Heats of Formation and Strain Energies for $[CH]_8$ Isomers Calculated by All-valence-electron Semi-empirical SCF–MO Theories

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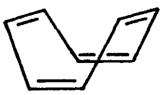
Summary Theoretical heats of formation and strain energies of all the possible $[CH]_8$ isomers were calculated by the MINDO/1 method, and were found to be in good agreement with the experimental data and the relative stability of these hydrocarbons estimated by thermal interconversion.

OF great recent interest are syntheses and thermal and photochemical transformations of the possible $[CH]_8$ isomers. In this paper we report a reliable prediction by theoretical methods of their heats of formation and strain energies and relate these to the ease of and direction of interconversion between isomers. The calculations were performed by the all-valence-electron semi-empirical SCF–MO methods elaborated by Pople *et al.*[1] and Dewar *et al.*[2] Since the experimental data concerning the geometry of these molecules are unavailable except for cyclo-octatetraene (I) and cubane (XII), an attempt was made to predict optimal geometries with respect to heat of formation; the geometry which gives the minimum heat of formation by the MINDO/2 method is considered to correspond to the equilibrium geometry of the actual molecule. Heats of formation by the MINDO/1 method were calculated by substituting the standard bond lengths of Baird and Dewar[2] for the optimal lengths of the MINDO/2. Strain energies were then estimated by substracting the strain-free heats of formation calculated by the additivity rules[3] of Franklin and Cox from the heats of formation obtained by the MINDO/1 method.



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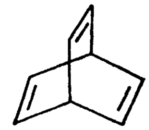

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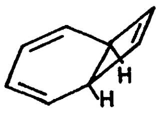

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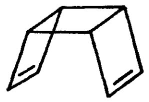

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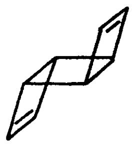

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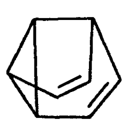

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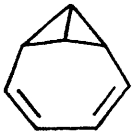

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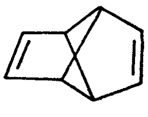
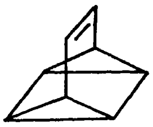


(VIII)

In the second version of the MINDO method, special interest is paid to reproduction of the actual geometry of the molecules. The effort appears incompatible with the strain energies of the cyclopropane and cyclobutane rings; the calculated heats of formation are 3·8 and −2·2 kcal/mol in contrast with those observed; 12·7 and 6·4 kcal/mol, respectively.[2] Thus in the second column of the Table, the MINDO/2 results for (IV), (V), and (X)—(XIV) are con-



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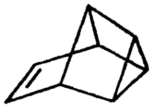
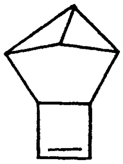
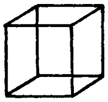


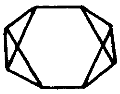
(X)



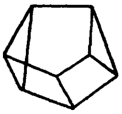
(XI)



(XII)



(XIII)



(XIV)

siderable underestimates. The MINDO/1 method is considered to give better results for the heat of formation; even the greatly strained cyclobutene deviates only by 3·4 kcal/mol from the observed value.[2] The experimental heats of formation of (I) and (XII) are 71·1 and 148·7 kcal/mol, respectively.[4,5] Based on the equilibrium concentration of bicyclo[4,2,0]octa-2,4,7-triene (III) in (I), the former is estimated to be less stable than the latter by about 4 kcal/mol.[6] Qualitatively, octamethylcyclo-octatetraene isomerizes completely on heating to the corresponding semibullvalene[7] and the tricyclo-diene (VIII) has been shown to isomerize spontaneously to (VI).[8,9] These experimental findings are all reproduced in the MINDO/1 calculations as summarized in the Table. As discussed in our previous papers and shown in the fourth column of the Table,[10] the total energies by the CNDO/2 method are not related to the experimental and estimated stability of the $[CH]_8$ isomers, and depend upon the number of the double bonds present in the molecule. This false trend indicates that the total energy values of the CNDO/2 approximation are not reliable in that different bond types cannot be compared directly. The deviation appears to be because the empirical parameters involved in this method are not yet optimized with respect to heat of formation. Improvement of these parameters by Fischer's[11] method may yield better results.

The strain energies and heats of formation are not directly related to the practical (*i.e.* kinetic) stability of these hydrocarbons. Less strained (III) and (VIII), for example, are too unstable to be isolated at room temperature,[6,8,9] while one of the most strained (XII) is indefinitely stable. This apparently paradoxical relation affords good support for the notion that the practical stability of a given compound is governed above all by lack of a symmetry-allowed or stabilized-biradical 'leaking path' available to the molecule. The potential energy surfaces interrelating the $[CH]_8$ isomers are currently under theoretical investigation.

(*Received, July* 1*st*, 1971; *Com.* 1108.)

TABLE

Heats of formation and strain energies of $[CH]_8$ *isomers*

Isomer	Heat of formation (kcal/mol) MINDO/2	MINDO/1	Total energy (atomic unit) CNDO/2	Strain energy (kcal/mol) Franklin's	Cox's
(I)	56·7	66·4	−62·69	−9·1	10·4
(II)	38·6	78·0	−62·90	23·5	26·8
(III)	42·9	77·9	−62·85	23·4	30·5
(IV)	46·3	120·8	−62·90	87·5	82·3
(V)	42·9	120·2	−62·92	86·8	81·7
(VI)	27·0	53·0	−63·06	19·6	14·5
(VII)	48·8	95·1	−62·92	59·8	67·3
(VIII)	46·7	64·8	−62·95	31·5	26·3
(IX)	35·2	76·8	−63·15	64·6	67·9
(X)	66·3	155·0	−63·00	142·8	146·1
(XI)	40·4	115·4	−63·05	103·2	106·5
(XII)	19·9	116·9	−63·30	125·6	125·7
(XIII)	34·3	121·0	−63·17	129·8	129·8
(XIV)	17·0	106·0	−63·28	114·8	114·8

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