Tetrahedron Letters, No. 8, pp.4-7, 1959. Pergamon Press Ltd. Printed in Great Britain.

CYCLOÖCTADECANONAENE: A THEORETICAL STUDY

D. W. Davies

Varo Terrace, Stockton, Durham

(Received 1 June 1959)

THE recent report of the preparation of cycloöctadecanonaene[1] suggests that a brief discussion of the results of a simple molecular orbital calculation on this system of 18 π-electrons might be of interest. Detailed results do not seem to be available in the literature, although they can readily be obtained from the general formulae for cyclic polyenes.

The calculations were made by the standard Hückel method.[2] The energy of the N-V transition was also obtained by a perturbation method due to Dewar.[3] The results for the resonance energy, the energy of the N-V transition, the free valency, the bond order and the corresponding bond length are shown in Table 1.

---

[1] F. Sondheimer and R. Wolovsky, Tetrahedron Letters No. 3, 3 (1959).

[2] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. A **192**, 16 (1947).

[3] M. J. S. Dewar, J. Chem. Soc. 3532 (1952).

TABLE 1. Molecular orbital calculations for $C_{18}H_{18}$

Method	Resonance energy		Energy of N-V transition	Wavelength of N-V transition	Bond order	Bond length	Free valency
	(β)	(kcal/mole)	(β)	(Å)	(Å)	(Å)	
Hückel	5.03	103	0.69	6030	1.640	1.404	0.452
Dewar			0.80	5200			
Expt.				4080			

The value in kcal/mole for the resonance energy is based on a value of 41 for benzene. This does not take into account compression energy. The energy per π-electron is somewhat less than in benzene, indicating that cycloöctadecanonaene is likely to be somewhat less stable than benzene. The free valency is about the same as that of the α-position in naphthalene; so there should be a similar reactivity to free radical reagents.

The bond order is the same for all the bonds, and the bond length shown in Table 1 was obtained from an empirical formula due to Longuet-Higgins and Salem.[4] On the basis of their work it seems probable that a more refined calculation would also give the result that all bonds are equal in length. The X-ray study mentioned in reference 1 should settle this question.

---

[4] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A **251**, 172 (1959).

The reported U.V. spectrum has maxima at 4480, 4080, 3690 and 2780 Å with extinction coefficients of 21800, 7500, 303000 and 8100 respectively. These may be identified with Clar's α, p, β, and β' bands[5] respectively, giving a ratio of 1.2 for the wavelengths of the α and β bands compared to the usual ratio of 1.3. This supports the assignment of the longest wavelength transition as α rather than p. The theoretical values given in Table 1 refer to the p band, and the agreement is rather disappointing, even if the argument given above is wrong and the longest wavelength transition is in fact the p band.

A tentative assignment of the symmetries of the excited states can be made for a structure having D_{6h} symmetry by arguments similar to those used by Dewar and Longuet-Higgins.[5] The symmetries and energies of the two highest filled orbitals and the two lowest unfilled orbitals are shown in Table 2. They may be called B', A', and A, B respectively.

TABLE 2. Lowest unfilled and highest filled orbitals

Designation	Energy (β)	Symmetry
B'	-1.0000	a_{2u}, a_{1u}
A'	-0.3472	e_{1g}
A	0.3472	e_{2u}
B	1.0000	e_{1g}

---

[5] M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Phys. Soc. A **57**, 795 (1954).

The first electronic transition A→A' gives rise to excited singlet states having B_{1u}, B_{2u}, and E_{1u} symmetry. Only the transition to the E_{1u} state is allowed. This may be identified with the intense band at 3690 Å. This has been called the β band above. The transition is similar to that in benzene, and by analogy the weaker bands at 4480 and 4080 Å may be identified with the forbidden transitions to the $^1B_{2u}$ and $^1B_{1u}$ states respectively. The next group of excited states involves the degenerate transitions B→A' and A→B'. These states have symmetries A_{1g}, A_{2g}, and E_{2g}, and the transitions are all forbidden. The band at 2780 Å may be identified with one of these. The next excited state involves the transition B→B', and it has E_{1u} symmetry. This transition is allowed and as the energy is still only 2β, a strong band at about 2000 Å may occur. It would, however, be unwise to carry this discussion further until more detailed information is available about the U.V. spectrum.