Photoelectron Spectroscopic Study of Skew Compounds. III. *N,N'*-Dimethylhydrazine, Dimethyl Peroxide, and Dimethyl Disulfide[1)]

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He I photoelectron spectra of $CH_3HNNHCH_3$, $(CH_3)_2O_2$, and $(CH_3)_2S_2$ have been measured and the spectra below 18 eV have been resolved into nine ionization bands corresponding to p-type localized molecular orbitals. Orbital assignments of the resulting vertical ionization energies have been carried out with CNDO/2 calculations in which orbital energies were calculated as a function of the dihedral angle in the region 0—180 °. The separation of the nonbonding photoelectron bands suggests that $CH_3HNNHCH_3$ exists in outer-inner skew form, whereas $(CH_3)_2O_2$ is in *trans* form. The sum rule consideration previously proposed by the present authors has been applied to the compounds studied here. The total sum of the vertical ionization energies in the p-type region for each compound has been well reproduced in terms of appropriate empirical parameters based on the photoelectron spectra of simple molecules. The effects of methyl substitution on the ionization-energy total sums for N_2H_4, H_2O_2, and H_2S_2 have been found to be very similar to those for ethane and ethylene.

Previously, on the basis of Walsh-type diagrams, the present authors have studied the He I photoelectron spectra of the simplest skew compounds, hydrazine[3)] and hydrogen peroxide.[4)] From these photoelectron studies,[3,4)] it was indicated that the whole of the spectra may be interpreted in terms of possible dihedral angles through semi-empirical calculations and that the splittings of the ionization bands corresponding to the nonbonding orbitals largely depend on the dihedral angles.[5)] In the present work, we have extended our photoelectron study to symmetric methyl-disubstituted skew compounds, $CH_3HNNHCH_3$, CH_3OOCH_3, and CH_3SSCH_3, to analyze their full He I spectra.

A high-resolution photoelectron spectroscopy using He I (584 Å) line is now well known as a powerful method to study valence orbital structure.[6)] Recently, dependences of the dihedral angle on nonbonding splittings in skew compounds including alkyl hydrazines,[7,8)] disulfides,[9–11)] and peroxides[12)] have been received much attention in molecular photoelectron spectroscopy. Recently, Rademacher[7)] and Nelsen *et al.*[8)] have studied photoelectron nonbonding splittings for a variety of alkyl hydrazines; Wagner and Bock[9)] and Baker *et al.*[10)] for several alkyl disulfides; Colton and Rabalais[11)] for S_2Cl_2, S_2Br_2, and $(CH_3)_2S_2$; and Batich and Adam[12)] for mono- and di-*tert*-butyl peroxide. Earlier He I photoelectron works of $CH_3HNNHCH_3$ and $(CH_3)_2S_2$ were carried out by Dewar *et al.*[13)] and Frost *et al.*,[14)] respectively, using a retarding grid technique. Kroto and Suffolk[15)] have recently reported a high-resolution He I spectrum of $(CH_3)_2S_2$. Most of these authors[7–15)] have also carried out semi-empirical SCF MO calculations to interpret the photoelectron spectra. Very recently, Davies[16)] has carried out *ab initio* calculations for H_2O_2 and H_2S_2 to interpret the available photoelectron data. Apart from the theoretical studies associated with photoelectron spectra, many other theoretical treatments for simple skew compounds have been carried out to study angular dependences of electron density, total energy, transition energy, nonbonding interaction, rotational barrier, *etc.*[17,18)]

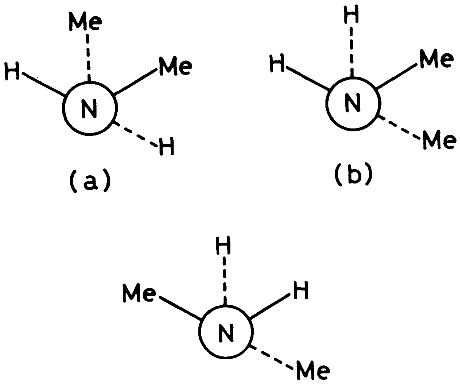

Fig. 1. *Gauche* forms of $CH_3HNNHCH_3$: (a) inner-inner form, (b) outer-inner form, (c) outer-outer form.

Conformation of $CH_3HNNHCH_3$, $(CH_3)_2O_2$, and $(CH_3)_2S_2$ have been studied by several workers.[19–21)] Aston *et al.*[19)] suggested for $CH_3HNNHCH_3$ that its entropy data may be interpreted with either a single outer-inner skew form or a 70%: 30% mixture of the outer-outer and outer-inner skew forms which are shown schematically in Fig. 1. A recent infrared and Raman study by During and Harris[20)] indicated that $CH_3HNNHCH_3$ in the liquid phase consists of a mixture of *gauche* forms. For $(CH_3)_2S_2$, an experimental value of 84°42′ for the dihedral angle was obtained by Sutter *et al.*[21)] using a microwave technique. There are no available data for the dihedral angle for $(CH_3)_2O_2$.

