Ionization Potentials of Some Organic Molecules. V. Heterocyclic Compounds Containing Nitrogen

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What kind of electron is actually responsible for the first ionization potential of a heterocyclic compound containing a nitrogen atom or nitrogen atoms? There are two contradicting views on the problem. One is to ascribe the most loosely bound electron to one of the non-bonding electrons belonging to the N atom, while the other regards one of the π-electrons of the conjugated system most easy to be removed¹⁾. In previous reports²⁾ dealing with ionization potentials of pyridine and picolines, the present writers tried to interpret the results of their measurement from the former viewpoint.

As a continuation of the study on ionization potentials, measurements were conducted on three isomers of diazines, three isomers of lutidines and *s*-triazine in the hope that they would provide a fresh clue to knowledge on this point. The results of the measurements on these seven heterocyclic compounds will be fully described in the present article with the possible interpretations.

Experimental Materials

Pyridazine.—3,6-Dichloropyridazine prepared by the chlorination of 3,6-pyridazinediol was hydrogenated in ammonia-ethanol solution with palladium-charcoal at atmospheric pressure. The filtered solution was made alkaline with potassium hydroxide, extracted with ether, dried with potassium carbonate, evaporated and distilled. B.p. 84-86°C (at 14 mm) (Mizzori and Spoerri³⁾ give b.p. 86-87°C/14 mm).

Pyrimidine.—3,4-Dichloropyrimidine, obtained by the chlorination of uracil, was hydrogenated as in the case of pyridazine to give pyrimidine. Pyrimidine mercurichloride was precipitated from the filtered solution, and distilled with sodium sulphide (nonahydrate). The aqueous distillate was saturated with potassium hydroxide. The separating pyrimidine layer was extracted with ether, dried with potassium hydroxide, evaporated and fractionated to give pyrimidine. B.p. 123°C (Hilbert and Johnson⁴⁾ give b.p. 124°C/758 mm).

Pyrazine. — Pyrazine - 2,3 - dicarboxylic acid (kindly provided by Sankyo Pharm. Co., Ltd.) was decarboxylated in acetic acid solution, made alkaline with sodium hydroxide and steam-distilled⁵⁾. Pyrazine was purified through mercurichloride as in the case of pyrimidine. B.p.

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1) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954)

2) K. Higasi, I. Omura and H. Baba, *J. Chem. Phys.*, **24**, 623 (1956); H. Baba, I. Omura and K. Higasi, This Bulletin, **29**, 521 (1956).

3) R. H. Mizzori and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1873 (1951).

4) G. E. Hilbert and T. B. Johnson, ibid., **52**, 1152 (1930).

5) S. Gabriel und A. Sonn, *Ber.*, **40**, 4852 (1907).

113°C; m.p. 53-54°C (from ether) (Wolff[6] gives m.p. 55°C).

s-Triazine.—s-Triazine was prepared by Grundmann's method[7] from formamidine[8] and sodium diformamide. M.p. 81-82°C (purified by sublimation). (Grundmann[7] gives m.p. 85°C).

Three isomers of lutidines were obtained from Kwanto Chem. Co., Inc., Tokyo. They were distilled before use. 2,3-*Lutidine*, b.p. 161°C. 2,4-*Lutidine*, 157.5-157.8°C. 2,6-*Lutidine*, b.p. 142.2°C. All the temperatures recorded here were uncalibrated.

Experimental Method and Result

The measurement of the first appearance potentials was made by the use of the apparatus described in a previous report[9]. Regarding the evaluation of the ionization potentials, a modified critical slope method was employed. The ionization efficiency curves were plotted on a semilog scale. The pressure of the reference gas, argon, was adjusted so that the initial portions of the curves for the sample and reference gases became nearly parallel to each other. The distance between the two curves along the voltage axis was taken to be the difference between the ionization potentials of the sample and the reference gase*.

