n,π-Conjugation in *N*-methylvinylamine. A photoelectron spectroscopic study

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The unstable species *N*-methylvinylamine was prepared by the thermal decomposition of gaseous 2-methylaziridine in a flow system and its UV photoelectron spectrum was recorded. The first two bands were observed at 8.00 and 11.00 eV. The methyl substituent shows the effect of reducing the degree of conjugation between the n_N and π_{CC} orbitals, as revealed by a comparison with the spectrum of the parent compound vinylamine.

Enamines play an important role as intermediate species in many synthetic processes.[1–4] The chemical properties of an enamine are largely dependent on the degree of conjugative interactions involving the n_N orbital and the π_{CC} orbital at the α,β-position. There have been many theoretical and experimental studies on the structural properties of enamines, with emphasis on those aspects which bear direct relationship to the n,π-conjugative interaction. Such aspects include the planarity of enamine molecules,[5,6] the amount of 2s character possessed by the n_N orbital,[7] the separation between the first two ionization energies,[8] the torsional twist around the carbon–nitrogen bond,[9] and n,π-electron interaction as reflected in the shielding of the β-proton in NMR spectra.[10] Most of the experimental studies have been confined to tertiary enamines, which can usually be readily synthesized and are stable toward tautomerism, and relatively few studies were performed on primary or secondary enamines.

The preparation of the simplest but unstable secondary enamine, *N*-methylvinylamine (NMVA), through pyrolysis of 2-methylaziridine, was reported in 1985 along with studies of its microwave[11] and IR[12] spectra. A *cis* conformation was suggested from the rotational constants obtained.[11] From the calculated angle between C–N bond and the NH_2 or $NH(CH_3)$ plane and the frequency values of the out-of-plane NH-wagging, it was inferred that the n,π-conjugation in NMVA must be stronger than that in the parent compound, vinylamine.[12]

In the present work the He(I) photoelectron spectrum of NMVA was investigated with the help of molecular orbital calculations. Comparison with the spectrum of vinylamine reveals a smaller degree of n,π-conjugation in the secondary enamine, contrary to the conclusion based on the IR study.

Experimental

NVMA was generated by the pyrolysis of 2-methylaziridine (MA). The pyrolysis was carried out at a pressure of about 1 Torr in a flow system by passing the MA vapour through a quartz tubing, 40 cm long and 1.1 cm in internal diameter, and lightly packed with quartz wool to improve thermal contact. Heating was achieved by using a tube-oven which was 30 cm in length. One end of the quartz tubing was connected to the inlet system of a Leybold-Heraeus UPG-200 photoelectron spectrometer. The MA sample had 98% purity and was obtained from Aldrich Chemical Company (bp 66–67 °C; lit.,[13] 66–67 °C), it was used without further purification except for initial degassing. No extraneous bands were detected in its photoelectron (PE) spectrum.

Pyrolysis of MA was performed at 750 °C. The main products, identified as NMVA and *N*-methylethylidenimine (MEIM; *vide infra*), could be collected by condensation in a cold trap placed downstream of the heated zone and maintained at the liquid nitrogen temperature. To record the spectra of the individual products, the components in the trapped mixture were released through differential vaporization using a cold bath of N_2/EtOH slurry.

The resolution of the photoelectron spectrometer was about 24–30 meV. Spectra were calibrated with reference to the Ar^+ ($^2P_{\frac{3}{2}}$) and CH_3I^+ ($^2E_{\frac{3}{2}}$) peaks.

Semi-empirical AM1[14] calculations were carried out using MOPAC 6.0 program[15] on a Silicon Graphics workstation, model 4D-20G. *Ab initio* 6-311++G** calculations were performed using the GAUSSIAN 92 program[16] on a NEC SX-1A computer.

