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Electronic Structure of Lone Pairs. III.[1] H_2S_2, H_2O_2, N_2H_4, and Diimides

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The electronic structure, the electronic transition, and the interaction of lone pairs of H_2S_2, H_2O_2, and N_2H_4 for several dihedral angles are studied by the semi-empirical ASMO SCF method, and their dependencies on the dihedral angle is discussed. Also, the interaction of the lone pairs of diimides, N_2H_2, N_2F_2, and $(CH_3)_2N_2$, the relative stability of the *cis* forms and of their *trans* form, and the electronic transition energies of these molecules are calculated. The stable forms of N_2H_2 and $(CH_3)_2N_2$ are calculated to be of the *trans* form, but that of N_2H_2 is the *cis* form. An energy component analysis of these compounds has been made. The main factor in the lack of stability of the *cis* form of N_2H_2 is shown to be the core-core repulsion term, V_{nn}. On the other hand, in H_2S_2 and N_2H_4 not only the V_{nn} term but also the electrostatic interaction term, $\sum_{i,j}^{\text{occ}}(2J_{ij}-K_{ji})$, contributes to their instability.

In a previous paper,[3] the electronic structure and the interaction of lone pairs of $(CH_3)_2S_2$ and cyclic disulfides were studied theoretically and their dependence on the dihedral angle, ϕ, was discussed.

Hydrogen peroxide, H_2O_2,[4,5] and hydrazine, N_2H_4,[5,6] are known to have dihedral angles of approximately 111° and 90° respectively from the investigation by means of X-ray analysis, by a study of the IR spectra, and so on. Recently, the dihedral angle of H_2S_2 was revealed to be 90°36′ by a microwave study.[7,8] In these molecules, the oxygen and the nitrogen atoms having lone pairs are bonded by a single bond, as in the case of disulfides. The problem of the rotational barriers of these compounds has been studied quantum-mechanically by many authors.[6,8–10] In the present paper, focusing our attention upon the electronic structure of the lone pair, calculations similar to the previous ones for several disulfides[3] are carried out for H_2S_2, H_2O_2, and N_2H_4. The dependence of the total energy and the interaction of the lone pairs on the dihedral angle is discussed, and an energy-component analysis of these molecules is reported.

In this paper we will also discuss the interaction of the lone pair of diimides, RN=NR, in which the nitrogen atoms are bonded by a double bond. The mutual

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[3] T. Yonezawa, H. Yamabe, and H. Kato, "Electronic Structure of Lone Pairs. II. Disulfides and Acyl Thiol" (to be published in this Bulletin).

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stability of their *cis* and *trans* forms[11] and the electronic transition energy are calculated. Moreover, the substituent effect of an electronegative atom, such as the F atom, or of a CH_3 group to the lone pairs of the sp^2 type of nitrogen atom is investigated. As Robin *et al.* pointed out in their paper, a few works[12-14] on the electronic states of azoalkanes have been performed. They studied the electronic structure by a non-empirical SCF CI method, using Gaussian-type orbital basis functions. Here, the electronic states of *cis* and *trans* diimides, N_2H_2, $(CH_3)_2N_2$, and N_2F_2 are calculated by the semi-empirical ASMO SCF method.[15]

Calculations

In the calculation by the semi-empirical ASMO SCF method,[15] the approximation and parameters used in the case of the disulfides are adopted. The coordinate axes, bond lengths, and bond angles of H_2S_2, H_2O_2, and N_2H_4 are given in Fig. 1, together with their dihedral angles, ϕ's, while those of the diimides are given in Fig. 2. The conformation of N_2H_4 in the dihedral angle, $\phi=0°$, is assumed to be as follows: The atoms, H_4 and H_6, are placed downward to the x-y plane, as in Fig. 1. The ∠NNH angle is put as 112°. In the conformation of the 90° dihedral angle, the group containing the N_2 atom is rotated by 90° around the N-N bond.

