Tetrahedron Letters No.52, pp. 4575-4578, 1970. Pergamon Press. Printed in Great Britain.

TOTAL ENERGY OF $(CH)_8$ ISOMERS CALCULATED BY THE CNDO/2 METHODS

Hiizu Iwamura, Kazuhiko Morio, Michinori Ōki, and Tosiyasu L. Kunii*
Department of Chemistry, Faculty of Science, and *Computer Center,
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

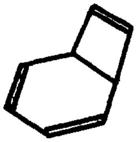
(Received in Japan 30 September 1970; received in UK for publication 13 October 1970)

The CNDO/2 calculations have since introduction by Pople and coworkers [1] proved quite satisfactory in reproducing molecular geometry. The method includes all valence electrons and yet is simple enough for organic chemist to perform the calculation of the equilibrium conformation and the charge distribution of large molecules. However, it has recently been recognized that the total energy calculated by the CNDO/2 approximations appears to be lower for the cyclic form than the corresponding linear models.[2] Further inspection of the literature seems to indicate that the calculated energy barriers to conformational changes which proceed through the planar transition state are usually higher than those experimentally observed.[3] On the contrary, the energy calculated by the CNDO/2 methods of the more or less folded transition state or the eclipsed conformation of the ethane-like molecules comes out lower than the observed value.[4]

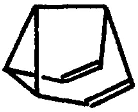
In the course of our theoretical study on the thermal isomerization of $(CH)_8$ hydrocarbons, we found an interesting but unrealistic structure – total energy correlation pertinent to the discrepancies mentioned above and to the limitation of the CNDO/2 approximations.

The calculations were performed on a HITAC 5020E computer by the use of the modified CNDO/2 program originally written in ALGOL by Segal and distributed by the QCPE organization.[5] The experimentally determined structures of cyclooctatetraene (I)[6] and cubane (V)[7] were well reproduced.[3c] The energy

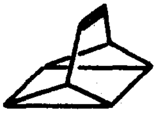
I



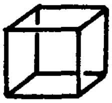
II



III



IV



V

minimization was carried out as usual by changing the bond lengths and angles for the hydrocarbons II to IV for which the observed structural parameters are not available. The C-H bond length was kept constant at 1.10 Å. The structures thus assumed are in reasonable agreement with those constructed by a Prentice-Hall framework molecular model.

In Table I are summarized the total energy of the $(CH)_8$ hydrocarbons I to V. The heat of formation (ΔH°_f) of I and V has been shown by the combustion data to be 71.1 and 148.7 ± 1.0 kcal/mole, respectively.[8,9] Based on the observed equilibrium concentration of II in I, II is expected to be less stable than I by about 3.8 kcal/mole.[10] Thus the order of stability is $I > II \gg V$, and the calculated total energies do not reflect the experimental data at all. Instead plot of the formers vs. number of rings in the $(CH)_8$'s gives an unexpectedly linear correlation as shown in Figure 1. Reparametrization of the resonance integral proportionality constants β in the CNDO/2 method according to Wiberg[11] did not improve the calculated total energy.

Table I. The Electronic and Total Energies of the $(CH)_8$ Isomers

	Electronic energy (a.u.)	Total energy (a.u.)
I	-227.44	-62.71
II	-232.00	-62.86
III	-240.67	-63.01
IV	-240.09	-63.13
V	-252.05	-63.34

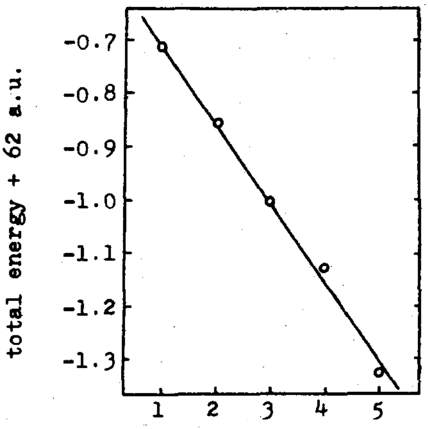


Figure 1. Total energy vs. number of rings in the $(CH)_8$

The erratic trend in Figure 1 appears to demonstrate the same general defect of the CNDO/2 methods as pointed out earlier; the compact molecules tend to become too stable. Thus the discrepancies seem to be originated from underestimation of the two-center electron repulsion integrals in the CNDO/2 approximations. Alternatively, the apparent stabilization by 360 kcal/mole when going from I to V might be due to overestimation of the energy gain by a carbon to carbon σ bond formation at the expense of a double bond.[12] The abscisa of Figure 1 corresponds to the increase in the number of σ bonds and to the decrease in the number of the double bonds in the $(CH)_8$ isomers. The partitioning study of the total energy into physical components is in progress to clarify the situations.

The CNDO/2 methods have already been used in many cases for studying reaction mechanisms with reasonable success.[13] In view of the present findings, however, the methods with presently available empirical parameters appear too naive to discuss quantitatively the mechanism of isomerization of the $(CH)_8$ hydrocarbons.[14]

REFERENCES

(1) J. A. Pople and G. A. Segal, J. Chem. Phys., **44**, 3289 (1966).

(2) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen and P. von R. Schleyer, J. Am. Chem. Soc., **91**, 5350 (1969).

(3) (a) M. S. Gordon and H. Fischer, ibid., **90**, 2471 (1968); (b) B. Tinland, Theoret. chim. Acta, **11**, 452 (1968); (c) H. Iwamura, K. Morio and T. L. Kunii, unpublished work.

(4) M. S. Gordon, J. Am. Chem. Soc., **91**, 3122 (1969); R. B. Davidson, W. L. Jorgensen and L. C. Allen, ibid., **92**, 749 (1970).

(5) Quatum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana 47401.

(6) M. Traetteberg, Acta Chim. Scand., **20**, 1724 (1966).

(7) E. B. Fleischer, J. Am. Chem. Soc., **86**, 3889 (1964).

(8) E. J. Prosen, W. H. Johnson and F. D. Rossini, ibid., **72**, 626 (1950).

(9) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave and J. L. Franklin, ibid., **88**, 626 (1966).

(10) R. Huisgen and F. Mietzsch, Angew. Chem., **76**, 36 (1964).

(11) K. B. Wiberg, J. Am. Chem. Soc., **90**, 59 (1968).

(12) H. Fischer and H. Kollmar, Theoret. chim. Acta, **13**, 213 (1969).

(13) For a review see H. H. Jaffe, Accounts Chem. Res., **2**, 136 (1969). H. Fischer, H. Kollmar, H. O. Smith and K. Miller, Tetrahedron Letters, 5821(1968); D. T. Clark and G. Smale, ibid., 3673 (1968); D. T. Clark, Theoret. chim. Acta, **10**, 111 (1968); K. B. Wiberg, Tetrahedron, **24**, 1083 (1968).

(14) Refinement of the CNDO/2 in conjunction with experimental data and *ab initio* calculations is expected. Treatment of the present systems by MINDO methods is also in progress in these laboratories.