Results and discussion

The PE spectrum of MEIM, shown in Fig. 1(*a*), was recorded when the gas was released by differential evaporation from a trapped mixture at −60 °C. The spectrum agreed well with the one published previously.[17] Fig. 1(*b*) shows another spectrum obtained when a gas was released at a bath temperature of −36 °C. It indicates the presence of MEIM as a minor component and another product as the major species. Due to similar volatilities, the two components could not be separated. However, upon removal of the signal due to MEIM through digital subtraction, the resultant spectrum of the 'pure' main species was obtained [Fig. 1(*c*)]. Monitoring of the spectral signal, which diminished with time, indicated that the main species has a lifetime of 20 s. This is approximately the same as the reported lifetime for NMVA.[11,12] The experimental ionization potentials also matched well the calculated orbital energies for NMVA (Koopmans' approximation). The spectrum was thus attributed to the secondary enamine.

The spectrum of NMVA is characterized by two well separated bands at 8.00 and 11.00 eV, followed by a group of higher energy bands which overlap extensively. This feature of the spectrum was predicted by the molecular orbital calculations, the results of which are shown in Table 1. On the basis of the calculations, the first two bands can be assigned to ionizations from the π^-_{CCN} and the π^+_{CCN} orbitals, which respectively arise from the out-of-phase and in-phase combinations between the nitrogen lone-pair (n_N) orbital of the amine moiety and the π_{CC} orbital of the olefin moiety. Note that the first band shows a slightly larger bandwidth than the second band, reflecting the expected shift toward a more planar structure around nitrogen upon removal of an electron from the π^-_{CCN} orbital, which is predominantly n_N in character. The bands at energies higher than 11 eV also have broad bandwidths and are assigned to ionizations from the σ_{CH}, π_{CH_2} and σ_{CN} orbitals.

