Molecular Orbital Theory of the Electronic Structure of Organic Compounds. VIII. Geometries, Energies, and Polarities of C_3 Hydrocarbons

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Abstract: *Ab initio* molecular orbital theory with a minimal basis set closely related to Slater-type orbitals (STO-3G) is used to find theoretical equilibrium geometries for the six C_3 hydrocarbons, propyne, allene, cyclopropene, propene, cyclopropane, and propane. These geometries compare well with experimental data. Isomerization energies, however, are poorly given by the STO-3G basis. Some improvement in the calculated relative energies is obtained if an extended basis of contracted gaussian functions (4-31G or 6-31G) is used for single calculations at the optimized STO-3G geometries. The magnitudes of electric dipole moments calculated using the extended 6-31G basis set are close to experimental values. However, the sign of the moment for cyclopropene disagrees with a recent experimental determination.

In an earlier paper in this series,[1] we have made a systematic LCAO (linear combination of atomic orbital) molecular orbital study of the equilibrium geometries and energies of the C_1 and C_2 hydrocarbons and their cations. Two basis sets were used, the simpler (STO-3G) being closely related to a minimal basis of Slater-type orbitals[2] and the other (4-31G) an extended contracted gaussian set with valence atomic orbitals split into inner and outer parts.[3] Minimization of the STO-3G total energy was carried out by variation of all geometrical parameters subject only to certain symmetry restrictions, and the final STO-3G geometry was then used for single calculations at the 4-31G level. In this paper we report the extension of this work to the six stable C_3 molecules, propyne, allene, cyclopropene, propene, cyclopropane, and propane. In addition, we present the results of calculations with the recently developed and larger 6-31G basis set.[4]

This research has three main aims. In the first place, it makes possible a more extensive comparison of theoretical (STO-3G) and experimental equilibrium geometries to test the ability of the theory to reproduce finer structural details. The second aim is to find how well the three basis sets reproduce energies of isomerization. These are energy differences between separate local minima on the same potential surface. Finally, the more accurate 6-31G wave functions can be used to make a study of electron distributions leading to the electric dipole moments for propane, propene, propyne, and cyclopropene. This extends our earlier study[5] using the STO-3G minimal basis. For the six molecules above, of course, all the experimental results are well established, but it is useful to make as wide a comparison as possible to give some indication of the value of predictions for systems where experimental facts are lacking.

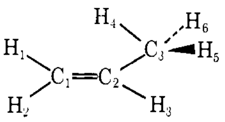
Methods and Results

The theoretical procedure is similar to that used in ref 1. Given an assumed symmetry (identical with the experimentally determined symmetry for all six molecules), all remaining geometrical parameters are varied until the theoretical STO-3G energy is minimized. The computational error in the equilibrium geometry is estimated to be about 0.001 Å for bond lengths and 0.1° for bond angles.[6] Finally, the STO-3G geometry is used for single calculations with the extended 4-31G and 6-31G basis sets. The complete set of energies obtained in this way is listed in Table I. Included in this table are the corresponding results for the hydrogen molecule and the C_1 and C_2 hydrocarbons. The STO-3G equilibrium geometries[7] for the C_3 compounds are given in Table II with the notation for propene and propane shown in I and II. The geometry for propyne has been reported previously[6] but is included here for completeness. The STO-3G geometries for H_2 and the smaller hydrocarbons are listed in ref 1. Orbital popu-

Table I. Theoretical Total Energies (Hartrees)

Molecule	STO-3G	4-31G[a]	6-31G[a]
Hydrogen	−1.11751[b]	−1.12658[b]	−1.12658
Methane	−39.72686[b]	−40.13976[b]	−40.18055
Acetylene	−75.85625[b]	−76.70999[b]	−76.79092
Ethylene	−77.07393[b]	−77.92188[b]	−78.00395
Ethane	−78.30618[b]	−79.11582[b]	−79.19748
Propyne	−114.44898	−115.69969	−115.82156
Allene	−114.42172	−115.69836	−115.82089
Cyclopropene	−114.40116	−115.64168	−115.76540
Propene	−115.66030	−116.90459	−117.02768
Cyclopropane	−115.66616	−116.88350	−117.00777
Propane	−116.88642	−118.09360	−118.21601

[a] Energy calculated using STO-3G optimized geometry. [b] From ref 1.



