*The Electronic State and Dipole Moment of Diazine Mono-N-oxide**

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In previous studies undertaken as part of a programme of physicochemical investigations of various heterocyclic *N*-oxides, one (T. K.) of the present authors has calculated simple molecular orbitals (SMO) and anti-symmetrized molecular orbitals taking into account configuration interactions (ASMO-CI) to elucidate their electronic structures and electronic spectra.[1,2] These results have been compared with these of some physicochemical experiments, such as electronic spectra, dipole moments, infrared spectra, reactivities, etc. As a result, the following set of parameters have been found to be most reasonable for SMO calculation:[3]

$$\alpha_{N^{\delta+}} = \alpha + 1.6\beta, \ \alpha_{O^{\delta-}} = \alpha + 0.8\beta, \ \rho_{NO} = 1$$

where $\alpha_{N^{\delta+}}$, $\alpha_{O^{\delta-}}$ and α are the Coulomb integrals of nitrogen, oxygen and carbon atoms respectively; β is the usual exchange integral between two carbon atoms in benzene; and ρ_{NO} represents the exchange integral of the N–O bond in the β unit. The exponential decrease of inductive effect due to the $N^{\delta+}$ atom, which is the same form as in Jaffé's procedure,[4] was taken into account:

$$\text{Inductive effect} = (1/3)^n \times 1.6\beta$$

where n is the number of bonds between the nitrogen atom and the carbon atom in question.

Further, it was shown that the SMO's and ASMO-CI's calculated under these conditions can reasonably explain the above physicochemical and chemical properties of basic such heterocyclic *N*-oxides[1,2,5] as pyridine *N*-oxide, and quinoline *N*-oxide. Now, as a further extension of these studies, the present authors have investigated the electronic state and the dipole moments of three diazine mono-*N*-oxides, which are convenient in confirming the adequacy of these parameters, from experimental and theoretical (SMO calculation under the conditions described above) points of view.

Experimental

The measurements of dipole moments were carried out at 25°C on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[6] For each solute, determinations were made on solutions of four different concentrations, appropriately chosen below 3 weight per cent. The graphical plot of the dielectric constant, as well as the density of solutions against the concentration in weight per cent, gave a linear dependence within the range of experimental error. The slopes of these straight lines were evaluated by the least-squares method. The molar polarization of the solute was calculated by a method similar to that introduced by Halverstadt and Kumler[7]; it differed, however, in that densities were used rather than the specific volumes. The deformation polarization of each compound was assumed to be 1.05 times the molar refraction approximated with the sum of

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[1] T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 578 (1959).

[2] T. Kubota, This Bulletin, **35**, 946 (1962).

[3] The details on the derivation of these paramters have been discussed in Refs. 1 and 2.

[4] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952); *J. Am. Chem. Soc.*, **76** 3527 (1954).

[5] Cf. T. Kubota, *J. Spectroscopical Soc. Japan*, **10**, 83 (1962).

[6] Y. Kurita and M. Kubo, *J. Am. Chem. Soc.*, **79**, 5460 (1957).

[7] I. F. Halverstadt and W. D. Kumler, ibid., **64**, 2988 (1942).

TABLE I. DIPOLE MOMENTS OF SOME DIAZINE MONO-*N*-OXIDES IN BENZENE SOLUTIONS AT 25°C

Compound	α	β g./cc.	P_2 cc.	MR_D cc.	μ D
Pyrazine 1-oxide	3.38	0.31	82.3	24.6	1.66
4-Methyl-pyrimidine 1-oxide	13.26	0.22	314.0	29.2	3.72
Pyridazine 1-oxide	31.02	0.35	581.3	24.8	5.21

atomic refractions for the D line. Since the values of moments are great, no serious errors are introduced by this assumption, the probable errors being estimated at less than 0.05 D.

