

$\text{-C}\equiv\text{C-}$

The chemistry of the carbon-carbon triple bond

Part 1

Edited by

SAUL PATAI

The Hebrew University, Jerusalem

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Contributing authors

J. Bastide	Centre Universitaire, Perpignan, France
D. A. Ben-Efraim	The Weizmann Institute of Science, Rehovot, Israel
K. A. Connors	School of Pharmacy, University of Wisconsin, Madison, Wisconsin, USA
J. D. Coyle	The Polytechnic, Wolverhampton, England
J. I. Dickstein	College of Du Page, Glen Ellyn, Illinois, USA
A. Gavezzotti	Istituto di Chimica Fisica e Centro CNR, Università di Milano, Milan, Italy
J. L. Hencher	University of Windsor, Windsor, Ontario, Canada
O. Henri-Rousseau	Centre Universitaire, Perpignan, France
A. C. Hopkinson	York University, Downsview, Ontario, Canada
A. M. Hudrlik	Rutgers University, New Brunswick, New Jersey, USA
P. F. Hudrlik	Rutgers University, New Brunswick, New Jersey, USA
W. D. Huntsman	Ohio University, Athens, Ohio, USA
Sir Ewart R. H. Jones	The Dyson Perrins Laboratory, Oxford University, Oxford, England
T. Kaneda	ISIR, Osaka University, Suita, Osaka, Japan
J. Klein	The Hebrew University, Jerusalem, Israel
J. C. Lavalley	U.E.R. de Sciences, Université de Caen, 14032 Caen Cedex, France
C. Lifshitz	The Hebrew University, Jerusalem, Israel
R. Lines	Chemical Centre, University of Lund, Lund, Sweden
A. Mandelbaum	Technion-Israel Institute of Technology, Haifa, Israel
S. I. Miller	Illinois Institute of Technology, Chicago, Illinois, USA
S. Misumi	ISIR, Osaka University, Suita, Osaka, Japan
M. Nakagawa	Osaka University, Toyonaka, Osaka 560, Japan
J. Saussey	U.E.R. de Sciences, Université de Caen, 14032 Caen Cedex, France
G. H. Schmid	University of Toronto, Toronto, Ontario, Canada
R. Shaw	Sunnyvale, California 94087, USA

M. Simonetta**Istituto di Chimica Fisica e Centro CNR, Università di Milano,
Milan, Italy****V. Thaller****The Dyson Perrins Laboratory, Oxford University, Oxford,
England****F. Théron****Université de Clermont-Ferrand, France****J. H. P. Utleý****Queen Mary College, London, England****M. Verný****Université de Clermont-Ferrand, France****R. Vessière****Université de Clermont-Ferrand, France**

Foreword

The present volume deals with the chemistry of the carbon-carbon triple bond. This is presented and organized again on the same general lines as described in the 'Preface to the series' printed on the following pages.

Some chapters originally planned for this volume did not materialize. These include a chapter on 'Free radical attacks involving carbon-carbon triple bonds', and a chapter on 'Arynes and hetarynes'. Tragically, the chapter on 'Directing and activating effects' is missing from this book owing to the untimely death of Professor Pentti Salomaa, a good friend, an excellent chemist and a devoted teacher, missed by all who knew him. It is hoped to include chapters on these subjects in 'Supplement C: The Chemistry of Triple-bonded Functional Groups', which is planned to be published in several years' time.

Jerusalem, October 1977

SAUL PATAI

The Chemistry of Functional Groups

Preface to the series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group tested and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

- (a) An introductory chapter dealing with the general and theoretical aspects of the group.
- (b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.
- (c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra; a chapter dealing with activating and

directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenenes' is included in the volume *The Chemistry of Alkenes*). In other cases certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the titles listed below:

- The Chemistry of Alkenes (two volumes)*
- The Chemistry of the Carbonyl Group (two volumes)*
- The Chemistry of the Ether Linkage*
- The Chemistry of the Amino Group*
- The Chemistry of the Nitro and Nitroso Group (two parts)*
- The Chemistry of Carboxylic Acids and Esters*
- The Chemistry of the Carbon-Nitrogen Double Bond*
- The Chemistry of the Cyano Group*
- The Chemistry of Amides*
- The Chemistry of the Hydroxyl Group (two parts)*
- The Chemistry of the Azido Group*
- The Chemistry of Acyl Halides*
- The Chemistry of the Carbon-Halogen Bond (two parts)*
- The Chemistry of Quinonoid Compounds (two parts)*
- The Chemistry of the Thiol Group (two parts)*
- The Chemistry of Amidines and Imidates*
- The Chemistry of the Hydrazo, Azo and Azoxy Groups*
- The Chemistry of Cyanates and their Thio Derivatives*
- The Chemistry of Diazonium and Diazo Groups*
- The Chemistry of the Carbon-Carbon Triple Bond (two parts)*
- Supplement A: The Chemistry of Double-bonded Functional Groups (two parts)*

