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Photoelectron Spectra and Sum Rule Consideration. Higher Alkyl Amines and Alcohols[1]

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Photoelectron spectra of higher alkyl amines and alcohols (Me, Et, *n*- and *i*-Pr, and *n*-Bu) have been measured with the 584 Å line of helium. Seven photoelectron bands corresponding to p-type MO's were identified for ethylamine and ethanol. Nine bands were observed for *n*- and *i*-propylamine and *n*- and *i*-propanol, and eleven for *n*-butylamine and *n*-butanol, in addition to the first C_{2S} bands appearing at about 19 eV. The sum rule previously proposed by Kimura *et al.* has further been applied to the compounds studied here. Total sums of vertical ionization energies in the region below 18 eV have been found to be well reproduced by the sums of appropriate energies estimated for the p-type localized MO's, using Koopmans' theorem. Information on orbital character has also been obtained from the sum rule in each symmetry species.

Recent advances in vacuum-ultraviolet photoelectron spectroscopy have made it possible to determine ionization energies of molecular valence orbitals with high precision and possible to obtain quantitative information on valence orbital energies on the basis of Koopmans' theorem.

Recent photoelectron works by Kimura *et al.*[2-5] have suggested that "sum rule" holds for vertical ionization energies to a considerably wide extent. Briefly speaking, for each alkyl halide, a total sum of experimental vertical ionization energies below about 17 eV was well reproduced by a simple summation of empirical energy values assumed for p-type localized MO's, using Koopmans' theorem. It should be mentioned that the empirical values used in those works were estimated on the basis of accurate photoelectron data of simple related molecules. In the present work, we have considered it very interesting to investigate how far such a sum rule holds for other kinds of compounds, and have undertaken to study series of alkyl amines and alcohols, by placing major emphasis on the sum rule.

The alkyl amines and alcohols studied here have partly been studied with a retarding grid-type technique for the first time by Al-Joboury and Turner[6,7] and later by Dewar and Worley.[8] Methanol has also been studied by ESCA by Siegbahn *et al.*[9] Recently, high-resolution photoelectron spectra of several alkyl alcohols have been reported by Baker *et al.*[10] and by

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[1] Part 5 of "Photoelectron Spectroscopic Studies."

[2] Part 1: K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, This Bulletin, **46**, 373 (1973).

[3] Part 2: S. Katsumata and K. Kimura, *ibid.*, **46**, 1342 (1973).

[4] Part 3: K. Osafune, S. Katsumata, and K. Kimura, *Chem. Phys. Lett.*, **19**, 369 (1973).

[5] Part 4: T. Yamazaki, S. Katsumata, and K. Kimura, *J. Electron Spectrosc.*, in press.

[6] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

[7] M. I. Al-Joboury and D. W. Turner, *ibid.*, *Ser. B*, 373 (1967).

[8] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

[9] K. Siegbahn *et al.*, "ESCA Applied to Free Molecules," North-Holland Publ. Co., Amsterdam (1969), p. 98.

[10] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).

Robin and Kuebler,[11] and those of methylamine and its related compounds by Cornford *et al.*[12] For higher alkyl amines, however, no high-resolution spectra have been published so far.

Price *et al.*[13] have recently reported He II photoelectron spectra of many organic compounds including methylamine and methanol, and have shown that the photoelectron bands due to 2s electrons of C, N, and O atoms appear in the region from 20 to 40 eV.

On a theoretical side, orbital calculations of methylamine[12,14] and methanol[8,9,11,15] have been carried out by Fink and Allen (*ab initio*),[14,15] Dewar and Worley (MINDO),[8] Siegbahn *et al.* (CNDO),[9] Cornford *et al.* (INDO),[12] and Robin and Kuebler (GTO).[11] According to these theoretical treatments, the valence orbital structures of methylamine and methanol have well been established to be (1a″)(5a′)(6a′)(2a″)(7a′) and (5a′)(1a″)(6a′)(7a′)(2a″), respectively. For the higher alkyl compounds, no such orbital structures have been reported.

Experimental

Commercial samples of the alkyl amines and alcohols were used after purification. Measurements of photoelectron spectra were carried out several times for each compound with a JASCO PE-1 high-resolution photoelectron spectrometer described before,[2] using He 584 Å resonance line. Calibration of an ionization energy scale was carried out using known ionization energies of Xe as a standard substance.

