2736 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2736—2738 (1975) [Vol. 48, No. 10

Photoelectron Spectroscopic Study of Skew Compounds. Methylhydrazine and Unsymmetrical Dimethylhydrazine

Katsumi Kimura, Shunji Katsumata, and Kazuteru Osafune1)

Physical Chemistry Laboratory, Institute of Applied Electricity, Hokkaido University, Sapporo 060

(Received June 28, 1975)

The He I photoelectron spectra of unsymmetric hydrazines CH_3HNNH_2 and $(CH_3)_2NNH_2$ have been measured and CNDO/2 calculations have been carried out, in which *gauche* (outer- and inner-skew) forms and *trans* form were taken into account for CH_3HNNH_2 and *gauche* and *trans* form for $(CH_3)_2NNH_2$. It has been found that nonbonding splittings in the photoelectron spectra are well reproduced by CNDO/2 calculations with *gauche* forms. The present results of conformation are supported by available conformational studies. The following conclusions have been obtained on orbital assignments of the photoelectron spectra: 1) The first and second bands are due to the methylated and unmethylated nitrogen lone pairs, respectively. 2) The third bands are attributed to the N–N bonding orbitals. 3) The rest of the photoelectron spectra up to 18 eV can be explained in terms of other p-type orbitals (C–N bonding, CH_3 pseudo π, and NH_2 pseudo π).

Previously, the He I photoelectron spectra of typical skew compounds, hydrazine2) and hydrogen peroxide,3) have been interpreted in terms of Walsh-type diagrams based on the CNDO/2 method. The separations of the first two photoelectron ionization bands due to nonbonding orbitals in these skew compounds have well been reproduced by CNDO/2 calculations at available dihedral angles. Recently, for a series of symmetrical dimethyl derivatives of hydrazine, hydrogen peroxide, and hydrogen disulfide, a similar analysis of He I photoelectron spectra4) suggested conformations that CH_3OOCH_3 has a *trans* planar form, while $CH_3HNNHCH_3$ and CH_3SSCH_3 are in *gauche* form. In connection with the previous studies,2–4) in the present work we have extended our photoelectron work to two kinds of unsymmetrical hydrazines in order to study nonbonding splittings as well as variations in inner valence orbitals with possible different conformations.

Nelsen and Buschek5) studied the nonbonding splittings of the photoelectron spectra of CH_3HNNH_2 and $(CH_3)_2NNH_2$ together with many other hydrazines, and indicated from INDO calculations that nonbonding splittings may be interpreted with a dihedral angle of 90°. Independently, Rademacher6) estimated the dihedral angles of various hydrazines by analyzing photoelectron nonbonding splittings. Bodar *et al.*7) earlier suggested in their He I photoelectron spectra of retarding-potential type for hydrazines that the nonbonding splitting reflects the skew angle.

From an entropy consideration, Janz and Russell8) indicated that the gaseous methylhydrazine exists predominantly as an outer-skew form. This compound can exist in either of two possible *gauche* conformations, "outer" or "inner" form. The *gauche* form with the methyl group farthest from the hydrogens of the amino group is called the outer form, while the other is known as the inner form.8) The outer form of methylhydrazine was later supported by an infrared and Raman study by Durig *et al.*9) For $(CH_3)_2NNH_2$ it was also indicated by Durig and Harris10) that the compound mainly exists in *gauche* rather than *trans* form.

Experimental

Measurements of He I photoelectron spectra were carried out with a high-resolution photoelectron spectrometer used previously.2–4) Calibration of the ionization energy scale was carried out using known ionization energies of Xe as an internal standard. Gaseous samples were introduced through a vacuum glass line with a teflon needle valve. The compounds studied are liberated from commercial hydrochloride salts in aqueous alkaline solution, and then were dehydrated by barium oxide and finally distilled in vacuum.