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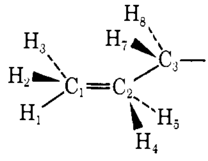

II

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(1) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(2) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(3) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(4) W. J. Hehre, R. Ditchfield, and J. A. Pople, *ibid.*, to be published.

(5) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970).

(6) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(7) All bond lengths in this paper are in ångströms, angles in degrees.

Table II. Equilibrium Geometries

Molecule[a]	Symmetry constraint	Parameter	STO-3G	Experimental
Propyne[b]	C_{3v}	$r(\mathrm{C{\equiv}C})$	1.170	1.206
		$r(\mathrm{C{-}C})$	1.484	1.459
		r(methyl CH)	1.088	1.105
		r(ethynyl CH)	1.064	1.056
		$\angle\mathrm{HCH}$	108.4	108.7
Allene[c]	D_{2d}	$r(\mathrm{C{=}C})$	1.288	1.308
		$r(\mathrm{C{-}H})$	1.083	1.087
		$\angle\mathrm{HCH}$	116.2	118.2
Cyclopropene[d]	C_{2v}	$r(\mathrm{C{=}C})$	1.277	1.300
		$r(\mathrm{C{-}C})$	1.493	1.515
		r(methylene CH)	1.087	1.087
		r(vinyl CH)	1.075	1.070
		$\angle\mathrm{HCH}$	112.5	114.7
		$\angle\mathrm{C{=}CH}$	150.3	149.9
Propene[e]	C_s	$r(\mathrm{C_1{=}C_2})$	1.308	1.336
		$r(\mathrm{C_2{-}C_3})$	1.520	1.501
		$r(\mathrm{C_1{-}H_1})$	1.081	1.091
		$r(\mathrm{C_1{-}H_2})$	1.081	1.081
		$r(\mathrm{C_2{-}H_3})$	1.085	1.090
		$r(\mathrm{C_3{-}H_4})$	1.085	1.085
		$r(\mathrm{C_3{-}H_5})$	1.088	1.098
		$\angle\mathrm{H_1C_1C_2}$	122.2	120.5
		$\angle\mathrm{H_2C_1C_2}$	121.9	121.5
		$\angle\mathrm{C_1C_2C_3}$	125.1	124.3
		$\angle\mathrm{H_3C_2C_1}$	119.8	119.0
		$\angle\mathrm{C_2C_3H_4}$	111.1	111.2
		$\angle\mathrm{H_4C_3H_5}$	108.5	109.0
		$\angle\mathrm{H_5C_3H_6}$	107.6	106.2
Cyclopropane[f]	D_{3h}	$r(\mathrm{C{-}C})$	1.502	1.510
		$r(\mathrm{C{-}H})$	1.081	1.089
		$\angle\mathrm{HCH}$	113.8	115.1
Propane[g]	C_{2v}	$r(\mathrm{C{-}C})$	1.541	1.526
		$r(\mathrm{C_1{-}H_1})$	1.086	1.091
		$r(\mathrm{C_1{-}H_2})$	1.086	1.091
		$r(\mathrm{C_2{-}H_4})$	1.089	1.096
		$\angle\mathrm{H_1C_1C_2}$	110.7	111.2
		$\angle\mathrm{H_2C_1C_2}$	110.7	111.2
		$\angle\mathrm{H_2C_1H_3}$	108.2	107.7
		$\angle\mathrm{C_1C_2C_3}$	112.4	112.4
		$\angle\mathrm{H_4C_2H_5}$	107.2	106.1

[a] References are to experimental geometries. [b] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). [c] A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965). [d] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). [e] D. R. Lide and D. Christensen, *ibid.*, **35**, 1374 (1961). [f] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). [g] D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

lations are calculated using Mulliken's method,[8] summing over inner and outer parts for the extended basis sets.