Results

Photoelectron spectra obtained for the amines and alcohols in the region below about 20 eV are shown in Fig. 1 (where only those of *n*-butylamine and *n*-butanol are not shown), no distinct vibrational structure being observed. As seen from Fig. 1, methylamine shows five bands which are clearly separated from one another and well correspond to those reported by Cornford *et al.*[12] For ethylamine, a total of seven bands including a slight shoulder at 13.8 eV were distinguished. This shoulder was carefully checked to be correct in the present measurement, because it is missing in literature. Ten and twelve bands were identified for propylamines and *n*-butylamine, respectively.

The spectrum of methanol consists of five bands, while that of ethanol shows six maxima and one slight shoulder at about 14.5 eV, which we consider as one of the ionization bands. In addition to seven bands reported previously for *n*-propanol by Baker *et al.*,[10] we observed two more bands appearing as slight shoulders at about 13.4 and 15.3 eV, and a maximum at 19.51 eV, so that a total of ten bands were identified in the region studied here. Similarly, for *i*-propanol, a slight shoulder at about 14 eV and a maximum at 19.52 eV were observed in addition to the bands already reported.[10] Twelve bands were found for *n*-butanol, including five new bands not reported previously.

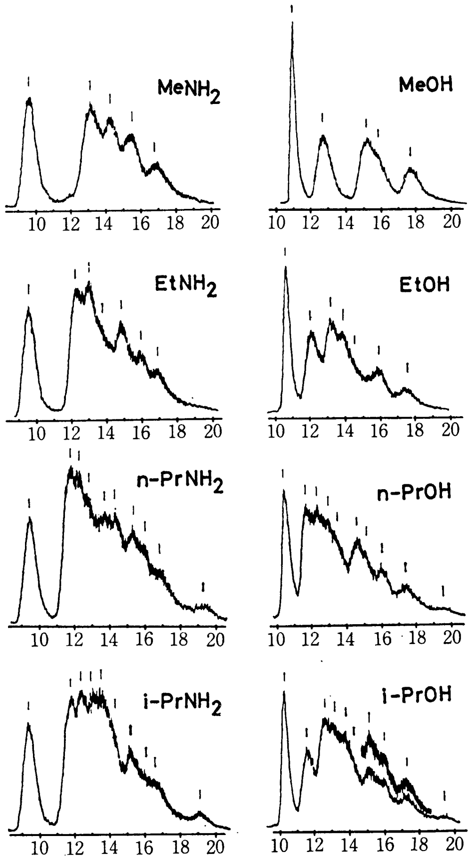

Fig. 1. Photoelectron spectra of alkyl amines and alcohols (methyl, ethyl and *n*- and *i*-propyl). Abscissas are in eV units. Vertical lines indicate the locations of the vertical ionization energies given in Tables 1 and 2.

Vertical ionization-energy (IE) values thus obtained from the maxima and shoulders of the photoelectron spectra are summarized in Tables 1 and 2. The IE values estimated from the shoulders are somewhat uncertain, which are shown in parentheses.

TABLE 1. VERTICAL IE'S OF METHYLAMINE AND METHANOL (in eV)

	MeNH$_2$			MeOH		
	This work	Other works[a]		This work	Other works[a]	
		Ref. 12	Ref. 14		Ref. 10	Ref. 11[b]
I_1	9.64(7a′)	7.9	(7a′)	10.94(2a″)	10.96	10.96(2a″)
I_2	13.22(2a″)	13.2	(2a″)	12.68(7a′)	12.72	12.62(7a′)
I_3	14.42(6a′)	14.5	(6a′)	15.19(6a′)	15.15	15.21(6a′)
I_4	15.45(5a′)	15.6	(5a′)	15.66(1a″)	15.55	15.64(1a″)
I_5	16.85(1a″)	17.1	(1a″)	17.50(5a′)	17.50	17.62(5a′)

a) High-resolution data.
b) Also, Refs. 9 and 15 for theory.

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[11] M. B. Robin and N. A. Kuebler, *J. Electron Spectry.*, **1**, 13 (1972—1973).