Titles in press:

*The Chemistry of Ketenes, Allenes and Related Compounds**Supplement B: The Chemistry of Acid Derivatives*

Future volumes planned include:

*The Chemistry of Cumulenes and Heterocumulenes**The Chemistry of Organometallic Compounds**The Chemistry of Sulphur-containing Compounds**Supplement C: The Chemistry of Triple-bonded Functional Groups**Supplement D: The Chemistry of Halides and Pseudo-halides**Supplement E: The Chemistry of $-NH_2$, $-OH$, and $-SH$ Groups and their Derivatives*

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these is Dr Arnold Weissberger, whose reassurance and trust encouraged me to tackle this task, and who continues to help and advise me. The efficient and patient cooperation of several staff-members of the Publisher also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Israel and overseas helped me in the solution of various major and minor matters, and my thanks are due to all of them, especially to Professor Z. Rappoport. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

The Hebrew University
Jerusalem, ISRAEL

SAUL PATAI

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CHAPTER 1

General and theoretical aspects of the acetylenic compounds

M. SIMONETTA and A. GAVEZZOTTI

*Istituto di Chimica Fisica e Centro CNR,
Università di Milano, Milan, Italy*

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I. INTRODUCTION

The presence of a triple bond in a molecule gives it many peculiar chemical and physicochemical properties. This chapter is devoted to a description of the general and theoretical aspects of the acetylenic linkage, with the aim of providing a basic background to the understanding of its properties and reactivity.

Our survey includes essentially results that have become available very recently. In some cases, this choice was a must, since some investigation techniques, such as for example photoelectron spectroscopy or the X-ray crystal structure analysis of acetylene-metal complexes, have developed in a substantial way only in the past decade. Also theoretical studies have in very recent times received a strong impulse. For the more traditional techniques of approach to the study of molecular structure and reactivity, the subject of acetylene chemistry has been covered prior to 1970 in a number of reviews, in which exhaustive surveys of early data can be found. In any case, data of special importance, although not new, have been included when essential to our discussion.

The valence molecular orbitals of acetylenes are outlined in Section II, since they are referred to in many cases when they are needed to explain molecular properties. To obtain them, use is made of the Extended Hückel Theory, which is known to be a straightforward way of calculating qualitatively good valence molecular orbitals. The results of more sophisticated quantum-mechanical calculations are reviewed in a separate section. Also in Section II, structural data are discussed in connection with the accuracy of the various diffraction techniques.

Section III on energetics contains an account of the molecular mechanics method, which has been shown to provide reliable thermodynamic information on organic compounds. The section on ionization potentials has been linked to the recent outburst of photoelectron spectroscopy data. In Section IV accounts of infrared and n.m.r. data have been compiled to give tabulations of vibrational frequencies, force constants, chemical shifts and coupling constants. A special section has been devoted to spectroscopic and X-ray investigations on acetylene in the solid state, including n.m.r. results on molecular motions in the crystal.

Section V on the interaction of acetylenes with transition metal atoms is opened by a survey of crystal structure data on the complexes, since these are thought to give a basic idea of the geometry of the interactions. A discussion of the various arguments used in describing the bonding follows. The importance of this subject can hardly be overemphasized, since it provides a key to the understanding of the metal-adsorbate interactions in olefin and acetylene adsorption on catalysts. The experimental and computational results obtained in this field, one of the most prominent in chemical research, have been reviewed for the part concerning more specifically acetylene.

II. GENERAL STRUCTURAL FEATURES

A. The Molecular Orbitals of the Acetylenes

I. An elementary picture of acetylene

The essential structure of a carbon-carbon triple bond can be explained by putting together two sp hybridized carbon atoms, (see Figure 1a). A σ bond is then formed;

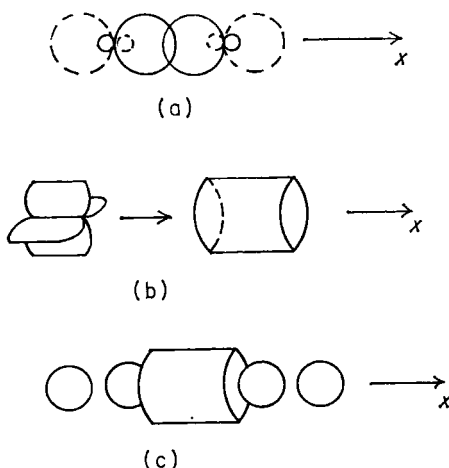


FIGURE 1. A simple picture of the electronic structure of acetylene.

