

CALCULATION OF THE EXCITED LEVELS OF INDENE

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(Received for publication, July, 7, 1953)

ABSTRACT The energy of the excited levels of indene is calculated by the method of anti-symmetrised Molecular Orbitals. The observed band system at 252Å is assigned to a ${}^1L_1 - {}^3M_1$ transition. The results of the M.O. and the A.O. methods of treatment are compared.

INTRODUCTION

It may be generally stated that the concept of unique electron configuration is valid for molecules also. This electron configuration is assigned for a given molecule by two methods usually called the Atomic Orbital (A.O.) and the Molecular Orbital (M.O.) methods. In the first method, a molecule is treated as compounded of several atoms and ions. The electron configuration is made up of the electron configurations of the different atoms. The wavefunctions of the molecule are written down as products of atomic orbitals (A.O.'s)—one electron wavefunctions in atoms. Energy values are then obtained by a variation method, as the roots of a secular equation. In the second method, the molecule is treated, as far as possible, as a unit. The wavefunction of the molecule is written down as (anti-symmetrised) product of a set of molecular orbitals (M.O.'s). These are solutions of Schrodinger's equation for an electron in the field due to the nuclei and all other electrons. In practice, this equation cannot be solved. The M.O.'s are written as linear combinations of a complete set of functions. This set might well be the A.O.'s of any one of the atoms of the molecule. But the difficulty, in this case is that the M.O.'s thus constructed converge too slowly. The use of orbitals of all the atoms of the molecule leads to better convergence. M.O.'s thus constructed as linear combinations of the A.O.'s of the concerned atoms, are called the L.C.A.O. forms of the M.O.'s. Having thus assigned the electron configuration, the calculation of energy levels was carried out on the basis of the theorem that the value of energy in a state ϕ is $\int \phi^* H \phi d\tau$, H being the Hamiltonian.

The A.O. method has been employed by Viswanath (1953) recently to calculate the energy levels of indene. Excited levels are predicted with energy values 3.84, 8.25, 105.67 eV above the ground level. All the levels conform to singlet symmetrical states 1A . In benzene and other molecules, the M.O. method is sometimes stated to give a better approximation than the A.O. method (Longuet-Higgins, 1948). The purpose

of this paper is to apply the second, antisymmetrised molecular orbital method to the indene molecule. The treatment of the problem is similar to that followed by Goepfert-Mayer and Sklar (1938) for benzene. The results are presented, in detail, in the following sections. A brief preliminary report has been published in "Current Science" (Ramamurty, 1953).

ANALYTICAL PART

The structure of indene is shown in figure 1. The molecule belongs to the symmetry group C_{2v} . In indene (as in benzene) only the $2p\pi$

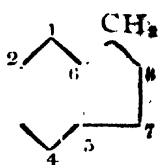


FIG. 1

electrons are spectroscopically active and hence only the molecular states of these electrons need be considered. These have a node in the plane of the molecule. There are eight $2p\pi$ electrons in indene, as was assumed by Viswanath in the A.O. calculations previously. The same assumption is made here also. The numbering of the electrons is shown above.

Representing the electrons by Greek letters μ, ν (ranging from 1 to 8) and the $2p\pi$ eigenfunction on the k th atom by $K(\nu)$ (ranging from I to VIII) and taking these to be positive on the same side of the indene plane, the molecular orbitals employed in this work are

$$\phi_l = \frac{1}{\sqrt{8\sigma_l}} \sum_{\nu=1}^8 e^{i2\pi l\nu} K(\nu)$$

with $l=0, \pm 1, \pm 2, \pm 3, 4$. σ_l 's are normalising factors. Evidently $\phi_l = \phi_{-l}^*$. ϕ_l, ϕ_{-l} have the same energy (ϵ_l , say). Also neglecting overlap integrals and integrals over products of non-neighbouring A.O.'s, the energy of the ϕ_l 's rises with $|l|$.

The energy of the molecule is lowest if the eight electrons are distributed in $\phi_0, \phi_1, \phi_{-1}, \phi_2$ two in each. The eigenfunction for the whole molecule is therefore

$$\psi_0 = \phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6)\phi_2(7)\phi_2(8).$$

The excited levels arise by a ϕ_2 electron jumping into ϕ_3, ϕ_{-3} or ϕ_4 . They are

$$\begin{aligned} &\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6)\phi_2(7)\phi_3(8) \\ &\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6)\phi_2(7)\phi_{-3}(8) \\ &\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6)\phi_2(7)\phi_4(8). \end{aligned}$$

All states belong to the symmetry type A_1 .

