$$\psi = \frac{e^{ikR}}{R} \cdot \frac{ik}{2\pi} \int\int_{-\infty}^{+\infty} e^{i(xq_x + yq_y)} \left(1 - e^{-\frac{i}{2k}\int_{-\infty}^{+\infty}(-V)dz}\cdot\right) dx\,dy = \frac{e^{ikR}}{R} A(k_f, k_0), \tag{1}$$

$q = k_0 - k_f$, k_f and k_0 being of magnitude k and having the directions respectively of scattering and of φ, R is the distance from the center of the sphere to the point of observation, $V = \hbar^2 U/2\mu$, U is the scattering potential, μ is the mass of a scattering particle; and $\hbar$ is Planck's constant. Formula (1) is true for vibrations of electric type, but these coincide with the magnetic ones for $kr \gg 1$ [5]. We may put $+V$ as $+V = (m^2 - 1)k^2$ within the sphere and $+V = 0$ elsewhere, for then Helmholtz's equation formally coincides with Schrödinger's equation, whose solution is (1). The first term in (1) is the formula for Fraunhofer diffraction with this choice for $+V$.

From (1) and this $+V$ we may calculate the scattered intensity $I = |\psi|^2$ and the attenuation factor $\sigma = (4\pi/k)\mathrm{Im}\,A$ (k_0, k_0) for $|m - 1| \to 0$, which gives us all the results of chapter 11 of [6].

The following formula is readily derived for the refractive index α of a medium containing N particles per unit volume:

$$\alpha = 1 + Nr^2 \frac{2\pi}{k} \left\{ -e^{-\rho\,\mathrm{tg}\,\beta} \frac{\cos\beta}{\rho} \cos(\rho - \beta) + \right.$$
$$+ e^{-\rho\,\mathrm{tg}\,\beta} \frac{\cos^2\beta}{\rho^2} \sin(\rho - 2\beta) + \left. \frac{\sin 2\beta \cos^2\beta}{\rho^2} \right\},$$
$$\rho = 2(n-1)kr, \quad \mathrm{tg}\,\beta = \varkappa(n-1), \quad m = n - i\varkappa.$$

Also, (1) enables us to calculate the characteristics of a multilayer sphere; for instance, the attenuation factor of a transparent ($\chi = 0$) two-layer spherical particle is

$$\sigma = \pi r_2^2 (2 - X_1 - X_2); \quad X_1 = [2 - K(\rho_2, \beta_2)] \cdot [1 - r_1/r_2],$$
$$X_2 = 4 \int_0^{r_1\,r_2} \cos\left[\rho_2\sqrt{1 - \xi^2} + \rho_2[(n_1 - 1)/(n_2 - 1) - 1]\sqrt{(r_1/r_2)^2 - \xi^2}\right] \xi\,d\xi.$$

Subscript 1 relates to the core and subscript 2 to the outer shell; $K = \sigma'/\pi r_2^2$, in which σ' is the attenuation factor for a sphere of radius r_2 and having $m = n_2$ in this approximation.

REFERENCES

1. H. S. Green and E. Wolf, Proc. Phys. Soc., 66A, 1129, 1953.
2. E Wolf, Proc. Phys. Soc., 74, 269, 1956.
3. P. Roman, Acta Phys. Hung., 4, 209, 1955.
4. L. Schiff, Phys. Rev., 103, 443, 1956.
5. M. Born, Optics [Russian translation], ch. 6, GONTI, 1937.
6. H. van der Holst, Scattering of Light by Small Particles [Russian translation], IIL, Moscow, 1961.

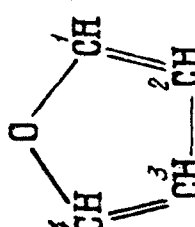# CALCULATION OF THE π-ELECTRON STRUCTURE OF SOME VINYL ETHERS BY THE SEMIEMPIRICAL SELF-CONSISTENT FIELD METHOD

Yu. L Frolov

Values are discussed for the resonance integral of $C-O(\beta_{C-O})$ and for the parameter $\delta\omega_O$ of the oxygen atom for use in π-electron calculations for vinyl ethers by means of a semiempirical form of the MOLCAO self-consistent field method; $\delta\omega_O$ equals $\omega_O - \omega_C$, in which, in general, ω_i is the part of the coulomb integral $\alpha_i = \omega_i - \sum_{j(\neq i)} N_j \gamma_{ij}$ dependent only on the type and valency state of atom i in the approximation used. The subscripts O and C correspond to oxygen and carbon, the γ_{ij} are the two-electron repulsion integrals, and N_j is the number of p- or π-electrons brought into the molecular structure by atom j.

The sequence of operations is as follows. First the electronic absorption spectrum (band with peak at 192 mμ [1],