two sp hybrids are unused, one at each side, while the unmixed p_y and p_z orbitals of each atom are paired to form two π bonds. These two perpendicular π bonds, in turn, overlap to give a cylindrically symmetric cloud, as shown in Figure 1b. σ Bonding with hydrogen in acetylene, or with substituents in acetylene derivatives, is provided by the two lobes of the sp hybrids that emerge on each side, as shown in Figure 1c. Even from this oversimplified picture, the delocalization of the π electrons, and the linearity of the acetylenic grouping, can easily be explained.

2. The molecular orbitals of acetylene

The $2s$ and the three $2p$ orbitals of the carbon atom, and the $1s$ orbital of hydrogen, can be used as a starting point in the construction of semilocalized molecular orbitals for a CH group. Two sp hybrids centred on carbon can be obtained, and these are shown in Figure 2(a). One of them mixes with the hydrogen $1s$ orbital in a bonding and antibonding manner, while the other remains unchanged, as shown in Figure 2(b). The two p orbitals that mix with neither the $2s$ orbital of carbon nor the

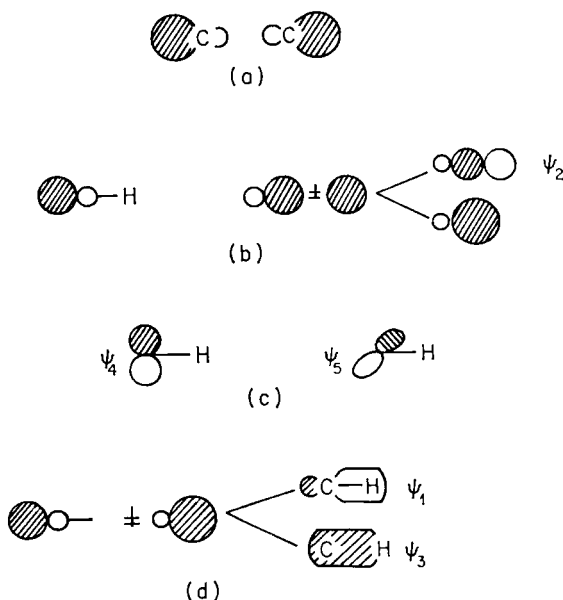


FIGURE 2. Successive orbital delocalizations to form the semilocalized molecular orbitals of the CH group. See text for further explanations.

$1s$ orbital of hydrogen will be called p_y and p_z , and are shown in Figure 2(c). A further delocalization, that will prove useful in the construction of the molecular orbitals of acetylene, is shown in Figure 2(d).

By mixing the molecular orbitals of two CH fragments, ψ_1 – ψ_5 , the molecular orbitals of acetylene can be drawn. A and B label the orbitals of the two CH groups that join to give the acetylene molecule:



The complete interaction diagram is given in Figure 3. The energies shown in this figure result from Extended Hückel calculations, as explained below.

An excellent three-dimensional pictorial view of the molecular orbitals of acetylene is available¹.

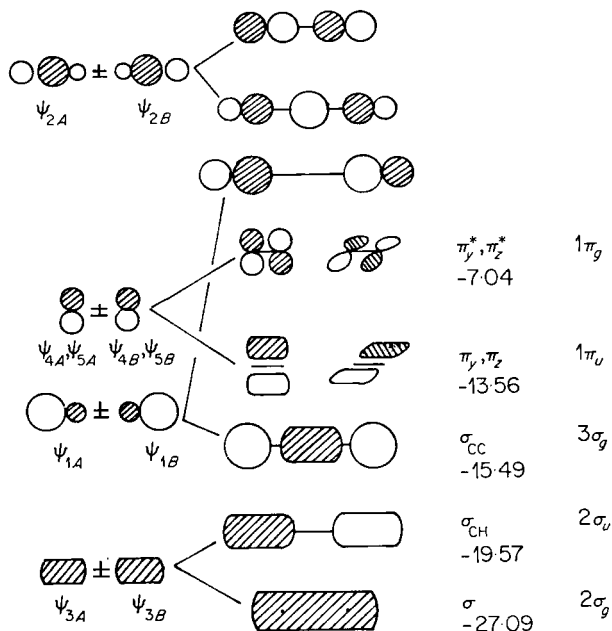


FIGURE 3. The molecular orbitals of acetylene. Energy values (eV) as resulting from EHT calculations.