[12] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **49**, 1135 (1971).

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[14] W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2276 (1967).

[15] W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261 (1967).

TABLE 2. VERTICAL IE'S OF HIGHER ALKYL AMINES AND ALCOHOLS (in eV)[a)]

	$EtNH_2$	n-$PrNH_2$	i-$PrNH_2$	n-$BuNH_2$	EtOH		n-PrOH		i-PrOH		n-BuOH	
	This work	This work	This work	This work	This work	Other work[10)]	This work	Other work[10)]	This work	Other work[10)]	This work	Other work[10)]
I_1	9.50	9.44	9.31	9.40	10.64	10.65	10.49	10.48	10.36	10.42	10.37	10.37
I_2	12.26	11.63	11.79	11.41	12.18	12.20	11.70	11.73	11.75	11.71	11.49	11.48
I_3	12.97	12.24	12.38	11.86	13.21	13.31	12.24	12.34	12.58	12.68	11.80	11.95
I_4	(13.8_0)	(13.0_2)	13.06	(12.2_3)	13.86	13.82	12.79	13.04	13.06	13.08	12.30	12.25
I_5	14.84	13.55	13.62	12.87	(14.5_5)		(13.4_4)		13.66	13.75	12.82	12.55
I_6	15.80	14.19	(14.1_0)	13.33	15.85	15.85	14.52	14.60	(14.0_0)		13.46	13.55
I_7	16.77	15.11	15.16	14.13	17.35	17.35	(15.3_2)		15.11	15.14	(14.1_3)	
I_8		15.84	(16.0_0)	14.74			16.03	16.00	15.88	15.80	14.91	15.10
I_9		16.70	16.55	15.26			17.23	17.14	17.22	17.20	15.36	
I_{10}		[19.32]	[19.16]	16.02			[19.51]		[19.52]		16.00	
I_{11}				16.76							17.14	
I_{12}				[18.93]							[19.19]	

a) Only high-resolution data are shown. Robin and Kuebler[11)] also report I_1 values for ethanol (10.62 eV), n-propanol (10.50 eV) and i-propanol (10.42 eV). Values in parentheses are shoulders and those in square brackets show the C_{2s}-orbital bands.

Discussion

Photoelectron Bands and Ionization Energy Data. Most of the amines and alcohols studied here have previously been studied with a retarding-potential technique.[6-8)] Agreements between the high-resolution and the retarding-potential IE's are not always good and some values are lacked in the latter. The high-resolution data already reported for the alkyl amines and alcohols[10,12)] are compared in Tables 1 and 2. As far as comparison is possible in Tables 1 and 2, the present experimental IE's are generally in good agreement with the literature values, although some IE values are missing in the previous works.[10)]

It should be pointed out that in each compound the number of the photoelectron bands observed here in the region below 18 eV is in accord with the number of p-type localized MO's. In fact, there should exist five, seven, nine, and eleven p-type localized MO's in the methyl, ethyl, n- and i-propyl and n-butyl compounds, respectively. The highest ionization-energy bands appearing at about 19 eV for the propyl and butyl compounds should be attributed to the first C_{2s} bands, since these bands correspond to the C_{2s} bands of propane and butane observed at about 19 eV by Potts *et al.*[13)] using a He II source. According to these authors,[13)] the first C_{2s} band of ethane appears at about 20.3 eV, and the O_{2s} band of methanol as well as the N_{2s} band of methylamine appear in the region higher than 20 eV.

In our previous works of higher alkyl halides,[2,5)] we have identified all the p-type bands appearing in the He I region, which are the halogen nonbonding orbitals, the C–C and C–halogen bonding orbitals, and the methyl- and methylene-group pseudo-π orbitals. A similar situation can be expected to occur in the alkyl amines and alcohols. Namely, the photoelectron bands are expected to correspond to the O and N nonbonding (n) orbitals, the C–C, C–O, C–N, and O–H σ orbitals, and the pseudo-π orbitals of the CH_3–,–CH_2–, and NH_2–groups.

