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# The $\pi$-Electronic Structures of Five-membered Heterocycles Containing Two or Three Heteroatoms and Their Benzo-derivatives

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The semiempirical Pariser-Parr-Pople SCF method combined with configuration-interaction has been applied for calculation of the electronic spectrum, ionization potential and electron affinity, $\pi$-electron distribution and total $\pi$-energy of such heterocycles as oxazole, isoxazole, oxadiazoles, imidazole, pyrazole, triazoles and their monobenzo-derivatives, and the theoretical results have been compared with the available spectral data and miscellaneous chemical properties including the position-dependency on substitution reactions, novel photochemical isomerization of several compounds and so forth.

The $\pi$-electronic structures and chemical properties of the titled compounds are of interest because the parent five-membered heterocycles are known as small aromatic molecules exhibiting unique chemical behaviour, and it is only recently that the chemistry of these compounds has made a remarkable progress. Several molecular orbital calculations have been performed for such compounds; Hückel-type calculations, both simple and modified, have been applied chiefly for evaluating dipole moment, reactivity index and resonance energy,[1-7] and an extended Hückel method including all valency electrons has also been used for the calculation of charge distribution of imidazole, pyrazole, *v*-triazole, and the four possible oxadiazoles,[8] which indicates that the calculated $\sigma$-polarizations are almost independent of the $\pi$-electron distributions. SCF calculations have also been performed for explanation of electronic spectra and dipole moments of the several molecules and have given good agreement with the experimental data by adopting proper semiempirical para-

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meters.[9-13]

It seems, however, that no attempts have been made for SCF calculations which systematically treat both the electronic spectra and chemical properties of the molecules mentioned above. In this work the standard Pariser-Parr-Pople SCF method with configuration-interaction procedure has been carried out for all the molecules in the title, such as oxazole, isoxazole, oxadiazoles, imidazole, pyrazole, triazoles, and their benzo-derivatives.

## Calculation Method

Calculations have been performed on the basis of the Pariser-Parr-Pople method[14] with configuration-interaction including all singly excited configurations. The elements of F matrix are taken as

$$F_{\mu\mu} = -I_\mu + (1/2)q_\mu\gamma_{\mu\mu} + \sum_{\nu\neq\mu}(q_\nu - n_\nu)\gamma_{\mu\nu},$$

$$F_{\mu\nu} = \beta_{\mu\nu} - (1/2)p_{\mu\nu}\gamma_{\mu\nu},$$

where $q_\mu$ and $p_{\mu\nu}$ are the diagonal and off-diagonal elements, respectively, of the bond order-charge density matrix, and $n_\nu$ is the number of electrons donated to the π-electron system by the $\nu$th atom. The values of valence-state ionization potential (I) and electron affinity (A) are determined as follows referring to the paper of Hinze and Jaffe.[15]

$I$ (eV): 11.16 (-C=), 14.12 (-N=), 26.70 (-N(H)-), 32.90 (-O-)

$A$ (eV): 0.03 (-C=), 1.78 (-N=), 9.26 (-N(H)-), 11.37 (-O-)

The two-center repulsion integral ($\gamma_{\mu\nu}$) is computed according to the Nishimoto-Mataga approximation. The core-resonance integral ($\beta_{\mu\nu}$) is evaluated using the equation $\beta_{\mu\nu} = -1/2\, S_{\mu\nu}(I(\mu)+I(\nu))$, where the overlap integral ($S_{\mu\nu}$) is calculated using Slater-type atomic orbital.[16] For comparison the calculation is performed both including and neglecting the $\beta_{\mu\nu}$ over non-neighbouring atomic pairs.

The comparison is meaningful in view of the present purpose of explaining both electronic spectra and chemical properties at the ground state; it is well-known that a good description of the ground state by using semiempirical parameters, in particular the core-resonance integral $\beta_{\mu\nu}$ adjusted to experimental spectral data is difficult, since the ground state which can be represented by a single Slater determinant does not mix with any of the corresponding singly excited states.

Molecular structures of all the heterocycles studied herein are tentatively approximated as a regular hexagon and pentagon with a bond length of 1.395 Å on account of lack in enough available expermental data.

The present calculations have been performed using HITAC 5020-E computer at the University of Tokyo.

## Results and Discussion

**Optical Properties.** The calculated results of singlet π–π* transition energy, corresponding oscillator strength and polarization direction, and excitation energy of the lowest $^3(\pi, \pi^*)$ state are summarized in Table 1(a) and 1(b), the experimental spectral data being collected in Table 2.

In the case of the five-membered heterocyclic molecules the predicted values of the first π–π* transition energy are remarkably (0.4—1.0 eV) lowered by the calculation including the $\beta_{\mu\nu}$ over non-neighbouring atomic pairs (This procedure will be denoted as method I and the other as method II), and these values tend to be slightly smaller than those observed. It is of interest to note that the predicted first π–π* transitions of vicinal-triazoles are more bathochromic and stronger in intensity than those of symmetrical-ones. It is also known that the direction of the first transition moment tends to be of a positive angle for isoxazole and pyrazole, and of a negative angle for oxazole and imidazole.