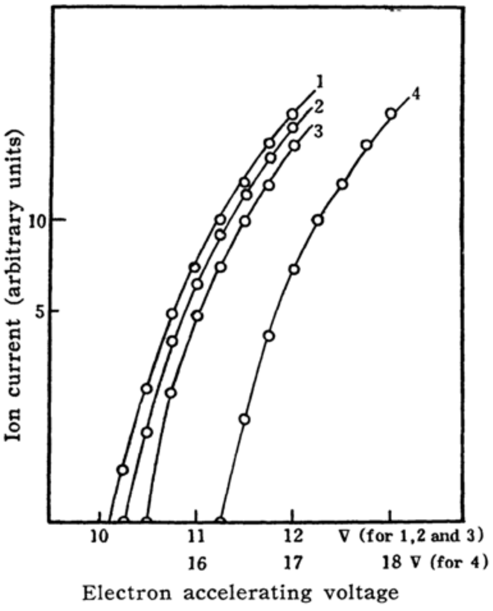

Fig. 1. Relative ionization efficiency curves. 1, pyridazine; 2, pyrimidine; 3, pyrazine; 4, argon.

In Fig. 1 some representative ionization efficiency curves are shown. For s-triazine the linear extrapolation method was also used for the sake of comparison.

In a previous report[9] the question was considered as to whether or not the choice of argon as the standard gas is suitable. For the samples treated so far, its use was justified. On account of the following facts the decision then reached is not ultimate nor fully acceptable. The energy spread of emitting electrons is greatly affected by the filament temperature, i.e., about 1800°K in this experiment. Further, the effect of contact potentials contributes to this spread of the energy. As a result the energy difference 0.18 eV between the doublet states, $^2P_{1\frac{1}{2}}$ and $^2P_{\frac{1}{2}}$ of argon ion[14] becomes much smaller in comparison with the energy spread of the bombarding electrons used in this sort of experiment*.

In benzene there appears to exist an energy level just under the highest occupied level, the energy separation being only 0.5 eV. It is pointed out by Morrison[15] that the existence of this level becomes a dominant cause of error in the apparent ionization potentials of benzenoid molecules when measured by the ordinary electron impact method. Consequently, if diazines or lutidines are not lacking in respect to such a neighboring level or levels, the measured first potentials of this experiment will correspond to some average values of the first, second and other ionization energies.

The remaining implications come from the space charge effects[16]. With a view to eliminate

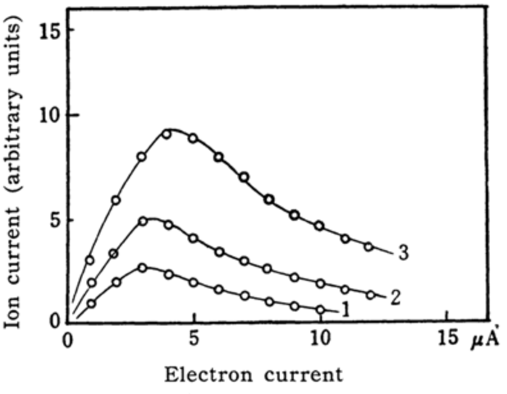

Fig. 2. Dependence of positive ion current (pyridazine) upon electron-beam current. Electron accelerating voltage: 1, 11eV; 2, 12eV; 3, 13eV.

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6) L. Wolff, ibid., **26**, 723 (1893).

7) C. Grundmann, H. Schröder und W. Ruske, ibid., **87**, 1866 (1954).

8) D. J. Brown, *J. Appl Chem.*, **2**, 202 (1952).

9) I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 501 (1956).

* This procedure has actually been adopted in the work of the previous papers[2,9]. It is a modified application of Honig's method[10], and is essentially the same as employed by Dibeler et al.[11], Lossing et al.[12] and others[13].

10) R. E. Honig, *J. Chem Phys*, **16**, 105 (1948).

11) V. H Dibeler, R M Reese and F. L Mohler, *J. Chem. Phys*, **20**, 761 (1952).

12) F. P. Lossing, A W Tickner and W A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

13) A. Jacobson, J. Steigman, R. A Strakna and S. S. Friedland, *J. Chem. Phys.*, **24**, 637 (1956); R W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956).