These must be multiplied by the appropriate spin factors. If two electrons are in the same M.O., they must have opposite spins. Thus for the ground state, the spin factor is

$$\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\alpha(7)\beta(8).$$

For the excited levels the ϕ_2 , ϕ_3 or the ϕ_2 , ϕ_{-3} or the ϕ_2 , ϕ_4 electrons may have their spins opposed or parallel. In the first case, the spin factor must be anti-symmetric and is

$$\frac{1}{\sqrt{2}} \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) [\alpha(7)\beta(8) - \alpha(8)\beta(7)].$$

In the second case, the spin factor must be symmetric; there are three of them and these are

$$\begin{aligned} &\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\alpha(7)\alpha(8) \\ &\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\beta(7)\beta(8) \end{aligned}$$

$$\frac{1}{\sqrt{2}} \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) [\alpha(7)\alpha(8) + \beta(7)\beta(8)].$$

In the first case, the states are said to be singlets. In the second case, they are said to be triplets. As we neglect in our calculation the spin-orbit interaction, the triplet will not be separated.

The totally anti-symmetrised wavefunction is then obtained by multiplying the orbital with the spin factor and applying the anti-symmetrising operator. Thus the anti-symmetrised wavefunction of the ground state is

$$\begin{aligned} \Psi_0 = & \frac{1}{\sqrt{8!}} \sum (-1)^P P \phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6)\phi_2(7)\phi_2(8) \\ & \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\alpha(7)\beta(8). \end{aligned}$$

The energy of the state is then equal to the sum of the energies of the separate M.O.'s and the energy due to the interaction of the electrons. The latter has the potential

$$H^{(1)} = \sum_{\nu=1}^8 \sum_{\mu < \nu} \frac{e^2}{r_{\nu\mu}}$$

The energy of the ground state is thus

$$2\epsilon_0 + 4\epsilon_1 + 2\epsilon_2 + \int \Psi_0^* H^{(1)} \Psi_0 d\tau.$$

The integral expressing the average value of $H^{(1)}$ can be expanded in terms of two types of integrals, viz.,

$$\gamma_{\mu\nu} = \iint \frac{e^2}{r_{\nu\mu}} |\phi_i(\nu)|^2 |\phi_i'(\mu)|^2 d\tau_\nu d\tau_\mu$$

$$\delta_{\mu\nu} = \iint \frac{e^2}{r_{\nu\mu}} \phi_i(\nu)\phi_i'(\mu) [\phi_i(\mu)\phi_i'(\nu)]^* d\tau_\nu d\tau_\mu$$

The energies including the electronic interaction for the ground state and the excited singlet and triplet levels are

$$\begin{aligned}
 E_g &= 2\epsilon_0 + 4\epsilon_1 + 2\epsilon_2 + \gamma_{0,0} + 8\gamma_{0,1} + 4\gamma_{0,2} + 6\gamma_{1,1} + 8\gamma_{1,2} + \gamma_{2,2} \\
 &\quad - 4\delta_{0,1} - 2\delta_{0,2} - 2\delta_{1,-1} - 2\delta_{1,2} - 2\delta_{-1,2} \\
 (\phi_2 \rightarrow \phi_1)E_s &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,3} + 6\gamma_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,3} + \gamma_{2,3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,3} - 2\delta_{1,-1} - \delta_{1,2} \\
 &\quad - \delta_{1,3} - \delta_{-1,1} + \delta_{2,1} \\
 (\phi_2 \rightarrow \phi_{-3})E_s &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,-3} + 6\gamma_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,-3} + \gamma_{2,-3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,-3} - 2\delta_{1,-1} \\
 &\quad - \delta_{1,2} - \delta_{-1,2} - \delta_{1,-3} - \delta_{-1,-3} + \delta_{2,-3} \\
 (\phi_2 \rightarrow \phi_1)E_t &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,3} + 6\gamma_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,3} + \gamma_{2,3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,3} - 2\delta_{1,-1} \\
 &\quad - \delta_{1,2} - \delta_{-1,2} - \delta_{1,3} - \delta_{-1,3} + \delta_{2,3} \\
 (\phi_2 \rightarrow \phi_1)E_t &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,-3} + 6\gamma_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,3} + \gamma_{2,3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,3} - 2\delta_{1,-1} \\
 &\quad - \delta_{1,2} - \delta_{-1,2} - \delta_{1,3} - \delta_{-1,3} - \delta_{2,3} \\
 (\phi_2 \rightarrow \phi_{-3})E_t &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,-3} + 6\delta_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,-3} + \gamma_{2,3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,-3} - 2\delta_{1,-1} \\
 &\quad - \delta_{1,2} - \delta_{-1,2} - \delta_{1,-3} - \delta_{-1,-3} - \delta_{2,-3} \\
 (\phi_2 \rightarrow \phi_1)E_t &= 2\epsilon_0 + 4\epsilon_1 + \epsilon_2 + \epsilon_3 + \gamma_{0,0} + 8\gamma_{0,1} + 2\gamma_{0,2} + 2\gamma_{0,3} + 6\gamma_{1,1} \\
 &\quad + 4\gamma_{1,2} + 4\gamma_{1,3} + \gamma_{2,3} - 4\delta_{0,1} - \delta_{0,2} - \delta_{0,3} - 2\delta_{1,-1} \\
 &\quad - \delta_{1,2} - \delta_{-1,2} - \delta_{1,3} - \delta_{-1,3} - \delta_{2,3}
 \end{aligned}$$