Results and Discussion

The He I photoelectron spectra obtained here for methylhydrazine and unsymmetrical dimethylhydrazine are shown by curves (a) and (b), respectively, in Fig. 1. Since the previous photoelectron works11–14) of various series of alkyl compounds have indicated that

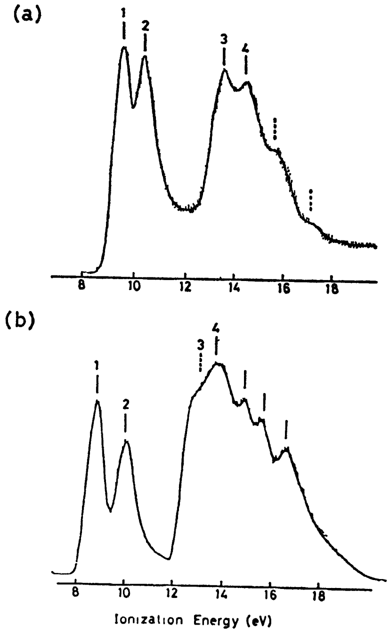

Fig. 1. He I Photoelectron spectra of (a) methylhydrazine and (b) unsymmetric dimethylhydrazine.

all photoelectron bands due to p-type localized molecular orbitals (LO's) are located below about 18 eV, the same situation may be expected to occur in the compounds studied. There are seven and nine p-type LO's in methylhydrazine and unsymmetrical dimethylhydrazine, respectively, the LO's being represented by n_N(nitrogen nonbonding), σ_{NN}(N–N bonding), σ_{CN} (C–N bonding), π_{NH_2}(NH_2 pseudo π), and π_{CH_3}(CH_3 pseudo π) orbitals. From the spectral shapes (maxima and shoulders) of the photoelectron spectra in Fig. 1, six and seven ionization bands can be identified in the region below about 18 eV. However, the remaining p-type bands are concealed under the photoelectron spectra in Fig. 1. The vertical ionization energies obtained from the photoelectron spectra in Fig. 1 are summarized in Table 1.

TABLE 1. VERTICAL IONIZATION ENERGIES (eV) OF METHYLHYDRAZINE AND UNSYMMETRICAL DIMETHYLHYDRAZINE

CH_3HNNH_2	9.36, 10.28, 13.38, 14.32, 15.5[a], 17.1[a]
$(CH_3)_2NNH_2$	8.85, 10.07, 13.0[a], 13.50, 14.75, 15.40, 16.35

a) Shoulder.

The first two vertical ionization energies slightly differ from those reported by Nelsen and Buschek (9.32 and 10.24 eV for CH_3HNNH_2; 8.88 and 10.13 eV for $(CH_3)_2NNH_2$),[5] but our separations (0.92 and 1.22 eV, respectively) are in good agreement with the reported ones (0.92 and 1.25 eV, respectively).[5] For higher ionization energies, there have been reported no high-resolution photoelectron data available for comparison.

In the present work, CNDO/2 calculations[15] were carried out for the outer, inner, and *trans* forms of methylhydrazine and for the *gauche* and *trans* forms of unsymmetrical dimethylhydrazine. Electron diffraction data of Beamer[16] were used for structural parameters. The calculated results of the p-type orbitals are illustrated in the energy level diagrams in Fig. 2, in which main characters are indicated in terms of the p-type LO's. (An ordinary 4 eV correction was made in the calculated energies.) The experimental levels based on Koopmans' theorem[17] are also compared with the calculated levels of the different conformations.

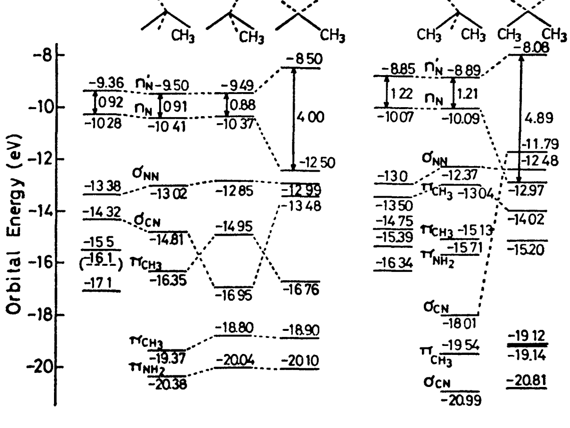

Fig. 2. Experimental and calculated (CNDO/2) energy levels for (a) methylhydrazine and (b) unsymmetric dimethylhydrazine.