Under these circumstances, we considered it interesting to obtain conformational information from He I photoelectron spectra for the skew compounds studied here. From previous He I photoelectron studies of several series of aliphatic organic compounds, Kimura *et al.*[22)] have indicated that the total sum of vertical ionization energies in the p-type region for each molecule may be reproduced in terms of vertical ionization energies of simple molecules. Therefore, such a sum rule consideration may be interesting for the compounds studied.

Experimental

Measurements of He I photoelectron spectra were carried out with the high-resolution photoelectron spectrometer used previously.[22] Calibration of the ionization energy scale was carried out using known ionization energies of Xe as an internal standard.[23] Gaseous samples were introduced through a vacuum glass line with a teflon needle valve. No metal tube was used to avoid decomposition.

sym-Dimethylhydrazine was librated from commercial dihydrochloride salt in aqueous alkaline solution, and then was dehydrated by barium oxide and finally distilled in vacuum. Dimethyl peroxide was prepared from dimethyl sulfate and hydrogen peroxide according to the method described by Hanst and Calvert[24] and purified by distillation in vacuum. Commercial dimethyl disulfide was purified by distillation in vacuum.

Theoretical Calculations

We carried out SCF MO calculations for $CH_3HNNHCH_3$, $(CH_3)_2O_2$, $(CH_3)_2S_2$, and H_2S_2, using the CNDO/2 method with the same parameterization as in the original paper.[25] The geometrical parameters used were taken from available structural studies,[26–28] which are summarized in Table 1. The CNDO/2 calculations of $(CH_3)_2O_2$, $(CH_3)_2S_2$, and H_2S_2 were performed for various dihedral angles from 0 to 180° with an interval of 10°. For $CH_3HNNHCH_3$, the calculations were carried out for the following conformations: 1) *cis* form, C_2; 2) *trans* form, C_2; 3) inner-inner skew form, C_2; 4) outer-inner skew form, C_1; and 5) outer-outer skew form, C_2. We used a FACOM-230/60 digital computer at the Computing Center of Hokkaido University.

Table 1. Geometrical parameters

$CH_3HNNHCH_3$[26]	$(CH_3)_2O_2$[27]
$r_{NN}=1.45$ Å	$r_{OO}=1.475$ Å
$r_{NC}=1.47$ Å	$r_{OC}=1.445$ Å
$r_{NH}=1.04$ Å	$r_{CH}=1.09$ Å
$r_{CH}=1.09$ Å	$\angle OOC=105°$
$\angle NNC=110°$	$\angle OCH=109°28'$

$(CH_3)_2S_2$[21]	H_2S_2[28b]
$r_{SS}=2.038$ Å	$r_{SS}=2.055$ Å
$r_{SC}=1.810$ Å	$r_{SH}=1.352$ Å
$r_{CH}=1.09$ Å	$\angle SSH=91°57'$
$\angle SSC=102°48'$	
$\angle SCH=109°28'$	

Results

The He I photoelectron spectra of $CH_3HNNHCH_3$, $(CH_3)_2O_2$, and $(CH_3)_2S_2$ are illustrated in Figs. 2—4, respectively. According to our previous photoelectron studies of various series of aliphatic compounds,[22] all the photoelectron bands due to p-type localized molecular orbitals (LO's) are located below about 18 eV. The same situation may also occur for the compounds studied. As done previously,[22] in the present work, the resolution of the photoelectron spectra into individual bands was carried out on the basis of 1) spectral shape (maxima and shoulders), 2) the number of p-type LO's, and 3) the sum rule consideration. The numbers of p- and s-type LO's for several related compounds are summarized in Table 2, from which it is seen that there are five p-type LO's in N_2H_4, H_2O_2, and H_2S_2 and nine in the methyl-disubstituted compounds. The p-type bands in the photoelectron spectra

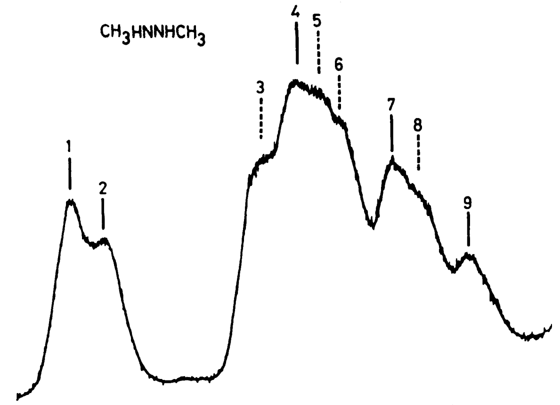

Fig. 2. He I photoelectron spectrum of $CH_3HNNHCH_3$.

