

## Empirical Correlation of CNDO/2 and Extended Hückel Ionization Energies for the Azines

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Empirical corrections to orbital energies from CNDO/2 and Extended Hückel calculations for benzene are used in an attempt to calculate ionization energies of the azines. Some experimental tendencies are reproduced but the results are markedly inferior to those obtained by the same technique using *ab initio* wavefunctions.

Koopmans' theorem makes possible relatively simple calculations of molecular ionization energies but does not always give sufficient accuracy for the assignment of photoelectron spectra. For the azines, Koopmans' theorem seems to give the wrong ordering of ionization energies for  $n$  and  $\pi$  orbitals. Almlöf *et al.*<sup>1</sup> have performed *ab initio* calculations for benzene and the azine series adding empirical corrections to the calculated energies. These corrections were obtained for each orbital with a photoelectron line of definite assignment, in general from the benzene assignment by Lindholm *et al.*<sup>2</sup> With a "topological" classification of the orbital symmetries these corrections could be transferred also to the other molecules. The resulting assignment of the azines was in essential agreement with the work of Gleiter *et al.*<sup>3</sup>

It is well known that semi-empirical MO methods often introduce additional inaccuracies to those caused by Koopmans' theorem, and in their standard versions they are not accurate enough for the direct assignment of the azines.<sup>4,5</sup> Still, one may ask whether the procedure of Almlöf *et al.*, gauged to the benzene photoelectron spectrum might not give useful results for the azines. The present note shows this not to be the case using standard CNDO/2 and Extended Hückel wavefunctions.

Thus, we have first estimated the differences between experimental and calculated ionization energies for benzene using Koopmans' theorem and the assignment by Lindholm and coworkers.<sup>2</sup> We have then classified the orbitals of the azines according to the topological scheme of Almlöf *et al.* and assumed that the same corrections to Koopmans' theorem apply for each orbital in the azines as in benzene.

The classification scheme of Almlöf *et al.* is based upon an idealized cylinder symmetry ( $D_{\infty h}$ ). Orbital labels are of the form  $nA_p$ , where  $n$  is a "principal quantum number" describing node planes encircling the cylinder symmetry axis ( $n=1$ , no node plane;  $n=2$ , one plane, *etc.*), and  $A$  is an "angular" quantum number used for nodes passing through the cylinder axis (orbitals with 0, 1, 2, and 3 such planes are labelled  $S$ ,  $P$ ,  $D$ , and  $F$ ). The subscript indicates inversion symmetry ( $g$  for symmetric and  $u$  for antisymmetric orbitals).

Apart from benzene, the molecules considered are all nitrogen heterocycles which may be notionally derived from benzene by the successive replacement of CH-groups by nitrogen: pyridine has one N-atom, pyridazine, pyrimidine, and pyrazine two N-atoms, 1,3,5-triazine three N-atoms and 1,2,4,5-tetrazine four N-atoms. All molecules are planar and have 30 valence electrons and consequently 15 occupied valence molecular orbitals, counting degenerate orbitals separately.

### RESULTS

Table 1 shows the calculated and the observed ionization energies for benzene. For CNDO/2<sup>6</sup>

Table 1. Experimental and calculated (Koopmans' theorem) ionization energies of benzene (eV).

Orbital	Experi- mental	CNDO/2	Diff.	Extended Hückel	Diff.
$\sigma$ orbitals					
$1S_g$	25.9	51.2	-25.3	26.9	-1.0
$1P_{u'}^g, 1P_{u''}^g$	22.7	38.0	-15.3	23.7	-1.0
$1D_{g'}^g, 1D_{g''}^g$	19.1	30.5	-11.4	18.9	0.2
$2S_g$	16.9	29.3	-12.4	16.2	0.7
$1F_{u'}^g, 1F_{u''}^g$	14.9	21.7	-6.8	13.7	1.2
$1F_{u'}^g, 1F_{u''}^g$	15.6	20.0	-4.4	16.5	-0.9
$2P_{u'}^g, 2P_{u''}^g$	14.1	19.3	-5.2	14.4	-0.3
$2D_{g'}^g, 2D_{g''}^g$	11.8	14.4	-2.6	12.8	-1.0
$\pi$ orbitals					
$1S_u$	12.2	23.6	-11.4	13.9	-1.7
$1F_{g'}^g, 1F_{g''}^g$	9.3	14.1	-4.8	12.3	-3.0

the difference between these quantities is greatest for the innermost orbitals. This is to be expected from the known errors of Koopmans' theorem but is due mainly to the choice of parameters as may be seen by comparison with the *ab initio* calculations of Almlöf *et al.*<sup>1</sup> For the Extended Hückel method<sup>7</sup> ionization energy corrections are much smaller, especially for the  $\sigma$  orbitals.

The ionization energies from CNDO/2 calculations using Koopmans' theorem change relatively little with increasing nitrogen content, a result which is unchanged by the empirical corrections taken from benzene. The photoelectron spectra, however, show increasing

ionization energies with nitrogen substitution. After correction the deviations between observed and calculated ionization energies using CNDO/2 lie within 1.1 eV for pyridine, within 1.8 eV for the diazines and within 2.2 eV for 1,3,5-triazine. Exceptions are found for one level each of pyridazine, pyrazine, and 1,3,5-triazine. Even larger deviations are obtained for 1,2,4,5-tetrazine.