14) T. Mariner and W. Bleakney, *Phys Rev.*, **72**, 807 (1947).

15) J. D. Morrison, *J. Chem. Phys.*, **22**, 1219 (1954).

16) J. Marriott and J. D. Craggs, "Applied Mass Spectrometry", London (1954), p. 173.

these effects as nearly as possible, the variation of ion currents with electron currents was closely examined (See Fig. 2). From the curves shown in Fig. 2 such an intensity of electron currents was chosen as to give a maximum intensity of ion currents.

The results of the measurement are collected in Table I. No data for comparison appear to exist in the literature[17].

TABLE I

IONIZATION POTENTIALS OF THE HETEROCYCLIC COMPOUNDS, eV.

Substance	Potentials
Pyridazine	9.86±0.05
Pyrimidine	9.91±0.05
Pyrazine	10.01±0.02
s-Triazine	10.07±0.05 (10.10±0.02)
2,6-Lutidine	9.57±0.02
2,3-Lutidine	9.68±0.02
2,4-Lutidine	9.43±0.02

The value in parenthesis was obtained by the linear extrapolation method, while all others refer to a modified critical slope method, argon being used as the standard gas.

Discussion

Lutidines.—In previous reports[2] dealing with the ionization potentials of xylenes and picolines it was found that the lowering in the potential by methyl substitution was less pronounced in pyridine than in benzene. From this observation it was suggested that the first ionization potentials of pyridine derivatives are largely determined by non-bonding electrons of the N atom, while those of benzene derivatives are determined by π-electrons.

In lutidines two hydrogen atoms of a pyridine molecule are replaced by methyl groups, while in picolines one hydrogen atom is replaced by a methyl group. In all these molecules methyl substitutions always result in the lowering in the potential, but they are not so large as in benzene derivatives. This trend will be clear upon a comparison of the two curves, 1 and 2, in Fig. 3. The ionization potentials obtained for three isomers of lutidines are thus in good accord with the view of the previous papers[2].

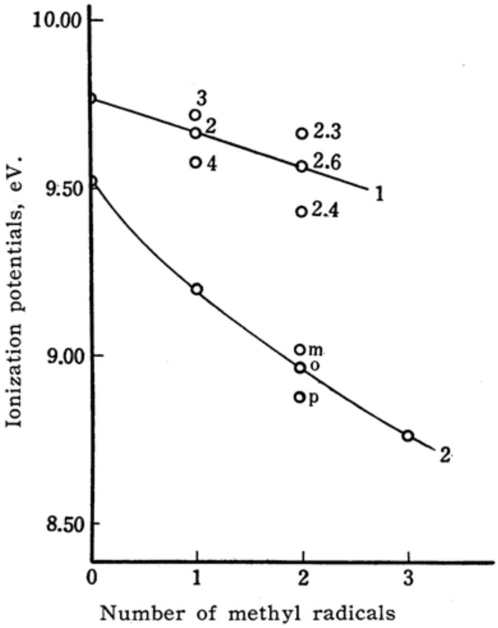

Fig. 3. Ionization potential and methyl substitution. 1, pyridine derivatives; 2, benzene derivatives.

Diazines and Triazine.—In previous studies[2] it was found that the replacement of a C–H group of a benzenoid molecule by an N atom always elevates the appearance potential. What would happen, if two or three C–H groups were replaced by the corresponding number of N atoms? The answer will be as follows. If the appearance potential is actually due to non-bonding electrons of the N atom, it will be affected by such a replacement in even the slightest degree. On the contrary, if π-electrons are responsible for the appearance potential, the magnitude of

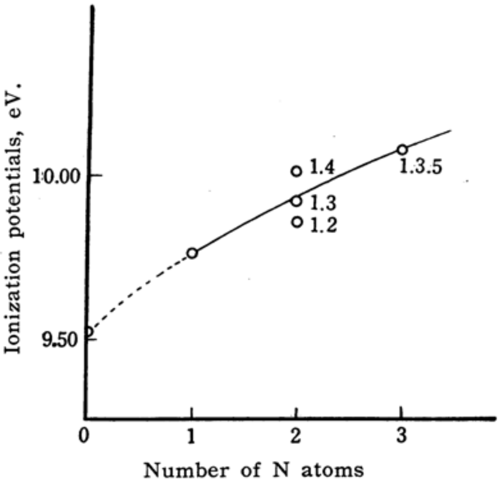

Fig. 4. The effect upon ionization potential of replacement of a C-H group by one or more N atoms.