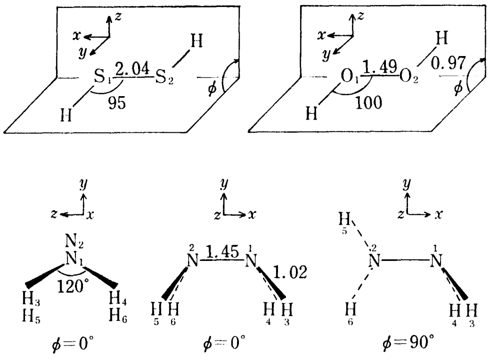

Fig. 1. Bond lengths (in Å) and bond angles (in degree), the dihedral angle ϕ of H_2S_2 and H_2O_2, the employed conformations of N_2H_4 for $\phi=0°$ and $\phi=90°$, and the coordinate axes are shown.

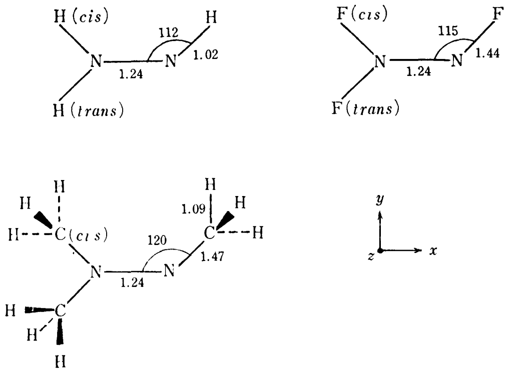

Fig. 2. Bond lengths (in Å), bond angles (in degree), and coordinate axes.

Results and Discussion

The angular dependencies of the atomic density and the atomic orbital (AO) densities of H_2S_2, H_2O_2, and N_2H_4 are given in Tables 1—3. The lone-pair levels and the lowest vacant level (LV) of H_2S_2 and H_2O_2 of various dihedral angles are given in Figs. 3 and 4 respectively.

TABLE 1. ELECTRON DENSITIES OF H_2S_2 AND ATOMIC BOND ORDER P_{s,p_i} OF THE SULFUR FOR VARIOUS CONFIGURATIONS

	$\phi°$	0	45	90	180
Atomic density	S_1	6.171	6.172	6.177	6.184
	H_3	0.829	0.829	0.823	0.816
Atomic orbital density	S_1 s	1.623	1.625	1.627	1.630
	x	1.142	1.142	1.140	1.136
	y	1.406	1.406	1.411	1.417
	z	2.000	2.000	1.999	2.000
	S_2 s	1.623	1.625	1.627	1.630
	x	1.142	1.139	1.140	1.136
	y	1.406	1.710	1.999	1.417
	z	2.000	1.709	1.411	2.000
P_{s,p_i}	S_1 s-x	0.300	0.300	0.300	0.298
	s-y	−0.337	−0.338	−0.338	−0.339
	s-z	0.000	0.005	0.005	0.000
	S_2 s-x	−0.300	−0.299	−0.300	−0.298
	s-y	−0.337	−0.235	0.005	0.339
	s-z	0.000	−0.242	−0.338	0.000

TABLE 2. ELECTRON DENSITIES OF H_2O_2 AND ATOMIC BOND ORDER P_{s,p_i} OF THE OXYGEN ATOM FOR VARIOUS CONFIGULATIONS

	$\phi°$	0	45	90	180
Atomic density	O_1	6.323	6.329	6.337	6.349
	H_3	0.677	0.674	0.663	0.651
Atomic orbital density	O_1 s	1.808	1.807	1.807	1.806
	x	1.008	1.013	1.011	1.012
	y	1.507	1.509	1.519	1.531
	z	2.000	2.000	2.000	2.000
	O_2 s	1.808	1.807	1.807	1.806
	x	1.008	1.005	1.011	1.012
	y	1.507	1.767	2.000	1.531
	z	2.000	1.761	1.519	2.000
P_{s,p_i}	O_1 s-x	0.114	0.114	0.116	0.116
	s-y	−0.285	−0.285	−0.282	−0.278
	s-z	0.000	0.000	0.000	0.000
	O_2 s-x	−0.114	−0.114	−0.116	−0.116
	s-y	−0.285	−0.199	0.000	0.278
	s-z	0.000	−0.200	−0.282	0.000

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TABLE 3. ELECTRON DENSITIES AND ATOMIC BOND ORDER P_{s,p_i} OF THE NITROGEN ATOM OF N_2H_4

