

TETRAHEDRAL "CYCLOBUTADIENE" ?

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RECENT experimental evidence<sup>1</sup> that  $C_4H_4$  is stabilized in the ion  $AgC_4H_4^+$  and that decomposition yields gas molecules which form  $AgC_4H_4^+$  elsewhere from  $Ag^+$  suggest reconsideration of the geometrical and valence structures of  $C_4H_4$  itself. It is suggested here that a tetrahedral structure geometrically similar to that<sup>2</sup> of  $B_4Cl_4$ , might be stable.

The instability of planar cyclobutadiene has been discussed many times since it was first pointed out<sup>3,4</sup> that the simplest LCAO treatments lead to a triplet ground state showing orbital degeneracy, which, in non-linear molecules should lead to molecular rearrangement.<sup>5,6</sup> A more recent study<sup>7</sup> has shown that electron - electron interaction splits the  $(a_{2u})^2(e_g)^2$  configuration into the four levels,  $^1A_{1g}$ ,  $^1B_{2g}$ ,  $^3A_{2g}$  and  $^1B_{1g}$ , none of

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<sup>1</sup> M. Avram, E. Marica and C. D. Nenitzescu, Chem. Ber. 92, 1088 (1959).

<sup>2</sup> M. Atoji and W. N. Lipscomb, J. Chem. Phys. 21, 172 (1953); Acta Cryst. 6, 547 (1953).

<sup>3</sup> E. Hückel, Grundzüge der Theorie ungesättigter und aromatischer Verbindungen, Verlag Chemie, Berlin (1938).

<sup>4</sup> G. W. Wheland, Proc. Roy. Soc. A 164, 397 (1938).

<sup>5</sup> H. A. Jahn and E. Teller, Proc. Roy. Soc. A 161, 220 (1937).

which is orbitally degenerate. Hence, the Jahn - Teller theorem in its exact form does not apply; nevertheless, the presence of both filled and unfilled electronic levels at so nearly the same energy is extremely rare in polyatomic molecules containing an even number of electrons. Presumably such molecules, if not diatomic, are unstable with respect to distortions that yield filled levels which are more stable and unfilled levels which are less stable. A planar distortion would most likely lead to acetylene, whereas a non-planar distortion could lead to a tetrahedral structure.

In order to examine molecular orbitals in tetrahedral  $C_4H_4$ , the LCAO approximation already given<sup>6</sup> for  $B_4H_4$  has been extended here to include resonance integrals  $\epsilon$  between approximately tetrahedral orbitals on the same carbon atom, and resonance integrals  $\eta$  between orbitals non-coplanar with the C-C bond. The  $a_1$  level lies at  $H_0 + \beta + 2\gamma + 4\delta + 2\epsilon + 2\eta$ , the e pair of levels at  $H_0 + \beta - \gamma - 2\delta - \epsilon + 2\eta$ , with a triply degenerate t levels between these.<sup>8</sup> Thus while  $B_4H_4$  would have the configuration  $(a_1)^2(t_1)^6$ ,  $C_4H_4$  would have the configuration  $(a_1)^2(t_1)^6(e)^4$ . Reasons that the  $(e)^4$  level is possibly slightly bonding include an argument based on approximate relative values of the integrals, and a comparison with the established structure of  $B_4Cl_4$ .

Assumption of reasonable hybrid orbitals in a range about that found<sup>8</sup> for cyclopropane yields values of overlap integrals corresponding to  $\gamma$  and  $\delta$  about 1/3 of that corresponding to  $\beta$ . The term  $\beta - \gamma - 2\delta$  would, with the

<sup>6</sup> H. A. Jahn, Proc. Roy. Soc. A 164, 117 (1938).

<sup>7</sup> W. Moffitt and J. Scanlan, Proc. Roy. Soc. A 220, 530 (1954).

<sup>8</sup> W. H. Eberhardt, B. L. Crawford, Jr. and W. N. Lipscomb, J. Chem. Phys. 22, 985 (1954).

hopeful assumption of proportionality to resonance integrals, lead to approximate non-bonding of these levels. Moreover, it is probable that  $\eta$  is negative, as are  $\beta$ ,  $\gamma$  and  $\delta$ , but comparison with the filled-orbital valence bond analogue<sup>9</sup> suggests that  $\epsilon$  is positive essentially because of distortion of bonds from the tetrahedral configuration. Both of these additional interactions tend to stabilize further the highest filled e degenerate pair of levels in tetrahedral  $C_4H_4$ . It is more difficult to estimate either the strain energy or the nearly compensating additional resonance energy of various pairing schemes, but the additional interactions, particularly those between orbitals on the same carbon atom, may require even more bend in the equivalent bonds along tetrahedral edges than that found<sup>8</sup> in cyclopropane.

A stronger argument is that  $B_4Cl_4$  exists, but that  $B_4H_4$  has not yet been discovered. Although to a first approximation<sup>8</sup> the filled electron configuration is  $(a_1)^2(t_1)^6$ , it has been argued<sup>10</sup> that the interaction of the lone  $\pi$  pairs of Cl with the e levels is at least partly responsible for the existence of  $B_4Cl_4$  as contrasted with  $B_4H_4$ . This interaction of levels with the same symmetry characteristics certainly suggests that the e pair of levels of the tetrahedral  $B_4$  group cannot lie at a high energy, relative to the lone pairs of Cl, and probably that they lie at weakly bonding energy levels.

Whereas in  $B_4Cl_4$  the e levels are filled by interaction with an electron donor, in tetrahedral  $C_4H_4$  the e levels are already filled.

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<sup>9</sup> C. A. Coulson and W. Moffitt, Phil. Mag. 40, 1 (1949).

<sup>10</sup> H. C. Longuet-Higgins, Quart. Rev. 11, 121 (1957).

Hence it is suggested that stable molecules based upon a tetrahedral  $C_4$  arrangement might be prepared if an electron acceptor, such as  $-COOH$ ,  $-BCl_2$ ,  $-NO_2$  or  $-CN$  is substituted for  $-H$  in  $C_4H_4$ .

The geometry of the  $AgC_4H_4^+$  complex depends upon whether one  $Ag^+$  is bonded to  $C_4H_4$ , as it might be in solution, or whether each  $Ag^+$  is bonded to two  $C_4H_4$  and each  $C_4H_4$  is bonded to two  $Ag^+$  as may occur in the crystal. In either case, the symmetrical  $5s$  orbital of  $Ag^+$  would lie off the four-fold axis and off the molecular plane if  $C_4H_4$  is planar or nearly so, or towards an opened edge, not a face, of the tetrahedron if the initially tetrahedral geometry is approximated.

In summary, it cannot be strongly argued that if  $C_4H_4$  or one of its substitution derivatives exists, it must be tetrahedral, but this possibility of a closed shell electronic structure for this elusive molecule appears not to have been previously suggested.