The results are shown in Table I, in which α and β denote the changes in the dielectric constant and in the density of the solutions with the weight fraction of the solute; the other notations have their usual meanings. The samples of pyrazine mono-*N*-oxide,[2] 4-methylpyrimidine mono-*N*-oxide[2] and pyridazine mono-*N*-oxide (hygroscopic colorless crystal of m. p. 38∼39°C)[8,9] used in this investigation were the same as those reported in detail in previous papers.[2,9] Here, we have employed 4-methylpyrimidine mono-*N*-oxide instead of pyrimidine mono-*N*-oxide because of the difficulty of preparing the latter. Moreover, although the position of the N-O group in 4-methylpyrimidine *N*-oxide has not yet been established, Position 1 in Fig. 2 was inferred to be the most plausible.[10]

MO Calculations and Discussion

The electronic structures of pyrazine mono-*N*-oxide, pyrimidine mono-*N*-oxide and pyridazine mono-*N*-oxide have been calculated by using a simple LCAO-MO (SMO) method, disregarding overlap integrals and electronic interactions.

The various parameters necessary to carry out the calculation are the same as those described at the beginning of this paper, except for the Coulomb integral of pyridine-type nitrogen, which was taken to be the $\alpha+0.4\beta$ derived by Hameka et al.[11] on the basis of the theoretical treatment of the dipole moment of the compounds like pyridine and which was added to the Coulomb potential due to the inductive effect of the $\gt N^{\delta+}$-group.

In this calculation, pyrazine mono-*N*-oxide was reasonably assumed to belong to the point group C_{2v}. The SMO's of the other two molecules, however, were directly obtained from the original secular equations.

The molecular diagrams thus obtained are shown in Figs. 1, 2 and 3, along with the numbering of atoms. Providing that the benzene heterocyclic ring of these molecules consists of a regular hexagon, with a bond length of 1.38 Å,[12] and that the N-O distance is 1.28 Å,[1,2,13] we have calculated the π-moments on the basis of the π-electron densities given in Figs. 1, 2 and 3. The results are demonstrated in each of the above figures. As in the case of basic heterocyclic *N*-oxides, it is clear from Figs. 1, 2 and 3 that the direction of the π-moment in each diazine mono-*N*-oxide indicates the π-electron transfer from the oxygen atom to the ring, the magnitude of which is greater than that (0.76 D) of pyridine *N*-oxide[2] to be discussed below. This fact is in good agreement with the accepted general tendency; that is, the replacement of one ring carbon atom by a nitrogen atom, which is a more electronegative element than carbon, brings about a greater charge transfer from the N→O group to the ring.

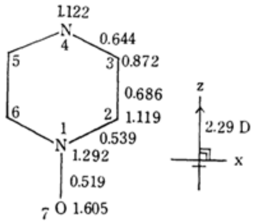

Fig. 1. Molecular diagram and π-moment of pyrazine mono-*N*-oxide.

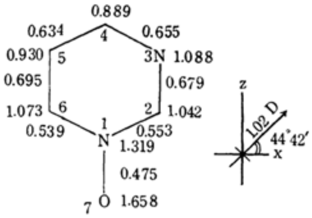

Fig. 2. Molecular diagram and π-moment of pyrimidine mono-*N*-oxide.

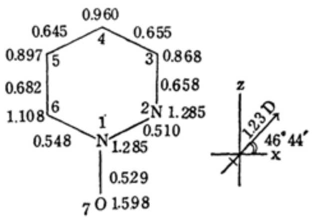

Fig. 3. Molecular diagram and π-moment of pyridazine mono-*N*-oxide.

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[8] C. F. Koelsch and W. H. Gumprecht, *J. Org. Chem.*, **23**, 1603 (1958).

[9] H. Watanabe, M. Ogata and H. Kano, *Chem. & Pharm. Bull.*, **11**, 29 (1963).

[10] E. Ochiai and H. Yamanaka, *Pharm. Bull.*, **3**, 175 (1955).

[11] H. F. Hameka and A. M. Liquori, *Mol. Phys.*, **1**, 9 (1958).

[12] This length corresponds to the averaged value of each bond length determined experimentally on pyridine.

[13] Y. Namba, T. Oda and T. Watanabe, This Bulletin, **36**, 79 (1963).

