The Effect of *d* Orbitals on the Calculated Ultraviolet Spectra of Organosulphur Compounds

By **John R. Grunwell** * and **Howard S. Baker**, Hughes Laboratories, Miami University, Oxford, Ohio 45056

The virtual orbital approximation to excited states using the results of CNDO/2–SCF–MO calculations has been used to evaluate the effect of *d* orbitals on the absorption spectra of thiolesters and sulphur–nitrogen compounds. In general, the predicted absorption maxima for $\pi \longrightarrow \pi^*$ transitions are too large; and although the inclusion of *d* orbitals improves the agreement with thiolesters this is not so for nitrogen–sulphur compounds. It is impossible to draw meaningful conclusions from such calculations about the necessity of *d* orbital participation.

THE electronic spectra of organosulphur compounds have provoked a great deal of speculation on the importance of *d* orbitals in the bonding of ground and excited states.[1,2] Recently, Williams and Kontnik[3] employed the virtual orbital method of Kroto and Santry[4] based on the CNDO/2–SCF–MO method of Pople,[5] as modified for third row elements by Segal and Santry,[6] in an effort to evaluate the importance of *d* orbitals in the determination of the electronic spectra of such cyclic sulphides as thiiran. The calculated absorption maxima agreed quite well with experiment, but only on inclusion of *d* orbitals in the basis set.

The calculations were limited to saturated molecules; and in consideration of our interest in the photochemistry of thiolesters and the structures of nitrogen–sulphur compounds containing the N:S:N system,[7,8] we also decided to investigate the importance of *d* orbitals to the excited states of unsaturated sulphur compounds where $\pi \longrightarrow \pi^*$ transitions represent the absorption maxima of longest wavelength. We have also used the CNDO/2 method of Santry[4] to calculate the transition energies E_{i-j} given by the relationship of equation (1) wherein ε_j and ε_i are respectively the unoccupied and

$$E_{i-j} = (\varepsilon_j - \varepsilon_i) - J_{ij} + 2K_{ij} \qquad (1)$$

occupied molecular orbitals, and J_{ij} and K_{ij} are expressed in (2) and (3). D and E are defined by equations (4) and (5), wherein C represents the coefficients of the

$$J_{ij} = \sum_{\mathrm{A}}\sum_{\mathrm{B}} D_i^{\mathrm{A}} D_j^{\mathrm{B}} \gamma_{\mathrm{AB}} \qquad (2)$$

$$K_{ij} = \sum_{\mathrm{A}}\sum_{\mathrm{B}} E_{ij}^{\mathrm{A}} E_{ij}^{\mathrm{B}} \gamma_{\mathrm{AB}} \qquad (3)$$

appropriate molecular orbitals, and γ_{AB} is the repulsion

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[1] G. Cilento, *Chem. Rev.*, 1960, **60**, 147.

[2] W. G. Salmond, *Quart. Rev.*, 1968, **22**, 253.

[3] D. R. Williams and L. T. Kontnik, *J. Chem. Soc.* (*B*), 1971, 312.

[4] H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, 1967, **47**, 792.

[5] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.

[6] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

[7] J. L. Downie, R. E. Maruca, and J. R. Grunwell, *Chem. Comm.*, 1970, 298.

[8] J. R. Grunwell and W. G. Danison, jun., *Tetrahedron*, 1971, **27**, 5315.

integral. Calculations were made with standard bond lengths and angles.[9]

$$D_i^{\mathrm{A}} = \sum_{\mu} {}^{\mathrm{A}}C_{\mu i}^2 \qquad (4)$$

$$E_{ij}^{\mathrm{A}} = \sum_{\mu} {}^{\mathrm{A}}C_{\mu i}C_{\mu j} \qquad (5)$$

RESULTS AND DISCUSSION

Examination of Tables 1 and 2 shows that the calculated value for the longest wavelength $\pi \longrightarrow \pi^*$ transition is too large by a factor of about two, For chlorobenzene and thioesters the inclusion of *d* orbitals in the basis set results in a reduction of the calculated transition energy by some 1·5—3·0 eV. Two effects contribute to this reduction in energy; thus, J_{ij} is larger, and the difference $(\varepsilon_j - \varepsilon_i)$ smaller when *d* orbitals are included in the calculation. That J_{ij} is larger derives from an increase in γ_{AB} when one of the atoms A is sulphur or chlorine.