As for the benzo-derivatives, such as 1,2-benzisoxazole (indoxazene), 2,1-benzisoxazole (anthranil) and benzimidazole, fairly good agreement is found between the calculated (by method I) and experimental spectra, even though the core-resonance integral ($\beta_{\mu\nu}$) is not chosen so as to reproduce individual transition energy. The observed spectrum of indazole is in better agreement with the calculated one (by method I) of 1*H*-tautomer rather than that of 2*H*-tautomer for the relative intensities of the lowest two bands. In the case of benzotriazole also, the observed transition energies of the lowest two bands seem to be in better agreement with the calculated values (by method I) of the 1*H*-tautomer rather than those of the 2*H*-

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10) W. C. Mackrodt, A. Wardley, P. A. Curnuck, N. L. Owen and J. Sheridan, *Chem. Commun.*, **1966**, 692.
11) D. W. Davies and W. C. Mackrodt, *ibid.*, 345 (1967).
12) L. Paoloni and M. Cignitti, *Tetrahedron*, **24**, 485 (1968).
13) R. D. Brown and B. A. W. Coller, *Theor. Chim. Acta*, **10**, 435 (1968).
14) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
15) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
16) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

TABLE 1 (a)

| | Spectral data calculated by Method I | | | | | |
|---|---|---|---|---|---|---|
| | $\Delta E_s$ (eV) | $f$ | $\alpha$ (°) | | $\Delta E_s$ (eV) | $f$ | $\alpha$ (°) |
| Oxazole | 5.26 | 0.24 | −16 | Imidazole | 5.64 | 0.20 | −23 |
| | 6.31 | 0.11 | 28 | | 6.41 | 0.12 | 19 |
| | 8.26 | 0.79 | 66 | | 7.93 | 0.51 | 23 |
| | 2.13* (eV) | | | | 2.73* | | |
| Isoxazole | 5.74 | 0.33 | 3 | Pyrazole | 5.95 | 0.17 | 19 |
| | 6.29 | 0.07 | −26 | | 6.42 | 0.19 | −25 |
| | 7.90 | 0.90 | 81 | | 7.66 | 0.76 | 71 |
| | 2.07* | | | | 2.59* | | |
| 1, 2, 3-Oxadiazole | 5.07 | 0.30 | −8 | 1, 2, 3-Triazole | 5.44 | 0.25 | −9 |
| | 6.41 | 0.06 | 17 | | 6.46 | 0.06 | 39 |
| | 7.80 | 0.92 | 73 | | 7.59 | 0.87 | 68 |
| | 1.53* | | | | 2.18* | | |
| 1,2,4-Oxadiazole | 5.68 | 0.21 | 7 | 1,2,4-Triazole | 5.95 | 0.01 | 26 |
| | 6.01 | 0.11 | −7 | | 6.24 | 0.23 | −2 |
| | 7.79 | 0.68 | 75 | | 7.36 | 0.58 | 56 |
| | 2.19* | | | | 2.64* | | |
| 1,2,5-Oxadiazole | 5.78 | 0.13 | 90 | 1,2,5-Triazole | 5.62 | 0.19 | 90 |
| | 5.95 | 0.40 | 0 | | 6.29 | 0.29 | 0 |
| | 7.81 | 0.80 | 90 | | 7.72 | 0.64 | 90 |
| | 1.69* | | | | 2.28* | | |
| 1,3,4-Oxadiazole | 5.65 | 0.27 | 0 | 1,3,4-Triazole | 5.78 | 0.09 | 90 |
| | 5.73 | 0.08 | 90 | | 6.10 | 0.22 | 0 |
| | 7.77 | 0.19 | 0 | | 7.37 | 0.40 | 0 |
| | 2.19* | | | | 2.70* | | |
| Benzoxazole | 4.69 | 0.13 | −4 | Benz-imidazole | 4.70 | 0.08 | −8 |
| | 5.13 | 0.26 | −27 | | 5.11 | 0.18 | −65 |
| | 5.69 | 0.24 | 37 | | 5.94 | 0.65 | 9 |
| | 6.25 | 0.15 | 54 | | 6.35 | 0.34 | 26 |
| | 6.73 | 0.52 | 44 | | 6.57 | 0.50 | 40 |
| | 2.13* | | | | 2.40* | | |
| Indoxazene | 4.59 | 0.09 | 66 | 1*H*-Indazole | 4.47 | 0.18 | 84 |
| | 5.07 | 0.37 | −29 | | 4.88 | 0.13 | −48 |
| | 5.99 | 0.71 | 31 | | 6.11 | 0.94 | 7 |
| | 6.42 | 0.04 | −43 | | 6.22 | 0.56 | 18 |
| | 6.61 | 0.46 | 6 | | 6.53 | 0.36 | −16 |
| | 1.84* | | | | 1.84* | | |
| Anthranil | 3.99 | 0.35 | 89 | 2*H*-Indazole | 4.36 | 0.32 | 89 |
| | 4.75 | $0.00_2$ | 44 | | 4.78 | 0.02 | 59 |
| | 5.54 | 0.01 | −14 | | 5.80 | 0.01 | 23 |
| | 6.02 | 0.04 | −41 | | 6.28 | 1.61 | −4 |
| | 6.37 | 1.89 | −1 | | 6.37 | 0.18 | 10 |
| | 1.04* | | | | 1.59* | | |
| Benzofurazan | 3.84 | 0.26 | 90 | 2*H*-Benzo-triazole | 4.25 | 0.26 | 90 |
| | 4.60 | 0.11 | 0 | | 4.60 | 0.13 | 0 |
| | 5.61 | 0.16 | 90 | | 5.91 | 0.09 | 90 |
| | 6.10 | $0.00_1$ | 90 | | 5.94 | 0.86 | 0 |
| | 6.12 | 1.29 | 0 | | 6.33 | 0.09 | 90 |
| | 0.69* | | | | 1.31* | | |
| 1,2,3-Benzo-xadiazole | 4.34 | 0.17 | 39 | 1*H*-Benzo-triazole | 4.47 | 0.18 | 52 |
| | 4.58 | 0.35 | −25 | | 4.66 | 0.24 | −43 |
| | 5.61 | 0.29 | 21 | | 5.85 | 0.71 | 8 |
| | 6.23 | 0.01 | 56 | | 6.10 | 0.01 | 51 |
| | 6.72 | 0.33 | 34 | | 6.64 | 0.64 | 64 |
| | 1.29* | | | | 1.56* | | |