The gap between the first two bands, 3.00 eV, is indicative

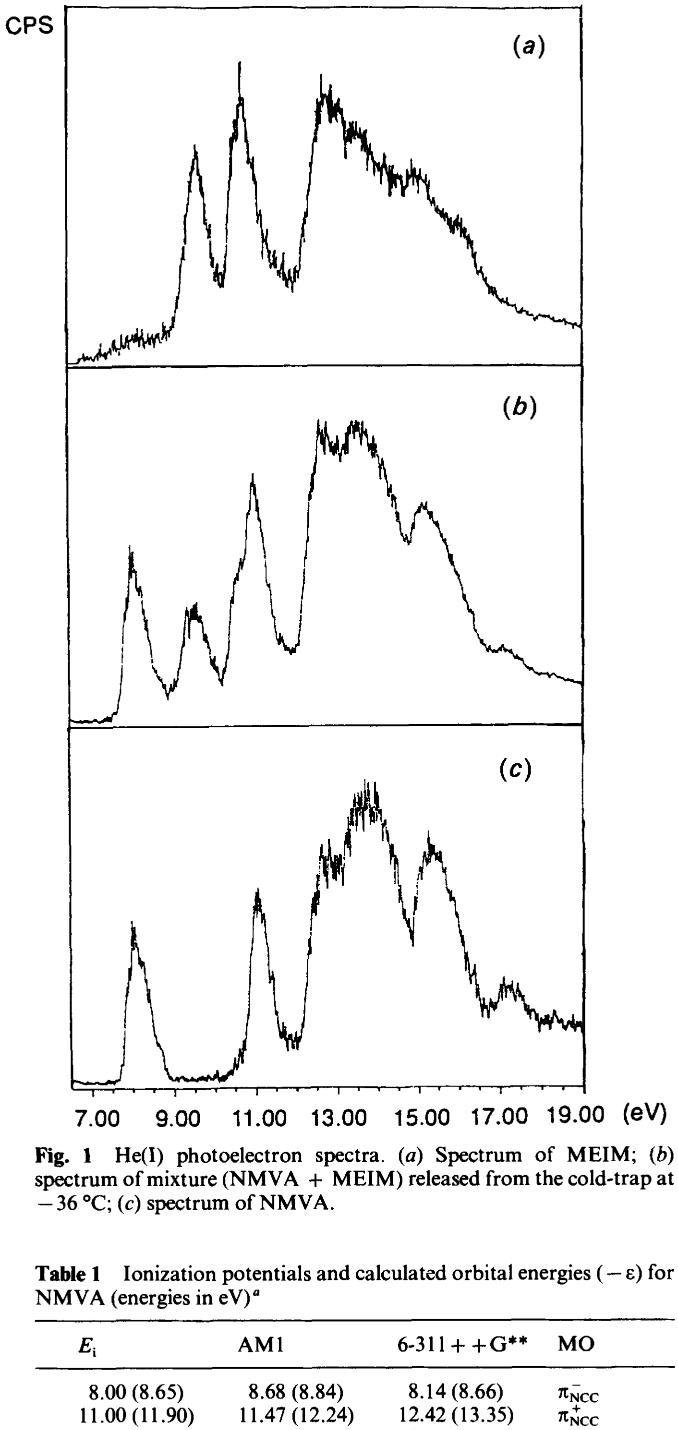

Fig. 1 He(I) photoelectron spectra. (*a*) Spectrum of MEIM; (*b*) spectrum of mixture (NMVA + MEIM) released from the cold-trap at −36 °C; (*c*) spectrum of NMVA.

Table 1 Ionization potentials and calculated orbital energies (−ε) for NMVA (energies in eV)[a]

E_i	AM1	6-311++G**	MO
8.00 (8.65)	8.68 (8.84)	8.14 (8.66)	π^{-}_{NCC}
11.00 (11.90)	11.47 (12.24)	12.42 (13.35)	π^{+}_{NCC}
12.6	12.22	13.88	σ_{CH}
13.6	12.74	14.75	$\pi_{\mathrm{CH_2}}$
13.9	13.79	15.60	σ_{CH}
15.2	15.00	16.55	σ_{CH}
15.5	15.90	17.07	σ_{CN},σ_{CH}
17.1	17.97	19.41	σ_{CH}

[a] The values in parentheses are for vinylamine; the ionization potentials of vinylamine were taken from ref. 18. The orbital energies of NMVA are for the *cis* conformation.

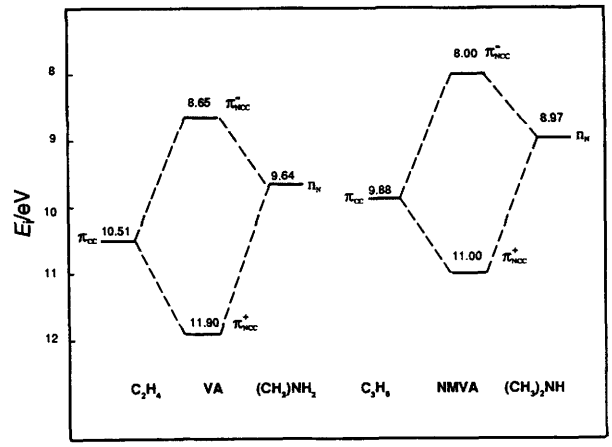

Fig. 2 Correlation diagram for the experimental vertical ionization potentials of vinylamine, *N*-methylvinylamine, ethene, propene, methylamine and dimethylamine. The value for propene was taken from ref. 20 and those for ethene and the alkyl amines were taken from ref. 21.

