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MOLECULAR DEFORMATION IN CYCLOÖCTADECANONAENE

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Abstract—Calculations are reported which show that the large cyclic polyene $C_{18}H_{18}$ recently synthesized by Sondheimer and Wolovsky cannot possibly be planar as a result of steric forces. The most likely deformation is one of D_{3d} symmetry in which the six inner hydrogen atoms suffer displacements of the order of $\pm 0{\cdot}9$ Å perpendicular to the mean plane. The resulting loss of π-electron resonance energy is about 70 kcal/mole.

IN a recent paper[1] Sondheimer and Wolovsky have reported the successful synthesis of cycloöctadecanonaene $C_{18}H_{18}$ (Fig. 1). They claimed that this hitherto unknown molecule showed definite aromatic character, being strikingly more stable than its acyclic analogue, although not so stable as a classical benzenoid system. From some preliminary considerations they suggest that the molecule should be exactly, or nearly, planar. Shortly afterwards Davies[2] published some theoretical calculations for this molecule, using the standard molecular-orbital (M.O.) method for π-electrons in the Hückel form. He also assumed that the molecule was planar. But steric considerations (see later) show that this cannot be the case, so that a reconsideration of some of his results seems to be necessary. In this paper we propose to discuss the shape of this molecule, and shall make predictions concerning the most probable type of deformation.

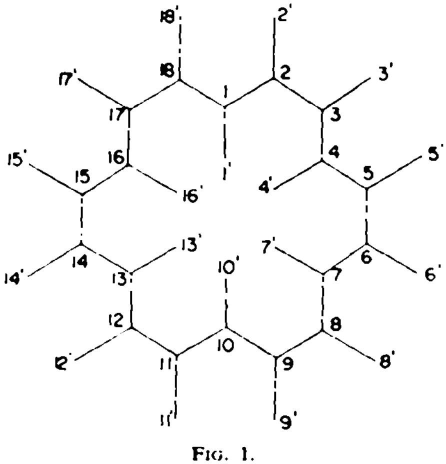

FIG. 1.

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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).

At first we shall suppose that, as a result of π-electron resonance, all the C—C bond lengths are equal, with a value 1·40 Å, and that all the bond angles are equal to 120°. There may be some slight failure in this assumption. Thus Ooshika[3] and Longuet-Higgins and Salem[4] have shown that in sufficiently long conjugated planar molecules the configuration with equal bond lengths is at most metastable. The stable configuration is characterized by an alternation of bond lengths, with a difference of about 0·035 Å. According to Longuet-Higgins and Salem this effect is expected from $C_{34}H_{34}$ upwards, though it cannot definitely be excluded in $C_{18}H_{18}$. However, in some unpublished calculations by one of us (A. G.) it seems likely that the higher, rather than the lower, value is the more probable.

Let us number the atoms as in Fig. 1, and let z_i and h_i denote any possible displacements of carbon atom i and hydrogen atom i' from an original assumed planar configuration where all z_i and h_i are zero. Now if the C—C bond lengths are equal to 1·40 Å and the angles are all 120°, it follows that in a hypothetical plane configuration the distance between neighbouring hydrogen atoms "inside" the molecule would be only 1·72 Å. This is exceedingly unlikely, because the shortest H . . . H distances in aliphatic hydrocarbon crystals are known to be 2·49–2·50 Å.[5] We must therefore expect some molecular deformation. There seem to be two extreme ways of maintaining the usual van der Waals distances:

(a) a change of C—C bond lengths, and perhaps a simultaneous change of bond angles, keeping the molecule planar,

(b) a buckling of some part or parts of the molecule out of the plane. We can easily show that there is very little probability for (a), because it involves too large a set of changes in bond lengths and bond angles. For example, if we remove the overcrowding by an equal increase in all C—C bond distances, these must be changed from 1·40 Å to 1·74 Å. Such an increase requires very large energy. And we know, from earlier theoretical and experimental arguments for other molecules of polynuclear type,[5] that this type of relief of steric strain is energetically far less satisfactory than out-of-plane buckling, as in (b). We have made some calculations to verify that this is also true for $C_{18}H_{18}$, and shall show later that (b) really is much more probable.

Deformations of type (b)

We make use of the method developed by Coulson and Senent[5,6], and some extensions obtained by the present authors.[7] According to this method we set up the total vibronic potential energy of the molecule $V(z_i, h_i)$, and choose the displacements z_i and h_i so that V is a minimum. So we set

$$\frac{\partial V}{\partial z_i} = 0 \qquad \text{for all } z_i \tag{1}$$

and

$$\frac{\partial V}{\partial h_i} = 0 \qquad \text{for all external hydrogens} \tag{2}$$

For the internal hydrogens we suppose (see later) that the displacements from the

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[3] Y. Ooshika, *J. Phys. Soc. Japan* **12**, 1238, 1246 (1957).

