

TABLE I. Calculated bond lengths (in Å).

N	a		b		c	
	x ₁	x ₂	x ₁	x ₂	x ₁	x ₂
2	1.34	1.41	1.34	1.43	1.34	1.43
3	1.35	1.40	1.34	1.42		
4	1.35	1.40				
5	1.36	1.40			1.35	1.41
6	1.36	1.39				
⋮						
∞	1.38	1.38			1.36	1.40

^a First approximation of Lennard-Jones.
^b Second approximation of Lennard-Jones.
^c Present calculations.

expressions for $\beta(x)$ and $E_\sigma(x)$ we have actually drawn the energy surfaces for $N=2$ (butadiene) and $N=5$ (decapentane) and found the minimum points. The case of $N \rightarrow \infty$ is explained separately in the next section. The results are listed in Table I together with the values obtained by Lennard-Jones.¹

Next let us consider the subject more generally. The actual shapes of the energy surfaces we have drawn suggest that for intermediate and large values of N we may put safely as

$$x_1 = x_0 - \xi, \quad x_2 = x_0 + \xi,$$

where x_0 is the bond length which minimizes the total energy under the restriction of $x_1 = x_2$. Then at $x = x_0$ we have the relation

$$0 = \partial E_T / \partial x \simeq (2N-1)(\partial E_\sigma / \partial x) + [4(2N+1)/\pi](\partial \beta / \partial x), \quad (9)$$

where

$$E_T(x) = (2N-1)E_\sigma(x) + 2N\alpha + 2\beta \sum_{m=1}^N \cos[m\pi/(2N+1)].$$

Next, assuming that ξ is small, we expand $\beta(x_1)$ and $\beta(x_2)$:

$$\begin{aligned} \beta(x_1) &\simeq \beta_0 - \frac{\partial \beta}{\partial x} \xi + \frac{1}{2} \frac{\partial^2 \beta}{\partial x^2} \xi^2, \\ \beta(x_2) &\simeq \beta_0 + \frac{\partial \beta}{\partial x} \xi + \frac{1}{2} \frac{\partial^2 \beta}{\partial x^2} \xi^2, \end{aligned} \quad (10)$$

where $\beta_0 \equiv \beta(x_0)$. By using these expressions and the approximate formula for θ_m due to Lennard-Jones,¹

$$\theta_m \simeq \frac{2m}{2N+1} \pi - (2N+1)^{-1} \left(1 - \frac{\beta_2}{\beta_1}\right) \tan \frac{m\pi}{2N+1}, \quad (11)$$

we finally arrive at the next expression for finite values of N after some manipulations,

$$\frac{\partial E_T}{\partial \xi} \simeq \frac{4}{\pi} \left\{ \frac{2N+1}{2N-1} - \log \frac{4(2N+1)}{\pi} \right\} \frac{\partial \beta}{\partial x}. \quad (12)$$

This formula tells us that if $\partial \beta / \partial x > 0$, we find the real minimum point of the energy surface in the positive side of ξ , namely, in the region of $x_1 < x_2$ for finite values of N .

3. INFINITELY LONG CHAINS ($N \rightarrow \infty$)

This case requires and permits separate treatment. Now it is justifiable to replace the sum in (7) by the integral

$$\begin{aligned} (E_T/N) &\rightarrow 2\alpha - (2/\pi) \int_0^\pi (\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\theta)^{1/2} d\theta \\ &\quad + E_\sigma(x_1) + E_\sigma(x_2) \quad (13) \\ &= 2\alpha - (4/\pi) |\beta_1 + \beta_2| E\left(\frac{1}{2}\pi, k\right) \\ &\quad + E_\sigma(x_1) + E_\sigma(x_2). \end{aligned}$$

Here

$$E\left(\frac{1}{2}\pi, k\right) = \int_0^{1/2\pi} (1 - k^2 \sin^2 \phi)^{1/2} d\phi, \quad k^2 \equiv 4\beta_1\beta_2 / [\beta_1 + \beta_2]^2,$$

is the complete elliptic integral of the second kind. Again let us expand the final expression of (13) with respect to ξ . By using (10) and an expansion formula of $E(\frac{1}{2}\pi, k)$, we find that

$$\begin{aligned} \left(\frac{E_T}{N}\right)_{\substack{x_1=x_0-\xi, \\ x_2=x_0+\xi}} &= \left(\frac{E_T}{N}\right)_{x_1=x_2=x_0} + \left[\mp \frac{4}{\pi} \frac{\partial^2 \beta}{\partial x^2} + \frac{\partial^2 E_\sigma}{\partial x^2} \right. \\ &\quad \left. + \frac{4}{\pi} \left(\frac{1}{2} - \log \frac{4|\beta|}{|\partial \beta / \partial x|} \right) |\beta| \left(\frac{\partial \beta / \partial x}{\beta} \right)^2 \right] \xi^2 \\ &\quad + \frac{4}{\pi} |\beta| \left(\frac{\partial \beta / \partial x}{\beta} \right)^2 \xi^2 \log |\xi|, \quad (N \rightarrow \infty), \quad (14) \end{aligned}$$

where the sign of the first term in the second bracket coincides with the sign of $\beta \cdot \partial \beta / \partial x$ and we neglect the terms higher than $O(\xi^4)$. The formula (14) is an even function of ξ and $\partial(E_T/N) / \partial \xi = 0$ at $\xi = 0$. Further, if $\partial \beta / \partial x \neq 0$, we always find that

$$(E_T/N)_{x_2=x_0+\xi}^{x_1=x_0-\xi} < (E_T/N)_{x_1=x_2=x_0}, \quad (N \rightarrow \infty), \quad (15)$$

provided that $|\xi|$ is appropriately small. This means that the energy surface (x_1, x_2) of E_T/N ($N \rightarrow \infty$) has a saddle point at $x_1 = x_2 = x_0$ and the true minimum point should be found in the off-diagonal region where $\xi \neq 0$. In other words we always have bond alternation in very long chains when $\partial \beta / \partial x \neq 0$ regardless of the functional forms of $\beta(x)$ and $E_\sigma(x)$.