Experimental Total Energies for p-Type Orbitals. Assuming Koopmans' theorem, a total sum of MO energies are given by

$$T = -\sum_i I_i \tag{1}$$

where I_i denotes the ith ionization energy. The 2s-type ionization energies (I_{10} for propylamines and propanols, I_{12} for n-butylamine and n-butanol) are removed in the calculations of the total sums. The results of such total sums for all the compounds studied here are summarized in Table 3, indicating that differences in T between two successive alkyl anologues approximately equal one another with an average value of $\Delta T = -26.04 \pm 0.25$ eV. This value should correspond to the orbital-energy change due to the substitution by the –CH_2– group in alkyl compounds.

TABLE 3. THE TOTAL ORBITAL ENERGIES (T, in eV) OF THE p-TYPE MO'S FOR THE ALKYL AMINES AND ALCOHOLS, OBTAINED ON THE ASSUMPTION OF KOOPMANS' THEOREM

Alkyl amines	T	ΔT	Alkyl alcohols	T	ΔT
$MeNH_2$	−69.58	−26.36	MeOH	−71.97	−25.67
$EtNH_2$	−95.94	−25.78	EtOH	−97.64	−26.12
n-$PrNH_2$	−121.72	−26.29	n-PrOH	−123.76	−26.02
(i-$PrNH_2$)	(−121.97)		(i-PrOH)	(−123.62)	
n-$BuNH_2$	−148.01		n-BuOH	−149.78	
		ΔT (average) = −26.04±0.25			

Using vertical IE's obtained for twelve alkyl halides (RX: R=Me to *n*-Bu; X=Cl, Br, I),[2] an average value of $\Delta T=-26.07\pm0.47$ eV was obtained, in excellent agreement with the above value (−26.04 eV). Furthermore, using IE values reported for methane, ethane, propane, isobutane, and neopentane,[16] an average value of −26.0 eV was obtained for ΔT, again very close to the above. Therefore, the ΔT value −26.04 eV obtained here may undoubtedly be allotted to the p-type localized orbitals consisting of the CC σ and CH_2 pseudo-π orbitals. In fact, it is interesting to see that the ΔT value is almost equal to the sum of −11.75 and −14.30 eV which have previously been proposed for σ_{CC} and π_{CH_2} by the present authors.[2] The comparison of T's in Table 3 also suggests that the present PE measurements were correctly carried out without missing any right bands or taking any wrong bands into account.

It should be pointed out that according to a theoretical study by Hoffmann,[17] $(2n+1)$ p-type MO's of alkanes (C_nH_{2n+2}) are located higher than about −17 eV whereas 2s-type MO's are below about −20 eV. Dewar and Worley[8] have also indicated from their MINDO method that in several alkyl alcohols the number of MO's with ionization energies higher than 20 eV is in agreement with that expected for 2s-type MO's and all the p-type MO's show ionization energies smaller than about 15 eV. These theoretical treatments seem to suggest that 2s- and 2p-type MO's in an alkyl compound may reasonably be distinguished.

TABLE 4. LOCALIZED ORBITAL ENERGIES (in eV) USED FOR PARTIAL AND TOTAL SUMS

$\varepsilon^0(n_N)=-10.80$	$\varepsilon^0(\sigma_{CN})=-14.42$	$\varepsilon^0(\pi_{NH_2})=-15.77$
$\varepsilon^0(n_O)=-12.61$	$\varepsilon^0(\sigma_{CO})=-15.19$	$\varepsilon^0(\sigma_{OH})=-15.57$
$\varepsilon^0(\sigma_{CC})=-11.75$	$\varepsilon^0(\pi_{CH_2})=\varepsilon^0(\pi_{CH_3})=-14.30$	

p-Type Localized MO's. Generally speaking, in a secular equation, the total value of all eigenvalues is equal to the sum over all diagonal elements, independent of off-diagonal elements. Therefore, such a sum rule may approximately be applied to our problem of orbital energies. When a molecule has a certain symmetry, the sum rule holds for orbital energies in each symmetry species, so that such a partial sum is helpful for assigning the observed IE's to MO's. We used empirical values given in Table 4 as localized MO energies which were selected in such that (1) the values for n_N and n_O were taken from the first IE's of ammonia and water, respectively, (2) the values for σ_{CN} and σ_{CO} were from the third IE's of methylamine and methanol, respectively, (3) the values for π_{NH_2} and σ_{OH} were taken so as to reproduce the total experimental orbital energies of methylamine and methanol, respectively, (4) the values for σ_{CC}, π_{CH_3}, and π_{CH_2} were the same as those previously used.[2]