$\Delta E_s$ = singlet $\pi$-$\pi^*$ transition energy.

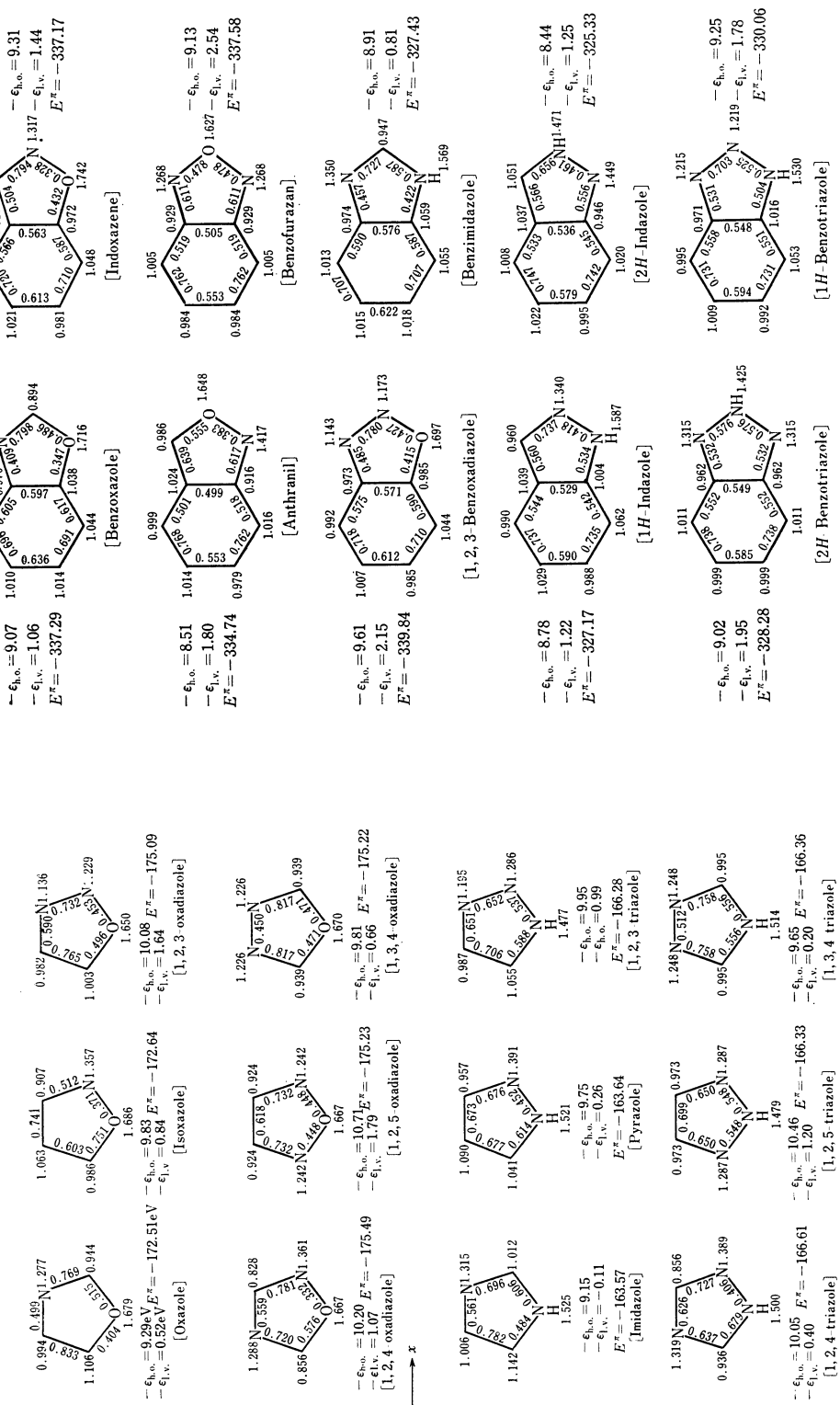
* = excitation energy of the lowest $^3(\pi$-$\pi^*)$ state.

$f$ = oscillator strength, where the transition moment of $i \rightarrow j$ singly excited transition is obtained as $(\boldsymbol{m}_{i\rightarrow j})_x = \sqrt{2}\sum_r C_r^i C_r^j \bar{x}_{rr}$, $(\boldsymbol{m}_{i\rightarrow j})_y = \sqrt{2}\sum_r C_r^i C_r^j \bar{y}_{rr}$ and $(\boldsymbol{m}_{i\ j})_z = 0$.