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

[5] C. A. Coulson and S. Senent, *J. Chem. Soc.* 1819 (1955).

[6] C. A. Coulson and S. Senent, *J. Chem. Soc.* 1813 (1955).

[7] C. A. Coulson and A. Golebiewski, in press.

planar configuration are such that the difference between the z-values of all adjacent internal hydrogen atoms is at least equal to R, the particular value of R being such that the conventional van der Waals distances are preserved. There are actually 30 equations of types (1) and (2), but on account of the molecular symmetry this number is reduced to only 3 functionally different equations.

Following the notation of references 5–7 we let the ratio of the bond lengths r_{CC}/r_{CH} $(A_{ii'})$ be denoted by λ, so that $\lambda = 1{\cdot}40/1{\cdot}08 = 1{\cdot}2963$, and we note that $A_{i,i+1} = 1$ since all C—C bonds are supposed equal. Let us also put

$$\xi_i = \lambda h_i \tag{3}$$

$$\text{and } \chi = \frac{k_2}{k_1} = \text{ratio of torsion and out-of-plane force constants}$$

$$= \frac{0{\cdot}0603}{0{\cdot}1345} = 0{\cdot}4483 \tag{4}$$

where the values of k_1 and k_2 are taken from our other paper.[7] In the same way as there, equations (1) and (2) now take the form:

$$\frac{1}{k_1}\frac{\partial V}{\partial z_1} = \alpha z_1 - \beta z_2 + z_3 - \chi z_4 - \chi z_{16} + z_{17} - \beta z_{18} - \gamma\xi_1 + (1 - \chi\lambda)\xi_2 + \chi\xi_3 + \chi\xi_{17} + (1 - \lambda\chi)\xi_{18} = 0 \tag{5}$$

$$\frac{1}{k_1}\frac{\partial V}{\partial z_2} = -\beta z_1 + \alpha z_2 - \delta z_3 + z_4 + \chi(z_5 + z_{17}) + (\gamma - \lambda - 1)z_{18} + (1 - \lambda\chi)\xi_1 - \gamma\xi_2 + \varepsilon\xi_3 - \chi(\xi_4 + \xi_{18}) = 0 \tag{6}$$

$$\frac{1}{k_1}\frac{\partial V}{\partial \xi_2} = (1 - \lambda\chi)z_1 - \gamma z_2 + \varepsilon z_3 + \chi(z_4 - z_{18} + \xi_1) + (1 + 2\chi)\xi_2 - \chi\xi_3 = 0 \tag{7}$$

where

$$\begin{aligned}
\alpha &= (2 + \lambda)^2 + 2 + \chi(2\lambda^2 - 4\lambda + 4) = 13{\cdot}8409\\
\beta &= 4 + 2\lambda - \chi(\lambda^2 - 1) = 6{\cdot}2876\\
\gamma &= 2 + \lambda + 2\chi(\lambda - 1) = 3{\cdot}5620\\
\delta &= 4 + 2\lambda + \chi(\lambda^2 - 4\lambda + 3) = 6{\cdot}3663\\
\varepsilon &= 1 - \chi(2 - \lambda) = 0{\cdot}6845\\
\lambda &= 1{\cdot}2963\\
\chi &= 0{\cdot}4483
\end{aligned} \tag{8}$$

and the remaining equations can be written down by an appropriate permutation of indices. We have not yet made any assumptions as to the symmetry of the deformed molecule. It is natural to expect that the molecule will become "corrugated" in such a way as to preserve D_{3d} symmetry. But we have also considered the alternative possibilities C_{3v}, D_2, C_s. Since, however, these all lead to greater strain energies, we shall not report any details of the calculation, and shall only describe the D_{3d} case, in which the central hydrogen atoms have displacements $\pm\frac{1}{2}R = 0{\cdot}907$ Å. Nor shall we consider any deformations of still lower symmetry. In the D_{3d} case the equations (5)–(7) take the simpler form