TABLE 1

Calculated and observed electronic transitions for *para*-disubstituted benzene derivatives p-XC_6H_4Y[a,b]

X	Y	E_{i-j}(obs)	E_{i-j}(calc.)	$(\varepsilon_j - \varepsilon_i)$	J_{ij}	$2K_{ij}$
H	F	4·744[e]	11·2678	16·8357	7·9145	2·3466
H	Cl[c]	4·697[f]	11·1707	16·2507	6·6123	1·5322
H	Cl[d]		9·8253	15·5513	7·5577	1·8317
H	CN	4·567[f]	10·8402	16·0222	7·8799	2·6981
H	NO_2	4·654[f]	9·4885	22·8740	8·6812	−4·7042
H	NH_2	4·472[f]	10·1470	15·3745	7·1786	1·9511
H	SCOH[c]	5·385[g,h]	10·5176	15·2494	5·6902	0·9586
H	SCOH[d]		7·4882	13·8044	7·1566	0·8404
NO_2	SCOH[c]	4·351[g,h]	9·2986	13·2383	4·7243	0·7846
NO_2	SCOH[d]		8·0198	12·5228	5·2382	0·7352
NH_2	SCOH[c]	4·580[g,h]	9·5016	14·2778	6·3131	1·5369
NH_2	SCOH[d]		7·8254	13·3772	6·5367	0·9859

[a] All transitions are $\pi \longrightarrow \pi^*$ type. [b] Energies in eV. [c] No *d* orbital in the basis set. [d] With *d* orbitals. [e] ' U.v. Atlas of Organic Compounds,' Plenum Press, London, 1968, vol. 4D 7/3. [f] Ref. 10, ch. 12, p. 257. [g] The observed value is for X = $SCOCH_3$ and Y = Me_2N. [h] J. R. Grunwell and S. I. Hanhan, *Tetrahedron*, in the press.

TABLE 2

Calculated and observed electronic transitions for carbonyl compounds Me COX[a,b]

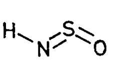
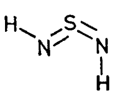
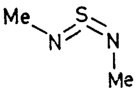
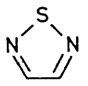
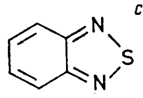
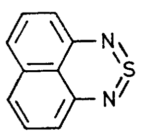
X	E_{i-j} (obs.)	E_{i-j}(calc.)	$(\varepsilon_j - \varepsilon_i)$	J_{ij}	$2K_{ij}$
Me[c]	4·502[g]	11·0910	17·2929	6·2087	0·0068
Me[d]		13·3640	19·2358	11·4016	5·5298
$H_2C{=}CH$[d]	3·870[h]	6·1357	15·6847	9·5509	0·0019
$H_2C{-}CH$[d]	5·827[h]	11·8105	16·7813	9·8941	4·9233
MeO[c]	5·896[i]	6·7191	18·4385	11·7390	0·0196
MeO[d]		12·7068	18·8848	10·5311	4·3531
Me_2N[c]		6·8883	17·9705	11·1023	0·0201
Me_2N[d]	5·680[j]	11·1723	17·0671	9·3784	3·4836
MeS[c,e]		6·1901	16·3241	10·1336	−0·0004
MeS[d,e]	5·385	10·2476	16·2398	7·3852	1·3930
MeS[c,f]		4·9675	15·0724	10·1064	0·0015
MeS[d,f]		7·2585	14·6942	8·7589	1·3182
$H_2C{=}CHS$[c,e]		6·8705	15·9541	9·0832	−0·0004
$H_2C{=}CHS$[d,e]	4·995	10·0152	15·5814	6·6668	1·1006
$H_2C{=}CHS$[c,f]		6·3014	14·3895	8·0873	−0·0008
$H_2C{=}CHS$[d,f]		7·0503	13·7854	8·0709	1·3358

[a] Energies in eV. [b] Structures have C–X–R of 109° and are cisoid. [c] $n \longrightarrow \pi^*$ Transitions. [d] $\pi \longrightarrow \pi^*$ Transitions. [e] No *d* orbitals in basis set. [f] With *d* orbitals. [g] Ref. 10, ch. 9, p. 187. [h] American Petroleum Institute Research Project 44I, 1949. [i] J. G. Calvert and J. N. Pitts, jun., ' Photochemistry,' Wiley, New York, 1966, ch. 5, p. 429. [j] P. P. Sherigin, *Izvest Akad. Nauk S.S.S.R. Otdel khim Nauk*, 1959, 2209.

Unlike thioesters, however, for compounds such as sulphur di-imides or thiadiazines which contain the N⁚S bond the inclusion of *d* orbitals has the opposite effect as shown by the results of Table 3. In these molecules, the principal effect of the inclusion of *d* orbitals in the basis set is to lower the energy of the HOMO ε_i thus causing the calculated transition energies for sulphur-nitrogen compounds to be greater than those calculated when *d* orbitals are excluded. The calculated stabilization of the HOMO can be as high as 2·5 eV.

