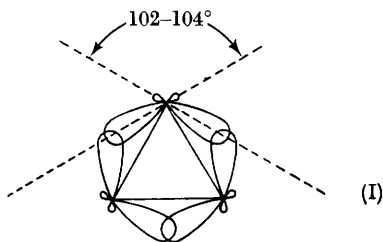


## “Twist” Bent Bonds

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THE nature of the bonding in cyclopropane and related strained systems has been considered from a theoretical point of view in several recent Papers.<sup>1-5</sup> Coulson and Moffitt have pointed out<sup>1</sup> that while the lines joining the carbon atoms in cyclopropane would be at angles of  $60^\circ$ , the orbitals of carbon could not be distorted from the tetrahedral ( $sp^3$ ) angle of  $109.5^\circ$  to a value as small as  $60^\circ$ . They suggested that the smallest possible angle between the orbitals of carbon would be  $90^\circ$  (*i.e.*, the angle between pure  $p$ -orbitals). Even if the C-C bonding in cyclopropanes was due to pure  $p$ -orbitals the centre of density of the bonding electron cloud would lie outside of a straight line connecting the carbon atoms. It thus becomes obvious that the overlapping orbitals which form the cyclopropane C-C bonds are not linearly oriented. The Coulson-Moffitt picture of cyclopropane would have the orbitals at an angle somewhere between  $109.5^\circ$  and  $90^\circ$  with the most probable angle being  $102-104^\circ$  as shown in structure (I).<sup>1,4,5</sup>



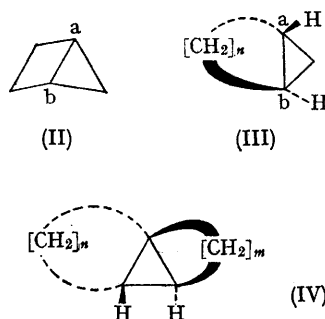
The calculations of Coulson and Moffitt have indicated<sup>1</sup> that certain characteristic properties should be found in cyclopropane. According to their calculations the energy of the system should be at a minimum when the H-C-H angle is  $116^\circ$ . Furthermore, the bonds connecting carbons are predicted to be more like those of ethylene than those of ethane. These predictions are in good agreement with experimental results.

Since the “strain” incorporated into a cyclopropyl ring causes this system to have unique properties, any increase in this strain due to the incorporation of the cyclopropyl ring into a polycyclic molecule would be expected to result in a magnification of the unusual characteristics of the cyclopropyl ring. Thus, we might expect that

† *trans*-Fused bicyclo[4,2,0]octanes and bicyclo[3,2,0]heptanes have been prepared (ref. 7). However, the conformational flexibility of the cyclobutane ring would be expected to drastically reduce the effect of the *trans*-fusion on the “symmetry” of the orbital overlap.

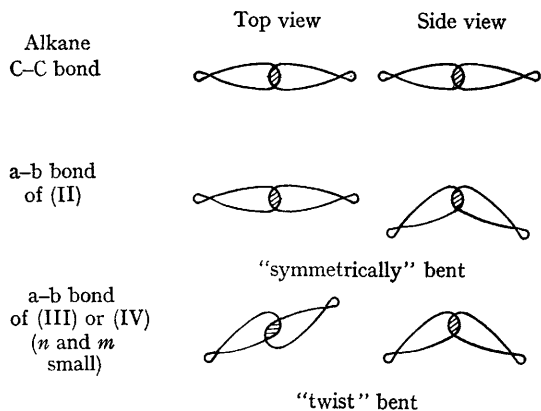
the bent bonds of highly strained polycyclic molecules will be unusually reactive.

I suggest that two distinctly different categories of bent bonds exist in polycyclic molecules containing highly strained rings. For lack of better terminology I suggest that these bonds be called “symmetrically” bent and “twist” bent. Molecules such as bicyclo[2,1,0]pentane and bicyclo[1,1,0]butane would contain “symmetrically” bent bonds similar in orbital overlap to cyclopropane but with less actual orbital overlap than cyclopropane. In contrast “twist” bent bonds would be expected to exist in molecules such as (III) and (IV). In (III), the “twisting” or torquing of the cyclopropane by the *trans*-fused bridge would result in an