ϕ°		0	90	
Atom		N_1	N_1	N_2
Atomic density		5.509	5.516	5.516
Atomic orbital density	s	1.408	1.408	1.408
	x	0.979	0.983	0.983
	y	1.820	1.822	1.303
	z	1.301	1.303	1.821
P_{s,p_i}	s-x	0.076	0.079	−0.079
	s-y	0.292	0.290	0.004
	s-z	0.000	0.004	0.290

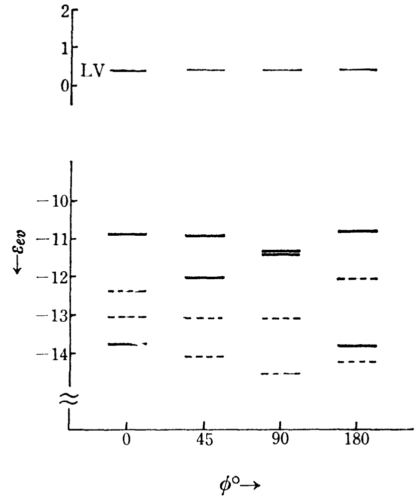

Fig. 3. Lone-pair levels and the lowest vacant level of H_2S_2 *vs.* dihedral angle ϕ. The heavy lines and the dashed lines designate the levels of the p-type lone pair and the sp^2-type lone pair, respectively.

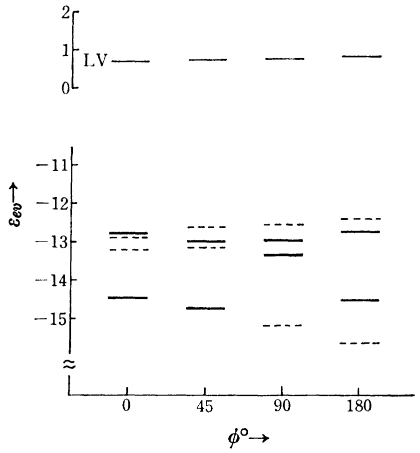

Fig. 4. Lone-pair levels and the lowest vacant level of H_2O_2 *vs.* dihedral angle ϕ. The heavy lines and the dashed lines designate the levels of the p-type lone pair and the sp^2-type lone pair, respectively.

1) H_2S_2: As is shown in Table 1, when the dihedral angle of H_2S_2 is equal to 0°, the p-type lone-pair AO becomes the p_z orbital of the S_1 atom (S_1z). The direction of the lone-pair orbital rotates, keeping its electron density approximately 2.00, following the change in the ϕ angle. When the dihedral angle increases, the atom density of the sulfur atom increases and that of the hydrogen atom decreases. That is, the electron flows from the s orbital of the hydrogen atom to the p_y orbital of the sulfur atom. This tendency has been pointed out for $(CH_3)_2S_2$ by the present authors[3] and for H_2O_2 by Morokuma *et al.* in their ab initio calculation[5] and also by Pitzer *et al.*[10] H_2S_2 also has sp^2-type lone pairs due to the hybridization of $3s$ and $3p$ electrons. These sp^2-type lone pairs rotate according to the change in the dihedral angle, ϕ. That is, the atomic density and the AO density of the sulfur atom of H_2S_2 and their angular dependence resemble those in the case of $(CH_3)_2S_2$. The lowest n–σ^* transition energies are given in Table 4. These transition energies are approximately equal to those of $(CH_3)_2S_2$. Therefore, it is noted that the main factor showing the angular dependency of the atomic density, the AO density, and the transition energy is not a group bonded to a sulfur atom, such as CH_3 and H, but a part of the S–S bond. The total energy decreases monotonically from a maximum at 0° to a minimum at 180°. The experimentally-obtained minimum (about 90.5°) can not be obtained.[16]

TABLE 4. DIFFERENCE OF TOTAL ENERGIES (eV)[a] AND TRANSITION ENERGIES[b] (eV)

	ϕ°	0	45	90	180
H_2S_2	Difference of the total energy	0.17	0.14	0.00	−0.04
	Transition energy	4.23	4.30	4.82	4.22
H_2O_2	Difference of the total energy	0.27	0.22	0.00	−0.16
	Transition energy	2.99	4.65	5.73	5.93
N_2H_4	Difference of the total energy	0.16	—	0.00	—
	Transition energy	4.21	—	4.94[c]	—

a) Difference of total energies referred to that in 90°.
b) Lowest $n \to \sigma^*$ transition.
c) Observed value is about 5.39 eV (S. Imanishi, *Nature*, **127**, 782 (1931)).