TABLE II. THE VALUES OF EMPLOYED σ-MOMENTS (D)
(See text)

Bond	Condition 1	Condition 2
$\overset{(+)}{N}\rightarrow\overset{(-)}{O}$	4.55	4.30**
N—O	0.40	0.40
≫N*:	1.0	—
C—N	O[C(sp^2)—N(sp^2)]	0.45

* The moment due to the unshared electron pair. See text.

** This value was cited from Smyth's table. C. P. Smyth: "Dielectric Behaviour and Structure," McGraw-Hill Book Co., New York (1955), p. 244.

It is especially noteworthy to point out that in pyrazine mono-*N*-oxide, a considerable amount of π-electron density is accumulated on the nitrogen atom at position 4, which is furthest apart from the N→O group. On the other hand, the fact that in the case of pyrimidine mono-*N*-oxide the contribution of the meta nitrogen atom to the increase of the π-moment is relatively small shows that the electron migration ability to the meta (3-) N-atom is weak, as is expected from the usual electronic theory. Assuming the mutual interaction between π- and σ- (the moments due to each of the localized bonds) moments to be negligible, we calculated the total dipole moments by means of the vector summation of π- and σ-moments, the latter values of which are listed in Table II. Here the necessary estimation of σ-moments is important. Our estimations were made under two conditions:

Condition 1: In this case we explicitly took into account the moment due to the unshared electron pair (the lone pair moment) on the nitrogen atom in the ring. Recently, Sheibe et al.[14] have reported the NMR chemical shift of pyrimidine in detail, showing that the lone pair moment of the nitrogen atom is, semi-experimentally, 1.2 D by connecting of above chemical shift data with the MO calculation results concerning pyrimidine under the following reasonale conditions: the SMO parameters of the N-atom are 0.5 or 0.4, the C(sp^2)–N(sp^2) σ-moment is nearly zero, as was suggeted by Hameka and Liquori,[11] and the usual C–H σ-moment was adopted. However, since the C–H moment, 0.6 D, adopted by them was somewhat larger than the normal value, we applied 0.4 D[15] to their data to obtain the N-lone pair moment of 1.0 D.

The σ-moment of the N→O bond was assigned as 4.55 D so as to reproduce the observed moment of pyridine *N*-oxide by using the π-moment (0.76 D) estimated experimentally and theoretically by us[1,2] and by other workers[16] and by using the C–N and C–H σ-moments as stated above and as listed in Conditon 1 in Table II.

Condition 2: We have applied the same σ-moments as those employed by Orgel et al.[15] to analyze the dipole moments of many heterocyclic compounds theoretically.[17]

As may be seen from Table III, the agreement between the observed total moments and the calculated ones is relatively good. However, Condition 1 seems to be more reasonable in view of the reproducibility of the observed value and from the theoretical point of view.

Now, the SMO-parameter for aromatic-*N*-oxides, derived previously by us, seems to be suitable to explain the electronic dipole moments for these compounds, including diazine mono-*N*-oxides.

Table IV gives the frontier electron densities of the compounds studied here as defined by Fukui et al.,[19] densities which were successfully applied hitherto to explain the chemical reactivities of the various *N*-oxides.

The chemical reactivity of pyridazine mono-*N*-oxide, which was recently studied in detail by Ogata and Kano,[20] showed that position 4 in the molecule (the para position to the N→O bond) is very active; for example, substituent reaction by a nitrating agent leads to a 4-nitro derivative. These facts agree well with the theoretical prediction inferred

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[14] W. Seiffert, H. Zimmermann and G. Sheibe, *Angew. Chem.*, **74**, 249 (1962).

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

[16] A. R. Katritzky, E. W. Randall and L. E. Sutton, *J. Chem. Soc.*, **1957**, 1769.

[17] The values of many σ-moments have recently been given by R. Daudel et al.[18] on the basis of the theoretical treatment of a σ-bond like C-H, the $\overset{(+)}{C}\rightarrow\overset{(-)}{H}$ and $\overset{(+)}{C}\rightarrow\overset{(-)}{N}$ moments being assigned as 0.40 and 1.15 D respectively. It should be noted that the C→N bond moment is very large and that it partly contains the contribution from the lone pair moment of the N-atom, which was prorated to each of the σ-bonds bonded with the N-atom. It seems that the above C→N σ-moment, etc., can not be applied to the C→N bond in the *N*-oxides, because the N-atom in the ≫N→O bond has no lone pair electron. Formally, however, we could explain the observed values with a better accuracy than that of "Condition 2" in Table II by using the σ-moments given by the above authors.