$\alpha$ = polarization direction measured counterclockwise to the $x$-axis.

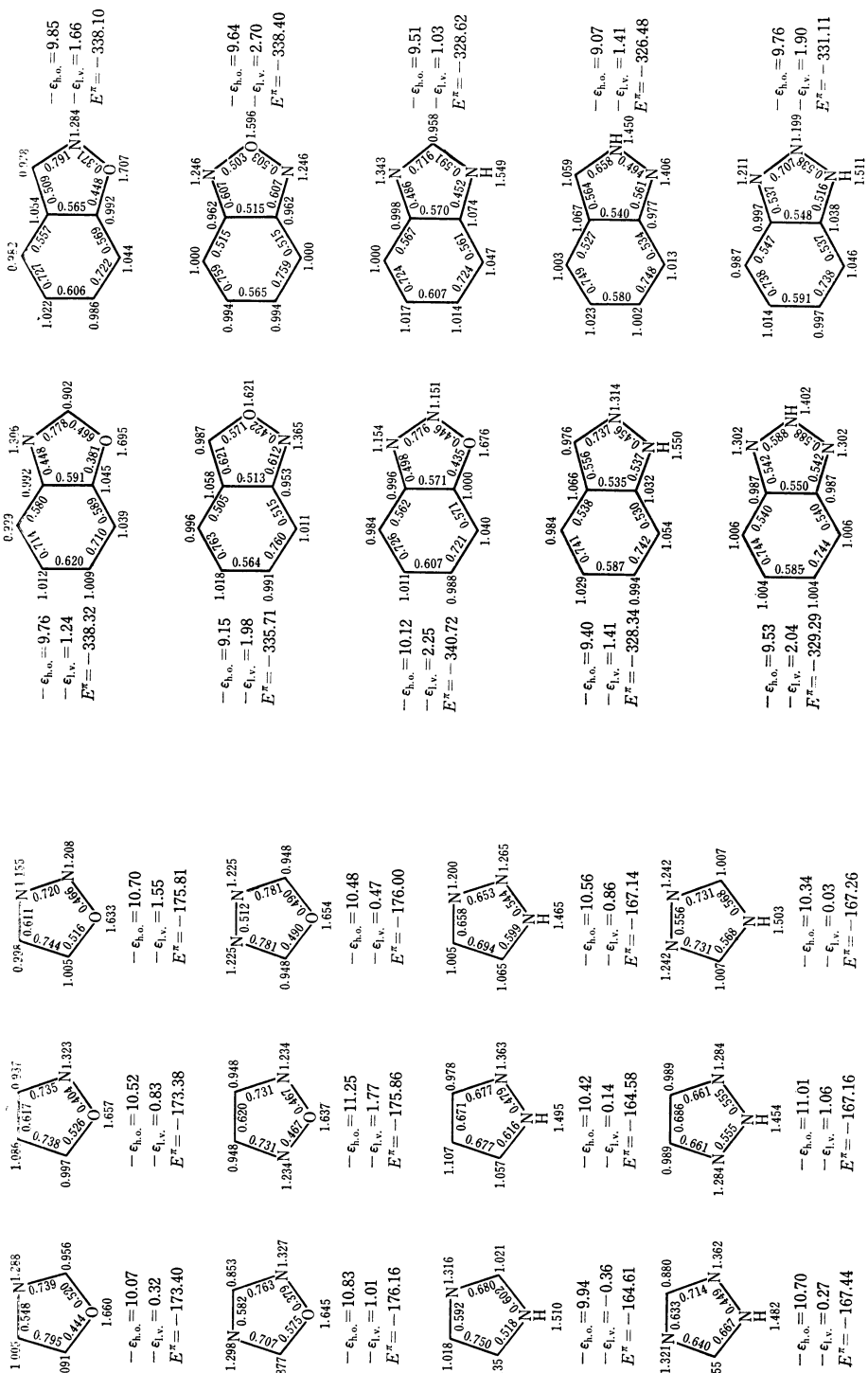
Table 1 (b)

