

**MTP International  
Review of Science**

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**Aliphatic Compounds**

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**Organic Chemistry  
Series One  
Volume 2**

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**Consultant Editor**  
**D H Hey FRS**  
**Volume Editor**  
**N B Chapman**

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**Volume 2**

# **Aliphatic Compounds**

Edited by **N. B. Chapman**  
University of Hull



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## **Aliphatic Compounds**

## MTP International Review of Science

### Publisher's Note

The MTP International Review of Science is an important new venture in scientific publishing, which we present in association with MTP Medical and Technical Publishing Co. Ltd. and University Park Press, Baltimore. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. We are starting with chemistry because the problems of literature survey are probably more acute in this subject than in any other. As a matter of policy, the authorship of the MTP Review of Chemistry is international and distinguished; the subject coverage is extensive, systematic and critical; and most important of all, new issues of the Review will be published every two years.

In the MTP Review of Chemistry (Series One), Inorganic, Physical and Organic Chemistry are comprehensively reviewed in 33 text volumes and 3 index volumes, details of which are shown opposite. In general, the reviews cover the period 1967 to 1971. In 1974, it is planned to issue the MTP Review of Chemistry (Series Two), consisting of a similar set of volumes covering the period 1971 to 1973. Series Three is planned for 1976, and so on.

The MTP Review of Chemistry has been conceived within a carefully organised editorial framework. The over-all plan was drawn up, and the volume editors were appointed, by three consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence, the 300 or so contributions to the MTP Review of Chemistry come from many countries of the world and provide an authoritative account of progress in chemistry.

To facilitate rapid production, individual volumes do not have an index. Instead, each chapter has been prefaced with a detailed list of contents, and an index to the 10 volumes of the MTP Review of Organic Chemistry (Series One) will appear, as a separate volume, after publication of the final volume. Similar arrangements will apply to the MTP Review of subsequent series.

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**INDEX VOLUME**

# **Organic Chemistry**

## **Series One**

Consultant Editor

**D. H. Hey, F.R.S.**

## Consultant Editor's Note

The subject of Organic Chemistry is in a rapidly changing state. At the one extreme it is becoming more and more closely involved with biology and living processes and at the other it is deriving a new impetus from the extending implications of modern theoretical developments. At the same time the study of the subject at the practical level is being subjected to the introduction of new techniques and advancements in instrumentation at an unprecedented level. One consequence of these changes is an enormous increase in the rate of accumulation of new knowledge. The need for authoritative documentation at regular intervals on a world-wide basis is therefore self-evident.

The ten volumes in Organic Chemistry in this First Series of biennial reviews in the MTP International Review of Science attempt to place on record the published achievements of the years 1970 and 1971 together with some earlier material found desirable to assist the initiation of the new venture. In order to do this on an international basis Volume Editors and Authors have been drawn from many parts of the world.

There are many alternative ways in which the subject of Organic Chemistry can be subdivided into areas for more or less self-contained reviews. No single system can avoid some overlapping and many such systems can leave gaps unfilled. In the present series the subject matter in eight volumes is defined mainly on a structural basis on conventional lines. In addition, one volume has been specially devoted to methods of structure determination, which include developments in new techniques and instrumental methods. A further separate volume has been devoted to Free Radical Reactions, which is justified by the rapidly expanding interest in this field. If there prove to be any major omissions it is hoped that these can be remedied in the Second Series.

It is my pleasure to thank the Volume Editors who have made the publication of these volumes possible.

London

D. H. Hey

## Preface

There are those who would readily sound the death-knell of Organic Chemistry. The fallaciousness of this attitude is vividly demonstrated by the contents of the present volume on Aliphatic Chemistry, which might *a priori* be expected to be the least lively part of a supposedly moribund subject.

