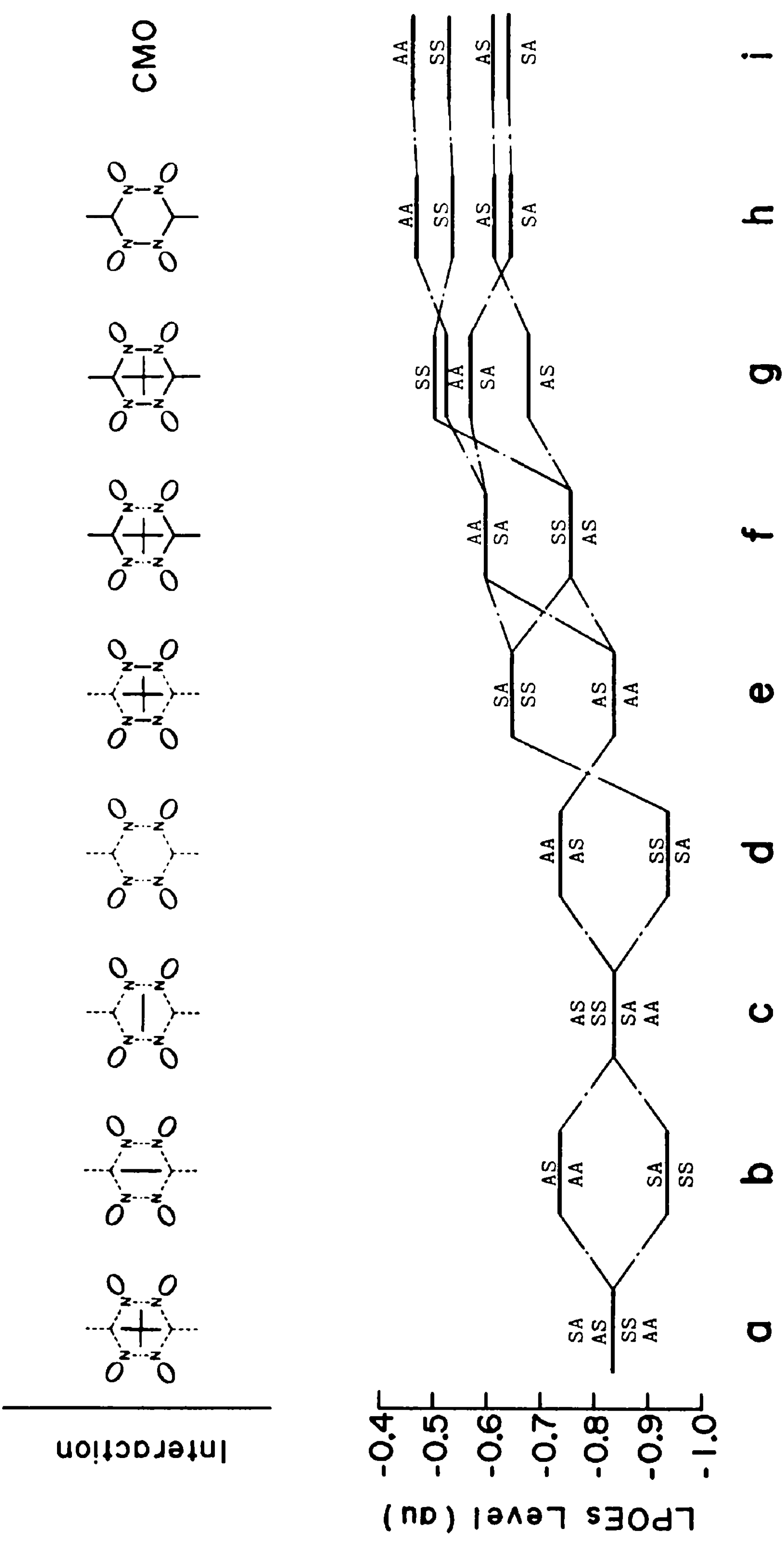


Fig. 4. LPO interaction diagram for s-tetrazine by the CNDO/2 calculations. Notations: see Fig. 2.