g indicates ground state ; *s*, singlet and *t*, triplet state

NUMERICAL CALCULATIONS

The integral γ 's and δ 's over M. O.'s are expressed in terms of integrals over A, O.'s by using the Huckel type orbitals written above.

First of all, the normalising factors σ_l 's are determined by the following equation :

$$\begin{aligned}
 \sigma_l &= \frac{1}{k} \int \sum e^{\frac{2\pi i l k}{8}} K(v) \sum e^{-\frac{2\pi i l k}{8}} K(v) d\tau, \\
 &= \frac{1}{k} \left[8 + \left(12 \cos \frac{\pi l}{4} + 2 \cos \frac{5\pi l}{4} \right) S_1 + \left(12 \cos \frac{\pi l}{2} + 4 \cos \pi l \right) S_2 \right. \\
 &\quad \left. + \left(8 \cos \frac{3\pi l}{4} + 2 \cos \frac{\pi l}{4} \right) S_3 \right]
 \end{aligned}$$

Where $S_1 = \int I(v)II(v)d\tau_v$, $S_2 = \int I(v)III(v)d\tau_v$, $S_3 = \int I(v)IV(v)d\tau_v$ and overlap integrals over electrons 1, 2, 3, 4 on the one hand and 7, 8 on the other are neglected.

Next, the expansions of integrals $\gamma_{ll'}$, $\delta_{ll'}$, will contain the following types of integrals :

$$A_K = \iint \frac{e^2}{rv\mu} I^2(v)(K+1)^2(\mu) d\tau_v d\tau_\mu$$

$$B = \iint \frac{e^2}{rv\mu} I^2(v)I(\mu)II(\mu) d\tau_v d\tau_\mu$$

$$C = \iint \frac{e^2}{rv\mu} I(v)II(v)I(\mu)II(\mu) d\tau_v d\tau_\mu$$

Interaction between electrons which are partially on atoms which are not closest neighbours as also between electrons 1, 2, 3, 4 on the one hand and 7, 8 on the other are neglected.

Lastly, we have

$$\begin{aligned} \epsilon_l &= \int \frac{1}{\sqrt{8\sigma_l}} \sum e^{-\frac{2\pi ilh}{8}} K(v)(T+H_0) \frac{1}{\sqrt{8\sigma_l}} \sum e^{-\frac{2\pi ilh}{8}} K(\gamma) d\tau_v \\ &= \frac{1}{8\sigma_l} \int I(v)(T+H_0) \left\{ 8I(v) + \left(2 \cos \frac{5\pi l}{4} + 12 \cos \frac{\pi l}{4} \right) II(v) \right. \\ &\quad \left. + \left(4 \cos \pi l + 12 \cos \frac{\pi l}{2} \right) III(v) + \left(2 \cos \frac{\pi l}{4} + 8 \cos \frac{3\pi l}{4} \right) IV(v) \right\} d\tau_v \end{aligned}$$

where T is the kinetic energy and H_0 the potential energy. Neglecting the effect of hydrogen atoms completely

$$H_0 = \sum H_K$$

where H_K is the potential of the attraction of the k th carbon nucleus and of the repulsion of the other five electrons on the k th nucleus. Obviously, H_K is the difference between the potential of a neutral carbon atom \bar{H}_K and the potential of a $2p\pi$ electron,