| | Spectral data calculated by method II | | | | | | |
|---|---|---|---|---|---|---|---|
| | $\Delta E_s$ (eV) | $f$ | $\alpha$ (°) | | $\Delta E_s$ (eV) | $f$ | $\alpha$ (°) |
| Oxazole | 6.32 | 0.28 | −11 | Imidazole | 6.68 | 0.19 | −20 |
| | 7.10 | 0.13 | 1 | | 7.35 | 0.14 | 1 |
| | 8.68 | 1.02 | 78 | | 8.65 | 0.94 | 62 |
| | 2.97* | | | | 3.64* | | |
| Isoxazole | 6.35 | 0.32 | 15 | Pyrazole | 6.63 | 0.21 | 27 |
| | 6.96 | 0.21 | −36 | | 7.24 | 0.26 | −31 |
| | 8.68 | 0.89 | 83 | | 8.63 | 0.82 | 76 |
| | 2.72* | | | | 3.35* | | |
| 1,2,3-Oxadiazole | 5.75 | 0.33 | −1 | 1,2,3-Triazole | 6.14 | 0.27 | −3 |
| | 6.97 | 0.14 | −44 | | 7.13 | 0.14 | −57 |
| | 8.35 | 0.88 | 75 | | 8.32 | 0.84 | 69 |
| | 2.18* | | | | 2.87* | | |
| 1,2,4-Oxadiazole | 6.52 | 0.02 | 35 | 1,2,4-Triazole | 6.69 | 0.01 | 29 |
| | 6.55 | 0.36 | 2 | | 7.04 | 0.27 | −1 |
| | 8.32 | 0.85 | 83 | | 8.18 | 0.74 | 64 |
| | 2.75* | | | | 3.34* | | |
| 1,2,5-Oxadiazole | 6.20 | 0.19 | 90 | 1,2,5-Triazole | 6.26 | 0.21 | 90 |
| | 6.47 | 0.44 | 0 | | 6.89 | 0.35 | 0 |
| | 8.61 | 0.81 | 90 | | 8.58 | 0.71 | 90 |
| | 2.23* | | | | 2.93* | | |
| 1,3,4-Oxadiazole | 6.45 | 0.05 | 90 | 1,3,4-Triazole | 6.57 | 0.09 | 90 |
| | 6.64 | 0.36 | 0 | | 7.09 | 0.20 | 0 |
| | 8.29 | 0.27 | 0 | | 8.09 | 0.56 | 0 |
| | 2.91* | | | | 3.47* | | |
| Benzoxazole | 5.23 | 0.06 | 8 | Benzimidazole | 5.26 | 0.06 | 1 |
| | 5.62 | 0.35 | −45 | | 5.52 | 0.27 | −72 |
| | 6.60 | 0.96 | 21 | | 6.81 | 1.69 | 7 |
| | 7.01 | 0.09 | 38 | | 7.08 | 0.03 | 19 |
| | 7.28 | 0.25 | 22 | | 7.34 | 0.24 | 76 |
| | 2.65* | | | | 2.77* | | |
| Indoxazene | 5.01 | 0.13 | 82 | 1*H*-Indazole | 4.97 | 0.23 | 86 |
| | 5.52 | 0.37 | −32 | | 5.41 | 0.16 | −46 |
| | 6.61 | 1.10 | 24 | | 6.71 | 1.30 | 5 |
| | 6.99 | 0.05 | −59 | | 6.96 | 0.53 | 18 |
| | 7.10 | 0.27 | −17 | | 7.14 | 0.06 | −28 |
| | 2.27* | | | | 2.32* | | |
| Anthranil | 4.49 | 0.41 | 88 | 2*H*-Indazole | 4.86 | 0.37 | 89 |
| | 5.21 | 0.04 | 24 | | 5.31 | 0.04 | 49 |
| | 6.09 | 0.06 | −20 | | 6.44 | 0.14 | 7 |
| | 6.56 | 0.02 | −58 | | 6.84 | 1.39 | −5 |
| | 6.78 | 1.73 | −2 | | 6.87 | 0.32 | 5 |
| | 1.52* | | | | 2.10* | | |
| Benzofurazan | 4.22 | 0.31 | 90 | 2*H*-Benzotriazole | 4.71 | 0.33 | 90 |
| | 4.95 | 0.15 | 0 | | 5.08 | 0.12 | 0 |
| | 5.99 | 0.17 | 90 | | 6.35 | 0.09 | 90 |
| | 6.54 | 1.23 | 0 | | 6.56 | 1.15 | 0 |
| | 6.57 | $0.00_0$ | 90 | | 6.79 | $0.00_3$ | 90 |
| | 1.10* | | | | 1.80* | | |
| 1,2,3-Benzoxadiazole | 4.81 | 0.16 | 64 | 1*H*-Benzotriazole | 4.94 | 0.24 | 69 |
| | 5.10 | 0.38 | −23 | | 5.17 | 0.23 | −38 |
| | 6.29 | 0.57 | 19 | | 6.54 | 1.08 | 7 |
| | 6.71 | 0.04 | 83 | | 6.62 | 0.03 | −37 |
| | 7.08 | 0.22 | 8 | | 7.07 | 0.16 | 7 |
| | 1.77* | | | | 2.04* | | |




(a)—1 (a)—2

Fig. 1(a). Molecular diagrams at the ground state calculated by method I.



(b)—1 (b)—2

Fig. 1(b). Molecular diagrams at the ground state calculated by method II.

TABLE 2. EXPERIMENTAL SPECTRAL DATA

| | | |
|---|---|---|
| Oxazole | 6.05 eV (3.59=log $\varepsilon$) | *1 |
| Isoxazole | 5.88 (3.60) | *2 |
| 1,2,5-Oxadiazole | Only end absorption | *3 |
| Imidazole | 5.99 (3.70) | *2 |
| Pyrazole | 5.90 (3.5) | *2 |
| *s*-Triazole | 5.79 | *4 |
| *v*-Triazole | 5.90 (3.6) | *5 |
| Benzoxazole | 4.49—4.59 (3.51—3.53)<br>4.71 (3.38) 5.37 (3.90) | *6 |
| Indoxazene | 4.43 5.06 | *7 |
| Anthranil | 4.04 4.77 | *8 |
| Benzimidazole | 4.55 (3.83) 5.08 (3.74)<br>6.14 (4.6) | *2 |
| Indazole | 4.19—4.37 (3.61)<br>4.90 (3.64) 5.60 | *9 |
| Benzotriazole | 4.42—4.56 (3.80—3.74)<br>4.66 (3.58) 5.08 (3.77) | *2 |