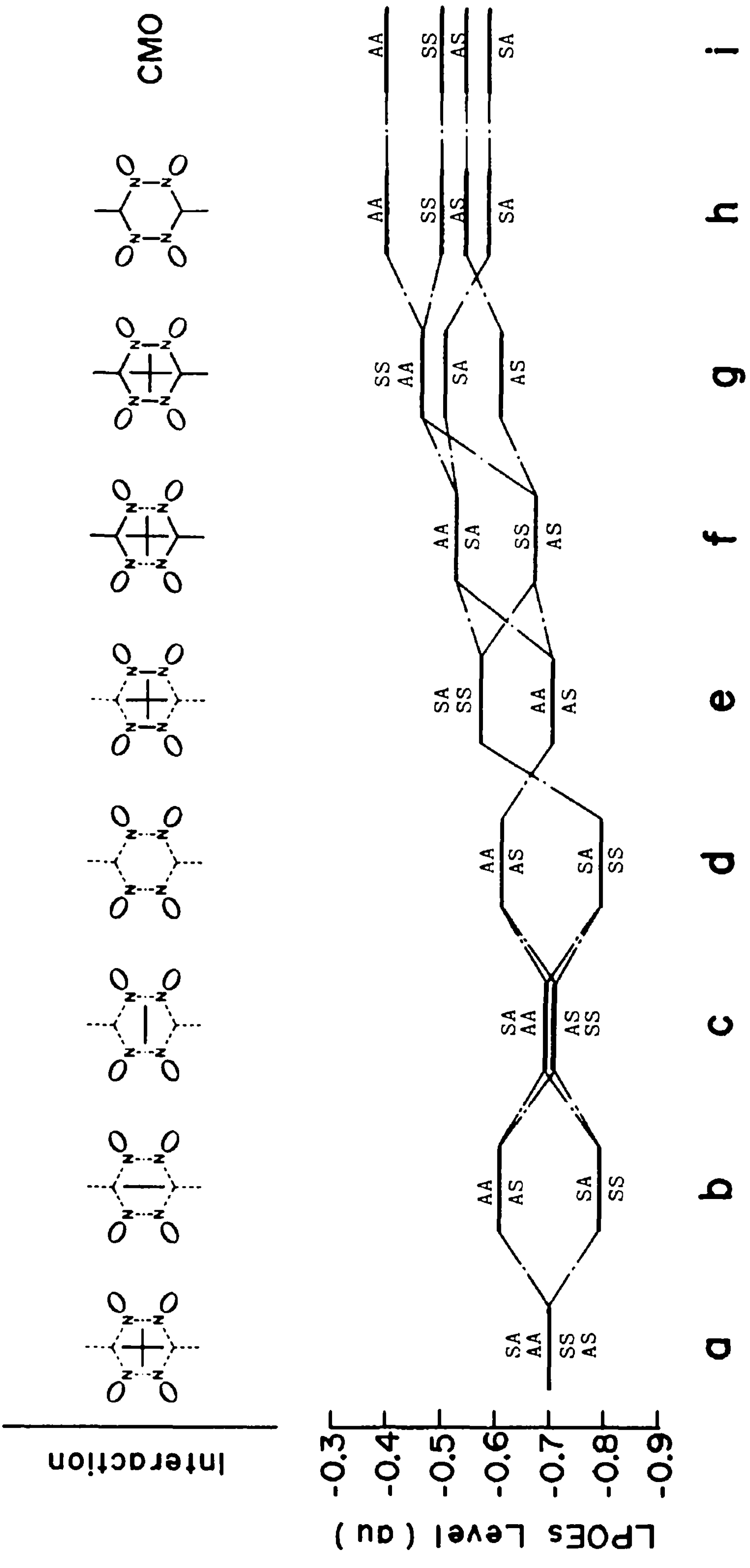
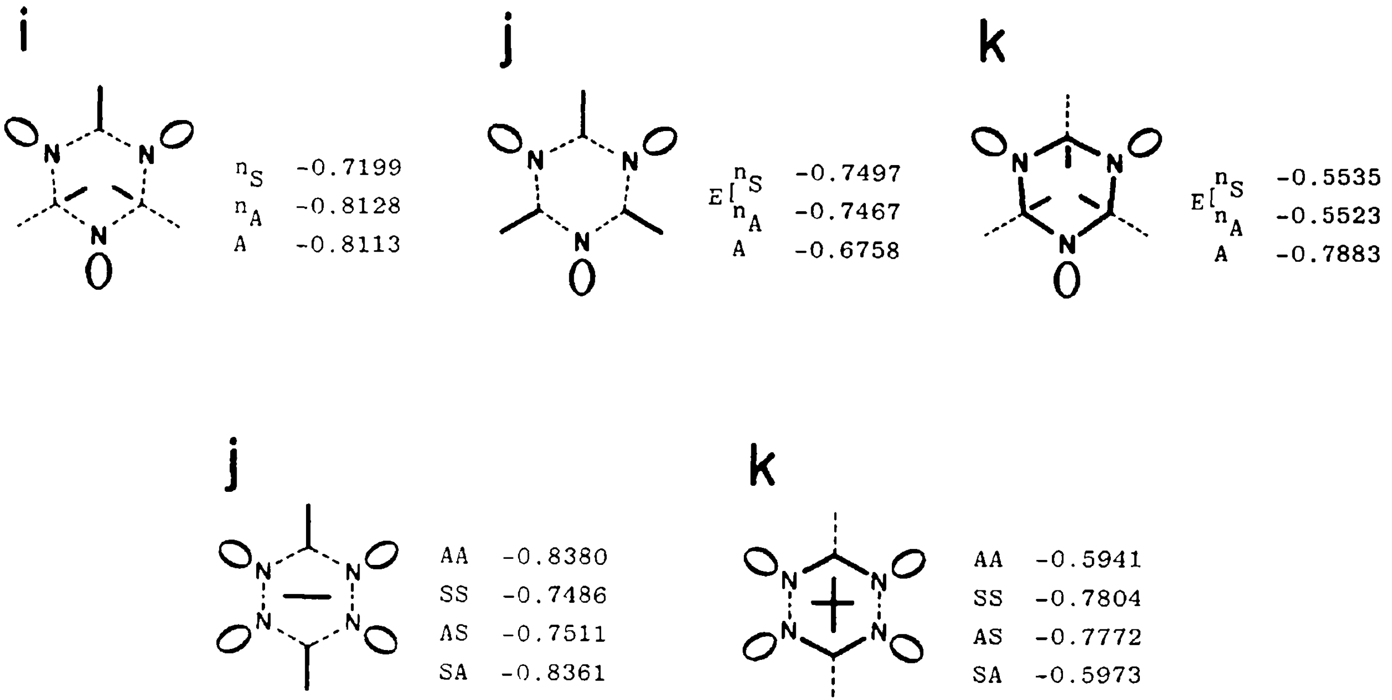