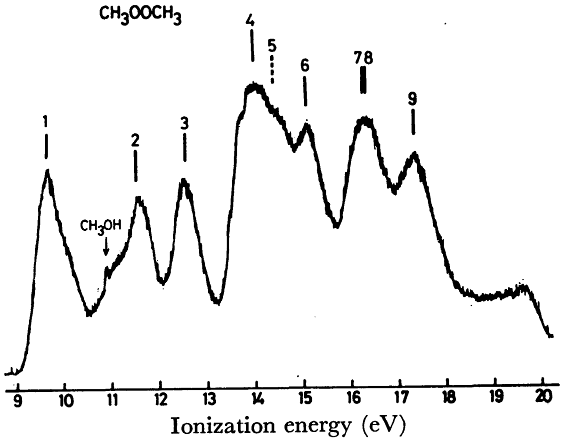

Fig. 3. He I photoelectron spectrum of $(CH_3)_2O_2$.

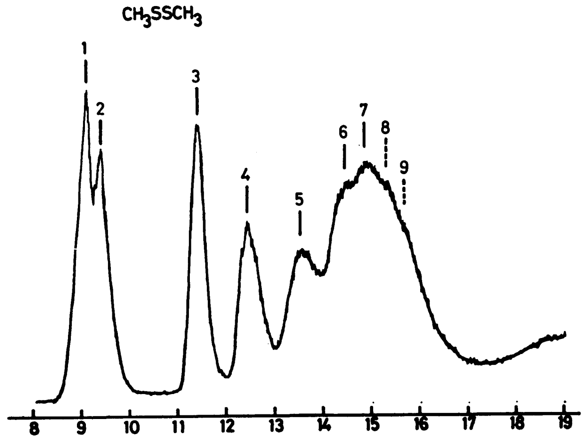

Fig. 4. He I photoelectron spectrum of $(CH_3)_2S_2$.

Table 2. Numbers of p- and s-type LO's[a)]

	p-type LO's[b)]						s-type LO's		
	n_X	σ_{XX}	σ_{XC}	σ_X'	π_{CH_3}	N_P	s_X	s_C	N_S
N_2H_4	2	1		2		5	2		2
H_2O_2	2	1		2		5	2		2
H_2S_2	2	1		2		5	2		2
$CH_3HNNHCH_3$	2	1	2		4	9	2	2	4
$(CH_3)_2O_2$	2	1	2		4	9	2	2	4
$(CH_3)_2S_2$	2	1	2		4	9	2	2	4

a) X=N, O, and S. N_P and N_S represent the total numbers of p- and s-type LO's respectively. b) σ_X' represents σ_{NH_2}, σ_{OH}, and σ_{SH} when X=N, O, and S, respectively.

Table 3. Vertical ionization energies obtained from the He I photoelectron spectrum and MO assignments based on CNDO/2 calculations for $CH_3HNNHCH_3$

	Vertical IE (eV)	MO assignment (CNDO/2) (outer-inner form)		
		Symmetry	Character	Energy (eV)[a)]
I_1	9.02	a	n_N^+	−9.19
I_2	9.69	b	n_N^-	−9.80
I_3	13.0_0	a	σ_{NN}	−11.92
I_4	13.70	b	σ_{NC}^-	−13.92
I_5	14.2_0	a	σ_{NC}^+	−14.94
I_6	14.6_0	b	π_{CH_3}	−15.37
I_7	15.70	a	π_{CH_3}	−18.21
I_8	16.3_0	b	π_{CH_3}	−19.48
I_9	17.27	a	π_{CH_3}	−21.03

a) Reduced by 4 eV.

Table 4. Vertical ionization energies obtained from the He I photoelectron spectra of $(CH_3)_2O_2$ and $(CH_3)_2S_2$ and orbital assignments deduced mainly from CNDO/2 calculations[a)]

	$(CH_3)_2O_2$			$(CH_3)_2S_2$		
	Vertical IE (eV)	MO assignment[b)] $\phi=180°$		Vertical IE (eV)	MO assignment $\phi=84°42'$	
		Sym.	Character		Sym.	Character
I_1	9.71	b_g	n_O^-	8.96	a	n_S^+
I_2	11.61	a_u	n_O^+	9.26	b	n_S^-
I_3	12.58	a_g	σ_{OO}	11.26	a	σ_{SS}
I_4	14.02	a_g	σ_{OC}^+	12.31	b	σ_{SC}^-
I_5	14.4_5	b_u	π_{CH_3}	13.42	a	σ_{SC}^+
I_6	15.08	b_g	π_{CH_3}	14.3_5	b	π_{CH_3}
I_7	16.3_0	b_u	σ_{OC}^-	14.7_5	a	π_{CH_3}
I_8	16.3_0	a_g	π_{CH_3}	15.1_5	b	π_{CH_3}
I_9	17.34	a_u	π_{CH_3}	15.5_5	a	π_{CH_3}

a) For orbital energies of the CNDO/2 calculations, see the diagrams in Fig. 5. b) The assignments for the second and third photoelectron bands are based on the consideration of the nonbonding splitting.