2) H_2O_2: The angular dependencies of the atomic density and the AO density of H_2O_2 (Table 2) are analogous to those of H_2S_2 and $(CH_3)_2S_2$.[3] That is the two p-type lone pairs are parallel at 0° and become orthogonal at 90°. The sp^2-type lone pairs are also seen. However, the AO density of the s orbital of the oxygen atom is larger than that of the sulfur atom (Table 2). The order of the lone-pair levels shown in Fig. 4 is different from that in the case of H_2S_2 of Fig. 3. The energy level of the sp^2-type lone pair becomes more unstable than the p type except for $\phi = 0°$, which may correspond to the larger s character and the smaller sp^2-type hybridization of the oxygen atom (see Tables 1 and 2). The splitting

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[16] This may be due to the inappropriate approximation of the calculation for such a small molecule with lone pairs. Recently, by using the basic set of Gaussian orbitals and the ab initio SCF MO method, Schwartz obtained an energy minimum of H_2S_2 for a dihedral angle in the range 90°—100° in fair agreement with the experimental value (about 90.5°) (Ref. 8).

between the p-type lone-pair levels is large when $\phi=0°$ and small when $\phi=90°$. That is, the interaction of the lone pairs aligned parallel is larger than those aligned in a rectangular manner. The total energies referred to that at 90° are shown in Table 4 for the various dihedral angles. The total energy decreases monotonically from a maximum at 0° to a minimum at 180°. The experimentally-obtained minimum (approximately 111°) can not be obtained, such as in the case of H_2S_2.[17] The lowest n–σ^* transition energy in 90° is calculated to be 5.73 eV. Urey *et al.*[18] and Fergusson *et al.*[18] reported that H_2O_2 is decomposed by light in the UV region, thus, the transition energy was not observed experimentally.

3) N_2H_4: The total energy at the dihedral angle of 90° is lower than that at 0°, which is compatible with the observation that the dihedral angle of the stable form is approximately 90°. In Table 3, when $\phi=0°$, the atomic bond order is zero, and it is noted that the lone pair of the nitrogen atom lies on the x–y plane and has a large electron density in the y direction. When $\phi=90°$, the lone pairs of the nitrogen atoms are perpendicular to each other. The splitting between the lone-pair levels at 0° (2.23 eV) is larger than that at 90° (0.22 eV).

Table 5. Some calculated results of N_2H_2

		cis		*trans*	
		N	H	N	H
Atomic density		5.254	0.746	5.277	0.723
Atomic orbital density	s	1.578	0.746	1.583	0.723
	x	1.092	—	1.104	—
	y	1.583	—	1.590	—
	z	1.000	—	1.000	—
Atomic bond order P_{s,p_i}	s–x	0.243	—	0.254	—
	s–y	−0.305	—	−0.304	—
	s–z	0.000	—	0.000	—
Total energy (eV)		−413.02		−413.31	
Δn[a] (eV)		2.33		5.20	

a) Splitting of lone-pair levels.

Table 6. Some calculated results of N_2F_2

		cis		*trans*	
		N	F	N	F
Atomic density		4.865	7.135	4.877	7.123
Atomic orbital density	s	1.775	1.962	1.768	1.962
	x	1.040	1.874	1.122	1.835
	y	1.033	1.315	0.971	1.342
	z	1.017	1.983	1.015	1.985
Atomic bond order P_{s,p_i}	s–x	0.280	—	0.323	—
	s–y	−0.240	—	−0.244	—
	s–z	0.000	—	0.000	—
Total energy (eV)		−1361.46		−1360.64	
Δn[a] (eV)		0.83		3.12	

a) Splitting of lone-pair levels.