Evaluation of Total Energy Sum for p-Type Orbitals. The total energies of p-type orbitals in alkyl amines ($C_nH_{2n+1}NH_2$) and alkyl alcohols ($C_nH_{2n+1}OH$) may be expressed by

$$T=\varepsilon^0(n_N \text{ or } n_O)+\varepsilon^0(\pi_{NH_2} \text{ or } \sigma_{OH})+\varepsilon^0(\sigma_{CN} \text{ or } \sigma_{CO})$$
$$+(n-1)\varepsilon^0(\sigma_{CC})+(n-1-2m)\varepsilon^0(\pi_{CH_2})$$
$$+(2+2m)\varepsilon^0(\pi_{CH_3}) \qquad (2)$$

where $m=1$ for *i*-propylamine and *i*-propanol and otherwise $m=0$.

TABLE 5. COMPARISON OF THE EXPERIMENTAL PARTIAL AND TOTAL SUMS (in eV) BETWEEN THE CALCULATED ONES

	Exptl	Calcd
Methylamine (C_S)	$T=-69.58$	−69.59
$(I_1, I_3, I_4)\rightarrow a'(n_N, \pi_{CH_3}, \sigma_{CN})$	$P=-39.51$	−39.52
$(I_2, I_5)\rightarrow a''(\pi'_{CH_3}, \pi_{NH_2})$	$P=-30.07$	−30.07
Methanol (C_S)	$T=-71.97$	−71.97
$(I_2, I_3, I_5)\rightarrow a'(\pi_{CH_3}, \sigma_{CO}, \sigma_{OH})$	$P=-45.37$	−45.06
$(I_1, I_4)\rightarrow a''(n_O, \pi'_{CH_3})$	$P=-26.60$	−26.91
Ethylamine	$T=-95.94$	−95.64
gauche-type interaction (C_1)		
$(I_1, I_4, I_6)\rightarrow(n_N, \pi_{CH_2}, \pi_{CH_3})$	$P=-39.10$	−39.40
$(I_2, I_3, I_5, I_7)\rightarrow(\sigma_{CC}, \pi_{CH_3}, \sigma_{CN}, \pi_{NH_2})$	$P=-56.84$	−56.24
trans-type interaction (C_S)		
$(I_1, I_3, I_4, I_5)\rightarrow a'(n_N, \sigma_{CC}, \pi_{CH_3}, \sigma_N)$	$P=-51.11$	−51.27
$(I_2, I_6, I_7)\rightarrow a''(\pi_{CH_2}, \pi'_{CH_3}, \pi_{NH_2})$	$P=-44.83$	−44.37
Ethanol	$T=-97.64$	−98.02
gauche-type interaction (C_1)		
$(I_1, I_3, I_4, I_6)\rightarrow(n_O, \sigma_{CC}, \pi_{CH_3}, \sigma_{CO})$	$P=-53.56$	−53.85
$(I_2, I_5, I_7)\rightarrow(\pi_{CH_2}, \pi_{CH_3}, \sigma_{OH})$	$P=-44.08$	−44.17
trans-type interaction (C_S)		
$(I_2, I_3, I_4, I_7)\rightarrow a'(\sigma_{CC}, \pi_{CH_3}, \sigma_{CO}, \sigma_{OH})$	$P=-56.60$	−56.81
$(I_1, I_5, I_6)\rightarrow a''(n_O, \pi_{CH_2}, \pi'_{CH_3})$	$P=-41.04$	−41.21
n-Propylamine	$T=-121.72$	−121.69
i-Propylamine	$T=-121.97$	−121.69
n-Propanol	$T=-123.76$	−124.07
i-Propanol	$T=-123.62$	−124.07
n-Butylamine	$T=-148.01$	−147.74
n-Butanol	$T=-149.78$	−150.12

The T's calculated from Eq. (2) using the values of Table 4 are shown in Table 5, compared with the corresponding experimental T's. The calculated T's for the higher alkyl amines and alcohols (Table 5) are generally in good agreement with experiment.

