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Note

MNDO Study of Helvetane and Israelane

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Applying MNDO approximation, the heats of formation (ΔH_f) and structures of the novel compounds helvetane (*1*) and israelane (*2*) have been calculated. The MNDO ΔH_f for *1* and *2* are 336 and 719 kcal/mol, respectively, in agreement with the previous prediction that *1* is more stable than *2*. In addition, in view of the structures calculated, the large positive ΔH_f values of *1* and *2* are most likely the result of these molecules' angular strain.

In a recent note,[1] the synthetic strategy for two isomeric members of the $(CH)_{24}$ series, helvetane (*1*) and israelane (*2*), was discussed. In addition, even though these two compounds were not prepared, it was predicted that *2* would rearrange thermally to *1*. Although the note was apparently written in jest,[2] the novel compounds *1* and *2* are undoubtedly of interest. Hence we have carried out MNDO[3] calculations on these two molecules in order to investigate their relative stability and their structures. Also, a comparison between these two compounds and related systems was made.

For the present calculations, D_{4h} and D_{6h} symmetries were assumed for *1* and *2*, respectively. The MNDO structures of these two molecules are depicted in Figures 1 and 2. The MNDO heats of formation (ΔH_f) for *1* and *2* are 336 and 719 kcal/mol, respectively.

Examining Figures 1 and 2, it is worth noting that the two twelve-mem-

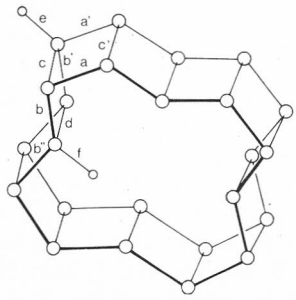

Figure 1. MNDO structure of helvetane (*1*). Bond lengths (Å): $a = a' = 1.60$, $b = b' = b'' = 1.56$ $c = c' = 1.57$, $d = 1.60$, $e = 1.09$, $f = 1.10$. Bond angles (°): a—$b = 114.0$, b—$b'' = 138.5$, a—$c = 90.0$, a'—$c' = 90.0$, b—$d = 89.5$, b'—$d = 90.5$, a'—$e = 115.4$, b'—$e = 118.5$, c—$e = 123.1$, b—$f = b''$—$f = 105.8$, a—$f = 128.3$. Only two hydrogens are shown.

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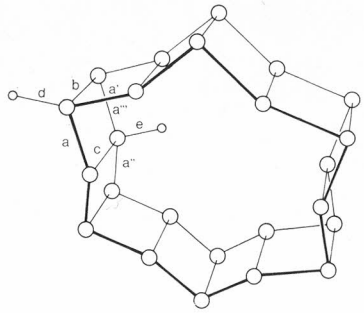
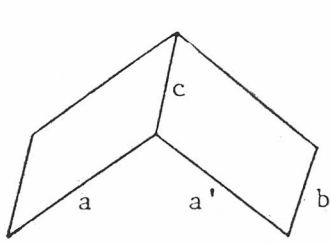


Figure 2. MNDO structure of israelane (*2*). Bond lengths (Å): $a = a' = a'' = a''' = 1.60$, $b = 1.56$, $c = 1.58$, $d = 1.09$, $e = 1.11$. Bond angles (°): $a—a' = 97.2$, $a''—a''' = 157.8$, $a—b = 90.4$, $a—c = 89.6$, $a—d = a'—d = 122.4$, $b—d = 124.9$, $a''—e = a'''—e = 99.1$, $c—e = 130.3$. Only two hydrogens are shown.

bered rings in both molecules have only very minor puckering and hence are nearly planar. When compared with the structure[4] of bicyclo[2.2.0]hexane (*3*) [$a = a' = 1.54$ Å, $b = 1.56$ Å, $c = 1.58$ Å, $a—a' = 113.5°$], significant lengthening



of all peripheral C—C distances (bond *a*) in *2* and eight »outer« C—C distances (bond *a*) in *1* is apparent. On the other hand, the bridging C—C lengths in *1* (bonds *c* and *d*) and *2* (bonds *b* and *c*) are on the whole comparable with that in *3*. The nonbonding distances between the »inside« hydrogens in *2* are 1.55 Å for *ortho*, 2.69 Å for *meta*, and 3.11 Å for *para* hydrogens, whereas the separations between the »inside« hydrogens in *1* are 1.68 Å for vicinal and 2.37 Å for diagonal hydrogens. Furthermore, it is noted that the C—C distance *d* in *1*, where two »inside« hydrogens are attached to the respective carbon atoms, is slightly longer than the bridging C—C bond in *3*.