$$\begin{aligned}
&(\alpha + 2\chi)z_1 - 2(1 + \beta)z_2 + 2(1 - \chi - \lambda\chi)\xi_2\\
&\quad = \tfrac{1}{2}\gamma\lambda R - (1 + \beta)z_1 + (\alpha - 2\chi + \gamma - \lambda + \delta - 1)z_2 - (\gamma + \varepsilon + \chi)\xi_2\\
&\quad = -\tfrac{1}{2}(1+\chi-\lambda\chi)\lambda R(1-\lambda\chi-\chi)z_1 - (\gamma+\varepsilon+\chi)z_2 + (1+3\chi)\xi_2 = -\tfrac{1}{2}\chi\lambda R
\end{aligned} \tag{9}$$

with solution

$$
\begin{aligned}
z_1 &= 0{\cdot}1571\,R &&= 0{\cdot}2850\ \text{Å}\\
z_2 &= 0{\cdot}0009\,R &&= 0{\cdot}0017\ \text{Å}\\
h_2 &= 0{\cdot}0926\,R &&= -0{\cdot}1680\ \text{Å}\\
h_1 &= \tfrac{1}{2}\,R &&= 0{\cdot}907\ \text{Å (assumed).}
\end{aligned}
\tag{10}
$$

The other displacements follow from symmetry. The corresponding numerical value of the strain function V is

$$V = 0{\cdot}4848\ 10^{-11}\ \text{ergs/molecule} = 69{\cdot}8\ \text{kcal/mole.} \tag{11}$$

Deformation of type (a)

We must now examine the relative energies of strain in out-of-plane buckling (b) and in-plane deformation (a). The most fundamental procedure would be to consider all possible deformations simultaneously. But this would be very tedious, and will not be necessary if we can show that the out-of-plane deformation energy V_z is much less than all reasonable in-plane deformation energies. For these latter we consider

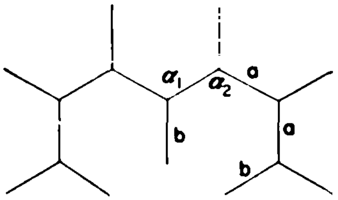

FIG. 2.

(1) V_x, caused by appropriate change of bond angles alone, chosen in such a way that the molecule remains planar and of symmetry D_{6h}.

(2) V_c, caused by changes in C—C bond lengths alone, still preserving symmetry D_{6h}.

In case (1) it can be seen from simple trigonometric considerations (Fig. 2) that the bond angles must become:

$$\alpha_1 = 2\alpha_2 - 2\pi/3,\ \alpha_2 = \sin^{-1}\left\{\frac{R_H - b - a}{2a}\right\} \text{ where } R_H \text{ is the H} \ldots \text{H distance } 2{\cdot}49\ \text{Å} \tag{12}$$

On putting $\Delta\alpha_1 = \alpha_1 - 2\pi/3$, $\Delta\alpha_2 = \alpha_2 - 2\pi/3 = \tfrac{1}{2}\Delta\alpha_1$ and using the potential function developed by Crawford and Miller[8] for the in-plane vibrations of benzene (but with neglect of the small terms representing *meta*- and *para*-interaction constants) we find that

$$V_x = 5{\cdot}9 \times 10^{-11}\ \text{erg/molecule}$$

This is about twelve times as large as the out-of-plane V_z given by (11).

Similarly in case (2) we remove the H . . . H overcrowding by increasing each

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[8] B. L. Crawford and F. A. Miller, *J. Chem. Phys.* **17**, 249 (1949).

C—C bond by 0·34 Å. The total energy which is thereby needed (once again neglecting *meta*- and *para*-interactions) is

$$V_c = 8{\cdot}1 \times 10^{-11} \text{ erg/molecule},$$

which is about seventeen times as large as V_z.

Because V_x and V_c have comparable values, we could reduce the strain energy by simultaneous change in both bond lengths and bond angles; and the deformation energy would be not smaller than

$$\tfrac{1}{2}(V_x + V_c) \sim 7 \times V_z$$

These calculations justify our conclusion that in the real molecule the release of steric overcrowding will take place almost entirely by out-of-plane displacements, and our value of 69·8 kcal/mole will be a good approximation to the best value that could be obtained by simultaneous adjustment of all the molecular parameters.

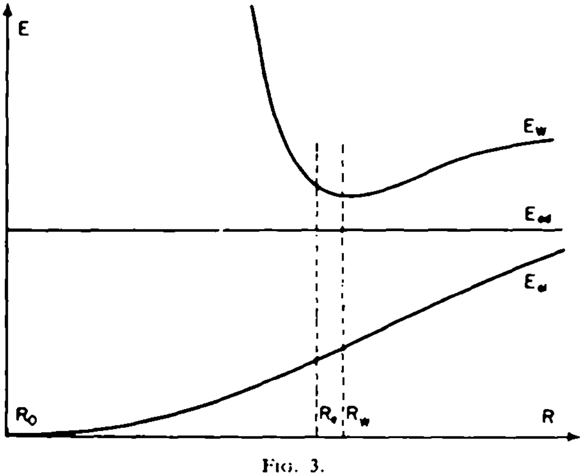

FIG. 3.

