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A Further Study on the CNDO/2 Structures of Water Dimer

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The structure of water dimer has been further studied by the CNDO/2 method. Some results have been found to be different from those in Thiel's paper.

Key words: Water dimer

According to Thiel [1], there are four CNDO/2 structures, (a)–(d), of water dimer, as shown in Fig. 1; (d) has the lowest energy. The results that I obtained recently from a CNDO/2 geometry optimization program [2] have been found to be in disagreement with Thiel's in the following respects:

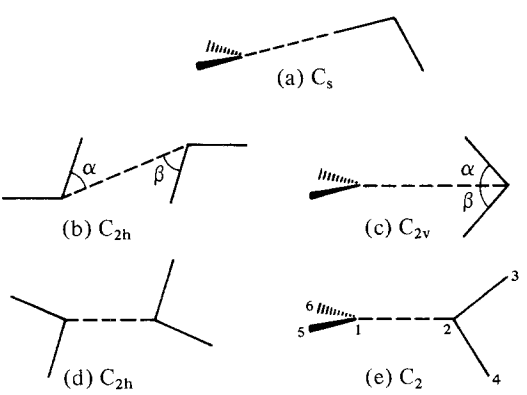

Fig. 1.

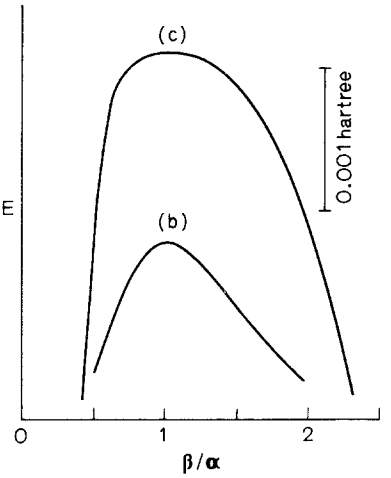

Fig. 2.

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1. Both (b) and (c) are not the equilibrium structures, but only the states at the saddle points. When the energy is plotted as a function of β/α (β and α as shown in Fig. 1) with restriction to C_s symmetry, either (b) or (c) arrives at a maximum (Fig. 2).
2. (d) is not the structure with the lowest CNDO/2 energy. When it is twisted about the O–O axis, it changes into a more stable structure, (e), belonging to C_2 point group. The dissociation energy of (e) has been found to be 14.5 kcal/mole, while that of (d) is 14.3 kcal/mole.

The geometry of (e) is as follows: $R_{12} = 1.455$ Å; $R_{23} = R_{15} = 1.054$ Å; $R_{24} = R_{16} = 1.041$ Å; $\measuredangle 123 = \measuredangle 215 = 142.7°$; $\measuredangle 124 = \measuredangle 216 = 118.1°$; the dihedral angle between plane 512 and plane 123 is 97.6°.

From the result of STO-3G, Thiel asserted that (d) is an artifact of CNDO/2. Similarly, it seems reasonable for us to believe that (e) is also an artifact. Therefore, it is fitting to conclude that among the equilibrium structures calculated by CNDO/2, only (a) agrees roughly with the real.

References

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2. Zhixing, C.: Study on the CNDO/2 Geometry Optimization, to be published

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