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# HUCKEL CALCULATIONS ON DECACYCLENE

P. N. SEN, B. CHAKRABARTI and S. K. BOSE
Department of Pure Chemistry, University College of Science, Cal-9, India

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**Abstract**—The Huckel calculations on decacyclene are reported together with the dynamical Jahn Teller distortion energies. The distortion energies are rather small, the value for the negative ion being smaller than that for the positive ion.

ELECTRON spin resonance measurement[1] shows that the dinegative decacyclene (Fig. 1) exists in a triplet state. This suggests that the first empty $\pi$-electron M.O. is doubly degenerate. Further, since this compound is a non-alternant hydrocarbon, the spin densities in positive and negative ions should be different. In order to get some useful information about this large conjugated ring system, simple Huckel calculations were made on decacyclene the results of which are reported in the present paper.

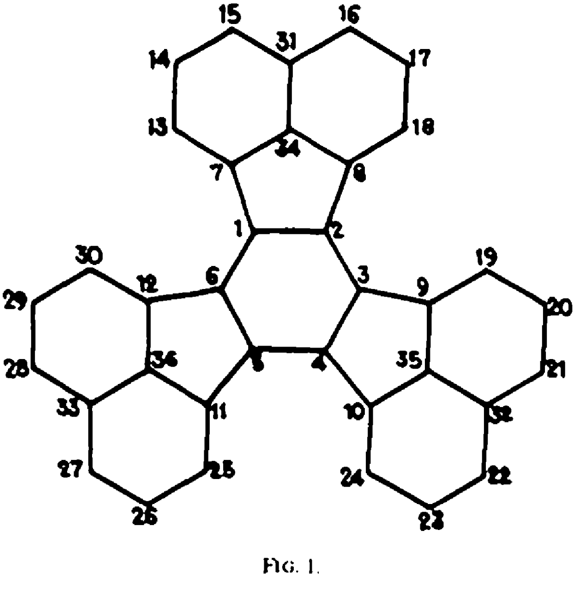

FIG. 1.

The molecular orbitals of decacyclene are obtained in terms of the irreducible representations of the point group $C_{3v}$ as:

$$\Gamma_{MO} = 7A_1 + 5A_2 + 12E.$$

The thirty six $\pi$-electrons of the molecule occupy the eighteen lowest levels.

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[1] R. E. Jesse, P. Biolen, R. Prins, J. D. W. Van Voorst and G. J. Hoijtink, *Mol. Phys.* 6, 633 (1963).

*Electron densities and bond orders.* From the values of the A.O. coefficients the electron densities $q_i$ and bond orders $p_{r,s}$ are calculated from the relation

$$q_i = 2\sum C_i^2 \cdot p_{r,s} = \sum C_r C_s$$

where $C_i$, $C_r$, $C_s$ refer to occupied M.O.s.

These are listed in Tables 1 and 2.

TABLE 1. CHARGE DENSITIES

$q_1 = q_2 = q_3 = q_4 = q_5 = q_6 = 1{\cdot}0313$

$q_7 = q_8 = q_9 = q_{10} = q_{11} = q_{12} = 1{\cdot}0300$

$q_{13} = q_{18} = q_{19} = q_{24} = q_{25} = q_{30} = 0{\cdot}9497$

$q_{14} = q_{17} = q_{20} = q_{23} = q_{26} = q_{29} = 1{\cdot}0051$

$q_{15} = q_{16} = q_{21} = q_{22} = q_{27} = q_{28} = 0{\cdot}9596$

$q_{31} = q_{32} = q_{33} = 0{\cdot}9988$

$q_{34} = q_{35} = q_{36} = 1{\cdot}0542$

TABLE 2. BOND ORDERS

$p_{1.2} = p_{3.4} = p_{5.6} = 0{\cdot}5686$

$p_{2.3} = p_{4.5} = p_{1.6} = 0{\cdot}5681$

$p_{1.7} = p_{2.8} = p_{3.9} = p_{4.10} = p_{5.11} = p_{6.12} = 0{\cdot}4113$

$p_{7.13} = p_{8.18} = p_{9.19} = p_{10.24} = p_{11.25} = p_{12.30} = 0{\cdot}6503$

