

THE EFFECT OF d-FUNCTIONS ON MOLECULAR ORBITAL ENERGIES FOR HYDROCARBONS

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Ab initio molecular orbital studies including d-functions in the basis set have been made on methane, acetylene, ethylene, ethane, propyne, allene, cyclopropene, propene and cyclopropane. It is shown that the strained cyclic molecules cyclopropene and cyclopropane are preferentially stabilized by the addition of d functions. If such functions are included, relative energies are given to an accuracy of 3 kcal/mole or better.

1. Introduction

Ab initio molecular orbital theory with limited basis sets has been quite widely applied to the structures and energies of small neutral hydrocarbons. Published work using an extended basis of s- and p-functions on carbon and s-functions on hydrogen indicates that calculated energies for cyclic forms are generally too high relative to corresponding energies for open-chain isomers. Peyerimhoff and Buenker [1], for example, studied the C_3H_4 isomers and found (with their largest basis) that cyclopropene was predicted to be 34.0 kcal/mole less stable than propyne, whereas the experimental separation (after correction for zero-point vibrational energy differences) is only 22.3 kcal/mole. Similar results for C_3H_4 and C_3H_6 were obtained in this laboratory [2]. This deficiency of the theory could be due either to the inadequacy of the basis set because of neglect of polarization functions (d-type on carbon and p-type on hydrogen) or to a difference of correlation energy between ring- and open-type isomers. Recent work on C_1 and C_2 carbonium ions [3] has already indicated that addition of polarization functions lowers the energy of cyclic (bridged) structures more than open structures. This appears to support the first possibility. In this note we report a study of the effect of carbon d-functions on the molecular orbital energies of stable C_1 , C_2 and C_3 hydrocarbons (except propene). This

provides further evidence that isomeric energy differences are well described by molecular orbital theory given an adequate basis set.

2. Method and results

The molecules considered are methane, acetylene, ethylene, ethane, propyne, allene, cyclopropene, propene and cyclopropane. We proceed by simple extension of work already presented [2, 4]. Theoretical geometries using a simple minimal basis set (STO-3G) [5] were first obtained and shown to be in reasonable agreement with experimental data. Single calculations at these geometries were then carried out using split-valence bases of contracted gaussian functions (4-31G [6] and 6-31G [7]). (Use of theoretical rather than experimental geometries has only a small effect on calculated energies [8].) The 6-31G basis has an improved inner-shell function but otherwise gives results similar to 4-31G. These calculations led to the already noted excessive separation between open and closed isomers. We now report further calculations for all molecules at the same nuclear geometry but with an additional set of second degree gaussian functions ($x^2, y^2, z^2, xy, yz, zx$) $\exp(-\alpha r^2)$ centered at each carbon atom. This is equivalent to the addition of a complete set of d-type gaussians together with an s-type function $r^2 \exp(-\alpha r^2)$. The value of the ex-

Table 1
Theoretical total energies ^{a)} (hartrees)

Molecule	6-31G	6-31G*	Difference
methane	-40.18055	-40.19517	0.01462
acetylene	-76.79092	-76.81700	0.02608
ethylene	-78.00395	-78.03145	0.02750
ethane	-79.19748	-79.22865	0.03117
propyne	-115.82156	-115.86337	0.04181
allene	-115.82089	-115.86070	0.03981
cyclopropene	-115.76540	-115.82294	0.05754
propene	-117.02768	-117.07111	0.04343
cyclopropane	-117.00777	-117.05872	0.05095

a) Energy calculated using geometry optimized with minimal STO-3G basis.

Table 2
Relative energies of isomeric C₃ hydrocarbons (kcal/mole)

Molecule		Calc.		Exp. ^{a)}
		6-31G	6-31G*	
C ₃ H ₄	propyne	0	0	0
	allene	0.4	1.7	2.1
	cyclopropene	35.2	25.4	22.3
C ₆ H ₆	propene	0	0	0
	cyclopropane	12.5	7.8	7.4

a) Calculated from observed heats of formation adjusted to 0°K with stationary nuclei. See ref. [8] for details.

ponent α is taken as 0.8 on the basis of optimization studies [9]. This augmented form of the basis set will be denoted by 6-31G⁺.

The total energies calculated in this way are listed in table 1. It is immediately evident that the addition of polarization functions on carbon lowers the energy more for cyclic than for open forms. The results may be assessed first by comparing energy differences between isomeric forms of C₃H₄ and C₃H₆ with experimental values (table 2). There is clearly a marked improvement. The value for cyclopropene relative to propyne is still about 3 kcal/mole too large, but the greater part of the discrepancy has gone. A second comparison with experiment can be made for the energies of bond separation reactions [8] which measure the non-additivity of energies of bonds between heavy atoms. The reactions relate the energies of C₃ hydrocarbons with the smaller systems. For the cyclic molecules, the bond separation energy is negative and is one measure of the strain. This comparison is displayed in table 3 and again shows improvement for cyclopropene and cyclopropane.

We should next consider whether the results would be further modified if p-type polarization functions were also added to the basis set for hydrogen atoms. At the present time, our computational facilities are inadequate for such calculations on the C₃ molecules. However, some indication is provided by the C₂ molecules where we have found [9] that addition of a single set of p-functions leads to energy lowerings per hydrogen atom of 1.00, 1.13 and 1.26 kcal/mole for ethane, ethylene and acetylene respectively. This suggests that the effect of hydrogen p-functions in a CH bond is nearly independent of the nature of the neighboring carbon. If this carries over to the C₃ molecules, the relative energies calculated for 6-31G* shown in tables 2 and 3 would be little changed.

Table 3
Bond separation energies (kcal/mole)

Molecule	Reaction	Bond separation energy		
		6-31G	6-31G*	exp ^{a)}
propyne	CH ₃ CCH + CH ₄ → C ₂ H ₂ + C ₂ H ₆	8.6	8.1	7.2
allene	CH ₂ CCH ₂ + CH ₄ → 2C ₂ H ₄	-4.1	-4.4	-4.1
cyclopropene	CH ₂ CHCH + 3CH ₄ → C ₂ H ₄ + 2C ₂ H ₆	-57.6	-50.4	-45.2
propene	CH ₃ CHCH ₂ + CH ₄ → C ₂ H ₄ + C ₂ H ₆	4.3	3.9	5.0
cyclopropane	CH ₂ CH ₂ CH ₂ + 3CH ₄ → 3C ₂ H ₆	-27.0	-26.2	-23.5

a) From ref. [8].

The general conclusion to be drawn from this work is that the relative energies of small cyclic and non-cyclic hydrocarbons are given with good accuracy (≈ 3 kcal/mole or better) by molecular orbital theory provided that the d-type functions are included in the basis set.

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References

- [1] S.D. Peyerimhoff and R.J. Buenker, *Theoret. Chim. Acta* 14 (1969) 305.
- [2] L. Radom, W.A. Lathan, W.J. Hehre and J.A. Pople, *J. Am. Chem. Soc.* 93 (1971) 5339.
- [3] P.C. Hariharan, W.A. Lathan and J.A. Pople, *Chem. Phys. Letters* 14 (1972) 385.
- [4] W.A. Lathan, W.J. Hehre and J.A. Pople, *J. Am. Chem. Soc.* 93 (1971) 808.
- [5] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2657.
- [6] R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.* 54 (1971) 724.
- [7] W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.* 56 (1972) 2257.
- [8] W.J. Hehre, R. Ditchfield, L. Radom and J.A. Pople, *J. Am. Chem. Soc.* 92 (1970) 4796.
- [9] P.C. Hariharan and J.A. Pople, to be published.