in Figs. 2—4 are indicated by solid and broken lines, the numbering of ionization bands being also shown. The vertical ionization energies thus obtained for $CH_3HNNHCH_3$ are summarized in Table 3 together with the MO assignments obtained from the CNDO/2 calculations, while the vertical ionization energies of $(CH_3)_2O_2$ and $(CH_3)_2S_2$ are shown in Table 4.

The Walsh-type diagrams[29)] based on the CNDO/2 calculations for $(CH_3)_2O_2$ and $(CH_3)_2S_2$ are illustrated in Fig. 5, in which the calculated orbital energies are plotted against the dihedral angle.

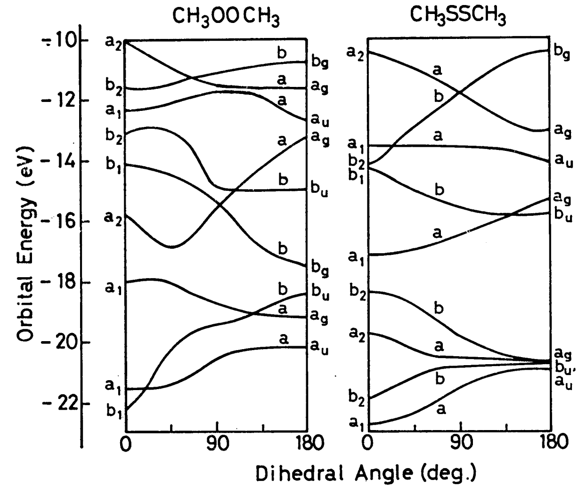

Fig. 5. Walsh-type orbital energy diagrams for $(CH_3)_2O_2$ and $(CH_3)_2S_2$, constructed on the basis of CNDO/2 calculations. (Energies for $(CH_3)_2O_2$ were reduced by 4 eV.)

Discussion

First we review the valence orbital structure of the simple skew compounds, N_2H_4, H_2O_2, and H_2S_2, using the available He I photoelectron spectra[3,4,9b)] shown in Fig. 6 as well as Walsh-type orbital energy diagrams shown in Fig. 7, in which the diagrams of N_2H_4 and H_2O_2 were previously reported[3,4)] and that of H_2S_2 was obtained from the present CNDO/2 calculations. It is seen that the orbital diagrams in Fig. 7 have the

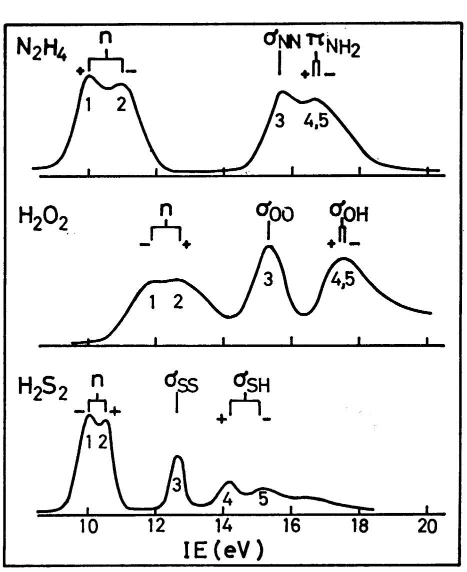

Fig. 6. Schematic drawing for the He I photoelectron spectra of N_2H_4, H_2O_2, and H_2S_2 reported in Refs. 3, 4, and 9b, respectively.

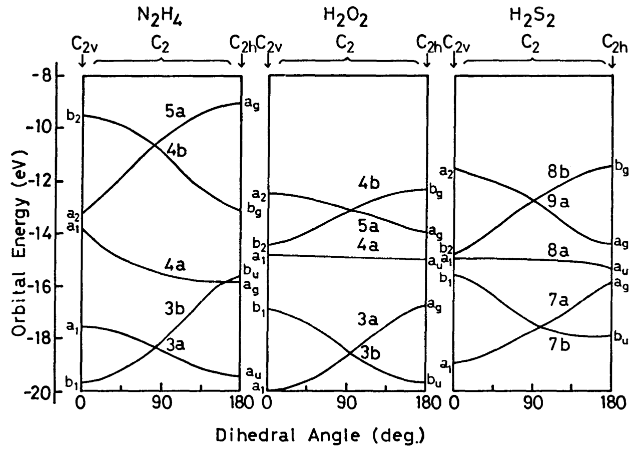

Fig. 7. Walsh-type orbital energy diagrams for N_2H_4, H_2O_2, and H_2S_2, constructed on the basis of CNDO/2 calculations. (Energies were reduced by 4 eV.)