of a high degree of n,π-interaction as it is larger than that observed for *N*-methyl-1,2,3,4-tetrahydropyridine by 0.17 eV;[19] the latter gives the largest difference between the first two vertical ionization potentials among a series of secondary enamines owing to its unique conformation which favours the n,π-conjugation.[9] It is interesting to compare NMVA and the parent compound, vinylamine (VA), with regard to the first two ionization potentials. The first two bands in the PE spectrum of the unsubstituted species occur at 8.65 and 11.90 eV,[18] showing a gap of 3.25 eV, slightly larger than that for NMVA. This order is also predicted by the molecular orbital calculations as illustrated in Table 1. The degree of conjugative interaction in the two compounds is illustrated in the correlation diagrams shown in Fig. 2, in which ionization potentials in the absence of such an interaction are approximately gauged with the π_{CC} ionization potentials of ethene and propene and the n_{N} ionization potentials of methylamine and dimethylamine. Note that the positions of the π^{-}_{CCN} and π^{+}_{CCN} levels for the two enamines are determined not just by the conjugative interaction but also by the inductive effect of the nitrogen on the alkene system, and the inductive effect of the alkene system on the nitrogen lone-pair. Both inductive effects have the same direction (stabilizing) and are almost equal in magnitude.[9] This implies that while the inductive effects tend to shift the π^{-}_{CCN} and π^{+}_{CCN} ionization potentials to higher values, the gap between the two levels can be taken as a reliable measure of the conjugative interaction. Thus the comparison between VA and NMVA seems to indicate that substitution of a hydrogen by a methyl group at the nitrogen position weakens the n,π-conjugation. While this observation is in contrast to the conclusion reached on the basis of comparisons of NH out-of-plane wagging frequencies and calculated geometries (as mentioned in the Introduction), it is in agreement with the observed reduction in basicity at the β-carbon position on going from vinylamine to *N*,*N*-dimethylvinylamine,[22] such basicity being a measure of the n,π-conjugation in the enamines.

References

1 S. F. Dyke, *The Chemistry of Enamines*, Cambridge University Press, London, 1973.
2 P. W. Hickmott, *Tetrahedron*, 1982, **38**, 1975.
3 C. Gadamasetti and M. E. Kuehne, in *Enamines: Synthesis, Structure, and Reactions*, ed. A. G. Cook, 2nd edn., Marcel Dekker, New York, 1988.
4 G. V. Boyd, in *The Chemistry of Enamines*, Part 2, ed. Z. Rappoport, Wiley, New York, 1994.
5 F. J. Lovas and F. O. Clark, *J. Chem. Phys.*, 1975, **62**, 1925.
6 C. Glidewell, *J. Mol. Struct.*, 1982, **89**, 349.
7 K. Yoshikawa, M. Hashimoto and I. Morishima, *J. Am. Chem. Soc.*, 1974, **96**, 288.

8 K. Muller, F. Previdoli and H. Desilvestro, *Helv. Chim. Acta*, 1981, **64**, 2497.

9 A. G. Cook, in *Enamines: Synthesis, Structure, and Reactions*, ed. A. G. Cook, 2nd edn., Marcel Dekker, Inc., New York, 1988.

10 W. D. Gurowitz and M. A. Joseph, *J. Org. Chem.*, 1967, **32**, 3289.

11 M. Sugie, H. Takeo and C. Matsumura, *Chem. Phys. Lett.*, 1985, **113**, 140.

12 Y. Amatatsu, Y. Hamada and M. Tsuboi, *J. Mol. Spectrosc.*, 1985, **111**, 29.

13 *Dictionary of Organic Compounds*, ed. J. Buckingham, vol. 4, 5th edn., Chapman and Hall, New York, 1982.

14 M. J. S. Dewar, E. G. Zoebisch, E. F. Healey and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

15 J. J. P. Stewart, MOPAC 6.0 (QCPE455), Quantum Chemistry Program Exchange, Indiana University, Bloominton, IN, USA, 1990.

16 M. J. Frisch, G. W. Trucks, M. Head-Gordon, Pm. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, *GAUSSIAN 92*, Gaussian Inc., Pittsburgh PA, 1992.

17 H. Bock and R. Dammel, *Chem. Ber.*, 1987, **120**, 1961.

18 B. Albrecht, M. Allan, E. Haselbach, L. Neuhaus and P. A. Carrupt, *Helv. Chim. Acta*, 1984, **67**, 220.

19 P. Beeken and F. W. Fowler, *J. Org. Chem.*, 1980, **45**, 1336.

20 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, 1981.

21 A. Katrib and J. W. Rabalais, *J. Phys. Chem.*, 1973, **77**, 2358.

22 J. Catalan and F. G. Blanco, in *The Chemistry of Enamines*, Part 1, ed. Z. Rappoport, Wiley, New York, 1994.

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