*1 H. Bredereck, R. Gompper and F. Reich, *Chem. Ber.*, **93**, 1389 (1960).
*2 G. Leandri, A. Mangani, F. Montanari and R. Passerini, *Gazz. Chim. Ital.*, **85**, 769 (1955).
*3 R. A. Olofson and J. S. Michelman, *J. Org. Chem.*, **30**, 1854 (1965).
*4 M. R. Atkinson, E. A. Parkes and J. B. Polya, *J. Chem. Soc.*, **1954**, 4256.
*5 L. W. Hartzel and F. R. Benson, *J. Amer. Chem. Soc.*, **76**, 667 (1954).
*6 R. Passerini, *J. Chem. Soc.*, **1954**, 2256.
*7 P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **8**, 101 (1941).
*8 R. Ramart-Lucas and M. Grumez, *ibid.*, **17**, 317 (1950).
*9 J. M. Barclay, N. Campbell and G. Dodds, *J. Chem. Soc.*, **1941**, 113.

tautomer. Experimentally, it is reported[17] that the first $\pi$–$\pi^*$ band of benzotriazole is characteristic of a quinoid chromophore and its second band is characteristic of a benzenoid chromophore.

The polarization direction of the initial three transitions are much affected by introducing benzene ring, but the general trends of variation are not affected appreciably by the replacement of the pyrrole-nitrogen with the furan-oxygen. In this case also, the first $\pi$–$\pi^*$ transition of the molecules with NH (O)-N bond tends to polarize along the bond, in contrast to the other-type molecule in which the corresponding transition polarizes in remarkably different directions. As to benzimidazole, indazole and benzotriazole it has been revealed[18] from fluorescence polarization data that the polarization directions of the lowest two absorptions are remarkably different to each other, and the first and third bands of benzimidazole have moderately close polarization directions. The calculated angle (by method I) between the two transition moments is 57° in benzimidazole, 48° (40°) in indazole and 85° (90°) in benzotriazole, the angle between the first and third transition moments in benzimidazole being 17°. According to method II the calculated angle is 73° in benzimidazole, 48° (40°) in indazole and 73° (90°) in benzotriazole, the angle between the first and third transition moments in benzimidazole being 6°. Such results are in line with the experimental facts.

The excitation energy of the lowest triplet state has been given for benzimidazole, indazole and benzotriazole as about 2.8, 2.6 and 2.8 eV, respectively.[18] The calculated excitation energy of the lowest triplet state of these molecules is by 0.4—1.2 eV (by method I) and 0.5—1.0 eV (by method II) lower as compared to the experimental values.

It may be said that the present calculations by method I on spectroscopic properties are in rather good correlation with the experimental results, although no specific adjustment of the core-resonance integral to the experimental transition energy is made. This encourages us to predict various chemical properties on the basis of the presently obtained $\pi$-electron distributions.

**Chemical Properties.** The calculated results on the $\pi$-electron distributions at the ground state, such as $\pi$-electron density and $\pi$-bond order, and the orbital energies of the highest occupied and lowest vacant ($\varepsilon_{h.o.}$ and $\varepsilon_{l.v.}$) are presented in Fig. 1(a), and for comparison the similar results evaluated by method II are also given Fig. 1(b). Comparative survey of the whole system will be useful especially for recognizing the effect of atom-rearrangements since the standardization of molecular geometry may remove complicated perturbations on the semiempirical integrals accompanied by geometrical variations.

As concerns oxazole and isoxazole molecules several features are eminent in the given molecular diagrams; the $\pi$-bond order of the N–O bond in isoxazole is very low as compared to those of the neighbouring bonds (particularly by method I), and the largest localized dipole is associated with the N–O bond. This predicts that the bond may be a preferred point of attack for any hydrolytic reagent. This bond, in fact, undergoes nucleophilic cleavage in sodium ethylate solution, differently from other azoles, and the cleavage is more facilitated in the state with a free 3-position than that with a free 5-position.[19] This preference of the position is also predicted by the presently given order of $q^{\pi}_{(C-3)} < q^{\pi}_{(C-5)}$. The present result indicates that oxazole gives less contribution of a shortly polarized ionic structure to hybrid resonance than isoxazole. The calcu-

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18) H. U. Schuett and H. Zimmerman, *Ber. Bunsenges. Phys. Chem.*, **67**, 54 (1963).
19) A. Quilico, *Atti. accad. nazl. Lincei, Rend. Classe sci. fis., mat. e nat.*, **15**, 357 (1953).

lated total $\pi$-energy of isoxazole is close to that of oxazole, and it seems probable that the $\pi$-energy stabilization in isoxazole is caused by the electrostatic interaction of the two oppositely polarized N and O atoms in spite of the reduced cyclic conjugation.

The relation of $q^{\pi}_{C(4)} > q^{\pi}_{C(2)}$ in oxazole is different from the result of a previous SCF calculation using the furan- and imidazole-type parameters for the empirical parameters.[9] The present result predicts that among the carbon atoms in oxazole ring the 5-atom has the largest $\pi$-electron density which is in line with a remark of other workers.[20] There is, however, a claim that the 2-atom should be expected to have a larger $q^{\pi}$ than the other two carbon atoms.[21] Electrophilic substitution on isoxazole is normally predicted to occur selectively at the C-4 position analogously to the $\beta$-position substitution in pyridine. This indicates that the influence of the nitrogen atom is predominant.