Fig. 5. LPO interaction diagram for s-tetrazine by the INDO calculations. Notations: see Fig. 2.



i

n_S	-0.7199
n_A	-0.8128
A	-0.8113

j

E	n_S	-0.7497
	n_A	-0.7467
	A	-0.6758

k

E	n_S	-0.5535
	n_A	-0.5523
	A	-0.7883

j

AA	-0.8380
SS	-0.7486
AS	-0.7511
SA	-0.8361

k

AA	-0.5941
SS	-0.7804
AS	-0.7772
SA	-0.5973

Fig. 6 Indirect through-space and skeletal through-bond interactions in s-triazine and s-tetrazine by the CNDO/2 calculations. Notations: see Fig. 2.

(**d**). AA and AS go up while SS and SA go down from **a**. When the short through-bond path is allowed (**e**), SA and SS go up markedly, however AS and AA does not vary at all from the **a** state as is expected from the symmetry of the included interactions. The long through-bond path is allowed (**f**). AA and SA go up considerably while SS and AS go upward a little from the diagram a. In this diagram, indirect through-space interaction via the C H bond is included. And this may play an important role to the LPO interaction as is already seen in the previous paper.[8] This point will also be discussed later.

To the diagram **f**, the short through-bond interaction is added (**g**), all of the energy levels go up. The diagram **h** shows that all the virtual orbitals are cut off from the interactions. That is, the interactions are allowed through the occupied orbitals. In comparison of **g** with **h**, the order between SS and AA, and that between SA and AS is reserved from **g** to **h**. This is a very interesting finding from view points of the through-space and through-bond interactions. Similar reversion of the LPOE order is also seen in pyridazine in the previous paper.[8] Full interaction state, i.e. the CMO state is indicated by **i**.

INDO calculation. We now discuss the interaction diagrams calculated by the INDO method using Fig. 5.