Table 7. Some calculated results of $N_2(CH_3)_2$

		cis		*trans*	
		N	C	N	C
Atomic density		5.197	4.066	5.231	4.013
Atomic orbital density	s	1.641	1.005	1.628	0.995
	x	1.044	1.041	1.066	1.032
	y	1.487	0.903	1.515	0.868
	z	1.026	1.116	1.023	1.118
Atomic bond order P_{s,p_i}	s–x	0.225	—	0.239	—
	s–y	−0.308	—	−0.303	—
	s–z	0.000	—	−0.001	—
Total energy (eV)		−740.23		−743.91	
Δn[a] (eV)		1.75		3.25	

a) Splitting of one-pair levels

Diimides. The electron density, the difference in the relative total energy, and the splitting of the lone-pair levels are listed in Tables 5—7 for the various diimides. Herzberg mentioned[19] that N_2H_2 should take a *trans* form in the ground state, and in our approximate calculation the *trans* form is calculated to be more stable.[20] For N_2F_2 and $(CH_3)_2N_2$, the stable forms are calculated to be the *cis* form and the *trans* form respectively. From the one-center bond orders of s–x, s–y, and s–z, the lone-pair orbital of the nitrogen atom may be approximately identified as a sp^2-type hybrid orbital for all the diimides studied here, and the lone pair of the N_1 atom lies on the molecular plane.

The splitting of the lone-pair levels is larger in the *trans* form than in the *cis* form for the three diimides, as is also pointed out by Robin *et al.*[11] This may be due to the fact that the overlap of the lone pairs is larger in the *trans* form than in the *cis* form. This tendency was also true in H_2S_2 and H_2O_2. (See the dotted line in Figs. 3 and 4. $\phi=0°$ and $\phi=180°$ correspond to the *cis* and *trans* forms respectively.) It is noted that, by the substitution of the fluorine atom, the lone-pair electron density of the nitrogen atom (mainly p_y AO) is greatly diminished and the splitting of the lone pair becomes small compared to N_2H_2. The atom density of the nitrogen atom of the *trans* diimide is larger in each case studied than that of the *cis* diimides, while that of the hydrogen atom of *trans* N_2H_2 is smaller than that of the *cis* form. Similar relations are shown for the atom density of the fluorine atom of N_2F_2 and that of the CH_3 group of $(CH_3)_2N_2$, which is the sum of the atom densities of the carbon atom and three hydrogen atoms.[21]

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[17] Pedersen and Morokuma have reported, in their ab initio calculation of H_2O_2 using a basic set of 26 Gaussian orbitals, that the energy decreases monotonically from a maximum at 0° to a minimum at 180° (Ref. 5).

[18] H. C. Urey, L. H. Dawsey, and F. O. Rice, *J. Amer. Chem. Soc.*, **51**, 1371 (1929); W. C. Fergusson, L. Slotin, and D. W. G. Style, *Trans. Faraday Soc.*, **32**, 956 (1936).

[19] G. Herzberg, *Kagaku to Kogyo*, **21**, 474 (1968).

[20] Lehn *et al.*, by their ab initio SCF LCAO MO calculations, that *trans* N_2H_2 is more stable than *cis* N_2H_2 by 10.5 kcal/mol (Ref. 12). On the other hand, Gordon *et al.*, in their ab initio calculations, fond that *cis* N_2H_2 and *cis* N_2F_2 are more stable than the corresponding *trans* diimides (Ref. 14).

[21] The atom densities of the CH_3 group of $(CH_3)_2N_2$ are 6.759 for the *trans* form and 6.803 for the *cis* form.

Some of the obtained transition energies are listed in Table 8, together with the values calculated and observed by Robin *et al.*[11] Among the calculated values of *trans* N_2F_2 and *trans* $(CH_3)_2N_2$, the lowest singlet-singlet transition is n–σ^* (^1B_g), and the next one is n–σ^* (^1B_u). This sequence is the same as that observed, but the values of these transitions are much smaller than the observed energies. Compared to the values calculated by Robin *et al.*,[11] our transition energies are small. The inclusion of the configuration interaction seems to be necessary. According to Herzberg,[19] the ground state of N_2H_2 is the triplet state. Our obtained transition energy of the $^3B_g(n\text{-}\sigma^*)$ of the *trans* N_2H_2 is remarkably low.