From comparison of the molecular diagrams of the four possible oxadiazole it is known that the $\pi$-electron density on the oxygen atom is almost invariant for all the molecules. This may indicate that with the same regular pentagon geometry the ionic structure with O(+) is equally predominant for all the molecules. It is of interest to note that the accepted mechanism for nucleophilic fission of the N–O bond in 1,2,4-oxadiazole is also accounted for by the low N–O $\pi$-bond order and $\pi$-electron density at the C-3. Electrophilic substitution such as nitration, halogenation or Friedel-Crafts' reaction are known not to occur at the C-3 or C-5 position of mono-substituted 1,2,4-oxadiazole.[22] This is in harmony with the present result which shows that these positions are markedly electron-deficient to favour nucleophilic substitutions.

In the case of the benzo-derivatives of oxazole, isoxazole and oxadiazoles the following effects of fused benzene-ring upon the $\pi$-electron distribution in each heterocyclic ring are known from the given molecular diagrams; in benzoxazole $\pi$-electrons on the hetero-ring are smoothly attracted toward the delocalized benzene-ring. In anthranil and benzofurazan the similar $\pi$-electron-migration occurs selectively along the O–N–C and O–N linkages, respectively. In 1,2,3-benzoxadiazole and indoxazene in which the $\pi$-dipole of the polar O(+)–N(−) bond is in direction against the fused benzene-ring, such migration is prohibitive. Electrophilic (nucleophilic) substitutions on indoxazene are predicted to occur in the increasing order of 7>5 (3>4,6), while the C-5 is assigned from experiment to the preferred point of electrophilic attack such as nitration[23] and bromination,[24] and the C-3 to the site of the initial nucleophilic attack in the N–O bond fission in alkaline solution,[25] respectively. Electrophilic (nucleophilic) substitution on anthranil is predicted to occur in the order of 5≈7 (3,6>4), and electrophilic halogenation[26] and nitration[27] are reported to occur at the 5-position. The corresponding orders in 1,2,3-benzoxadiazole and benzoxazole are 7>5 (6>4 by method I and 4>6 by method II), and 7>4,5,6 (2), respectively. The hydrolysis of benzoxazole in alkaline solution is possibly due to a nucleophilic attack on the C-2, but its electrophilic substitution such as nitration is known to occur at the C-6.

Concerning the negatives of the highest occupied orbital and lowest vacant orbital energies which represent ionization potential and electron affinity, respectively, it is of interest to note that the presence of the polar N–O bond in the benzo-derivatives as well as the five-membered heterocycles tends to increase both values so as to justify the contribution of the electrostatic interaction to $\pi$-energy stabilization. However, few experimental data are available to check the predicted tendency.

It is known[28] that indoxazene undergoes photochemical isomerization into benzoxazole and at the same time ring-cleavage into the nitrile of salicylic acid. The present calculation indicates that excitation into the lowest $^1(\pi, \pi^*)$ and/or $^3(\pi, \pi^*)$ state induces decrease of the $\pi$-bond orders in the O–N–C linkage of indoxazene and favours bond-lability (See the corresponding molecular diagrams in Fig. 2(a) and 2(b).).

More discussions will be made for the nitrogen-containing heterocycles; firstly, the experimental basic $pK_a$ values of five-membered heterocycles (6.95(imidazole), 2.53 (pyrazole), 2.55 (1,2,4-triazole))[29a] are found in bad correlation with the ordering of the $\pi$-electron density on the pyridine-type nitrogen. It is probable that the present disagreement is partly due to difference in the protonation energy except $\pi$-energy term, since a recent CNDO-type calculation of the total

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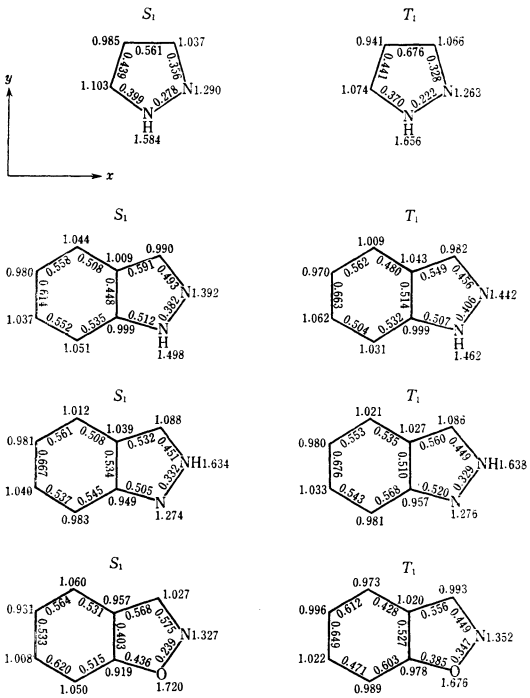


Fig. 2(a). Molecular diagrams at the lowest $^1(\pi, \pi^*)$—$S_1$— and $^3(\pi, \pi^*)$—$T_1$— states calculated by method I.