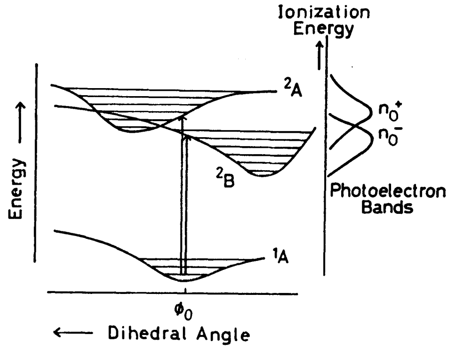

Fig. 8. Schematic drawing that explains the broadening of the nonbonding photoelectron bands of H_2O_2, using the potential curves of the ground and the ionic states expressed as a function of the dihedral angle. (ϕ_0 represents the equilibrium skew angle of the ground state molecule.)

following characteristics. 1) The two highest curves due to the ± combinations of the nonbonding orbitals cross each other at about 90°, the splitting being closely associated with the dihedral angle. Such angular dependences of the nonbonding orbital splitting have previously been reported by Yonezawa *et al.*[17] 2) The third curves due mainly to the N–N, O–O, and S–S bonds are quite insensitive to the dihedral angle. 3) The fourth and fifth curves also cross each other at about 90°.

Since experimental dihedral angles of 90—120° have been reported for N_2H_4, H_2O_2, and H_2S_2 from structural analysis studies,[30] it is seen from the Walsh-type diagrams in Fig. 7 that the orbital orderings are N_2H_4 [3a, 3b, 4a, 4b, and 5a], H_2O_2 [3b, 3a, 4a, 5a, and 4b], and H_2S_2 [7b, 7a, 8a, 9a, and 8b]. The difference in the orbital symmetry between N_2H_4 and H_2O_2 are due to the relative orientation of the nonbonding orbitals with respect to the C_2 axis. The recent *ab initio* calculations of Davies[16] gave rise to slightly different assignments that the above order of the 3b and 3a levels in H_2O_2 and that of the 7b and 7a levels in H_2S_2 are reversed. It should be mentioned that the experimental nonbonding splittings of N_2H_4, H_2O_2, and H_2S_2 (0.73,[3] 1.00,[4] and 0.27 eV,[9b] respectively) may be approximately reproduced by the CNDO/2 calculations using the available dihedral angles.

The photoelectron nonbonding bands in Fig. 6 are structureless and much broader compared with usual sharp nonbonding bands of aliphatic alcohols and amines.[6] It may be pointed out that the broadening of the nonbonding bands of the skew compounds may be interpreted in terms of differences in geometry between the ground and the ionized states. Since the original study by Walsh,[19] many workers have published qualitative and quantitative MO studies[31] using Walsh diagrams. Combining a ground-state orbital correlation diagram with the Walsh rule, we may qualitatively predict changes in geometry between the ground state and its ionized states. Now let us take H_2O_2 as an example. Ionization of an electron from the 4b orbital whose energy decreases with increasing dihedral angle (Fig. 7) gives rise to the ionized state ^2B which has a potential minimum at a smaller angle than the equilibrium ground-state dihedral angle (ϕ_0). The potential curves of the ground and the ionized states are schematically illustrated as a function of the dihedral angle in Fig. 8. On the other hand, in the case of the ionization from the 5a orbital, a reverse situation may occur, the orbital energy increasing with the dihedral angle (see Fig. 7). Therefore, the resulting potential curve (^2A) should have a minimum at a larger angle than ϕ_0 as shown in Fig. 8. The broadening of the nonbonding bands strongly suggests that the ^2B and ^2A ionized states are quite different in the equilibrium dihedral angle from the ground state.

N,N′-Dimethylhydrazine. The full photoelectron spectrum of $CH_3HNNHCH_3$ (Fig. 2) and its interpretation is reported here for the first time, although experimental nonbonding splittings for many alkyl hydrazines including $CH_3HNNHCH_3$ have previously been reported by Rademacher[7] and Nelsen *et al.*[8] There are only slight differences in vertical ionization energies between the literature values[7,8] and ours for the first two photoelectron bands which may be attributed to the nitrogen nonbonding orbitals.

As shown in Fig. 1, there may be three possible *gauche* configurations (inner-inner, outer-inner, and outer-outer forms). The present CNDO/2 calculations yielded nonbonding splittings of 2.72, 1.89, 0.62, 0.61, and 0.05 eV for *cis*, *trans*, inner-inner, outer-inner, and outer-outer forms, respectively. Our experimental nonbonding splitting was 0.67 eV which is close to the calculated splittings of the inner-inner and outer-inner forms, but largely differs from those of the *cis*, *trans*, and outer-outer forms. A possibility of inner-inner form may also be ruled out because of a steric interaction of the two methyl groups. Therefore, from the consideration of the nonbonding splitting, outer-inner skew form seems to be most plausible for $CH_3HNNHCH_3$.

