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BOND LENGTHS IN THE CYCLO-OCTATETRAENE DIANION $C_8H_8^{--}$

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Abstract—Simple molecular orbital calculations suggest that the $C_8H_8^{--}$ dianion is planar with equal bond lengths 1·409 Å.

IT has recently been shown by Katz and Strauss[1] using nuclear magnetic resonance and electron-spin resonance that the cylco-octatetraene dianion $C_8H_8^{--}$ must be highly stabilized by resonance, and probably be flat. Now it can be shown that the ground state of a hypothetical flat neutral C_8H_8 would have unequal bond lengths, in distinction to the case of benzene C_6H_6 where resonance causes all the bonds to be equal (the "4*n* + 2 rule"). It is important, therefore, to enquire whether the dianion is or is not a regular octagon.

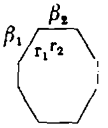

FIG. 1.

To do this consider a plane molecule (Fig. 1) with alternating lengths r_1, r_2 and corresponding molecular-orbital integrals β_1, β_2. If we suppose that $r_1 < r_2$, then $|\beta_1| > |\beta_2|$, and perfectly straightforward m.o. calculations with neglect of all overlap integrals show that the energies of the 8 allowed orbitals for the π-electrons are given by

$$\varepsilon_1 = (\beta_1 + \beta_2) = -\varepsilon_8$$

$$\varepsilon_2 = \varepsilon_3 = \sqrt{(\beta_1^2 + \beta_2^2)} = -\varepsilon_6 = -\varepsilon_7$$

$$\varepsilon_4 = (\beta_1 - \beta_2) = -\varepsilon_5$$

Fig. 2 shows the appearance of these energies, both for the case of $r_1 = r_2$ and $r_1 < r_2$. The most notable difference when the octagon is not regular, lies in the splitting of the previous degenerate zero-energy level. In the case of neutral cyclo-octatetraene with 8 π-electrons it can be seen that the previous degeneracy is removed (by the operation of a pseudo Jahn–Teller effect similar to that already known in cyclo-butadiene C_4H_4)[2] so that the molecule becomes distinctly more stable. In the case of the dianion, with 10 π-electrons, the lowest five orbitals are doubly occupied, and it is not immediately obvious whether or not the stability is increased as a result of the distortion. We can show, however, that although it turns out that the π-electrons favour a distorted

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[1] T. J. Katz, *J. Amer. Chem. Soc.* **82**, 3784 (1960); T. J. Katz and H. L. Strauss, *J. Chem. Phys.* **32**, 1873 (1960).

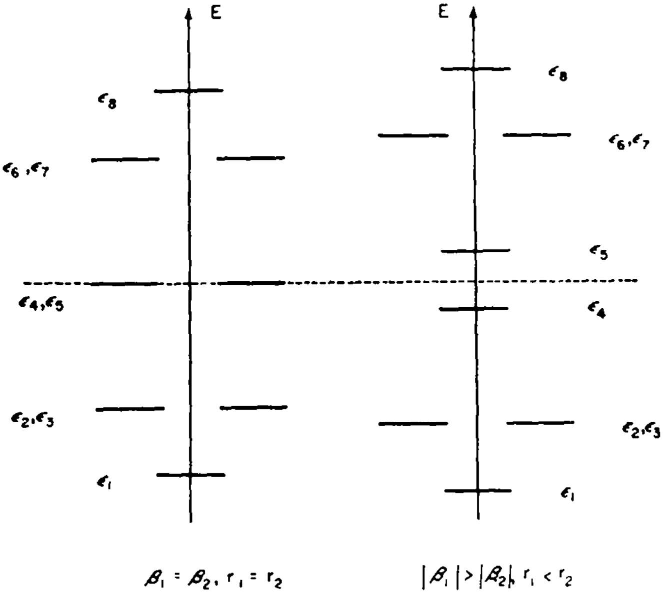
[2] C. A. Coulson, *J. Chem. Soc.* Special Publication No. 12, 85 (1958).

octagon, the influence of the underlying σ-bonds is sufficiently strong in favour of equal bonds as to cause the molecule to assume a regular octagonal shape.