The relatively large positive ΔH_f values of *1* and *2* are most likely the result of these molecules' angular strain. Here, again, compound *3* may be used as a reference. The strain energy for *3* is 51 kcal/mol at 25 °C.[5] Additionally, the cyclobutane moiety in *3* is puckered (puckering angle is 11.5°). For both *1* and *2*, all cyclobutane units are planar. In *1*, bond angle *a*—*b* is similar to *a*—*a'* in *3*, but angle *b*—*b''* is significantly larger. Hence, it is expected that the strain energy for *1* would be somewhat higher than the sum of those for six bicyclohexanes. Based on the classical mechanical model,[6] the strain contributed by angles *b*—*b''* in *1* would be 10.9 kcal per angle, or $10.9 \times 8 = 87$ kcal/mol. If it is assumed that the strain difference between *1* and the sum of six bicyclohexanes is mainly contributed by the *b*—*b''* angle strains, then the strain energy for *1* would be $6 \times 51 + 87 = 393$ kcal/mol. Alternatively,

applying Schleyer's group increment strain energy correction for CH groups[5], the strain energy for *1* based on the MNDO ΔH_f would be 387 kcal/mol, in excellent agreement with the classical mechanical model result.

Similar results can be obtained for *2*. As shown in Figure 2, bond angles a—a' and a''—a''' are severely distorted. The former is smaller than the angle a—a' in *3*, while the latter is considerably larger. In fact, an increase in angle a—a' wil occur at the expense of an increase in angle a''—a'''. If it is assumed that the difference in strain energy between *2* and the sum of six bicyclohexanes arises from the strain[6] of angles a—a' (57 kcal/mol) and a''—a''' (344 kcal/mol), the strain energy for *2* would be $6 \times 51 + 57 + 344 = 707$ kcal/mol. On the other hand, applying Schleyer's method,[5] the strain energy for *2* based on the MNDO ΔH_f would be 770 kcal/mol, in fair agreement with the classical mechanical model result.

To conclude, the present results are in accord with the prediction that helvetane is thermodynamically more stable than israelane. In addition, the large positive ΔH_f values for both *1* and *2* are due to these molecules' severe angular strain. The strain per CH unit is approximately 16 kcal/mol for *1* and 32 kcal/mol for *2*. It is interesting to note that the strain per CH unit for *1* is still somewhat less than those for several known $(CH)_n$ compounds,[7] such as cubane (20 kcal/mol) and prismane (23 kcal/mol).

REFERENCES

1. G. Dinsburg, *Nachr. Chem. Tech. Lab.* **30** (1982) 289; *Nouv. J. Chim.* **6** (1982) 175.
2. D. Ginsburg, private communication (1983).
3. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.* **99** (1977) 4899.
4. B. Anderson and R. Srinivasan, *Acta Chem. Scand.* **26** (1972) 3468.
5. E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **95** (1973) 8005.
6. The force constant k_Θ used is 35 cal/deg.^{2}. See F. H. Westheimer in M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York (1956).
7. A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York (1978).

SAŽETAK

MNDO studij helvetana i izraelana

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Izračunani su strukturni podaci i topline stvaranja slobodnih molekula helvetana (*1*) i izraelana (*2*), koje još do sada nisu sintetizirane. Pri tome je primijenjena semiempirijska MNDO metoda. Pokazano je da je spoj *1* za oko 380 kcal/mol stabilniji od *2*. To je posljedica manje kutne napetosti.