An early electron diffraction study by Beamer[26] indicated that its experimental results are unfavorable to the *cis* configuration. Aston *et al.*[19] could rationalize the entropy data of $CH_3HNNHCH_3$ in terms of either a single outer-inner (*gauche*) form or a 70% : 30% mixture of the outer-outer and outer-inner forms, respectively. The infrared and Raman study by During and Harris[20] also suggested that the molecule has more than a single form in its liquid and gaseous state. However, in the present study, the photoelectron spectrum may be interpreted in terms of only a single outer-inner form. This is supported by a very recent gas-phase electron diffraction study by Kuchitsu *et al.*[32]

The CNDO/2 results of $CH_3HNNHCH_3$ for the outer-inner form are summarized in Table 3, main orbital characters being also shown. For higher photoelectron bands, the present CNDO/2 calculations of $CH_3HNNHCH_3$ suggest that 1) the third band is of σ_{NN}, 2) the fourth and the fifth band are due to the ± combinations of the σ_{NC} orbitals, and 3) the last four bands are due to the methyl pseudo π orbitals.

Dimethyl Peroxide. For $(CH_3)_2O_2$ there are no available He I photoelectron spectra for comparison. This compound slightly decomposes at room temperature, the major products being methanol and carbon monoxide whose first vertical ionization energies are 10.91 eV[22d] and 14.01 eV,[6] respectively. The shoulder appearing at 10.9 eV in the spectrum may be due to a small amount of the decomposed methanol.

From the spectral shape as well as the number of p-type LO's we concluded that the spectrum below 18 eV in Fig. 3 consists of the nine p-type bands. The first three bands are well separated from one another. The CNDO/2 calculations indicated that the total energy becomes minimum at $\phi=180°$, where the nonbonding splitting amounts to 1.91 eV. This value is in good agreement with the experimental separation between the first and the second band, $11.61-9.71=1.90$ eV (Table 4). On the basis of the nonbonding splitting consideration, we tentatively propose that $(CH_3)_2O_2$ has a planar *trans* form in the gaseous phase. A similar situation was reported to occur for di-*tert*-butyl peroxide by Batich and Adam.[12]

The MO assignments of $(CH_3)_2O_2$ obtained by the CNDO/2 calculations are summarized in Table 4, in which the assignments for the second and the third photoelectron band are based on the consideration of the nonbonding splitting. The CNDO/2 calculations of $(CH_3)_2O_2$ in *trans* form indicated that the σ_{OO} level lies between the two nonbonding levels. This assignment may probably be incorrect, although the calculations gave rise to the reasonable nonbonding splitting, 0.91 eV. As shown in Table 4, we therefore concluded that the third photoelectron band to the σ_{OO} orbital.

Dimethyl Disulfide. The spectrum of $(CH_3)_2S_2$ in Fig. 4 is essentially the same as those previously reported by Kroto and Suffolk,[15] by Wagner and Bock,[9b] and by Colton and Rabalais.[11] However, our spectrum obtained here clearly shows the sixth band (appearing as a bump at 14.4 eV) which has not been pointed out by other workers, and also shows two slight shoulders at about 15.5 eV (indicated by broken lines in Fig. 4). On the basis of the number of p-type LO's in this compound, there should exist nine p-type ionization bands below 16 eV, therefore four ionization bands being located in the 14—16 eV range.

As has already been pointed out,[9b,11,15] the first and the second band of $(CH_3)_2S_2$ are due to the ± combinations of the sulfur nonbonding orbitals. The experimental nonbonding splitting ($9.26-8.96=0.30$ eV) was reproduced at dihedral angles of 84° and 98° in the present CNDO/2 calculations which showed that the total energy becomes minimum at 84°. It is interesting to see that this angle is very close to that (84°42′) determined by a microwave study by Sutter *et al.*[21] The MO symmetries and characters based on the CNDO/2 calculations (at $\phi=84°42'$) are summarized in Table 4. These MO symmetries are consistent with those reported by Wagner and Bock[9b] and Colton and Rabalais.[11]

According to the CNDO/2 calculations, the third inner orbital is of σ_{SS} in character and very insensitive to the variation of the dihedral angle (see Fig. 7). It may be pointed out here that the upper part of the correlation diagram of $(CH_3)_2S_2$ resembles those of H_2O_2, H_2S_2, and N_2H_4, but largely differs from that of $(CH_3)_2O_2$. This difference may be explained in terms of a difference in size between the sulfur 3p and oxygen 2p orbitals. In a photoelectron study by Sweigart and Turner,[33] it has been pointed out in oxygen- and sulfur-containing heterocyclic compounds that orbital interaction between sulfur nonbonding orbitals is mainly through-space interaction, whereas that between oxygen nonbonding orbitals is through bond dominant. Therefore, the difference in the pattern of the orbital energy diagrams between $(CH_3)_2O_2$ and $(CH_3)_2S_2$ in Fig. 5 may be attributed to the differences in the nonbonding orbital interactions.