Evaluation of Partial Orbital-Energy Sums. Methylamine and methanol are of symmetry C_{2s}, so that their MO's are divided into two groups; one (a') symmetric to the molecular plane and the other (a'') antisymmetric. Interactions in a' in methylamine are considered to occur among the n_N, π_{CH_3}, and σ_{CN}, while the π'_{CH_3} and π_{NH_2} in a'' are expected to mix considerably with each other. As seen from Table 5, the partial sums in a' and a'' for this molecule are in excellent agreement with $-(I_1+I_3+I_4)$ and $-(I_2+I_5)$, respectively, the agreement not only suggesting a validity of the selection of the orbital energy parameters but also providing an information about orbital character. Such orbital interactions are also shown in an energy diagram of Fig. 2, in which the experimental levels are correlated with the initial localized MO's. From the sum rule consideration, the orbital

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[16] J. N. Murrell and W. Schmidt, *J. Chem. Soc., Faraday Trans.*, II, **68**, 1709 (1972).

[17] R. Hoffmann, *J. Chem. Phys.*, **40**, 2047 (1963).

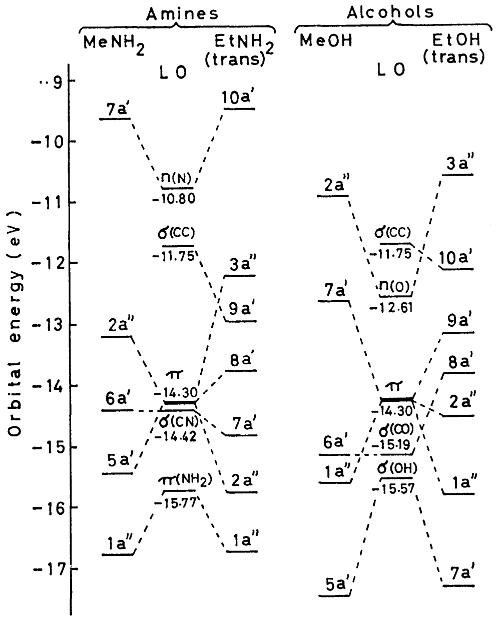

Fig. 2. Energy level diagrams of methylamine, ethylamine, methanol and ethanol. The experimental energy levels are correlated with the initial localized MO levels (I.O).

structure of methylamine may be concluded to be [1a'', 5a', 6a', 2a'', 7a'] in decreasing order of ionization energy. It should be mentioned that this orbital ordering is in completely agreement with the theoretical result reported by Fink and Allen.[14]

For methanol, a valence orbital structure of [5a', 1a'', 6a', 7a', 2a''] has already been established from the theoretical treatments.[9,11,15] It is interesting to see that the same orbital ordering can be obtained from the present calculation of partial sums (Table 5). I_1(2a'') and I_4(1a'') in this molecule result mainly from the conjugative interaction between the n_O and π'_{CH_3} orbitals belonging to a'', while I_2(7a'), I_3(6a'), and I_5(5a') are due to the interaction of the π_{CH_3}, σ_{CO}, and σ_{OH} orbitals. The orbital correlation are also shown in Fig. 2.

Ethylamine and ethanol in gaseous phase are known to exist in *trans* and *gauche* forms from a microwave spectroscopy,[18] although unknown about which form is predominant. In the present work, therefore, orbital assignments for these ethyl compounds were considered in the two types of conformations as shown in Table 5. (The diagram in Fig. 2 for these compounds shows the levels obtained on the basis of the *trans* conformations.) Even in the *gauche* form with no symmetry, orbital interactions seem to divide into two groups; one consisting of the MO's which are approximately in plane with regard to the N–C–C (or O–C–C) plane and the other being approximately out of plane. No partial sums are shown in Table 5 for the propyl and butyl compounds since there are no conformational informations available. Finally, it should be pointed out that, in the case of *trans* ethanol, the 10a' level may be correlated with the σ_{CC} level probably because of the inductive effect of the OH group (Fig. 2).

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[18] E. B. Wilson, *Chem. Soc. Rev.*, **1**, 293 (1972).