$p_{7.34} = p_{8.34} = p_{9.35} = p_{10.35} = p_{11.36} = p_{12.36} = 0{\cdot}5180$

$p_{15.31} = p_{16.31} = p_{21.32} = p_{22.32} = p_{27.33} = p_{28.33} = 0{\cdot}5507$

$p_{13.14} = p_{17.18} = p_{19.20} = p_{23.24} = p_{25.26} = p_{29.30} = 0{\cdot}6251$

$p_{14.15} = p_{16.17} = p_{20.21} = p_{22.23} = p_{26.27} = p_{28.29} = 0{\cdot}7098$

$p_{31.34} = p_{32.35} = p_{33.36} = 0{\cdot}5301$

The energies of the H.M.O. were corrected for overlap using the relation.

$$E_{\text{Huckel}} = \alpha - m\beta$$

$$E_{\text{corrected}} = \alpha - m'\gamma$$

where $m' = (m\ 1 - mS)$ with $\gamma = \beta - S\alpha$, $S$ being 0·25[2].

The transition energies in units of $\gamma$ is converted to cm$^{-1}$ by setting

$$\gamma = 23{,}000\ \text{cm}^{-1}.$$

The observed and calculated transition energies are listed in Table 3, and shown in the Fig. 2.

The transition $E \rightarrow E$ contains a symmetry forbidden component $A_1 \rightarrow A_2$, an electronically allowed component $A_1 \rightarrow E$, and a component $A_1 \rightarrow A_1$ which can appear only in conjunction with an out-of-plane bending vibration. Rather low intensity of the 5500 $A$ band and the existence of vibrational structure although not well developed, suggest that this band should be associated with the vibronic $A_1 \rightarrow A_1$

[2] G. W. Wheland, *J. Am. Chem. Soc.* **63**, 2025 (1941).

component of $E \rightarrow E$ transition. Preliminary measurement of polarization selectivity of this band appears to support this assignment.

TABLE 3

| Transition between levels | | Calculated | | Observed* | |
|---|---|---|---|---|---|
| | | $\nu$, cm$^{-1}$ | $\lambda$, Å | $\nu$, cm$^{-1}$ | $\lambda$, Å |
| −0·4291 (E) | 1·3333 ($A_1$) | 40,535 | 2467 | 40,900 | 2440 |
| −0·8000 ($A_1$) | 0·3630 (E) | 26,752 | 3738 | 26,400 | 3780 |
| −0·6368 ($A_2$) | 0·3630 (E) | 22,994 | 4349 | 32,800 | 4200 |
| −0·4291 (E) | 0·4754 ($A_2$) | 20,803 | 4807 | | — |
| −0·4291 (E) | 0·3630 (E) | 18,218 | 5489 | 18,100 | 5500 |

* Unpublished work of B.C.