Sum Rule Consideration. Using the experimental vertical ionization energies, we obtained the sum (T) over all the p-type bands in each compound by

$$T_{\text{expt.}} = \sum_i(-I_i) \qquad (1)$$

The results are summarized in Table 5, being plotted against the number (m) of substituted methyl groups

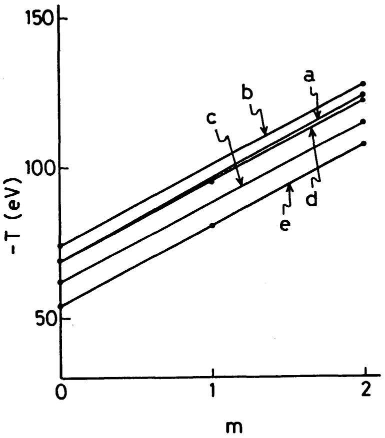

Fig. 9. Plots of the total sums of experimental vertical ionization energies *versus* the number of methyl groups for several series: (a) RHNNHR′, (b) ROOR′, (c) RSSR′, (d) RH_2CCH_2R', and (e) RHC=CHR′, where R=R′=H at $m=0$; R=H and R′=CH_3 at $m=1$; and R=R′=CH_3 at $m=2$.

TABLE 5. COMPARISON OF THE EXPERIMENTAL AND CALCULATED VALUES (in eV) ON THE PARTIAL SUM (P) AND THE TOTAL SUM (T) IN THE SUM RULE CONSIDERATION USING p-TYPE LO'S

(I's)→(p-type LO's)	Expt.	Calcd.
$N_2H_4(C_2)$[a]	$T=-69.5$	-69.5[d]
$(I_1, I_3, I_5)\rightarrow a(n_N, \sigma_{NN}, \pi_{NH_2})$	$P=-42.2$	-42.2
$(I_2, I_4)\rightarrow b(n_N, \pi_{NH_2})$	$P=-27.3$	-27.3
$H_2O_2(C_2)$[b]	$T=-74.5$	-74.5[d]
$(I_2, I_3, I_5)\rightarrow a(n_O, \sigma_{OO}, \sigma_{OH})$	$P=-45.5$	-45.3
$(I_1, I_4)\rightarrow b(n_O, \sigma_{OH})$	$P=-29.1$	-29.2
$H_2S_2(C_2)$[c]	$T=-62.1$	-62.1[d]
$(I_1, I_3, I_5)\rightarrow a(n_S, \sigma_{SS}, \sigma_{SH})$	$P=-37.7$	-37.3
$(I_2, I_4)\rightarrow b(n_S, \sigma_{SH})$	$P=-24.4$	-24.8
$CH_3HNNHCH_3$ (C_1)	$T=-123.5$	-124.0
$(I_1, I_2, I_3,\cdots I_9)\rightarrow(2n_N, \sigma_{NN}, 2\sigma_{NC}, 4\pi_{CH_3})$		
$(CH_3)_2O_2(C_{2h})$	$T=-127.4$	-128.9
$(I_1, I_2, I_6, I_9)\rightarrow$Out-of plane $(2n_O, 2\pi_{CH_3})$	$P=-53.7$	-53.8
$(I_3, I_4, I_5, I_7, I_8)\rightarrow$In-plane $(\sigma_{OO}, 2\sigma_{OC}, 2\pi_{CH_3})$	$P=-73.7$	-75.1
$(CH_3)_2S_2(C_2)$	$T=-114.9$	-115.5
$(I_1, I_3, I_5, I_7, I_9)\rightarrow a\,(n_S, \sigma_{SS}, \sigma_{SC}, 2\pi_{CH_3})$	$P=-63.9$	-64.0
$(I_2, I_4, I_6, I_8)\rightarrow b(n_S, \sigma_{SC}, 2\pi_{CH_3})$	$P=-51.0$	-51.5

a) The I_i's were taken from Ref. 3: $I_1=9.91$, $I_2=10.61$, $I_3=15.61$, $I_4=I_5=16.66$ in eV units. b) The I_i's were taken from Ref. 4: $I_1=11.69$, $I_2=12.69$, $I_3=15.33$, $I_4=I_5=17.4$ in eV units. c) The I_i's were taken from Ref. 9b: $I_1=10.01$, $I_2=10.28$, $I_3=(12.6)$, $I_4=(14.1)$, $I_5=(15.1)$ in eV, where the values in parentheses were estimated from the reported photoelectron spectrum. d) Assumed to be equal to the experimental value.