Methylhydrazine. As can be seen from Fig. 2, the calculated nonbonding splittings of the outer and inner forms (0.91 and 0.88 eV, respectively) are close to the experimental one (0.92 eV), whereas the calculated splitting of the *trans* form (4.00 eV) is quite large. The comparison of the nonbonding splitting between experiment and theory therefore strongly suggests that this compound exists in the skew rather than *trans* form. This result of conformation is consistent with that of Nelsen and Buschek[5] who interpreted the nonbonding splittings of 21 hydrazines including methylhydrazine in terms of a dihedral angle of 90° using INDO calculations. According to the entropy considerations of Janz and Russell[9] and Durig *et al.*,[10] methylhydrazine mainly exists as an outer form. It would be very difficult to distinguish the outer and the inner form from each other from a photoelectron study.

The CNDO/2 results indicated that the outermost orbital is assigned to the methylated nitrogen lone pair. (Its energy level is represented by n_N' in Fig. 2.) The third and fourth photoelectron bands may correspond to the N–N and C–N bonding orbitals, respectively. It is interesting to note that the σ_{NN} level is almost independent of the dihedral angle. This tendency was previously pointed out in hydrazine.[2]

The fourth band at 14.32 eV may be due to the σ_{CN} LO, close to the 14.42-eV band of methylamine previously assigned to the σ_{CN} LO.[12] As mentioned before, there may be a concealed band in the methylhydrazine spectrum. The 15—18 eV spectrum in Fig. 1(a) should be associated with three p-type LO's (two π_{CH_3}'s and one π_{NH_2}). The position of the concealed band may be estimated on the basis of the photoelectron data of simple molecules. Using the empirical energy parameters previously proposed,[4] we have a value of −96.08 eV for the total energy sum over all the p-type LO's of methylhydrazine. On the other hand, the summation of the experimental vertical ionization energies shown in Table 1 gives rise to 79.9 eV. Therefore, the remaining photoelectron band is expected to appear around 16.1 eV (=96.0—79.9), the corresponding level being shown by a dotted line in Fig. 2. It may be concluded that the 15—18 eV spectrum consists of three ionization bands (two π_{CH_3} and one π_{NH_2}).

Unsymmetrical Dimethylhydrazine. The photoelectron nonbonding splitting again suggests that this compound may exist as a *gauche* rather than *trans* form. It is seen from Fig. 2 that the experimental nonbonding splitting (1.22 eV) is in excellent agreement with that of *gauche* form (1.21 eV). The nonbonding splitting of *trans* form (4.89 eV) is very large compared with that of *gauche* form. According

TABLE 2. COMPARISON OF NONBONDING SPLITTINGS (in eV) BETWEEN EXPERIMENT AND CALCULATION (CNDO/2)

	N_2H_4[2]	H_2O_2[3]	$(CH_3)_2O_2$[4]	CH_3HNNH_2	$(CH_3)_2NNH_2$	$CH_3HNNHCH_3$[4]	$(CH_3)_2S_2$[4]
Exptl.	0.73	1.00	1.90	0.92	1.22	0.67	0.30
CNDO/2	0.60	0.58	1.91	0.88, 0.91[b]	1.21	0.71	0.28
ϕ_0[a]	95°	111°30′	180°	90°	90°	90°	84°42′

a) The dihedral angle used in the CNDO/2 calculations. b) Inner and outer forms, respectively.

to the entropy study of Durig and Harris,[11] the compound exists predominantly as a *gauche* form.

The CNDO/2 calculations indicated that the third and fourth levels may correspond to the σ_{NN} and π_{CH_3} LO's, respectively. The third, 13.0-eV band due to the σ_{NN} LO is fairly close to the 13.38-eV band of methylhydrazine. The fourth, 13.50-eV band is considered to arise from the orbital interaction of two methyl groups.