First let us show that the π-electron energy E_π favours a distorted octagon. E_π takes the form

$$\begin{aligned} E_\pi &= 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_3 + 2\varepsilon_4 \\ &= 2(\beta_1 + \beta_2) + 4\sqrt{(\beta_1^2 + \beta_2^2)}. \end{aligned}$$

We shall suppose that β varies with r according to the exponential law used by Longuet-Higgins and Salem[3], viz. $\beta = \beta_0\, e^{-a(r-r_0)}$. Then if we start with all links equal to r_0, with equal resonance integrals β_0, we may consider the particular distorted shape of Fig. 1 for which $r_1 = r_0 - x$, $r_2 = r_0 + x$, so that



$\beta_1 = \beta_2,\ r_1 = r_2$ $|\beta_1| > |\beta_2|,\ r_1 < r_2$

π-electron molecular-orbital energies in $C_8H_8^{--}$

FIG. 2.

$$\beta_1 = \beta_0 e^{ax}, \qquad \beta_2 = \beta_0 e^{-ax}.$$

Then

$$\begin{aligned} \varepsilon_1 &= 2\beta_0 \cosh ax &&= 2\beta_0(1 + \tfrac{1}{2}a^2x^2 + \ldots) \\ \varepsilon_2 &= 2^{1/2}\beta_0 \sqrt{(\cosh ax)} &&= 2^{1/2}\beta_0(1 + \tfrac{1}{4}a^2x^2 + \ldots) \\ \varepsilon_3 &= 2\beta_0 \sinh ax &&= 2\beta_0(ax + \tfrac{1}{6}a^3x^3 + \ldots). \end{aligned}$$

Thus as x increases from zero E_π is lowered by an amount roughly equal to Kx^2, where $K = (2 + \sqrt{2})\, a^2\, |\beta_0|$. This shows that E_π favours alternating bond lengths.

To determine the actual equilibrium configuration when the σ-bond energy E_σ is included, we write

$$E = E_\pi + E_\sigma$$

where

$$E_\sigma = 4[\tfrac{1}{2}k(r_1 - s)^2 + \tfrac{1}{2}k(r_2 - s)^2].$$

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

In this expression s is the length of a pure single carbon–carbon trigonal bond, and k is its force constant.

It is obvious that the energy E is stationary at $r_1 = r_2$. If we can show that it is a minimum at this point, then we have shown that the regular structure is preferred. By direct differentiation, using the fact that $d\beta/dr = -a\beta$;

$$\frac{\partial^2 E}{\partial r_1^2} = 4k + 2a^2\beta_1 + \frac{4a^2\,\beta_1^2(\beta_1^2 + 2\beta_2^2)}{(\beta_1^2 + \beta_2^2)^{3/2}}$$

and a similar equation for $\partial^2 E/\partial r_2^2$. Also

$$\frac{\partial^2 E}{\partial r_1 \partial r_2} = -\frac{4a^2\,\beta_1^2\,\beta_2^2}{(\beta_1^2 + \beta_2^2)^{3/2}}$$

If we put $s = 1{\cdot}50$ Å, and accept the value $a = 2{\cdot}683$ Å^{-1}, as used by Coulson and Golebiewski[4], and put $k = 4{\cdot}8\ 10^5$ dynes/cm, it is easily verified that the first term in the expression for $\partial^2 E/\partial r_1^2$ (which is due to the σ-bonds) is positive and about three times as large as the other two terms (which are negative and due to the π-bonds). Also $(\partial^2 E/\partial r_1^2)(\partial^2 E/\partial r_2^2) > (\partial^2 E/\partial r_1 \partial r_2)^2$. Thus the regular octagon is stable and this stability is independent of small changes that we might wish to made in the numerical values of s, a and k. The actual length in the equilibrium state comes out to be 1·409 ± 0·001 Å. This is notably longer than in benzene (1·397 Å) in agreement with the fact that although the anion does possess considerable resonance stability, its π bond order 0·604 is smaller than that of benzene 0·667. This difference accounts for the 0·012 Å increase in length. It may be worth adding that all reasonable order-length curves give approximately the same value for this increase.

[4] C. A. Coulson and A. Golebiewski, unpublished.