TABLE 8. TRANSITION ENERGIES (ΔE IN eV) AND TRANSITION MOMENTS (Q)

a) N_2H_2

	ΔE calcd	Q calcd	ΔE calcd[9]	Q calcd[9]
cis				
n_1-π^* $^1B_1$	1.52	0.17	3.36	0.20
n_2-π^* $^1A_2$	3.61	0.00	7.41	0.00
n_1-σ^* $^1A_1$	5.46	0.00	8.40,9.94	0.07,0.22
n_1-σ^{**} $^1B_2$	6.21	0.30	6.97,8.90	0.25,0.19
π-π^* $^1B_2$	6.64	0.88	—	—
n_1-π^* $^3B_1$	0.59	0.00	2.07	0.00
n_2-π^* $^3A_2$	2.64	0.00	—	—
n_1-σ^* $^3A_1$	4.46	0.00	—	—
n_1-σ^{**} $^3B_2$	5.65	0.00	—	—
π-π^* $^3B_2$	3.06	0.00	6.45	0.00
trans				
n_1-π^* ^1B_g	0.98	0.00	3.92	0.00
n_1-σ^* ^1B_u	5.02	0.09	7.80,8.53,9.68	0.23,0.19,0.16
n_2-π^* ^1A_u	6.36	0.24	10.94	0.26
n_1-σ^{**} ^1A_g	6.45	0.00	7.12,9.14	0.00,0.00
π-π^* ^1B_u	6.64	0.88	—	—
n_1-π^* ^3B_g	0.01		3.01	0.00
n_1-σ^* ^3B_u	4.01	0.00	—	—
n_2-π^* ^3A_u	5.17	0.00	—	—
n_1-σ^{**} ^3A_g	6.01	0.00	—	—
π-π^* ^3B_u	3.06	0.00	6.53	0.00

b) N_2F_2

	ΔE calcd	Q calcd	ΔE obsd[9]
cis			
n_2-π^* $^1A_2$	3.21	0.00	
n_1-π^* $^1B_1$	3.27	0.16	
n_2-σ^* $^1A_1$	3.79	0.10	
σ-σ^* $^1B_2$	5.24	0.04	
π-π^* $^1B_2$	5.99	0.84	
n_2-π^* $^3A_2$	2.44	0.00	
n_1-π^* $^3B_1$	2.74	0.00	
n_2-σ^* $^3A_1$	3.42	0.00	
σ-σ^* $^3B_2$	4.76	0.00	
π-π^* $^3B_2$	3.31	0.00	
trans			
n_1-π^* ^1B_g	1.99	0.00	>6.19
n_1-σ^* ^1B_u	3.15	0.82	8.06
n_1-σ^{**} ^1A_g	5.12	0.00	
n_2-π^* ^1A_u	5.83	0.13	
n_1-π^* ^3B_g	1.23	0.00	
n_1-π^* ^3B_u	1.31	0.00	
n_1-σ^{**} ^3A_g	3.85	0.00	
n_2-π^* ^3A_u	5.39	0.00	

c) $N_2(CH_3)_2$

	ΔE calcd	Q calcd	ΔE obsd[9]	ε max.[9]
cis				
n_1-π^* $^1B_1$	1.96	0.15		
n_2-π^* $^1A_2$	3.45	0.02		
n_1-σ^* $^1A_1$	5.56	0.29		
π-π^* $^1B_2$	5.82	0.93		
n_1-π^* $^3B_1$	1.15			
n_2-π^* $^3A_2$	2.71			
π-π^* $^3B_2$	3.09			
n_1-σ^* $^3A_1$	4.39			
trans				
n_1-π^* ^1B_g	1.21	0.03	3.65	5
π-π^* ^1B_u	5.73	0.94		
n_1-σ^* ^1B_u	4.52	0.23	6.7	
n_2-π^* ^1A_u	5.61	0.15		
n_1-σ^{**} ^1A_g	5.69	0.01		
n_1-π^* ^3B_g	0.37			
π-π^* ^3B_u	3.09			
n_2-π ^3A_u	4.96			
n_1-σ^{**} ^3A_g	5.03			