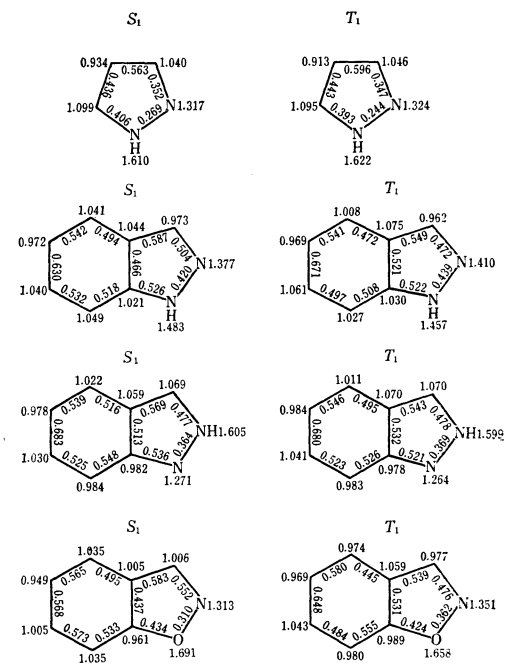


Fig. 2(b). Molecular diagrams at the lowest $^1(\pi, \pi^*)$—$S_1$— and $^3(\pi, \pi^*)$—$T_1$— states calculated by method II.

molecular protonation energy assuming the same regular pentagon geometry[29b] can predict correctly the experimental order of $pK_a$. Also, the predicted relations, $q^{\pi}_{=N-}$(pyrazole)$>q^{\pi}_{=N-}$(imidazole) and $q^{\pi}_{-\underset{H}{N}-}$(pyrazole)$\sim q^{\pi}_{-\underset{H}{N}-}$(imidazole) appear as incompatible with the observed order[30] of strength of the autoassociating hydrogen-bond in these molecules, indicating that the autoassociation involves complicated polymerization as usually accepted.

In the case of pyrazole the charge distribution predicts that electrophilic substitution occurs in the order of $4>5>3$, in agreement with the accepted fact that the ordinary electrophilic substitutions proceed readily at the 4-position. But the theoretical prediction for pyrazole should be modified because it is known that there is a tautomeric exchange of the position of the N–H bond so that the 3- and 5-positions should be considered as equivalent. As for imidazole the predicted order of electrophilic substitution is $5>2>4$, while nitration[31] and sulfonation[32] occur at the 5- and 4-positions. This may also be due to the equivalence of both positions associated with tautomerism. It should be mentioned here that diazonium coupling has been found to occur at the 2-position in imidazole, in disagreement with the predicted ordering. Electrophilic substitution on benzimidazole, 2*H*-indazole and 1*H*-indazole is predicted to occur in the order of $7\geqq6\geqq5\geqq4$ (by method I) and $7\geqq5\geqq6\geqq4$ (by methodII), $3>5>7>4$, and $7>5$, respectively, while it is known that nitration of benzimidazole occurs at the 5(6)-position,[33] and nitration[34] and halogenation[35] of indazole occur at the C-5 and C-3(5), respectively.

Electrophilic substitution on 1,2,3-triazole is predicted to occur at the 5-position, while actual bromination is known to give the 4,5-dibromo-derivative.[36] In the case of 1,2,4-triazole with $\pi$-electron-deficient C atoms, such electrophilic substitutions as halogenation, sulfonation and Friedel-Crafts' alkylation of the nucleus are unknown. Electrophilic substitution on 1*H*-benzotriazole is predicted to occur at the C-5 and C-7 positions, while nitration[37] and chlorination[38] are known to occur at the 4,7- and 4,5,6,7-positions,

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respectively.

It is known that the calculated ionization potential becomes higher by the increase of $\pi$-electron localization; among the five-membered diazoles and triazoles the largest value is found in 1,2,5-triazole with a polar N–NH–N linkage, and in the case of the molecules with one NH–N bond it is enhanced most for 1,2,4-triazole with alternate arrangement of plus and minus charges. The calculated electron affinity is in parallel relation with the corresponding ionization potential except for the case of 1,2,3- and 1,2,4-triazoles. So far as the present result is concerned, the effect of atom-rearrangement upon the relative orderings of both value is not affected by the replacement of pyrrole-nitrogen with furan-oxygen. On fusing the benzene-ring the ionization potential tends to be lowered, and the difference of the ionization potential and electron affinity is minimized at benzo-1,2,5-triazole in which the pyrrole-nitrogen mostly donates its $\pi$-electron to the whole conjugated system. Now, the lower ionization potentials calculated by method I are higher by $\sim$0.5 eV than those evaluated by a generalized free-electron model.[7]

It is known, by analogy with indoxazene, that 1*H*-indazole and pyrazole undergo photoisomerization into benzimidazole and imidazole, respectively.[39] But the mechanism in detail is unknown excepting that the presence of quinoid-type tautomer and the introduction of electron-donating group into the 5- or 6-position appears to favour the isomerization of 1*H*-indazole. For reference the $\pi$-electron distributions for the lowest $^1(\pi, \pi^*)$ and $^3(\pi, \pi^*)$ which were calculated with the CI procedure are given in Fig. 2(a) and 2(b). The result indicates that such excitations on 1*H*-indazole and pyrazole give rise to increased convertibility of 1*H*-indazole into 2*H*-tautomer as expected from the photoexcited change in the $\pi$-electronic state on the –NH–N–C– system, and to the increased lability of the pyrazole ring as expected from the much reduced $\pi$-bond orders.

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