3. Substituent effects: Extended Hückel calculations

The Extended Hückel Theory² (EHT) gives a qualitatively correct approach to the shapes and energies of the molecular orbitals of organic compounds. The effect of a substituent carrying a p orbital on the π system of acetylene is schematized in Figure 4(a); the amount of stabilization of the in-phase combination, and of destabilization of the out-of-phase one, depends on the amount of overlap between the two systems (which in turn depends on geometry) and on the initial separation of the interacting levels. EHT can provide an approach to the calculation of these effects; some examples are given below. The parameters used in the calculations are standard ones³⁻⁴, and the geometries are obtained from the structural data reported in the next section, except for the triple bond length, which is kept constant at 1.20 Å and the acetylenic C—H bond length which is kept constant at 1.05 Å.

a. Halogeno derivatives. Table 1 gives some results for the level shifts due to interaction with the substituent, as obtained by EHT. In the case of fluorine, there is a large separation between the π orbitals of acetylene and the p orbital of the heteroatom. In the case of chlorine, it is the larger C—X bond distance that prevents

a large stabilization. However, coupling with the low-lying p orbital of fluorine brings the π levels of fluoroacetylene below the highest σ -type orbital, which is the HOMO (Highest Occupied Molecular Orbital) for this compound.

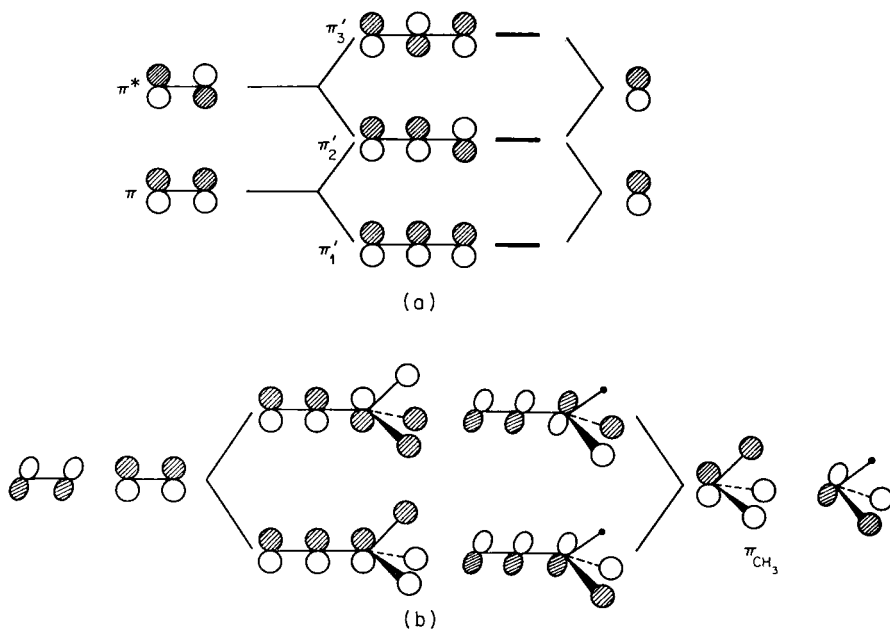


FIGURE 4. (a) Interaction of the π system of acetylene (left) with a p orbital. (b) The π orbitals of CH_3 (right) interacting with the π system of acetylene.

TABLE 1. Molecular orbital energy levels for compounds $\text{HC}\equiv\text{CX}$ as obtained from EHT (eV). π'_1 , π'_2 , π'_3 , as in Figure 4

X	π	π^*	$p(\text{X})$	π'_1	π'_2	π'_3
H	-13.56	-7.04	—	—	—	—
F	—	—	-18.10	-18.38	-13.14	-6.38
Cl	—	—	-13.99	-14.42	-13.13	-6.77

b. Methylacetylene. The ' π ' orbitals of the methyl group, which can be written as in Figure 4(b)¹, interact with the π system of acetylene in the usual way (Figure 4b). This can be described as the MO picture of hyperconjugation.

c. Nitrogen-containing derivatives. Inspection of the π -type MOs of aminoacetylene is interesting (Figure 5a). The bonding interaction of one p orbital of nitrogen with the two hydrogens of the amino group prevents further coupling with the π system of acetylene, while the other π -type orbital of the amino group (a pure p orbital) can couple with one π MO of acetylene.