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* The energy spread has not been accurately determined. But refer, for example, to R. H. Vought, *Phys. Rev.*, **71**, 93 (1947).

[17] Tables of Ionization Potentials of Molecules and Radicals, *Monogr. Res. Inst. Appl. Elec.*, Hokkaido University, **4**, (1954—7), appendix.

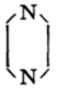
the change will be much greater. Probably its magnitude will be almost the same as in the change when a C–H group in benzene is replaced by one N atom.

With this expectation in mind, the present experiment on diazines and triazine was carried out. The results obtained are shown as a graph in Fig. 4. A smooth curve is obtained when the ionization potentials are plotted against the number of N atoms replaced.

To begin with, it would be better to leave the first view of non-bonding electrons out of consideration, and see if the second view of π-electrons can satisfactorily account for the data on potentials. Fortunately, there are available calculations on π-electron energies for pyridine and diazines[18]. In Table II the energy of the highest occupied level, ε_m in β unit*, is shown for each of these compounds. By the use of these values and the assumption $\beta=-2.75$ eV**, the differences in ionization potential between diazines and pyridine can be calculated. (See the values denoted by ΔI_π in Table II). It will be seen that the theoretical differences for 1,2- and 1,3-diazines are much greater than those observed. Contrary to this, the theoretical consideration gives the least change for 1,4-diazine, while the actual observation gives the greatest change.

TABLE II

IONIZATION POTENTIALS (I), π-ELECTRON DENSITY (q) AND ENERGY OF THE HIGHEST OCCUPIED LEVEL (ε_m)

	I (eV)	ΔI_{obs} (eV)	ε_m (β)	ΔI_π (eV)	q_{N}	ΔI_{n} (eV)
	9.76	—	1.051	—	1.29	—
	9.86	0.10	1.305	0.70	1.24	0.14
	9.91	0.15	1.209	0.43	1.28	0.03
	10.01	0.25	1.100	0.13	1.23	0.17

Next, let the problem be considered from the viewpoint of non-bonding electrons. Against the anticipation based upon this view, diazines were found to have larger ionization potentials than pyridine. But this might be a matter of natural consequence, if the N atoms in diazines have much smaller electron densities than the N atom in pyridine.

The interaction between the N atoms in diazines and a triazine may be better understood, when the electron transmission is grouped into those of π-electrons and σ-electrons. As is evident from the molecular orbital calculation[18], π-electron densities on the N atoms of diazines become smaller than that in pyridine. The decrease is marked at 1,2- and 1,4-positions (Compare the values of q_{N} in Table II). The decrease in density of σ-electron is also expected in diazines, the order of decrease being 1,2>1,3>1,4. Total electron densities of N atoms in diazines are thus smaller than that of pyridine. Consequently, the effective electronegativities of N atoms increase upon replacement by the N atom.

It will be evident from the above argument that, as far as a qualitative explanation is concerned, the increase in the ionization potentials in diazines and a triazine can be accounted for on the assumption of non-bonding electrons. As the next step, one must make a trial to see whether or not quantitative interpretation is possible on the same basis. In the last column of Table II the results of such a trial are summarized. Indeed, the calculated difference of the ionization potential ΔI_{n} is in better accord with the observed values than ΔI_π.

The principle of the calculation is as follows. The energy change of the π-electron system δE is expressed by

$$\delta E=\frac{\partial E}{\partial \alpha_r}\delta\alpha_r+\cdots\cdots\simeq q_r\delta\alpha_r, \tag{1}$$

where $\delta\alpha_r$ is the change of coulomb integral α_r of an atom r and q_r denotes the π-electron density of the atom r[19]. Attention is focussed on the N atom, so that its charge q_{N} and α_{N} are considered.