The energy levels calculated by the INDO method shifted upward in general in comparison with the results of the CNDO 2 calculations. However, the behavior of the interaction diagram by the INDO method resembles to that of the CNDO 2 one as seen in Fig. 4. A small difference appears in the diagram **g**. In the INDO calculation, SS and AA almost overlapped. However in the CNDO 2 calculation, they are separated. In the diagram e a small difference appeared.

GENERAL DISCUSSION

The indirect through-space interaction via the C H bond and the skeletal through bond interactions are discussed in some detail using Fig. 6.

The indirect through-space interaction shows, that the symmetrical interaction in relation to the axis a or b of s-triazine or s-tetrazine is destabilized by this type of interaction. For example, n_S in diagram **i**, and AS and SS in **j** of s-tetrazine are to some extent destabilized by this kind of indirect through-space interaction. The other levels are not affected much by this path but these are affected by the skeletal C-N σ-frame, although in the diagram i of s-triazine n_S cannot be expressed purely by the eqn (1) as was already discussed in the preceding paragraph.

Through skeletal through-bond interaction (**k**) in s-triazine, E is destabilized. From this, it is found that the LPOs of the E species can interact with the C N σ-bonds but not with C H bonds. In the case of s-tetrazine (**k**), SA and AA are destabilized through the C N σ-bonds and AS and SS are also destabilized through these bonds up to around the diagram **f** of Fig. 4. This will be quantitatively explained in the next paragraph. The behavior of A between **i** and **j** in s-triazine is the same as was already explained by the relation of the diagrams **d** and **e** in s-triazine.

Analyses of the LPOEs are summarized in Tables 2 and 3, and 5 and 6 for s-triazine and s-tetrazine, respectively. The procedure for the analysis is the same as that in the previous paper.[11]

Table 2. Analysis of LPOEs in s-triazine (CNDO 2)

	E				A		Descriptions[b]
	n_S [a]	%	n_A [a]	%	[a]	%	
Through-space	-16	-0.5	-3	-0.1	19	1.3	**c-a**
Through-bond	3187	99.1	3193	99.3	1372	97.0	**e-a**
Through-space through-bond coupling	14	0.4	-4	-0.1	-4	-0.3	(**f-a**)-[(**c-a**)+(**e-a**)]
Through-virtuals	31	1.0	31	1.0	28	2.0	**g**(CMO)-**f**
Total	3216	100	3217	100	1415	100	**g**(CMO)-**a**

[a] energy difference in $\times 10^{-1}$ au. See also Table 1. [b] See also Fig. 2.

Table 3. Analysis of LPOEs in s-triazine (INDO)

	E				A		Descriptions[b]
	n_S [a]	%	n_A [a]	%	[a]	%	
Through-space	65	2.6	46	1.9	-112	-13.2	**c-a**
Through-bond	2409	97.4	2422	97.8	892	105.1	**e-a**
Through-space through-bond coupling	-29	-1.2	-20	-0.8	24	2.8	(**f-a**)-[(**c-a**)+(**e-a**)]
Through-virtuals	28	1.1	28	1.1	45	5.3	**g**(CMO)-**f**
Total	2473	100	2476	100	849	100	**g**(CMO)-**a**

[a] See [a] of Table 2. [b] See also Fig. 3.

Table 4. LPOEs (au) under different interaction states[a] in s-tetrazine

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**[b]
CNDO									
AA	-0.8361	-0.7360	-0.8388	-0.7344	-0.8355	-0.5936	-0.5225	-0.4643	-0.4614
SS	-0.8354	-0.9358	-0.8327	-0.9289	-0.6457	-0.7530	-0.5044	-0.5325	-0.5279
AS	-0.8353	-0.7352	-0.8326	-0.7367	-0.8347	-0.7541	-0.6746	-0.6124	-0.6116
SA	-0.8342	-0.9347	-0.8368	-0.9417	-0.6448	-0.5969	-0.5670	-0.6125	-0.6388
INDO									
AA	-0.6981	-0.6049	-0.6935	-0.5975	-0.6983	-0.5166	-0.4559	-0.3880	-0.3860
SS	-0.7001	-0.7928	-0.7046	-0.7947	-0.5661	-0.6524	-0.4520	-0.4896	-0.4876
AS	-0.7001	-0.6087	-0.7044	-0.6160	-0.7002	-0.6603	-0.6038	-0.5356	-0.5332
SA	-0.6926	-0.7863	-0.6879	-0.7844	-0.5661	-0.5246	-0.4976	-0.5768	-0.5745

[a] See also Figs. 4 and 5. [b] Full interaction case (CMO).