Molecular Geometries. The overall agreement between calculated and experimental geometries is good, the mean absolute deviations being 0.01 Å in bond lengths (calculated from the 23 unique bond lengths) and 0.9° in bond angles (calculated from the 17 unique bond angles). The average deviation for the nine unique carbon–carbon bonds is 0.02 Å. The mean errors are smaller than those previously obtained[6] in an application of the STO-3G calculations to a wider selection of molecules, suggesting that hydrocarbons are particularly well treated by this basis set. It is important to note that the theory is equally successful for cyclic and acyclic systems.

Bond Lengths. Calculated bond lengths for carbon–carbon multiple bonds are consistently too low (by *ca.* 0.03 Å). However, the observed trends are given well. For example, the reduction in calculated C=C bond lengths in going from propene to allene to cyclopropene (1.308, 1.288, 1.277) agrees with experiment (1.336, 1.308, 1.300). The calculated C=C bond lengths in propene and ethylene[1] are very similar, as observed.

Although carbon–carbon single bond lengths in propane, propene, and propyne are all slightly overestimated, the reduction adjacent to multiple bonds observed in the above series (1.526, 1.501, 1.459) is reproduced by the theory (1.541, 1.520, 1.484).

Calculated carbon–hydrogen bond lengths are in close agreement with experiment, but minor variations in the experimental values for different C–H bonds are not always paralleled. Bigger effects such as the short ethynyl C–H in propyne and short vinyl C–H in cyclopropene are reproduced.

Bond Angles. The calculated HCH angles all agree closely with experimental values. Thus, the methyl HCH angles in propane, propene, and propyne are all less than tetrahedral, with propane having the smallest value. There is considerable widening of the HCH angle (above the tetrahedral value) in the methylene groups of cyclopropene and cyclopropane. The reduction of the HCH angles in allene and the vinyl group of propene from 120° is also reproduced.

An opening of the CCC angles (from trigonal and tetrahedral values, respectively) is observed in propene

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(8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(124.3°) and propane (112.4°), presumably because of steric interactions. This effect is given well by the theory (CCC angles 125.1° and 112.4°, respectively).

In concluding this section, we mention some previous work[9–13] that has been done on the variation of geometrical parameters for cyclopropane and cyclopropene. An early study by Preuss and Diercksen[9] using a rather smaller basis of gaussian functions gave a value of 1.54 Å for the C–C bond length in cyclopropane assuming experimental values for the other parameters. Frost and Rouse[10] made a complete geometry determination (assuming D_{3h} symmetry) with their floating spherical gaussian orbitals, obtaining a structure close to ours. A rather more extensive set of computations on cyclopropane was carried out by Buenker and Peyerimhoff[11] using an extended basis set based on gaussian lobe functions. They varied one CCC angle (C_{2v} symmetry) making a number of assumptions about other parameters. The lowest energy obtained was −116.9164 hartrees, which is intermediate between the 4-31G and 6-31G results quoted in Table I. In these computations they found an apparent minimum corresponding to a CCC angle of 63.5°, deviating slightly from the generally assumed D_{3h} symmetry. To test this further, we repeated the cyclopropane geometry optimization with the STO-3G basis, but giving the molecule *complete* freedom within the C_{2v} symmetry. This procedure led back to the more symmetric D_{3h} structure. We conclude that the STO-3G basis gives no evidence for distortion to C_{2v} symmetry in cyclopropane. Peyerimhoff and Buenker have also made a study[13] of cyclopropene in which they vary the CCC angle at the methylene group. They find a value of 53.4°, which is quite close to our result (50.7°).