Nowhere is this more obvious than in the first chapter on hydrocarbons: new methods jostle with deeper analyses of old problems, and in so doing proclaim the unitary character of modern chemistry. Wherever else one looks that mastery over subtle chemical transformation and potent determination of intricate molecular structure for which aliphatic chemistry is rightly renowned is richly exemplified. Nitrogen compounds have long occupied a major position in this field and continue to do so: the chapter on phosphorus chemistry reveals the competition for eminence from that element. Sulphur compounds and halogeno-compounds are also close contenders. Possibly some of the most novel and exciting chemistry is to be found in the short review on boron compounds, a topic now essential to a modern representative treatment of organic chemistry whether aliphatic or aromatic. In the field of oxygen-functional compounds, the paths may be well trodden, but new vistas appear and useful short-cuts are established. In relation to naturally occurring compounds carboxylic acids occupy pride of place: there is a continuing splendour about aliphatic organic chemistry in this area. Some subjects have been excluded because they are dealt with elsewhere in the series as a whole, e.g. amino acids and proteins, and compounds closely related to simple carbohydrates. One or two minor topics, e.g. carbonic acid derivatives are only treated incidentally, and systematic treatment of organometallic compounds is also yielded to other volumes in the series.

It is hoped that the present review will provide an up-to-date, critical and stimulating account of what is manifestly a vital feature of a still vigorously growing and fascinating subject.

# Contents



<b>Hydrocarbons</b>	1
D. E. Webster, <i>University of Hull</i>	
<b>Halogeno compounds</b>	65
G. M. Brooke, <i>Durham University</i>	
<b>Alcohols, ethers and related compounds</b>	91
S. G. Wilkinson, <i>University of Hull</i>	
<b>Nitrogen compounds</b>	131
P. Wilder, Jr., and J. M. Shepherd, <i>Duke University, Durham, North Carolina</i>	
<b>Phosphorus compounds</b>	217
Louis D. Quin, <i>Duke University, Durham, North Carolina</i>	
<b>Sulphur compounds</b>	259
D. R. Hogg, <i>University of Aberdeen</i>	
<b>Carbonyl compounds</b>	289
R. Brettle, <i>University of Sheffield</i>	
<b>Carboxylic acids</b>	317
N. Polgar, <i>University of Oxford</i>	
<b>Boron compounds</b>	357
K. J. Toyne, <i>University of Hull</i>	



# 1 Hydrocarbons

D. E. WEBSTER

University of Hull

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1.1	INTRODUCTION	2
1.2	THEORETICAL STUDIES	2
1.2.1	<i>Electronic structures</i>	2
1.2.2	<i>Woodward-Hoffman orbital symmetry rules</i>	8
1.3	ALKANES	10
1.3.1	<i>Preparation and isolation</i>	10
1.3.2	<i>Reactions</i>	10
1.3.2.1	<i>Radical processes</i>	10
1.3.2.2	<i>Electrophilic substitutions</i>	12
1.3.2.3	<i>Reactions in a plasma jet</i>	15
1.3.2.4	<i>Homogeneous catalysis</i>	15
1.3.2.5	<i>Enzyme catalysed oxidations</i>	17
1.4	ALKENES	17
1.4.1	<i>Preparation</i>	17
1.4.2	<i>Reactions</i>	19
1.4.2.1	<i>Isomerisation</i>	19
1.4.2.2	<i>Disproportionation</i>	20
1.4.2.3	<i>Reduction</i>	21
1.4.2.4	<i>Oligomerisation and polymerisation</i>	22
1.4.2.5	<i>Reactions with organic compounds</i>	23
1.4.2.6	<i>Carbonylation and hydroformylation</i>	29
1.4.2.7	<i>Hydrosilylation</i>	29
1.4.2.8	<i>Hydration</i>	30
1.4.2.9	<i>Oxidation</i>	32
1.4.2.10	<i>Reactions with sulphur compounds</i>	34
1.4.2.11	<i>Halogenation</i>	35
1.4.2.12	<i>Organometallic complexes</i>	38
1.4.2.13	<i>Miscellaneous</i>	39
1.5	ALKADIENES	39
1.5.1	<i>Alka-1,2-dienes</i>	39
1.5.1.1	<i>Preparation</i>	39
1.5.1.2	<i>Reactions</i>	40