Table 5. Analysis of LPOEs in s-tetrazine (CNDO/2)

	AA		SS		AS		SA		Descriptions[b]
	Δ[a]	σ	Δ	σ	Δ	σ	Δ	σ	
rough-space (short)	1001	26.7	-1004	-32.7	1001	44.7	-1005	-51.4	**b-a**
rough-space (long)	-27	-0.7	27	0.9	27	1.2	-26	-1.3	**c-a**
rough-bond (short)	6	0.2	1897	61.7	6	0.3	1894	96.9	**e-a**
rough-bond (long)	2425	64.7	824	26.8	812	36.3	2373	121.4	**f-a**
rough-space through-space coupling	43	1.1	42	1.4	-42	-1.9	-44	-2.3	**(d-a)-[(b-a)+(c-a)]**
rough-bond through-bond coupling	705	18.8	589	19.1	789	35.3	-1595	-81.6	**(g-a)-[(e-a)+(f-a)**
rough-space through-bond coupling	-435	-11.6	654	21.3	-364	-16.3	320	16.4	**(h-a)-[(d-a)+(g-a)**
rough-virtuals	29	0.8	46	1.5	8	0.4	37	1.9	**i(CMO)-h**
tal	3747	100.	3075	100.	2237	100.	1954	100.	**i(CMO)-a**

[a] Δ: energy difference in $\times 10^{-4}$ au. [b] See also Fig. 4 and Table 4.

Table 6. Analysis of LPOEs in s-tetrazine (INDO)

	AA		SS		AS		SA		Descriptions[b]
	Δ[a]	σ	Δ	σ	Δ	σ	Δ	σ	
rough-space (short)	932	29.9	-927	-43.6	914	54.8	-937	-79.3	**b-a**
rough-space (long)	46	1.5	-45	-2.1	-43	-2.6	47	4.0	**c-a**
rough-bond (short)	-2	-0.1	1340	63.1	-1	-0.1	1265	107.1	**e-a**
rough-bond (long)	1815	58.2	477	22.4	398	23.9	1680	142.3	**f-a**
rough-space through-space coupling	28	0.9	26	1.2	-30	-1.8	-28	-2.4	**(d-a)-[(b-a)+(c-a)**
rough-bond through-bond coupling	609	19.5	664	31.3	566	33.9	-995	-84.3	**(g-a)-[(e-a)+(f-a)**
rough-space through-bond coupling	-327	-10.5	570	26.8	-159	-9.5	126	10.7	**(h-a)-[(d-a)+(g-a)**
rough-virtuals	20	0.6	20	0.9	24	1.4	23	1.9	**i(CMO)-h**
tal	3121	100.	2125	100.	1669	100.	1181	100.	**i(CMO)-a**

[a] See a) of Table 5. [b] See also Fig. 5 and Table 4.

In s-triazine, the effects of the through-space, through-space through-bond coupling and through virtuals are very small. We easily recognized that largely the interaction between or among the LPOs is explained by the through-bond interaction. In the INDO calculations, the through-space interaction is larger than in the CNDO/2 calculations.

In s-tetrazine, the through-space (long), through-space through-space coupling, and through-virtuals do not have much of an effect on the lone-pair orbital energies. As for the through-space interactions, the symmetrical interaction in relation to the a axis makes LPOEs stabilize while the antisymmetrical one in relation to it destabilize. As for the through-bond interactions, SS and SA are destabilized through the short path, while through the long path all combinations are affected. Here AA and SA are destabilized more than SS and AS. As for the through-bond through-bond coupling, SA has a fairly large minus value, but the others have a positive value. With the through-space through-bond coupling the values of AA and AS are negative, while SS and SA are positive. These signs depend on the symmetry properties. The results of the INDO calculations show similar results of the CNDO/2 calculations except that the through-space interactions in the INDO calculations are a bit larger than those in the CNDO/2 calculations.

The procedure applied in the present article is very useful in order to analyse quantitatively the orbital interactions. The present analysis proposes new information in relation to the orbital interaction between LPOs and/or between LPO(s) and σ-frames. This procedure will also be used to explain the reactivity and reaction path of addition reactions.

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