Energy Component Analysis. The total energies of $(CH_3)_2S_2$, H_2S_2, N_2H_4, and N_2H_2 have been analyzed to their various contributions; the results are given in Table 9, where W, V_{nn}, and E_e denote the total energy, the core-core repulsion energy, and the total electronic energy respectively. The orbital energy and the core integral of the ith MO are designated by ε_i and H_i. The Coulombic and exchange integrals between the ith and the jth MO's are indicated by J_{ij} and K_{ij} respectively. The W and E_e quantities are written as follows:

$$W = E_e + V_{nn} \tag{1}$$

$$E_e = 2\sum_{i}^{\text{occ}} \varepsilon_i - \sum_{ij}^{\text{occ}} (2J_{ij} - K_{ij}) \equiv \varepsilon - G \tag{2}$$

or

$$E_e = 2\sum_{i}^{\text{occ}} H_i^{\text{core}} + \sum_{ij}^{\text{occ}} (2J_{ij} - K_{ij}) \equiv H + G \tag{3}$$

where ε, H, and G imply $2\sum_{i}^{\text{occ}}\varepsilon_i$, $2\sum_{i}^{\text{occ}}H_i^{\text{core}}$, and $\sum_{i}^{\text{occ}}(2J_{ij} - K_{ij})$ respectively. $\Delta H(E-H)$ in Table 9 denotes the electronic energy calculated by the extended Hückel method. We will first discuss the case of H_2S_2. As the dihedral angle, ϕ, decreases from 90° to 0°, the molecule becomes less stable. The unstabilization energy of H_2S_2 is given by the difference in the total energy, ΔW between 0° and 90°; it is 0.17 eV. Note that the difference in the core-core repulsion energy, ΔV_{nn}, is 1.26 eV, while that of the total electronic energy, ΔE_e, is −1.09 eV. Hence, the difference in the electronic interaction energy, ΔG, is 0.66 eV, which corresponds the fact that the two lone pairs become parallel at 0°. That is, the ΔW of H_2S_2 being decomposed to ΔV_{nn}, ΔH, and ΔG according to Eqs. (1) and (2), the tendencies of ΔV_{nn} and ΔG are parallel with that of ΔW.

TABLE 9. ENERGY COMPONENT ANALYSIS (IN eV)

	$(CH_3)_2S_2$			H_2S_2			N_2H_4		N_2H_2	
$\phi°$	0	45	90	0	45	90	0	90	0	180
ΔW	+ 1.98	+ 0.64	0	+0.17	+0.14	0	+0.16	0	+0.30	0
ΔV_{nn}	+47.46	+28.83	0	+1.26	+0.78	0	+0.84	0	+1.71	0
ΔE_e	−45.48	−28.19	0	−1.09	−0.64	0	−0.69	0	−1.41	0
ΔH	−88.87	−55.18	0	−1.75	−0.18	0	−0.82	0	−1.32	0
ΔG	+43.39	+26.99	0	+0.66	+0.54	0	+0.13	0	−0.09	0
$\Delta \varepsilon$	− 2.09	− 1.21	0	−0.43	−0.14	0	−0.56	0	−1.50	0
$\Delta H(E-H)$	+ 0.47	—	0	−0.03	−0.05	0	—	—	—	—

TABLE 10. DIFFERENCE OF $(2J_{ij}-K_{ij})$ BETWEEN 0° AND 90° OF N_2H_4

	1	2	3	4	5	6(*n*)	7(*n*)
1	−0.01	+0.02	−0.26	+0.10	−0.15	+0.18	+0.05
2		+0.03	−0.05	+0.04	−0.14	+0.32	+0.04
3			−0.64	−0.02	−1.40	+0.66	−0.06
4				+0.36	+0.15	+0.17	−0.26
5					−0.46	+0.17	+0.43
6(*n*)						+0.43	+0.20
7(*n*)							+0.04

(*n*): (*n*) denotes a lone-pair MO.

It is also noted that the instability of H_2S_2 towards 0° is contributed to by an increase in ΔV_{nn} and ΔG.[22]

It is noted that the core-core repulsion energy does not cancel the electronic energy. The sum of the orbital energy does not exhibit the same trend as the total energy with regard to the variation in the dihedral angle[24] (see $\Delta\varepsilon$ and ΔW in Table 9). That is, in this case, the stabilization of the molecule at 90° can not be interpreted by the extended Hückel calculation, as is shown in Table 9.