General conclusions

It is interesting to use the results just obtained to plot total energy curves for this molecule. But instead of adopting the final value of R involved in the hydrogen displacements, let us use R as a parameter, and plot (Fig. 3) the variation with R of:

(I) $E_{el}(R)$, defined as the total electronic energy of the system. This is the quantity which we have effectively been calculating hitherto, and takes account of the loss of π-electron energy due to the displacements z_t and h_t, but it does not include the H . . . H van der Waals energy,

(II) E_w, defined as the total van der Waals energy of the six central hydrogen atoms. This is approximately equal to six times the van der Waals energy between a pair of H atoms.

(III) E_{ad}, defined as the sum of the tabulated energies of the single and double bonds that occur in a Kekulé structure. Thus, in the absence of E_w, the conventional resonance energy would be simply $E_{ad} - E_{el}$. In Fig. 3 we have also used R_w to denote that value of R which leads to the usual van der Waals distance 2·49 Å.

But of course the true equilibrium value of R, here called R_e, will be a little less than R_w, since R_w is at the minimum of the E_w curve, and R_e is at the minimum of the $(E_{el} + E_w)$ curve. The length $R_w - R_e$ will be small, since we know that the repulsive part of the E_w curve rises very steeply.

If we define the resonance energy E_{res} as the difference between the energy of a Kekulé structure (E_{ad}), without any van der Waals correction, and the equilibrium total energy, then

$$E_{res} = E_{ad} - \{E_{el}(R_e) + E_w(R_e)\} \tag{13}$$

This is not the same as the value calculated by Davies[2] who neglected E_w and calculated E_{el} only for the planar molecule; in fact

$$E_{Davies} = E_{ad} - E_{el}(0) = 103 \text{ kcal/mole} \tag{14}$$

Our own calculations (11) of V are

$$V = E_{el}(R_w) - E_{el}(0) \tag{15}$$

It follows that

$$\begin{aligned} E_{Davies} - E_{res} &= \{E_{el}(R_e) - E_{el}(0)\} + E_w(R_e) \\ &= \{E_{el}(R_e) - E_{el}(R_w)\} + V + E_w(R_e) \end{aligned}$$

Now the total energy at R_e will be very slightly less than at R_w. So

$$E_{el}(R_e) + E_w(R_e) < E_{el}(R_w) + E_w(R_w),$$

from which it follows that

$$E_{Davies} - E_{res} < V + E_w(R_w) \tag{16}$$

So $E_{res} > E_{Davies} - V - E_w(R_w)$. Substituting for E_{Davies} and V we see that E_{res} should be a little more than $33 - E_w(R_w)$ kcal/mole. Thus the resonance energy is much smaller than its value for a benzenoid system with no overcrowding, and of the same order of magnitude as for an acyclic analogue. The molecule would, however, be expected to show aromatic-type behaviour in its reactivity, in general agreement with Sondheimer and Wolovsky.

There is, however, one difficulty connected with the spectrum of $C_{18}H_{18}$ in the u.v. range. Davies[2] calculated an N → V transition at 6030 Å, using the standard Hückel technique. But the experimental value is 4080 Å. This big difference would be still further increased if steric effects on the spectra were to be introduced in a way such as that discussed by one of us.[9] For these steric effects lead to red shifts and so increase the calculated wavelength. Perhaps, therefore, the model which is being used is not correct. If, for example, the bonds alternated in length along the carbon chain, then by analogy with the linear polyene chains we should expect a considerable blue shift relative to the value calculated by Davies. The X-ray work announced by Sondheimer and Wolovsky[1] will probably settle this question. But even if the bonds do alternate in this way, this is very unlikely to affect our discussion of the strain energy and the magnitudes of the various atomic displacements other than in a relatively minor way.

Acknowledgements– One of us (A. G.) would like to acknowledge the award of a Fellowship from The Rockefeller Foundation which has made this work possible.

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[9] C. A. Coulson, *Steric Effects in Conjugated Systems* [Proceedings of a Symposium by The Chemical Society, The University, Hull, 15–17 July (1958)] pp. 8–21. Butterworths, London (1958).