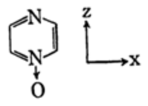
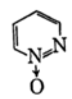
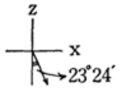
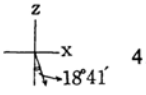
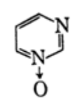
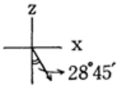
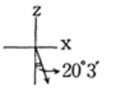
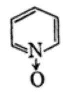
Moreover, although the direction of the C-H bond moment under conditions 1 and 2 is in the direction opposite to that expected theoretically,[18a, b] it should be pointed out that, in the case of Condition 1, the sum of "the lone pair moment of the N-atom" and "the C-H bond moment located at the para-position to the N-atom" is 1.40 D, the value and the direction of which are nearly of the same order as the 1.33 D obtained theoretically by Hameka and Liquori.[11]

[18] a) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience. Publ. Inc., New York (1959), p. 206; b) C. A. Coulson and M. T. Rogers, *J. Chem. Phys.*, **35**, 593 (1961).

[19] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).

[20] M. Ogata and H. Kano, *Chem. & Pharm. Bull.*, **11**, 29, 35 (1963).

TABLE III. THE CALCULATED VALUES OF TOTAL DIPOLE MOMENTS OF SOME *N*-OXIDE COMPOUNDS

Compound	Calculated moment and direction				Observed value*
	Condition 1		Condition 2		
		1.27 D		2.01 D	1.66 D
		5.18 D		4.94 D	5.21 D
		4.02 D		4.26 D	3.72 D**
		4.19 D		4.39 D	4.19 D[a,5,16]
$(CH_2)_3N\rightarrow O$		4.95 D		5.15 D	5.02 D[b,5,16]

* See Table I.

** This value was obtained on 4-methylpyrimidine *N*-oxide (see "Experimental"). The small effect owing to the methyl group was disregarded on comparison of calculated and observed values. This situation may be allowable for the purpose of the present discussion.

a) A. N. Sharpe and S. Walker, *J. Chem. Soc.*, **1961**, 4522.

b) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).

TABLE IV. FRONTIER ORBITAL ELECTRON DENSITIES*

	7	1	2	3	4	5	6	ψ_i**
Pyridazine mono-*N*-oxide	0.5780	0.0104	0.0906	0.0334	0.1522	0.0029	0.1324	$(\psi_{4j})^2$
	0.1694	0.2661	0.2368	0.0253	0.1492	0.1274	0.0259	$(\psi_{5j})^2$
Pyrimidine mono-*N*-oxide	0.6189	0.0178	0.1222	0.0099	0.1258	0.0107	0.0948	$(\psi_{4j})^2$
	0.0980	0.1667	0.0004	0.1846	0.1973	0.0322	0.3209	$(\psi_{5j})^2$
Pyrazine mono-*N*-oxide	0.6100	0.0086	0.1211	0.0017	0.1359	—	—	$(\psi_{4j})^2$
	0.1856	0.2876	0.1112	0.0443	0.2159	—	—	$(\psi_{5j})^2$

* The numbering of each atom is the same as that shown in Figs. 1, 2 and 3.

** ψ_4 and ψ_5 denote the highest occupied orbital and the lowest empty orbital, respectively.

from Table IV, in which the frontier electron density on the carbon atom located at position 4 is largest.

Summary

The dipole moments of pyrazine 1-oxide, 4-methylpyrimidine 1-oxide and pyridazine 1-oxide have been measured in benzene solutions and found to be 1.66, 3.72, and 5.21 D respectively. A comparison of these values with those obtained by the SMO calculation, in which the necessary parameters have been theoretically evaluated in detail by us in previous papers,[1,2] shows that the agreement between the observed and calculated values is good.

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