Next, as for N_2H_2, *trans* N_2H_2 is more stable than *cis* N_2H_2. The unstabilization energy, ΔW, is 0.30 eV. In contrast to the other three compounds in Table 9, the difference in the electronic interaction energy, ΔG, is negative. That is, the electronic interaction in the *cis* form is smaller than that in the *trans* form.

In order to known whether the lone-pair levels have a definite relation to the value of $G=\sum_i^{\mathrm{occ}}(2J_{ij}-K_{ij})$, each $(2J_{ij}-K_{ij})$ value of N_2H_4 and N_2H_2 is studied. In Table 10, the differences in these values of N_2H_4 between 0° and 90° are listed; they are also compared with the corresponding levels and a standard is made of the value of 90°.[25] That is, $\Delta(2J_{ij}-K_{ij})=(2J_{ij}-K_{ij})$ (at 0°) $-(2J_{ij}-K_{ij})$ (at 90°). The value of the $(2J_{ij}-K_{ij})$ is presented by the element of the ith raw and the jth column, namely, the (ij) element of Table 10. The order of the numbering is that of the level sequences obtained when $\phi=0$. Comparatively large repulsive values are seen in the elements with reference to the lone-pair levels, but they are not definitely large.

As has been noted in the previous section, the interaction of the lone pairs in N_2H_2 is larger at 180° (*trans* form) than at 0° (*cis* form), but the total energy at 180° is slightly lower than that at 0°. This relation between the interaction of the lone pair and the total energy is different from the previously-obtained relation that the stable conformation of such molecules as $(CH_3)_2S_2$, H_2S_2, H_2O_2, and N_2H_4 is the one where the interaction of the lone pairs is smaller. A similar relation appears in Table 9. That is, the electronic interaction, G, of N_2H_2 is large in the unstable conformation, while those of the other three compounds are small in the stable conformation.

TABLE 11. DIFFERENCE OF $(2J_{ij}-K_{ij})$ BETWEEN 0° AND 90° OF N_2H_2

	1	2	3	4	5(*n*)	6(*n*)
1	−0.06	+0.11	−0.01	−0.07	−0.10	−0.20
2		+0.17	+0.18	+0.16	+0.70	+0.07
3			+0.23	−0.10	−0.03	−0.83
4				0.00	+0.24	−0.32
5(*n*)					−0.12	+0.26
6(*n*)						−0.41

(*n*): (*n*) denotes a lone-pair MO.

Comparing Tables 10 and 11, we can also see the following relations with regard to the different contributions of the electronic interaction term $(2J_{ij}-K_{ij})$ to the energies of N_2H_2 and N_2H_4. The 5th and 6th raws and columns of Table 11 are referred to the lone-pair levels of N_2H_2. Among the elements concerned with the lone-pair levels of N_2H_2,[25] negative values are more often seen than in the case of N_2H_4 in Table 10. In fact, the sum of the elements concerning the lone-pair MO's in Tables 10 and 11 is 2.37 eV (repulsive) for N_2H_4 and −0.74 eV for N_2H_2. From these discussions, it may be concluded that one of the main factors in the instability of N_2H_4 at $\phi=0°$ is the lone-pair interaction or the electrostatic interaction in the lone-pair MO's.

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The calculations were carried out on the HITAC 5020 computer at the Computation Center of the University of Tokyo.

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[22] A parallelism between ΔV_{nn} and ΔW was also seen in the calculation of *cis*- and *trans*- butadienes and glyoxals (Ref. 23).

[23] H. Kato, H. Konishi, H. Yamabe and T. Yonezawa, This Bulletin, **40**, 2761 (1967).

[24] Fink and Allen also pointed out, in their SCF calculation of H_2O_2, the unparallel behavior of the sum of the orbital energies and the total energy. They said that this may be due to the highly localized ionic character associated with two sets of lone pairs in H_2O_2 (Ref. 9).

[25] For N_2H_2, the difference between 0° and 180° is calculated as follows: $\Delta(2J_{ij}-K_{ij})=(2J_{ij}-K_{ij})$(at 0°) $-(2J_{ij}-K_{ij})$(at 180°).