1.5.2	<i>Alka-1,3-dienes</i>	43
1.5.2.1	<i>Preparation</i>	43
1.5.2.2	<i>Reactions</i>	44
1.5.3	<i>Alka-1,4-dienes</i>	50
1.5.3.1	<i>Preparation</i>	50
1.5.3.2	<i>Reactions</i>	51
1.5.4	<i>Alka-1,5-dienes</i>	51
1.5.4.1	<i>Preparation</i>	51
1.5.4.2	<i>Reaction</i>	52
1.5.5	<i>Alkatrienes</i>	52
1.5.5.1	<i>Reactions</i>	52
1.6	ALKYNES	52
1.6.1	<i>Preparation and isolation</i>	52
1.6.2	<i>Reactions</i>	52
1.6.2.1	<i>Hydroboration</i>	52
1.6.2.2	<i>Reactions with organic compounds</i>	53
1.6.2.3	<i>Oxidation and reactions with sulphur compounds</i>	54
1.6.2.4	<i>Halogenation</i>	55
1.6.2.5	<i>Organometallic complexes</i>	55
1.6.2.6	<i>Miscellaneous</i>	55

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## 1.1 INTRODUCTION

This chapter is a review of part of the recent literature concerning aliphatic hydrocarbons. A search of the 1970 and 1971 journals revealed c. 1600 papers and patents that would be appropriate for this section. The space available will not allow discussion of more than c. 25% of these, so drastic selection has been necessary.

The criteria used were as follows. Two major topics, namely heterogeneous catalysis involving aliphatic hydrocarbons (about 200 references) and relevant patents (about 500), have been entirely omitted; there is insufficient space to include all the work, and selection of parts of either would be most arbitrary.

The remaining 900 papers were reduced by omitting those devoted to the physical chemistry of aliphatic hydrocarbons. The remaining papers, those of clear interest to organic chemists, form the basis of this chapter.

Although some mechanistic aspects of aliphatic hydrocarbon chemistry are discussed, the emphasis of the chapter is on compounds rather than mechanism. Reactions of aliphatic hydrocarbons that are catalysed homogeneously in solution by transition-metal complexes are included. A more complete review of such reactions is in another part of this series<sup>1</sup>. There are no recent reviews that cover the same area as the subject matter of this chapter.

## 1.2 THEORETICAL STUDIES

### 1.2.1 Electronic structures

There have been rapid advances during the past few years in the methods available for treating the electronic structures of organic molecules<sup>2</sup>, and

self-consistent field (SCF) methods are now widely used. A survey<sup>3</sup> of molecular orbital methods that treat all the valence electrons, and can be used for three-dimensional molecules or complexes in general, that discusses both semi-empirical and *ab initio* methods, and gives the results for methane, ethane, ethylene, acetylene, and propyne has appeared. Two more detailed papers having the same senior author<sup>4,5</sup> use a set of Gaussian fitted Slater-type orbitals (STO-3G)<sup>6</sup> and two extended sets of orbitals (4-31G)<sup>7</sup> and (6-31G)<sup>5</sup>, to obtain the geometries and energies of the neutral C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> hydrocarbons, and of the related C<sub>1</sub> and C<sub>2</sub> positive ions. The agreement between calculated and experimentally determined bond lengths and bond angles is good, as can be seen in Table 1.1, which lists the values for the neutral C<sub>1</sub> and C<sub>2</sub> molecules studied. Equally good agreement is obtained for the bond angles of propyne, allene, cyclopropene, cyclopropane and propane<sup>5</sup>. Structures of protonated methane and ethane<sup>4,8</sup> derived by the same methods are of interest, as these intermediates are found during the electrophilic substitution of alkanes (Section 1.3.2.2). CH<sub>5</sub><sup>+</sup> has been analysed by using three models. That of lowest energy [Figure 1.1(a) with  $r_1 = 0.1098$ ,  $r_2 = 0.1106$ ,  $r_3 = 0.1370$  and  $r_4 = 0.1367$  nm,  $\alpha = 140$ ,  $\beta = 83.8$ ,  $\theta = 37.2$  and  $\zeta = 117.7$  degrees] is of C<sub>s</sub> symmetry and is equivalent to a loose complex