TABLE 3

Observed and calculated electronic transitions for nitrogen–sulphur compounds[a,b]

Compounds	E_{i-j} (obs.)	E_{i-j}(calc.)	$(\varepsilon_j - \varepsilon_i)$	J_{ij}	$2K_{ij}$
 [c,d]		6·9716 7·8474	11·3200 15·1868	10·1126 10·8168	5·7642 3·9774
 [c,d]		6·5479 11·7458	10·4465 20·4549	9·7259 10·0609	5·8273 0·6759
 [c,d]	4·455[e]	4·6944 6·7499	8·5662 13·1785	9·1708 9·0773	5·2991 2·6486
 [c,d]		7·8512 6·3539	14·5772 13·3418	8·6908 9·1553	1·9648 2·1674
 [c,d]	4·061	7·0867 6·2246	10·6968 11·4289	7·6505 7·6500	4·0404 2·4457
 [c]	1·939[h]	0·0493 4·4305	8·8818 9·3580	9·1629 5·6924	0·3304 0·7649

[a] All transitions $\pi \longrightarrow \pi^*$. [b] Energies in eV. [c] No *d* orbitals in basis set. [d] With *d* orbitals. [e] Value for sulphur di-t-butyldi-imide. [f] D. Clemens, A. Bell, and J. O'Brien, *Tetrahedron Letters*, 1965, 1487. [g] J. L. Downie and J. R. Grunwell, unpublished results. [h] H. Behringer and K. Leiritz, *Chem. Ber.*, 1965, **98**, 3196.

Experimentally the $n \longrightarrow \pi^*$ transition occurs at longer wavelength than the $\pi \longrightarrow \pi^*$ transition for ketones and esters, although the $n \longrightarrow \pi^*$ transition occurs at much shorter wavelengths for esters than for ketones.[10] However, for amides[11] and thioesters, the

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[9] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, ch. 4. p. 111.

[10] H. H. Jaffe and M. Orchin, ' Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, ch. 9, pp. 179—180.

[11] E. B. Neilsen and J. A. Schellman, *J. Phys. Chem.*, 1967, **71**, 3914.

reverse situation occurs, *i.e.* the $\pi \longrightarrow \pi^*$ transition appears at the longer wavelength, with the thioesters at longer wavelength than amides.

However, the calculations show the $n \longrightarrow \pi^*$ transition to occur at lower energy for all the types of compound mentioned. The agreement between experiment and theory is poor, although better than for $\pi \longrightarrow \pi^*$ transitions. There are internal inconsistencies such as the prediction that the $n \longrightarrow \pi^*$ transition for acetone is of higher energy than that for methyl acetate.

The predicted longest wavelength transition for thioesters and amides is of the $n \longrightarrow \pi^*$ type despite the fact that the HOMO π type orbital is above that of the n type in energy so that the difference $(\varepsilon_j - \varepsilon_i)$ is greater for the $n \longrightarrow \pi^*$ transition. This energy difference $(\varepsilon_j - \varepsilon_i)$ is offset by J_{ij} which is some 1·0—2·0 eV larger for the $n \longrightarrow \pi^*$ transition, and by K_{ij} which is some 1·0—3·0 eV greater for the $\pi \longrightarrow \pi^*$ transition. The inclusion of *d* orbitals lowers the energy of the $n \longrightarrow \pi^*$ transition primarily because the energy of the π^* orbital is lowered, whilst that of the n orbital is virtually unchanged.

Conformational changes around the carbonyl C–X bond have but little effect on the transition energies of either the $n \longrightarrow \pi^*$ or $\pi \longrightarrow \pi^*$ type; and further, the individual terms of equation (1) are essentially constant. Changes in the $\widehat{\mathrm{C{-}X{-}C}}$ bond angle from 109 to 120° also have no effect on the calculated energies.

By Koopmans' theorem,[12] the ionization potential I_{p} of a molecule can be approximated by the orbital energy ε_i; but the CNDO/2 ε_i values are much larger (by 3—4 eV) than the observed ionization potentials. Therefore, the major source of error in the predicted $\pi \longrightarrow \pi^*$ transition energies is due to the large energy for the occupied molecular orbitals.

In view of this large error in the orbital energies, it is impossible to make a meaningful judgment as to whether or not the inclusion of *d* orbitals in the calculations is necessary to explain $\pi \longrightarrow \pi^*$ electronic transition energies. For sulphur–nitrogen compounds the absence of *d* orbitals which stabilizes the already over-stabilized ε_i values gives a more accurate prediction of the transitions; whilst the presence of *d* orbitals seems to improve the accuracy of the prediction for thioesters. However, *d* orbital participation did not change the prediction that $n \longrightarrow \pi^*$ transitions should occur at longer wavelength than $\pi \longrightarrow \pi^*$ transitions for thioesters. Therefore, we believe the results of Williams and Kontnik[3] to be fortuitous.

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[12] T. Koopman, *Physica*, 1933, **1**, 104.