With the Extended Hückel method the agreement between orbital energies and ionization energies is better and the same is true for the results after correction. With one or two exceptions for each molecule the results are within 0.6 eV for pyridine, and within 1.3 eV

Table 2. Calculated and experimental ionization energies of pyridine and pyrazine. The calculated results are obtained using Koopmans' theorem corrections for benzene (eV).

	Pyridine CNDO/2	EH	AI	Exp.	Pyrazine CNDO/2	EH	AI	Exp.
$1S_g$	26.4	28.3	29.2	—	26.6	28.9	30.7	—
$1P_{u'}^g, 1P_{u''}^g$	22.2	22.7	23.2	23.3	21.7	22.7	24.0	24.0
$1P_{u'}^g, 1P_{u''}^g$	24.0	24.1	24.8	24.2	25.2	27.0	28.6	—
$1D_{g'}^g, 1D_{g''}^g$	19.1	19.4	19.6	19.6	19.0	19.7	20.5	20.6
$1D_{g'}^g, 1D_{g''}^g$	19.7	19.5	19.8	20.0	20.2	20.2	21.2	21.0
$2S_g$	16.3	16.8	17.0	17.1	15.4	17.0	17.2	17.1
$1F_{u'}^g, 1F_{u''}^g$	15.6	16.1	15.8	15.7	16.2	16.5	17.0	17.0
$1F_{u'}^g, 1F_{u''}^g$	16.0	15.6	15.7	15.7	16.6	15.5	16.4	16.2
$2P_{u'}^g, 2P_{u''}^g$	13.7	14.0	14.5	14.4	13.4	13.9	15.0	15.0
$2P_{u'}^g, 2P_{u''}^g$	13.1	14.2	13.8	13.7	11.7	14.1	11.4	11.7
$2D_{g'}^g, 2D_{g''}^g$	12.1	12.1	12.6	12.5	12.6	13.1	13.6	13.3
$2D_{g'}^g, 2D_{g''}^g$	10.7	11.3	9.6	9.7	10.1	11.0	9.4	9.4
$1S_u$	12.4	13.4	12.9	13.2	12.4	13.7	13.9	14.0
$1P_{g'}^g, 1P_{g''}^g$	9.3	9.2	9.5	9.7	9.3	9.2	10.0	10.2
$1P_{g'}^g, 1P_{g''}^g$	9.9	10.1	10.4	10.5	10.3	11.7	11.8	11.4

for the diazines. For 1,3,5-triazine and 1,2,4,5-tetrazine the deviations are within 1.9 eV.

The order of ionization energies, after correction, is in essential agreement with experiment and with the *ab initio* calculations for the inner valence orbitals. This is an expected result since it is also obtained with the Extended Hückel method directly.<sup>8</sup> Notable deviations, however, are obtained for the outermost orbitals. Even after correction the semiempirical wavefunctions fail to predict the correct ordering of  $\sigma$  and  $\pi$  states. The lowest  $\sigma$  ionization energy, conventionally related to a nitrogen lone-pair is systematically stabilized relative to the  $\pi$  orbitals, leading to erroneous assignments for the first ionization energy for all azines except, possibly, for pyridine. Representative results for pyridine and pyrazine are given in Table 2. The *ab initio* results as well as the experimental assignments are from Almlöf *et al.*,<sup>1</sup> the latter in essential agreement with the work of Gleiter *et al.*<sup>3</sup>

The systematic increase of the deviations with increasing nitrogen substitution may be interpreted as due to non-optimal nitrogen parameters relative to those of carbon and hydrogen. A reparametrization might therefore give some improvement.

The conclusion of the present study is that the utility of the approach of Almlöf *et al.* in assigning photoelectron spectra of series of similar molecules with conventional semiempirical wavefunction is limited.

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## REFERENCES

- Almlöf, J., Johansen, H., Roos, B. and Wahlgren, U. *J. Electron Spectrosc. Relat. Phenom.* 2 (1973) 51.
- Jonsson, B. Ö., Lindholm, E. and Skerbele, A. *Int. J. Mass Spectrom. Ion Phys.* 8 (1972) 101.
- Gleiter, R., Heilbronner, E. and Hornung, V. *Helv. Chim. Acta* 55 (1972) 255.
- Ellis, R. L., Jaffé, H. H. and Masmamdes, C. A. *J. Amer. Chem. Soc.* 96 (1974) 2623.
- Palmer, M. H., Gaskell, A. J. and Findlay, R. H. *Tetrahedron Lett.* 47 (1973) 4659.
- Pople, J. A. and Segal, G. A. *J. Chem. Phys.* 44 (1966) 3289.
- Hoffmann, R. *J. Chem. Phys.* 39 (1963) 1397.
- Friedh, C., Åsbrink, L., Jonsson, B. Ö. and Lindholm, E. *Int. J. Mass Spectrom. Ion Phys.* 8 (1972) 101.

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