**Table 1.1**

(From Pople, Lathan and Hehre<sup>4</sup>, by courtesy of the American Chemical Society)

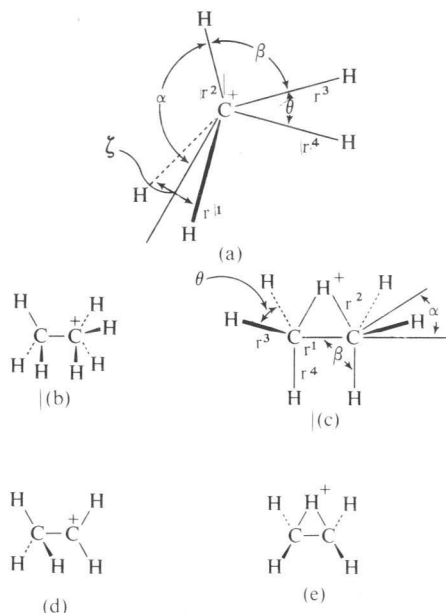
Molecule	Parameter	Calc. value (STO-3G)	Calc. value (4-31G)	Exptl. value
CH <sub>4</sub>	$r_{CH}$	0.1083 nm	0.1081 nm	0.1085 nm
C <sub>2</sub> H <sub>2</sub>	$r_{CC}$	0.1168 nm	0.1190 nm	0.1203 nm
	$r_{CH}$	0.1065 nm	0.1051 nm	0.1061 nm
C <sub>2</sub> H <sub>4</sub>	$r_{CC}$	0.1306 nm	0.1316 nm	0.1330 nm
	$r_{CH}$	0.1082 nm	0.1073 nm	0.1076 nm
	$\angle$ HCH	115.6 degrees	116.0 degrees	116.6 degrees
C <sub>2</sub> H <sub>6</sub>	$r_{CC}$	0.1538 nm	0.1529 nm	0.1548 nm
	$r_{CH}$	0.1086 nm	0.1083 nm	0.1086 nm
	$\angle$ HCH	108.2 degrees	107.7 degrees	107.8 degrees

of CH<sub>3</sub><sup>+</sup> and H<sub>2</sub>. The analogous model for C<sub>2</sub>H<sub>7</sub><sup>+</sup> [Figure 1.1(b)], which is equivalent to a loose complex between C<sub>2</sub>H<sub>5</sub><sup>+</sup> and H<sub>2</sub>, is not that of lowest energy; the complex with a bridging proton [Figure 1.1(c) with  $r_1 = 0.2362$ ,  $r_2 = 0.1251$ ,  $r_3 = 0.1097$  and  $r_4 = 0.1094$  nm,  $\alpha = 52.7$ ,  $\beta = 89.5$  and  $\theta = 115.6$  degrees] is 11 kcal mol<sup>-1</sup> lower in energy. In this complex the bridging proton is at the vertex of a very flat isosceles triangle with a long C—C distance, indicating that protonation of alkanes can easily lead to C—C cleavage. That C<sub>2</sub>H<sub>5</sub><sup>+</sup> has a smaller affinity than CH<sub>3</sub><sup>+</sup> for H<sub>2</sub> is presumably because the additional methyl group is donating electrons to the carbenium\* ionic centre.

The energy of the ethyl cation [Figure 1.1(d)] is found to be 11.42 and 6.76 kcal mol<sup>-1</sup> lower than that of the bridged structure [Figure 1.1(e)] by using the STO-3G and the 4-31G method respectively. Corresponding values obtained<sup>9</sup> by using two non-empirical LCAO—MO—SCF techniques are 5.16 and 3.39 kcal mol<sup>-1</sup>.

\*Cf. p.12.