The actual values of x_1 and x_2 which give the true minimum point can be obtained either by using the

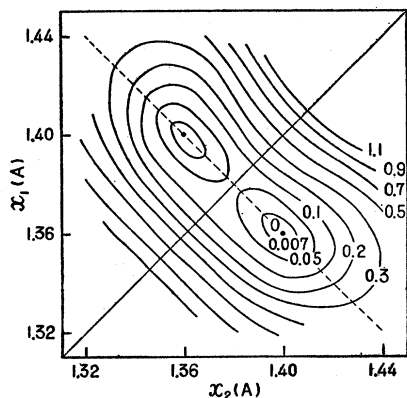


FIG. 1. Energy contours for E_T/N , ($N \rightarrow \infty$) (distance in Å and energy in kcal/mole).

formula (14) or by drawing the energy surface directly. We have done both by adopting Lennard-Jones' expressions for $\beta(x)$ and $E_\sigma(x)$ and found that $x_1 = 1.36$ Å and $x_2 = 1.40$ Å, while $x_0 = 1.38$ Å. In this case we have two minimum points situated symmetrically with respect to the ridge $x_1 = x_2$. We show schematically how the energy surface looks in Fig. 1.

4. CHAINS WITH $2N+1$ (ODD) CARBON ATOMS

The discussion of the preceding section ($N \rightarrow \infty$) includes both even and odd number carbon chains. However, there seems to be actually no bond alternation in shorter odd number carbon chains. Let us try to fix the critical number of carbon atoms theoretically at which the bond alternation begins to emerge as a bulk effect in the odd carbon chain.

According to Coulson,⁶ the total energy of $2N+1$ carbon chain is given as

$$E_T = N\{E_\sigma(x_1) + E_\sigma(x_2)\} + (2N+1)\alpha - 2 \sum_{m=1}^N \{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos[m\pi/(N+1)]\}^{\frac{1}{2}}. \quad (16)$$

As in the foregoing, we expand E_T in terms of ξ in the neighborhood of the minimum point x_0 of the diagonal line ($x_1 = x_2$) of the energy surface (x_1, x_2). The result

⁶ C. A. Coulson, Proc. Roy. Soc. (London) **A164**, 383 (1938).

turns out to be

$$E_T \approx 2NE_\sigma(x_0) + N(\partial^2 E_\sigma / \partial x^2)\xi + (2N+1)\alpha - 4|\beta| \sum_{m=1}^N \frac{\cos \frac{m\pi}{2(N+1)}}{2(N+1)} + 2 \left\{ \frac{\partial^2 \beta}{\partial x^2} \sum_{m=1}^N \frac{\cos \frac{m\pi}{2(N+1)}}{2(N+1)} - \frac{(\partial \beta / \partial x)^2}{\beta} \right. \\ \left. \times \sum_{m=1}^N \left[\frac{\sin^2 \frac{m\pi}{2(N+1)}}{2(N+1)} / \frac{\cos \frac{m\pi}{2(N+1)}}{2(N+1)} \right] \right\} \xi^2. \quad (17)$$

If we put the following approximate formula (with $\eta \approx 0.5$) into (17),

$$\sum_{m=1}^N \cos[m\pi/2(N+1)] \approx 2(N+1)/\pi, \\ \sum_{m=1}^N \left[\frac{\sin^2 \frac{m\pi}{2(N+1)}}{2(N+1)} / \frac{\cos \frac{m\pi}{2(N+1)}}{2(N+1)} \right] \\ \approx \frac{2(N+1)}{\pi} \left\{ \log \frac{4(N+1)}{\pi} + \eta \right\}, \quad (0 < \eta < 1), \quad (18)$$

and again adopt Lennard-Jones' $\beta(x)$ and $E_\sigma(x)$, we can find that the critical number is $N \approx 20$. That is, in the chains with odd ($2N+1$) carbon atoms the bond alternation occurs when $N > 20$. Labhart's conclusion⁵ is that $N > 31$.

5. CONCLUDING REMARK

The primary purpose of our investigation was to correct the wrong conclusion of Lennard-Jones' paper.¹ We have given the corrected numerical values and also general discussions on the conditions for the occurrence of the bond alternation.

Finally, it is to be noted that the reasoning of Lennard-Jones gives the right answers to shorter chains in which $\partial E_T / \partial \xi \neq 0$. This is seen in Table I: The second approximation of Lennard-Jones does actually give the correct values of x_1 and x_2 in the case of $N=2$. The same would be expected also for other cases of finite N . Unfortunately, however, in the case of $N \rightarrow \infty$ where $\partial(E_T/N) / \partial \xi = 0$, his procedure of successive approximation does not seem to work smoothly.