in Fig. 9. Lines a, b, and c in Fig. 9 are drawn through the plots for the hydrazines, peroxides, and disulfides, respectively, to show variations in the total sum with m. Similar plots (lines d and e) are also shown in Fig. 9 for the methyl-substituted compounds of ethane and ethylene, clearly indicating linear relationships between T and m.[34] Previously, we have reported such linear tendencies for several series of methyl-, chloro-, and bromo-substituted compounds.[22f,g] We may point out here that, as seen from Fig. 9, lines a, b, and c are almost parallel to one another as well as to lines d and e. These experimental results indicate that the methyl-substitution effects of T for the hydrazines, peroxides, and disulfides are very similar to those for the alkanes and alkenes. The difference in T in each methyl substitution is estimated to be 27.0 eV in the hydrazines, 26.4 eV in the peroxides, 26.5 eV in the disulfides, while it is 26.0 eV in the alkanes and 26.8 eV in the alkenes.[22g]

As shown previously,[22] the total sum may be expressed approximately with the sum of empirical orbital energies (ε_i) over all the p-type LO's. The total sums for N_2H_4, H_2O_2, and H_2S_2 may be expressed by

$$T_{\text{calc.}} = 2\varepsilon(n_X) + \varepsilon(\sigma_{XX}) + 2\varepsilon(\sigma_X') \tag{2}$$

where X=N, O, and S, and $\sigma_{X'}$ represents π_{NH_2}, σ_{OH}, and σ_{SH}, respectively. For $CH_3HNNHCH_3$, $(CH_3)_2O_2$, and $(CH_3)_2S_2$, the total sum may be given by

TABLE 6. EMPIRICAL ENERGIES (eV) USED FOR LOCALIZED MOLECULAR ORBITALS (LO'S) IN THE SUM RULE CONSIDERATIONS

$\varepsilon(n_N)=-10.88$	$\varepsilon(\sigma_{NN})=-14.90$
$\varepsilon(n_O)=-12.61$	$\varepsilon(\sigma_{OO})=-16.10$
$\varepsilon(n_S)=-10.48$	$\varepsilon(\sigma_{SS})=-12.31$
$\varepsilon(\sigma_{NC})=-14.42$	$\varepsilon(\pi_{NH_2})=-16.40$
$\varepsilon(\sigma_{OC})=-15.19$	$\varepsilon(\sigma_{OH})=-16.60$
$\varepsilon(\sigma_{SC})=-12.42$	$\varepsilon(\sigma_{SH})=-14.30$
	$\varepsilon(\pi_{CH_3})=-14.30$

$$T_{\text{calc.}} = 2\varepsilon(n_X) + \varepsilon(\sigma_{XX}) + 2\varepsilon(\sigma_{XC}) + 4\varepsilon(\pi_{CH_3}) \tag{3}$$

With Eqs. (2) and (3), we estimated the total sums using the empirical energies ε_i given in Table 6, the resulting $T_{\text{calc.}}$ being also included in Table 5. All the ε values in Table 6 were previously used in the sum rule considerations of alkyl amines,[22d] alcohols,[22d] and thioalcohols,[35] except the $\varepsilon(\sigma_{XX})$'s which were determined so as to reproduce the experimental total sums of the parent compounds. As can be seen from Table 5, it is interesting to note that the experimental total sums for $CH_3HNNHCH_3$, $(CH_3)_2O_2$, and $(CH_3)_2S_2$ are reproduced in terms of the empirical LO energies with errors of 0.5, 1.5, and 0.6 eV, respectively.

Since N_2H_4, H_2O_2, H_2S_2, and $(CH_3)_2S_2$ are of molecular symmetry C_2, the LO's may be divided into two symmetry groups a and b. Therefore, the partial sums, P, belonging to these symmetry species were also calculated, as shown in Table 5. For $(CH_3)_2O_2$ which is proposed here to have C_{2h} symmetry, the LO's may be divided into the out-of-plane and in-plane ones, the resulting partial sums being also shown in Table 5. On the other hand, the experimental partial sums were obtained by appropriate combinations of I_i's on the basis of the MO assignments described before (Tables 3 and 4). Although no orbital interactions were taken into account for each set of equivalent LO's, a considerably good agreement is generally obtained between the experimental and theoretical partial sums as shown in Table 5.

Finally, we may point out the following point in connection with the sum rule considerations. Koopmans' theorem[36] was assumed for selecting the ε_i's from the photoelectron data of the simple molecules. However, if we consider each empirical value (in Table 6) without a negative sign as a hypothetical ionization energy, which is due to the ionization of an electron from the original unperturbed LO, then the present sum rule consideration may be thought as an additivity rule of ionization energy, independent of Koopmans' theorem.

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