The first ionization may be illustrated as follows.

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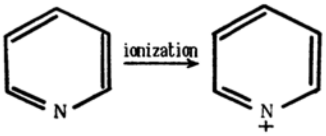
[18] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

* The energy ε_m is measured relative to the coulomb integral for a carbon atom. β is defined as the resonance integral of a carbon-carbon bond.

** The value of transition energy to the first excited state for benzene, -2β, derived from the LCAO MO method (neglecting overlap integral), was put as equal to the observed 5.5 eV (C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948)).

[19] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).



When one non-bonding electron is taken from the N atom, it is supposed that the unit positive charge is localized at the N atom: that is, N^+ is produced. The total energy change of π-electrons on ionization will be approximated by

$$\delta E = q_N \delta\alpha_N \tag{2}$$

where

$$\delta\alpha_N = \alpha_{N^+} - \alpha_N \tag{3}$$

and

$$0 > \alpha_N > \alpha_{N^+} \tag{4}$$

As a further approximation[18] one may put $\delta\alpha_N = \beta$* and $\beta = -2.75$ eV. The calculation for δE can be immediately made**, when use is made of q_N values of diazines of Table II.

The value δE thus obtained constitutes only a small fraction of the total energy change in the ionization process. The main part of the ionization energy is of course the energy for removing one electron from a molecule to infinity. But the latter energy is regarded as the same for both pyridine and diazines. By use of this approximation the difference in the ionization potentials between each of the diazines and pyridine may immediately be calculated from the difference in δE. (See ΔI_n in Table II).

In view of the assumptions involved, no strong claim will be made for the reliability of the calculated values ΔI_n. But it appears certain that interaction between N atoms can not be neglected safely and that the present results of these experiments and considerations on diazines and triazine do not contradict the writers' view which favors non-bonding electrons.

Lastly a few words must be added on the accuracy of ordinary electron-bombardment values at large. The ionization potential of benzene, 9.52 eV, obtained by electron bombardment[20] is greater by 0.3 eV than 9.24 eV which is given by both spectroscopic[21] and photoionization method[22]. For pyridine there are available two electron-bombardment values, 9.80 eV[23] and 9.76 eV[2], while photoionization gives a much lower value 9.23 eV[24]. The discrepancy among these values seems to indicate that in pyridine there exists a neighboring level or levels near the highest occupied level.

Under these circumstances one is not absolutely sure as to the accuracy of the values obtained in this sort of measurement. Emphasis in this article has been placed on the general effects of replacement upon the ionization potentials, but not on the fine differences among three isomers. The latter problem is in fact of great importance in chemistry, but at the present stage of research any detailed discussion on this point might be somewhat speculative.

Summary

First ionization potentials of the following substances were determined by a modified critical slope method. Pyridazine 9.86±0.05, pyrimidine 9.91±0.05, pyrazine 10.01±0.02, *s*-triazine 10.07±0.05, 2,3-lutidine 9.68±0.02, 2,4-lutidine 9.43±0.02, and 2,6-lutidine 9.57±0.02 eV. Interpretations of the results are given from the view-point that the ionization potentials of these compounds are largely determined by the non-bonding electrons at the N atom.

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* $\alpha(-N=) = \alpha + \beta$, $\alpha(-N^+=) \simeq \alpha(-\overset{|}{N}-) = \alpha + 2\beta$. Regarding the latter see H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954).

** For diazines one may consider that half the unit positive charge appears at each N atom upon the removal of one non-bonding electron. This will not alter the values of δE, if one assumes that the resulting change in coulomb integral of each N atom is $(1/2)\beta$.

20) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Soc.*, **20**, 1021 (1952).

21) W. C. Price, *J. Chem. Phys.*, **3**, 256, 365, 439 (1954).

22) K. Watanabe, *J. Chem. Phys.*, **24**, 1564 (1954).

23) A. Hustrulid, A. Kusch and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938).

24) K. Watanabe, Private communication.