Tetrahedron Letters No.11, pp.22-24, 1960. Pergamon Press Ltd. Printed in
Great Britain.

BOND ALTERNATION IN CYCLOÖCTADECANONAENE (CON)

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(Received 20 April 1960)

THE molecule CON, which has recently been synthesized by Sondheimer and co-workers,[1] is of great theoretical interest because its spectrum should be exactly predictable. If, as has been supposed, the molecule is fully conjugated,[1,2] the transition energies should be given by the Moffitt[3] theory of cyclic polyenes. According to this theory, which has proven highly successful in the interpretation of polyacene spectra, a cyclic polyene of length $(4\nu + 2)$ should have transitions with energy:

$$\Delta E(\Xi) = 4\beta\ (\Xi)\ \sin\phi, \left(\phi = \frac{\pi}{(4\nu + 2)}\right)$$

where the resonance integrals $\beta\ (\Xi)$ are set to fit the three benzene transitions $\Xi = E_{1u}, B_{1u}, B_{2u}$. This predicts for CON transitions with the same symmetries at 510, 580, and 730 mμ respectively, in striking discord with the reported transitions[1] 378, 415, and 456 mμ. (The band at 378 mμ, with ε roughly 10 times that of the other two bands, is identified with the allowed E_{1u} transition). The failure of a theory that has been so successful in other

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

[2] D.W. Davies, Tetrahedron Letters No.8, 4 (1959).

[3] W. Moffitt, J. Chem. Phys. 22, 320 (1954).

cases leads naturally to a reexamination of basic assumptions concerning this molecule.

The assumption that appears most suspect is that of equal bond lengths. It has been found empirically that the bond lengths in linear polyenes continue to alternate even as molecules tend to get very long.[4] Theoretical explanation for this fact was given by Labhart.[5] Further studies by Ooshika[6] and by Longuet-Higgins and Salem[7] indicate that the same behavior should hold in cyclic systems. It therefore seems reasonable to look for bond alternation in CON.*

The Moffitt theory allows for a most convenient calculation of the effect of bond alternation. We shall assume the double bonds are characterized by β_1 and the single bonds by β_2. (That this should send the transitions to shorter wave length may be seen intuitively from the fact that in the extreme limit the molecule appears as 9 ethylenes with $\lambda \sim 1800$ Å.) If one defines $\beta = (\beta_1 + \beta_2)/2$ and $\delta = (\beta_1 - \beta_2)/2$, it may be shown that the transition energy becomes:

$$\Delta E = 4\sqrt{\beta^2 \sin^2\phi + \delta^2 \cos^2\phi},$$

where $\phi = \pi/(4\nu + 2)$, as before. It is, however, no longer clear that the Moffitt procedure of choosing three values of β (Ξ) is justified. If we choose a single value of β=3.14 eV to fit the average of the benzene

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[*] It is a suggestive coincidence that the linear 18-membered polyene absorbs in the very same region as CON. See F. Bohlmann, *Ber.* **85**, 388 (1952).

[4] W. Drenth and E.H. Wiebenga, *Acta Cryst.* **8**, 755 (1955).

[5] H. Labhart, *J. Chem. Phys.* **27**, 957 (1957).

[6] Y. Ooshika, *J. Phys. Soc. Japan* **12**, 1246 (1957).

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

levels, it follows that $\delta = 0.175\beta$ will yield λ = 405 mμ agreeing with the average observed for CON.

The value of δ given above is rather large. In fact, comparison with the β values of butadiene[8] indicates that the alternation in CON is of the same order of magnitude. This would suggest a difference in bond lengths of about 0.1 Å in agreement with Ooshika's prediction of 0.12 Å. The treatment of Longuet-Higgins predicts bond alternation of about 0.04 Å beginning with systems $(4\nu + 2) \approx 34$; however, he points out that this result is very sensitive to details and alternation could begin at $(4\nu + 2) = 18$. The X-ray studies in progress[1] may settle these questions. Meanwhile, further theoretical studies are being carried out at this laboratory.

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[8] B. Pullman and A. Pullman, Les Théories Electroniques de la Chimie Organique p. 200.Masson et Cie., Paris (1952).