The main characteristics of the electronic spectra of small saturated hydrocarbons have been studied by using the CNDO (complete neglect of differential overlap), the INDO (intermediate neglect of differential overlap) and the RCNDO [CNDO including higher (Rydberg) atomic orbitals] methods<sup>10</sup>. All three correctly interpret the bathochromic shift in the electronic



**Figure 1.1** Models for protonated alkanes and alkenes  
(From Pople, Lathan and Hehre<sup>4</sup>, by courtesy of the American Chemical Society)

spectra of methane, ethane, propane, butane, n-pentane, isobutane, isopentane and neopentane. The RCNDO calculations show that electrons giving the first singlet-singlet and singlet-triplet transitions in the electronic spectra are almost entirely valence shell electrons, that the singlet-singlet transition involves principally C—H electrons for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ , and principally C—C electrons for  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$ , and that the singlet-triplet transition involves C—H electrons for all linear alkanes and C—C and C—H electrons for the branched alkanes.

Despite the view<sup>2</sup> that 'there no longer seems any point in carrying out calculations by less refined procedures (than SCF-LCAO-MO methods)' an interesting application of the Hückel method to  $\pi$ -resonance energies has classified single and double bonds into eight types according to the number of attached hydrogen atoms<sup>11</sup>. All acyclic and cyclic polyenes can be constructed by combinations of these eight types of bonds. The  $\pi$ -energies and resonance energies of cyclic polyenes, which can be readily calculated, correlate well with chemical behaviour, and may be compared with the values obtained by the more complex CNDO method<sup>2</sup>.

The continuing controversy as to whether or not C—C bond lengths depend on  $\pi$ -bond order or the degree of hybridisation (s-character) of the orbitals forming the  $\sigma$ -bond in unsaturated and conjugated hydrocarbons, has now been extended to saturated hydrocarbons<sup>12-14</sup>. There is a strong correlation between experimental bond lengths and the amount of s-character

calculated for hybrid orbitals forming single bonds<sup>12</sup>, and, in contrast, it has been shown that if  $\pi$ -overlap is neglected, the calculated bond lengths of ethylene and acetylene are essentially identical with those calculated for ethane, implying that  $\pi$ -bonding is entirely responsible for the shortening of the C—C bond in ethylene and acetylene<sup>13</sup>. Calculations<sup>14</sup> using the INDO method with ethane as the model indicate that the predominant effect is due to  $\pi$ -bonding, and a pseudo- $\pi$  description<sup>15</sup> with the H orbitals combined as a group ( $\sigma$ ,  $\pi_{\text{symmetric}}$ , and  $\pi_{\text{antisymmetric}}$ ) directly relates the s-character with the pseudo- $\pi$  overlap of the hydrogen  $\pi$ -orbitals with the  $p_y$  and  $p_z$  orbitals of the carbon atoms.

The pseudo- $\pi$  model has also been used in an 'explanation' of the long-standing problem of the origin of the barrier to internal rotation in ethane and other alkanes<sup>16</sup>. The behaviour of two occupied pairs of orbitals during the rotation from the staggered to the eclipsed form is suggested as the origin of the energy barrier. However, the problem is more complex. Two sets of SCF calculations<sup>17–19</sup> show how elusive is the source of this energy barrier. Comparison of the components making up the barrier energy from these two treatments (Table 1.2) shows that although the calculated barriers agree