Isomerization Energies. The energy differences between isomeric forms of C_3H_4 and C_3H_6 are listed (relative to propyne and propene) in Table III and compared with the experimental results. It is clear that the STO-3G minimal basis gives poor results here, the propene–cyclopropene pair actually being incorrectly ordered. On the other hand, the 4-31G and 6-31G results, which are very close together, are qualitatively more satisfactory, although the cyclic molecules are predicted to be relatively high in energy. It should be emphasized, however, that the N-31G results are based on the STO-3G geometries and do not represent the full prediction of the extended basis sets.

Table III. Relative Energies (kcal mol^{-1}) of Isomeric C_3 Hydrocarbons

Formula[a]	Molecule	Calculated STO-3G	Calculated 4-31G	Calculated 6-31G	Experimental[b]
C_3H_4	Propyne	0	0	0	0
	Allene	17.1	0.8	0.4	2.1
	Cyclopropene	30.0	36.4	35.2	22.3
C_3H_6	Propene	0	0	0	0
	Cyclopropane	−3.7	13.2	12.5	7.4

[a] Stoichiometric formula. [b] Calculated from observed heats of formation adjusted to 0°K with stationary nuclei using observed fundamental vibrational frequencies. Relevant experimental data are summarized in W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4796 (1970).

A comparable study of the relative energies of C_3H_4 isomers was carried out by Peyerimhoff and Buenker[13] using two basis sets based on Whitten's lobe functions. The better basis used inner and outer parts for valence orbitals and is quite similar in total energies to our 6-31G set. They found relative energies quite close to ours, the principal difference being that allene was incorrectly calculated to be more stable than propyne.

The results above are consistent with previous conclusions about the C_2 hydrocarbons.[1] It has been noted that the isotropic minimal STO basis set is unsuccessful in obtaining energies of reactions involving changes of bond type. In particular, the wrong sign is obtained for the energy of the reaction

$$C_2H_6 + C_2H_2 \longrightarrow 2C_2H_4 \qquad (1)$$

where ΔE(exptl) = −9.1 kcal mol^{-1} and ΔE(STO-3G) = +9.1 kcal mol^{-1}. In a similar way, we now find that the STO-3G energy of allene compared with propyne is much too high. On the other hand, the extended 4-31G basis has been shown[1,3] to be much more successful in predicting the energy change of reaction 1 (ΔE(4-31G) = −11.3 kcal mol^{-1}), and it is therefore not unexpected that it also gives the isomerization energy for the transformation of propyne to allene moderately well. The additional inner-shell functions in the 6-31G basis set, although leading to a considerable lowering in total energies, do not seem to have a significant effect on the calculated relative energies.

In general, the STO-3G basis appears to favor structures with single bonds, presumably because single bonds are less anisotropic and therefore relatively better described by an isotropic minimal basis. The low STO-3G energy of cyclopropane relative to propene shows a similar bias, favoring CC single bonds (three single bonds *vs.* a single and a double bond). The same applies to cyclopropene (two single bonds and a double bond) relative to allene (two double bonds), where the energy difference is underestimated but not by enough to reverse the order of stability. An additional factor, which has been noted previously[14] and is relevant to the discussion of isomerization energies, is that the energies of cyclic relative to acyclic molecules with the *same* types of bonds are consistently overestimated by the STO-3G and N-31G basis sets.

Dipole Moments and Charge Distributions. The dipole moments of propane, propene, propyne, and cyclopropene are of interest because these molecules are the simplest stable polar hydrocarbons. Previous *ab initio* calculations with various basis sets and experimental or standard geometries have been reasonably successful in the prediction of moments for these molecules.[5,15–20] We present here 6-31G calculated

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(9) H. Preuss and G. Diercksen, *Int. J. Quantum Chem.*, 1, 361 (1967).

(10) A. A. Frost and R. A. Rouse, *J. Amer. Chem. Soc.*, 90, 1965 (1968).

(11) R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, 73, 1299 (1969).