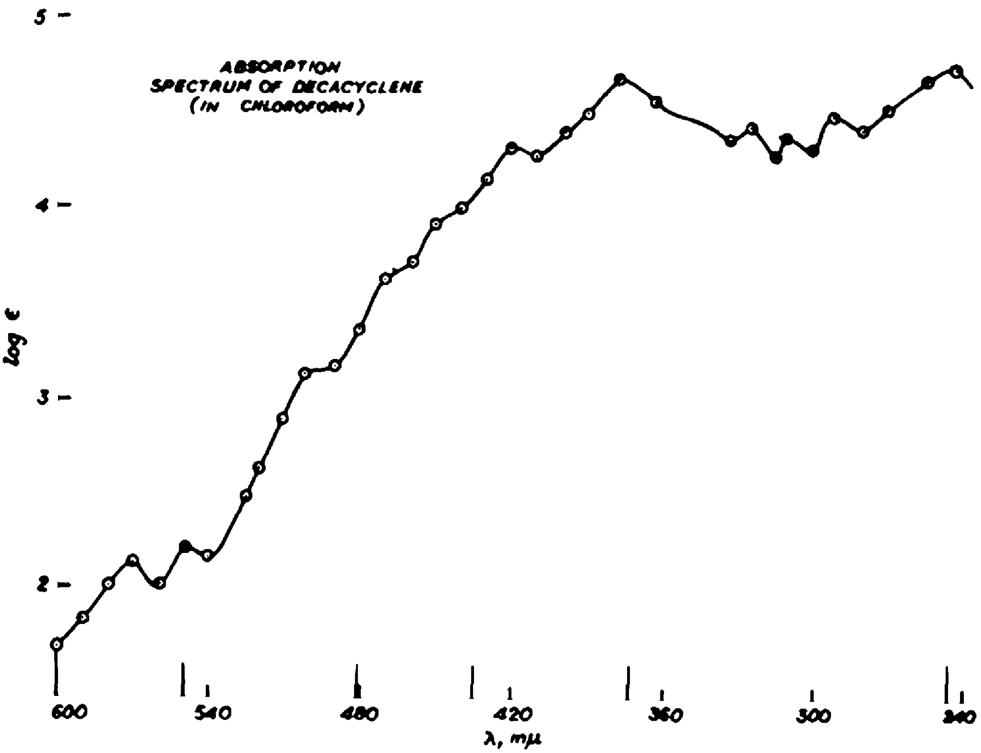

FIG. 2.

*Jahn–Teller effect for decacyclene ion.* The topmost filled level of decacyclene is doubly degenerate. In the case of positive ion the unpaired electron will be in a degenerate orbital consequently the molecule will be subjected to Jahn–Teller distortion of the type discussed by McLachlan. The distortion energy ($\Delta E$) and the difference in potential energy between two distorted structures ($\Delta U$) were calculated by method suggested by Hobey and McLachlan[3] and were found to be −0·2107

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[3] W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.* 33, 1695 (1960).

Kcal/mole and $-0{\cdot}0001$ Kcal/mole respectively. As the potential energy difference is much less than $kT$, the kinetic energy at room temperature, the molecule will be very little distorted by Jahn–Teller effect.

For alternant hydrocarbons the distortion energy and potential difference between two distorted structure come out to be equal for mono-negative and mono-positive ions because of the appearance of energy levels of unfilled orbitals in opposite pairs. In the case of non-alternant hydrocarbons this situation does not exist so the distortion energy for positive ion will be different from that for negative ion. Calculation shows that for negative ion

$$\Delta E = -0{\cdot}0859 \text{ Kcal/mole} \qquad \text{and} \qquad \Delta U = +0{\cdot}0002 \text{ Kcal/mole}.$$

In this case also the distortion will be small. Further we find that positive ion is distorted more than the negative ion.

*Spin densities.* These are calculated from the relation

$$\rho_r = C^2m + 1, r.$$

where $\rho_r$ is the spin density at atom $r$ and $Cm + 1$ is the corresponding atomic orbital of the M.O. with unpaired electron.[4] Since the highest filled and the lowest unfilled energy levels of the molecule are doubly degenerate two sets of values for spin densities are obtained for the mono-negative and mono-positive ions.

TABLE 4

| Spin density of position | Dinegative ion | Dipositive ion |
|---|---|---|
| 1, 2, 3, 4, 5, 6 | 0·0824 | 0·1171 |
| 7, 8, 9, 10, 11, 12 | 0·0408 | 0·0476 |
| 13, 18, 19, 24, 25, 30 | 0·0843 | 0·0489 |
| 14, 17, 20, 23, 26, 29 | 0·0113 | 0·0136 |
| 15, 16, 21, 22, 27, 28 | 0·1057 | 0·0748 |
| 31, 32, 33 | 0·0002 | 0·0018 |
| 34, 35, 36 | 0·0175 | 0·0609 |

The values reported in Table 4 are for dinegative and dipositive ions. These are twice the average of the two sets with one unpaired electron.

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[4] A. Streitwiesser, Jr., *Molecular Orbital Theory for Organic Chemists* p. 155. Wiley (1961).