**Table 1.2**

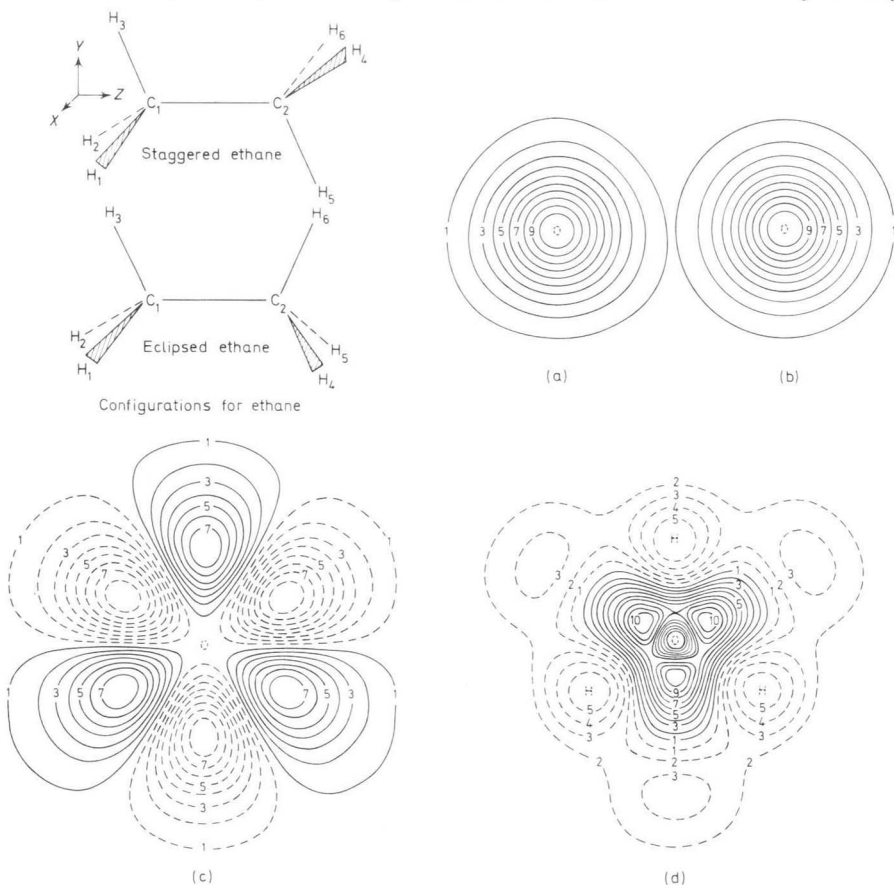
(From Epstein and Lipscomb<sup>19</sup>, by courtesy of the American Chemical Society)

	<i>Energy components (in atomic units) for ethane</i>	
	Ref. 17	Ref. 18
Kinetic	0.020 14	0.009 94
Nuclear repulsion	0.007 49	−0.118 48
Nuclear attraction	−0.048 98	0.201 13
Electron repulsion	0.026 57	−0.087 36
Barrier	*0.005 22	*0.005 23

\*Equal to 3.3 kcal mol<sup>−1</sup>.

to within 10<sup>−5</sup> of an atomic unit, three of the four contributing terms have different signs in the two methods. The total energies of the functions studied are large and energy decompositions for such functions are generally erratic. It is suggested that there are essentially two effects to be considered, namely the rotation of the methyl groups and the adjustment of the molecular geometry to the new configuration after rotation. For ethane the second point negates the first, but for cases where no change in the molecular geometry occurs (other than the rotation being studied) the explanation based on the pseudo- $\pi$  model<sup>16</sup> may be useful. Other recent *ab initio* LCAO–MO–SCF calculations<sup>20–24</sup> of the rotational energy barrier in ethane give respectively values of 2.58, 3.07, 3.17, 3.331 and 2.521 kcal mol<sup>−1</sup>. (The experimental value<sup>25</sup> is 2.928 ± 0.025 kcal mol<sup>−1</sup>). The origin of the barrier has been further discussed in terms of attractive (nuclear–electron), repulsive (nuclear–nuclear, electron–electron) and kinetic terms<sup>20, 24, 26</sup>. For ethane the barrier is due to the repulsive terms, and arises from ordinary chemical bonding by the action of the Pauli principle, although there are very substantial inherent difficulties in splitting up a molecular wave function clearly to bring out the

workings of the Pauli principle. Some insight is obtained by carrying out a charge density analysis of the barrier<sup>24</sup>. This clearly requires some care as the energy difference between the eclipsed and staggered forms of ethane is only 1/20 000 of the total molecular energy. The total molecular electron distributions for eclipsed and staggered ethane in the  $xy$  plane perpendicular to the centre of the C—C bond are shown in Figure 1.2(a) and (b). The three-fold symmetry of the eclipsed form is clear, but the six-fold symmetry