Parameters (eV) of Vinyl-n-Butyl Ether, Divinyl Ether, and Furan

Compound	α_{OO}	β_{C-O}	β_{C-C}	γ_i	γ_{ij}	ε_μ	Transition energies			
							Calculation		Measurements	
							Singlet	Triplet	Singlet	Triplet
$C_4H_9-O-\overset{1}{C}H=\overset{2}{C}H_2$	-16.5	-1.65	-2.92	$\gamma_0=15.05$ $\gamma_1=10.73$ $\gamma_2=10.61$	$\gamma_{01}=8.15$ $\gamma_{02}=5.75$ $\gamma_{12}=7.45$	-12.51 -9.72 -2.73	6.57 8.42	3.90 7.40	6.5 >7.4	
$\overset{3}{C}H_2=\overset{4}{C}H-O-\overset{1}{C}H=\overset{2}{C}H_2$	-16.5	-1.65	-2.92	$\gamma_0=15.10$ $\gamma_1=\gamma_4=10.70$ $\gamma_2=\gamma_3=10.63$	$\gamma_{01}=\gamma_{04}=8.15$ $\gamma_{02}=\gamma_{03}=5.75$ $\gamma_{14}=5.75$ $\gamma_{23}=3.00$ $\gamma_{12}=\gamma_{34}=7.45$ $\gamma_{13}=\gamma_{24}=3.95$	-13.31 -11.03 -9.39 $+2.16$ $+2.89$	6.05 7.05 8.40 8.55 9.05 9.60	4.85 5.40 6.60 7.25 8.50 8.90	6.05	
(furan ring structure)	-16.5	-1.65	$\beta_{12}=\beta_{34}=$ $=-2.75$ $\beta_{23}=$ $=-1.95$	$\gamma_0=15.20$ $\gamma_1=\gamma_4=10.63$ $\gamma_2=\gamma_3=10.63$	$\gamma_{01}=\gamma_{04}=8.15$ $\gamma_{02}=\gamma_{03}=6.00$ $\gamma_{12}=\gamma_{31}=7.40$ $\gamma_{14}=5.90$ $\gamma_{23}=7.20$ $\gamma_{13}=\gamma_{24}=5.80$	-13.65 -10.30 -9.72 $+1.94$ $+3.53$	5.75 6.50 7.50 7.40 8.50 10.60	4.05 4.60 5.80 6.30 7.40 10.00	6.05 6.5 7.8	4.9

supposed band in 130-160 mμ region) is used to select the parameters for vinyl-n-butyl ether; then these are used to calculate the structures of divinyl ether and furan, the results being compared with experiment (UV spectra). Pople's method [2, 3] is used, the two-center electron-repulsion integrals being calculated by the method of [4], while the γ_i are found from $\gamma_i = 3.29\, Z_i^{eff}$ [5], in which the Z_i^{eff} are the effective nuclear charges calculated from Slater's rule, but with allowance for the charge distribution of the mobile electrons:

$$\text{for C} \qquad Z_i^{eff} = 3{,}60 - 0{,}35\, p_{ii},$$

$$\text{for O} \qquad Z_j^{eff} = 5{,}25 - 0{,}35\, p_{jj};$$

in which p_{ii} and p_{ij} are the charges of the mobile electrons on the corresponding atoms.

The table gives the results, in which ε_μ is the energy of the molecular orbital; the numbers are those of the carbon atoms. The energies of the electronic transitions have been calculated without allowance for interaction between configurations. The β_{C-C} are from $\beta(r) = 2523 \exp(-5.0085\, r)$, the basic data for this coming from benzene and ethylene [4], i.e., $\beta(1.39 = -2.39$ eV and $\beta(1.35) = -2.92$ eV. The lengths of the C—C bonds in furan are from the microwave spectrum [6]. The 252 mμ band of furan is very weak [7, 8] (peak extinction coefficient about one), and this may be assigned to the transition to the triplet state (calculated energy 4.6 eV).

The results are in satisfactory agreement with experiment; the parameters can be applied to molecules with the structure R_1—O—R_2, R_1 and R_2 being unsaturated hydrocarbon radicals.

The calculated electron-density distributions are
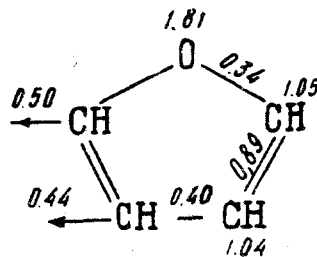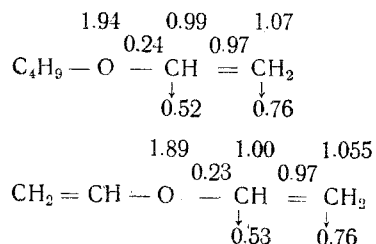
The results are in good agreement with the reactivity. The two ethers have negative charges on the β-carbon; they react with halogens in accordance with Markovnikoff's rule. The calculated electron-density distribution for furan indicates that the α-carbon is highly reactive in electrophilic attack and radical processes. The free-valency results for furan resemble those for aromatic compounds; in fact, the α-hydrogen is replaced by bromine [9], but the double bond is not broken. This is typical of aromatics.

REFERENCES

1. P. P. Shorygin, T. N. Shkurina, M. F. Shostakovskii, and E. P. Gracheva, Izv. AN SSSR, Otdel. Khim. Nauk, 1011, 1961.

2. J. A. Pople, Trans. Faraday Soc., 49, 1375, 1953.

3. J. A. Pople, Proc. Phys. Soc., London, A68, 81, 1955.

4. R. Pariser and R. G. Parr, J. Chem. Phys., 21, 767, 1953.

5. L. Paoloni, Nuovo Cimento, 4, 410, 1956.

6. B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. R. Andersen, and M. Schöttländer, J. Molec. Spectrosc., 9, 124, 1962.

7. L. W. Picket and N. J. Hoeflich, J. Amer. Chem. Soc., 73, 4865, 1951.

8. M. K. Orloff and D. D. Fitts, J. Chem. Phys., 38, 2334, 1963.

9. P. Carrer, Textbook of Organic Chemistry [Russian translation], Goskhimizdat, Leningrad, p. 959. 1962.

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