$$H_K = \bar{H}_K - \int \frac{e^2}{rv\mu} K^2(\mu) d\tau_\mu$$

Also as $K(v)$ is a $2p\pi$ eigenfunction,

$$(T+H_0)K(v) = W_{2p}K(v)$$

where W_{2p} is the energy of a $2p$ level in carbon atom in a valence state. Bearing this in mind and substituting for H_0 as above, two new kinds of integrals arise in the expression of ϵ_l namely,

$$Q = - \int \bar{H}_1(v)II^2(v) d\tau_v,$$

$$\text{and } R = - \int \bar{H}_1(v)I(v)II(v) d\tau_v.$$

All interaction between non-neighbours is neglected. Then

$$\epsilon_l = \frac{1}{\sqrt{8\sigma}} \left(8\sigma_l W_{2p} - 8(2Q + 2A_1 + 2A_2 + A_3) - \left(2 \cos \frac{5\pi l}{4} + 12 \cos \frac{\pi l}{4} \right) (R+B) \right)$$

Assuming the C=C distance in indene to be 1.39 Å *i.e.* equal to that in benzene, the values of the integrals $S_1, S_2, S_3, A_0, A_1, A_2, A_3, B, C, Q, R$ can be taken over from the benzene calculations of Goepfert-Mayer and Sklar (1938). The energy levels of indene, relative to the ground level, are obtained to be 0, 0.36, 3.89, 8.39, 10.615, 10.628, 11.82.

The energy levels are shown in figure 2. It is clear from it that the observed band system at 2952 Å arises from a jump $\phi_2 \rightarrow \phi_3$ (${}^1A_1 - {}^3A_1$) *i.e.*, from a singlet to triplet transition. Such transitions are highly probable in complex molecules (Kasha, 1950).

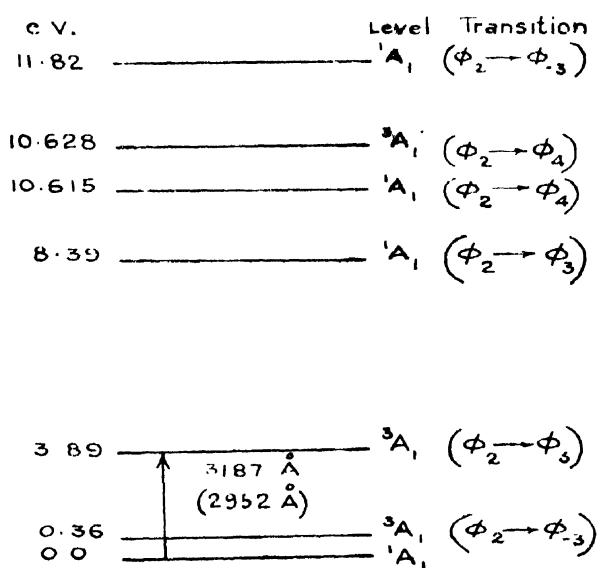


FIG. 2

Comparing the results of A.O. and M.O. calculations, they give nearly the same values for lower excited levels. The lower excited level at 0.36 eV, however, does not appear in the A.O. treatment. The M.O. method gives even in respect of lower excited levels a better approximation to the experimental values, for indene by 40 Å. Also the M.O. method enables us to calculate the energy levels state by state, taking the group-theoretical aspect also into account in the calculation itself. Further, the M.O. method is clear as to the multiplicity and symmetry character of the state.

SUMMARY

The energy levels of indene have been calculated by the method of anti-symmetrised molecular orbitals. In applying this method the following assumptions have been made

1. The molecule has eight $2p\pi$ electrons.
2. Huckel type M.O. forms are used

$$\varphi_k = \frac{1}{\sqrt{8}} \sum_{l=1}^{2\pi/lk} \sigma_l \bar{\epsilon}^{-1}$$

3. Interaction between electrons partially on non-neighbouring atoms as also between electrons 1, 2, 3, 4 on the one hand and 7, 8 on the other have been neglected. Effect of hydrogen atoms and spin-orbit interaction is also neglected.

4. The C=C distance in indene is taken as 1.39 Å.

Reckoning from the ground state the energy levels are obtained to be 0, 0.36, 3.89, 8.39, 10.615, 10.628, 11.82 eV. The observed band system at 2952 Å should arise, according to this treatment, from the ground state to a triplet excited level.

ACKNOWLEDGMENT

The author would like to express his indebtedness to Prof. K. R. Rao for his kind guidance and interest in the work.

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