**Figure 1.2** (a) and (b) Total charge density for eclipsed and staggered ethane respectively, perpendicular to the mid-point of the C—C bond. (c) Difference plot of the eclipsed ethane electron density minus the staggered ethane electron density at the same location as in (a) and (b). (d) As for (c) on the C—C bond 0.0263 nm from C-1. For (a) and (b) contour 1 is at 0.018 au and the contour interval is 0.018 au. For (c) and (d) contour 1 is at  $\pm 0.000\ 02$  au and the contour interval is  $\pm 0.000\ 02$  au

(From Jorgensen and Allen<sup>24</sup>, by courtesy of the American Chemical Society)

of the staggered form is obscure, and it is not clear from a comparison of these total molecular charge densities that there is a greater repulsion between the methyl groups in the eclipsed than in the staggered form. The difference in the electron densities (eclipsed minus staggered) [Figure 1.2(c)] shows that there is less electron density, hence greater repulsion, between the opposing

C—H bonds in the eclipsed than the staggered conformer since the negative contours (dotted lines) encompass more area than the equivalent positive contours (solid lines). An equivalent difference plot in an  $xy$  plane between the carbon atoms, but close to one of them [Figure 1.2(d)] clearly shows that there is an electron density decrease in the eclipsed relative to the staggered conformer in front of the C—H bonds, i.e. that an increase in the repulsion between eclipsing C—H bonds is the dominant factor in determining the nature of the ethane barrier. Barriers to rotation of methyl groups and C—C bonds in other molecules have also been calculated (Table 1.3)<sup>23, 27–29</sup>.

**Table 1.3**

(From Random and Pople<sup>23</sup>, by courtesy of the American Chemical Society, except for \* Ref. 27, † Ref. 28 and ‡ Ref. 29)

Hydrocarbon	Barrier (calc.) /kcal mol <sup>-1</sup>	Barrier (exptl.) /kcal mol <sup>-1</sup>
But-1-yne	3.46	—
But-2-yne	0.006	—
Propene	1.54	1.95–2.04
Propene*	1.48	1.95–2.04
Propene*	1.25	1.95–2.04
Buta-1,2-diene	1.40	1.59
Propane	3.45	3.40
2-Methylpropene	1.705	2.12–2.35
<i>cis</i> -But-2-ene	0.42	0.73
<i>trans</i> -But-2-ene	1.54	1.95
2-Methylpropane	3.88	3.90
Ethylene	138.6	65
Allene	91.9	—
Allene†	72.7	—
Butatriene	73.9	—
Vinylacetylene	137.7	—
Buta-1,3-diene	6.73	5.0
Buta-1,3-diene‡	5.15	5.0
<i>n</i> -Butane	3.40	—
But-1-ene ( <i>skew</i> )	3.46	3.16
But-2-ene ( <i>cis</i> )	4.96	3.99

A comparison of the electronic structure of ethylene and diborane by has recently appeared<sup>30</sup>.

A comparison of the electronic structure of ethylene and diborane by molecular S.C.F. calculations and high-resolution photoelectron spectroscopy<sup>31</sup> substantiates Pitzer's<sup>32</sup> view that diborane is very similar to ethylene with the double bond protonated, there being some changes in the ordering of the molecular orbitals, in particular the  $\pi$ -MO in B<sub>2</sub>H<sub>6</sub> is the fourth to be filled, whereas in ethylene it is of highest energy. There have been further studies of the photoelectron spectra of alkanes<sup>33–36</sup> and the spectra have been analysed by means of molecular orbital theory<sup>35</sup>.

A detailed description of the electronic structure of acetylene, obtained by using an extended set of S.C.F. wave functions<sup>37</sup>, shows that the  $\sigma$ -electronic charge in the C—C region is *c.* 2 as expected, but that the  $\pi$ -electronic charge is 1.2 electrons per  $\pi$ -bond, i.e. about 40 % of the  $\pi$ -charge of the C—C bond