The sum rule consideration mentioned above may help to estimate the remaining photoelectron bands. The total sum of LO energies is −124.68 eV. On the other hand, the sum of the experimental ionization energies given in Table 1 is 91.9 eV. A difference of 32.7 eV (=124.6—91.9 eV) suggests that there are two additional bands in the region 15—17 eV. In Fig. 2(b), it is not easy to correlate the experimental levels to the five deepest CNDO/2 levels of the *gauche* form which are shown by π_{CH_3}, π_{NH_2}, $\sigma_{CN(-)}$, π_{CH_3}, and $\sigma_{CN(+)}$ in this order. (These characters simply represent the largest contributions in the calculated MO's.) From our experiences,[11–14] however, the p-type LO's of this compound are considered to be $\sigma_{CN(-)}$ and $4\pi_{CH_3}$ instead of $\sigma_{CN(\pm)}$ and $3\pi_{CH_3}$, in addition to n_N', n_N, and π_{NH_2}. This conclusion was also supported by MINDO/2 calculations[18] which were also carried out in the present work. The MINDO/2 results of the *gauche* form showed that the five deepest levels mentioned above correspond to π_{CH_3}, π_{NH_2}, $\sigma_{CN(-)}$, π_{CH_3}, and π_{CH_3} in this order. The $\sigma_{CN(+)}$ orbital was indicated to give the first s-type one. (For methylhydrazine, the MINDO/2 calculations led to the same orbital assignments as the CNDO/2 calculations.) The MINDO/2 calculations were also found to give rise to somewhat smaller nonbonding splittings than the CNDO/2 calculations.

Potts *et al.*[19] indicated in their He II photoelectron spectra that s-type bands appear at 21.9 and 27.5 eV in methylamine, 20.6, 22.4, and 28.0 eV in dimethylamine, and 24.5 eV in hydrazine. The first s-type bands of the methylated hydrazines studied here are therefore expected to appear in the region 20—21 eV.

Table 2 summarizes experimental and calculated nonbonding splittings for the compounds so far studied in this laboratory. It is interesting to note that the experimental nonbonding splittings are well reproduced by CNDO/2 calculations with available skew angles.

References

1) Present address: Government Research Institute of Industry, Tosu-shi, Saga-ken.

2) K. Osafune, S. Katsumata, and K. Kimura, *Chem. Phys. Lett.*, **19**, 369 (1973).

3) K. Osafune and K. Kimura, *ibid.*, **25**, 47 (1974).

4) K. Kimura and K. Osafune, This Bulletin, **48**, 2421 (1975).

5) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973).

6) P. Rademacher, *Angew. Chem. Int. Ed. Engl.*, **12**, 408 (1973).

7) N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. O. Worley, *Tetrahedron*, **26**, 4109 (1970).

8) G. J. Janz and K. E. Russell, *J. Chem. Phys.*, **17**, 1352 (1949).

9) J. R. Durig, W. C. Harris, and D. W. Wertz, *ibid.*, **50**, 1449 (1969).

10) J. R. Durig and W. C. Harris, *ibid.*, **51**, 4457 (1969).

11) K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, This Bulletin, **46**, 373 (1973).

12) S. Katsumata, T. Iwai, and K. Kimura, *ibid.*, **46**, 3391 (1973).

13) K. Kimura, S. Katsumata, T. Yamazaki, and H. Wakabayashi, *J. Electron Spectrosc.*, **6**, 41 (1975).

14) K. Kimura and K. Osafune, *Mol. Phys.*, **29**, 1073 (1975).

15) J. A. Pople and D. L. Beveridge, "Approximate molecular orbital theory," McGraw-Hill, N. Y. (1970).

16) W. H. Beamer, *J. Amer. Chem. Soc.*, **70**, 2979 (1948).

17) T. Koopmans, *Physica*, **1**, 104 (1934).

18) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

19) A. W. Potts, T. A. Williams, and W. C. Price, *Discuss. Faraday Soc.*, **54**, 104 (1972).