(12) L. Salem, private communication.

(13) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, 14, 305 (1969).

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(15) M. L. Unland, J. R. Van Wazer, and J. H. Letcher, *ibid.*, 91, 1045 (1969).

(16) M. D. Newton and W. N. Lipscomb, *ibid.*, 89, 4261 (1967).

(17) D. T. Clark, *Theor. Chim. Acta*, 15, 225 (1969).

(18) E. Scrocco, J. Tomasi, R. Bonaccorsi, and C. Petrongolo, quoted in ref 17.

(19) E. Kochanski and J. M. Lehn, *Theor. Chim. Acta*, 14, 281 (1969).

(20) M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *J. Chem. Phys.*, 51, 45 (1969).

Table IV. Calculated (6-31G) and Experimental Dipole Moments (Debyes)

Molecule	Calculated	Experimental
Propane	0.06	0.083[a]
Propene	0.34	0.364[b]
Propyne	0.68	0.75[c]
Cyclopropene	0.54	0.45[d]

[a] D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960). [b] D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957). [c] J. S. Muenter and V. W. Laurie, *ibid.*, **45**, 855 (1966). [d] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *ibid.*, **30**, 512 (1959).

dipole moments for optimized geometries of the four molecules above. The magnitudes are given in Table IV and are in close agreement with experimental values.

In agreement with an earlier STO-3G study,[5] we find that in propane, the central methylene group is at the positive end of the small electric dipole. This polarity has been suggested from microwave determinations on deuterated species.[21]

For propene and propyne, the calculated moments are largely associated with a polarization of the π electrons in the multiple bond, this effect being larger than any transfer of electrons into the π system. The atomic π charges are

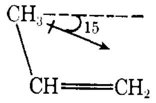
0.965 1.043

$CH_3—CH{=}CH_2$

1.972 2.048

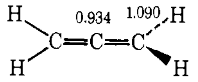
$CH_3—C{\equiv}CH$

These results confirm those of earlier calculations.[5,16,22] The calculated moment in propene is inclined at 15° to the C=C bond (the experimental inclination[23] is 22°).

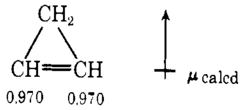


For propyne, we find the methyl group at the positive end of the dipole, which is again in accordance with the conclusion from studies of deuterated propynes.[21]

Polarization of the π electrons in allene takes place to a slightly greater extent than in propene or propyne. π-Electron populations in the plane of the paper are

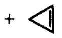


In cyclopropene, it is found that π electrons are *withdrawn* from the double bond into the CH_2 group. This leads to a theoretical dipole moment with its negative end on the methylene group and with the following π-charge densities.

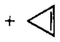


This dipole orientation was also obtained in previous *ab initio* studies.[19,20] It is the reverse of the usual polarity involving the interaction of saturated and unsaturated hydrocarbon fragments. Its origin can be understood qualitatively by noting that the empty antibonding π* orbital associated with the C=C group is of a_2 symmetry (point group C_{2v}) and is therefore not available to accept electrons from the π-like orbitals of the CH_2 group which all have b_1 symmetry. The only electron transfer that can occur (within the valence orbital framework), therefore, is from the occupied bonding π orbital of C=C (symmetry b_1) to the antibonding orbitals of the CH_2 group. This appears to be the main effect giving rise to the theoretical dipole.

The only experimental study of the dipole direction in cyclopropene is due to Benson and Flygare,[24] who find the opposite result



from the *g* values of cyclopropene and its 1,2-dideuterio derivative. This apparent conflict clearly merits further study. Further evidence supporting the



polarity is provided by the dipole directions of 1-methylcyclopropene and will be discussed in a future publication.[25]

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(22) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(23) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, 27, 868 (1957).

(24) R. C. Benson and W. H. Flygare, *ibid.*, **51**, 3087 (1969).

(25) W. J. Hehre and J. A. Pople, manuscript in preparation.