

Strain in NonTetrahedral Carbon Atoms

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appreciable contribution to the maximum height of the H^+ or D^+ peaks; such a behavior for H_2 was observed by Hagstrum and Tate⁷ with a mass spectrometer of somewhat similar type. The shapes of our H^+ and D^+ peaks become less symmetrical above 32 volts, indicating some contribution of high velocity ions to the shoulders of the peaks. Thus all of our R values should correspond predominantly to the production of monatomic ions by the single process of excitation of H_2 (or D_2) to H_2^+ (or D_2^+) in its lowest energy state. However, the possibility of smaller contributions from excited states of stable H_2^+ (or D_2^+) cannot be excluded.

We do not regard the apparent change of R with electron energy in the table as significant, since a relative shift of about 1 volt in the absolute values of electron energy used for each related pair of ionizing efficiency curves, would be sufficient to account for the observed differences in R between the low and high ends of the energy range. At these extremes the slopes of the ionizing efficiency curves are rather steep, whereas in the middle range of 50–90 volts, all curves are sufficiently flat to eliminate this source of error.

¹ W. Bleakney, E. U. Condon, and L. G. Smith, *J. Phys. Chem.* **41**, 197 (1937).

² D. P. Stevenson, private communication.

³ J. Delfosse and J. A. Hipple, *Phys. Rev.* **54**, 1060 (1938).

⁴ M. W. Evans, N. Bauer, and J. Y. Beach, *J. Chem. Phys.* **14**, 701 (1946).

⁵ W. Bleakney, *Phys. Rev.* **40**, 496 (1932).

⁶ H. W. Washburn and C. E. Berry, *Phys. Rev.* **70**, 559 (1946).

⁷ H. D. Hagstrum and J. T. Tate, *Phys. Rev.* **59**, 354 (1941).

Strain in Non-Tetrahedral Carbon Atoms

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IN view of the recent correspondence in this journal^{1–3} concerning the non-tetrahedral carbon atom, it seems desirable to call attention to certain results obtained by us which are now being prepared for publication.

Hybridization of s and p orbitals in carbon compounds was originally introduced to provide four atomic orbitals with strong directional properties, it being supposed that the attached groups were placed along the lines of greatest electron density. But, particularly in molecules which are "strained" in the original sense of Baeyer, we may expect that the lines of maximum charge density do not necessarily coincide with the directions of the attached atoms. In this way we are led to a treatment which regards the hybridization ratio λ as a variational parameter. The energy E of a molecule is expressed in terms of λ and $E(\lambda)$ is minimized. This leads to the best possible description of the molecule in terms of the pure valence state approximation of perfect pairing. We have treated the molecules cyclopropane, cyclobutane, and cyclobutadiene along these lines, discussing their stability, strain energy, and the orientation in space of their hydrogen atoms. We have also considered the compounds spiropentane, cyclobutene, and dibenz-cyclobutadiene (diphenylene) with special reference to the earlier treatment of the cyclic C_nH_n and

C_nH_{2n} by Penney.⁴ It has also been possible to account qualitatively for the anomalous bond shortening associated with these strained systems^{5,6}—anomalous, inasmuch as it is associated with a decreasing force constant.^{7–9}

Our chief results for cyclopropane may be summarized as follows:

(i) Each carbon atom is at the corner of an equilateral triangle and the hybridization is such (see Fig. 1) that the

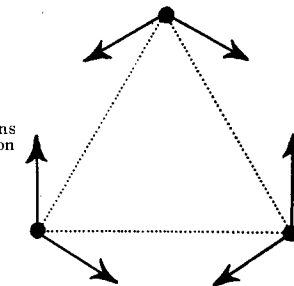


FIG. 1. Arrows denote directions of hybrid orbitals at the carbon atoms of cyclopropane.

two orbitals from any one carbon, in the plane of the ring, make an angle of about 106° with one another. In this way there is obtained a gain of about 5 ev per CH_2 group over a model in which¹ this angle is set at 90° . This means that less overlapping of the wave functions of paired electrons is more than offset by a decrease in strain energy at the carbon atoms.

(ii) The angle of 106° in the plane of the ring implies that the external valence angle should lie near 113° . A recent electron diffraction study⁶ of the dichlorocyclopropane molecule gives $112^\circ \pm 4^\circ$.

(iii) The bond length is expected to be shorter and the C—C stretching force constant less than the corresponding quantities for, say, ethane.

(iv) The error caused by neglect of resonance in the plane of the ring—a neglect which distinguishes our pure valence state model from the full HLSP treatment—is estimated at approximately 1 ev per CH_2 group. This is important when discussing strain energies.

Since the C—C bonding orbitals are not directed at one another, these bonds may be described as "bent"—a concept which may be usefully employed symbolically to illustrate the effects (i)–(iv) above.

Our predicted HCH angle for cyclopropane (113°) differs appreciably from that of Duffey¹ (180°), and that of Kilpatrick and Spitzer² (122°), but is apparently in complete agreement with what is observed for the dichloro compound. Duffey's paper seems to contain no more than a restatement of the implications of Van Vleck's " ω -model,"¹⁰ whereas Kilpatrick and Spitzer's treatment, though much more enlightening, involves certain *ad hoc* assumptions which we have managed to avoid.

¹ G. H. Duffey, *J. Chem. Phys.* **14**, 342 (1946).

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⁵ Pauling and Brockway, *J. Am. Chem. Soc.* **59**, 1221 (1937).

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⁷ F. Stitt, *J. Chem. Phys.* **7**, 297 (1939).

⁸ T. P. Wilson, *J. Chem. Phys.* **11**, 376 (1943).

⁹ Saksena, *Proc. Ind. Acad. Sci.* **A10**, 449 (1939).

¹⁰ J. H. Van Vleck, *J. Chem. Phys.* **1**, 219 (1933).