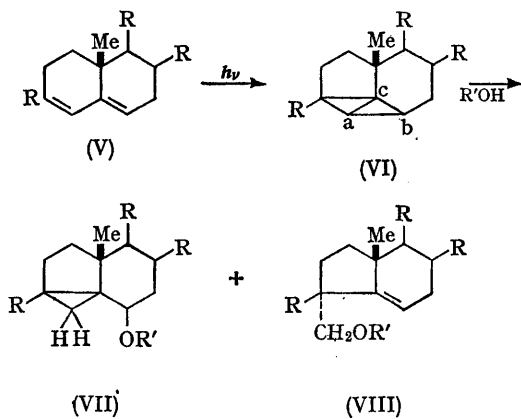


opposing horizontal displacement of the orbitals forming the a-b bond. This type of displacement is shown schematically below. From the side view the orbital projection for the a-b bonds in (II) and (III) might look quite similar. However, it is suggested that the top projection for this same bond would be very different. At present the most strained known *trans*-fused bicyclo[ $n$ ,1,0]-alkane is *trans*-bicyclo[6,1,0]nonane.<sup>6†</sup> This system probably does not possess enough strain to produce the postulated distortion. As  $n$  is reduced from six to five to four, the effects of bond “twisting” should be reflected in increased chemical reactivity.

Although *trans*-fused bicyclo[ $n$ ,1,0]alkanes with sufficient strain to demonstrate bond “twisting” are not yet known, examples of *di-cis*-fused cyclopropanes, such as (IV), do exist in unusually strained form. In principle the a-b bond of (IV) should be subjected to horizontal displacement



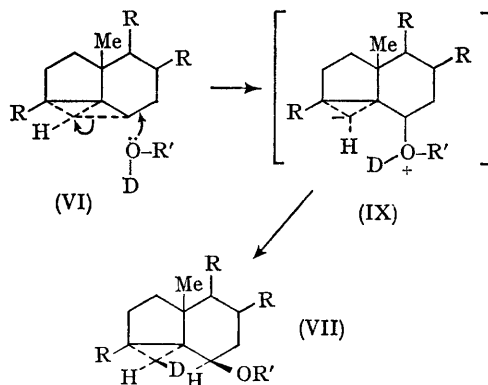
when *n* and *m* are sufficiently small. The initial photolytic products formed *via* irradiation of heteroannular dienes are examples of this class of di-*cis*-fused cyclopropanes and therefore should contain "twist" bent bonds. Such light-produced intermediates have been isolated<sup>8</sup> or suggested<sup>9</sup> in several reactions, most of which are exemplified by the conversion of (V) into (VI). The a-b bond of (VI) possesses unprecedented reactivity for a



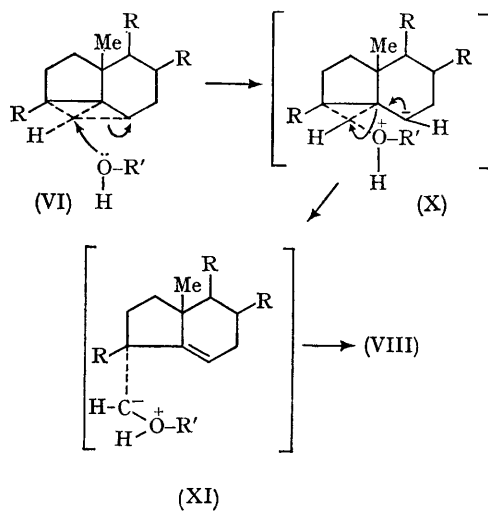
$\sigma$ -bond. From available data<sup>12</sup> it might have been expected that the a-c bond of (VI) would be the most reactive. However, the "twisted" a-b bond should have less orbital overlap than the a-c bond and therefore should be more reactive. Confirmation of this hypothesis is provided by the products obtained from (VI) by reaction with protic solvent at room temperature in a "dark reaction".<sup>8c</sup>

Previously, the a-b bond of (VI) has been described<sup>8c</sup> as "approaching something like an ion pair." Although an ion pair would be very reactive, the reactions of (VI) are not totally consistent with such an intermediate species. I

suggest that ethanol can add to either end of the "twist" bent bond a-b.



Addition of solvent to C<sub>b</sub> would result in a cyclopropyl carbanion, (IX), which by proton transfer would yield (VII). Since such a cyclo-



propyl carbanion should not invert readily, addition of ROD should produce a  $\beta$ -deuterium on the cyclopropyl ring. This is consistent with experimental results.<sup>10c</sup>

Addition of alcohol to C<sub>a</sub> would yield the carbanion (X), which *via* electron shifts would give the carbanion (XI). A concerted or subsequent proton transfer would yield (VIII).

The observed<sup>8b</sup> 4 : 1 ratio of (VII) to (VIII) would be expected if the transition state for addition of ROH involved considerable breaking of the a-b bond.

Although at present there are few examples of compounds containing "twist" bent bonds, those

examples which do exist have reactivity consistent with that predicted on the basis of a "twist" bent bond hypothesis. In addition to rationalizing the nature of this reactivity, the hypothesis adequately explains the products formed from these molecules.

Perhaps the most attractive feature of the "twist" bent bond hypothesis is the prediction that a variety of systems of types (III) and (IV) should possess reactivity analogous to that noted thus far only for structures related to (VI).

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