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**chemistry of acetylenes**

edited  
by  
H.G.  
VIEHE

# CHEMISTRY OF ACETYLENES

Edited by HEINZ GÜNTER VIEHE

UNION CARBIDE EUROPEAN

RESEARCH ASSOCIATES, S.A.

BRUSSELS, BELGIUM

*and*

UNIVERSITY OF ERLANGEN-NÜRNBERG, GERMANY

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## FOREWORD

About fifteen years ago I wrote a monograph which managed to comprise in the compass of a few hundred pages a reasonably comprehensive practical guide to the synthetic capabilities of acetylenic compounds as known at that time. At various intervals since then I have been prodded to bring it up to date but I have consistently demurred. Laziness and the miniscule monetary return for authorship have certainly played a part in this decision, but the main energy barrier has been the sheer magnitude of the task. Work on the reactions and utility of acetylenic compounds has mushroomed at such speed that a single-handed coverage of the present-day situation would require a superhuman dedication for any degree of adequacy. It is thus fortunate that the vigorous persuasion of Professor Viehe has assembled a gamut of experienced practitioners in various aspects of the acetylenic art who have shared the burden of this massive undertaking to produce the present definitive survey. The resulting coverage provides an authoritative appraisal of virtually every aspect of the rich tapestry of acetylene chemistry.

An expert compilation such as this not only underlines the versatile and frequently bizarre nature of acetylenic reactions but also reveals that their scope is so wide that they cannot fail to suggest potential uses to the reader in almost any organic field. The conjoint effort has been impressively thorough in its detailed comprehensiveness, and all organic chemists have reason to be indebted to the group of distinguished authors who have shouldered the burden of this enterprise. It will undoubtedly be the sourcebook and vade mecum for users of triple bonds for many years to come. I hope also that the editor will ignore my bad example and will arrange for modernizing supplements to appear at intervals to keep this most valuable reference work abreast of this still-developing region of organic chemistry.

R. A. RAPHAEL, F.R.S.  
*Regius Professor of Chemistry*  
*University of Glasgow*

## PREFACE

Research workers and students on all levels in chemistry have long wanted an adequate coverage of modern acetylene chemistry. More than ten years after the appearance of the excellent book "The Chemistry of Acetylenic Compounds" by R. Raphael, I was invited by Marcel Dekker to prepare the best possible description of this field of chemistry. Discussions with Professor Raphael, who stimulated and encouraged this endeavor, and friends and colleagues—particularly F. Arens, F. Bohlmann, P. Cadiot, and J. Fieth—made it clear that only the combined effort of many experts could find a satisfactory solution for the problem. The original nucleus of contributors soon grew to twenty-two from seven different countries, and we were given advice and support by many more colleagues. In addition to the individuals already mentioned I want to thank those who helped to start and to formulate this enterprise, namely Dr. R. H. Gillette, Sir Ewart Jones, and Professor G. Wittig. I am very thankful also to Dr. B. Phillips, G. Pevtchin, and the research management of Union Carbide for their permission and help.

After the time- and energy-consuming multistep synthesis of this book, I and the other authors now hope that it may prove sufficiently comprehensive to serve well the field of acetylenes and organic chemistry.

H. G. VIEHE

*Princeton University*  
*August, 1969*

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A

# I

## THEORETICAL



## CHAPTER I

# STRUCTURE AND PHYSICAL PROPERTIES OF ACETYLENIC COMPOUNDS; THE NATURE OF THE TRIPLE BOND

*Johannes Dale*

KJEMISK INSTITUTT, UNIVERSITETET I OSLO, BLINDERN, OSLO, NORWAY

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## I. INTRODUCTION

The most widely accepted theoretical picture of the triple bond, the molecular orbital picture of a sigma bond plus two equivalent pi bonds, is in many respects unsatisfactory, as will be shown throughout this chapter. There are alternative ways of describing the triple bond, such as the classic picture of three bent bonds and the Linnett double quartet (1, 2), which in many respects are preferable to

the sigma-pi picture, whose fundamental handicap is that of being based on one-electron orbitals with total neglect of interelectronic repulsion. Instead of starting out with a preconceived theoretical picture as a basis on which the observed chemical and physical properties of acetylenes are explained, the approach of the present treatment will rather be to present the facts, and only at the end try to evaluate the predictive merits of the various bonding models.

In discussing the geometric and dynamic structural data, results from spectroscopic methods (bond lengths and angles, force constants, etc.) will be included, although the primary spectroscopic data will be treated separately later. Throughout, a comparison of the structural data of the acetylenic bond will be made, on the one hand with other triple bonds, and on the other hand with double and single carbon-carbon bonds. A correlation with small-ring cycloalkenes and bicycloalkanes has also been found useful, acetylene being considered formally as "cycloethene" or "bicyclo[0,0,0]ethane"; this is in analogy with the well-known close relationship between olefins and small-ring cycloalkanes, ethylene being considered formally as "cycloethane."

To maintain simplicity in presentation, the spectroscopic and other data reproduced in tables and figures could not always be specified with respect to solvent, temperature, etc. For more accurate details the reader is referred to the sources or other compilations.

## II. STRUCTURAL DATA

### A. Simple Acetylenes

The length of the triple bond can be determined directly by diffraction methods (X-ray diffraction of the crystalline state, electron diffraction of the gaseous state) and from rotational spectra of the gaseous state. The molecular moments of inertia, from which the structure is derived, can be obtained not only from pure rotational spectra in the microwave region, but also from rotational structure in vibrational spectra, and, very rarely, from rotational-vibrational structure in electronic spectra. In Table 1 the data considered to be the most reliable are given both for the  $\text{C}\equiv\text{C}$  triple bond itself and for the single bonds next to it in typical alkynes and halogenoacetylenes; the two carbon atoms of the triple bond and the two substituent atoms lie on a straight line in all these cases. For comparison the corresponding data for similar alkenes and alkanes and for analogous nitriles have been included. It is quite clear that the triple-bond length (both  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{N}$ ), hence its strength, is largely independent of the nature of the substituents. The  $\text{C}\equiv\text{C}$  triple bond is appreciably shorter than the  $\text{C}=\text{C}$  double bond, which is again similarly shorter than the  $\text{C}-\text{C}$  single bond in alkanes. On the other hand, the formal single bonds adjacent to these CC bonds become appreciably shortened, hence stronger, as one passes from the alkane through the alkene to the alkyne. For halogen-carbon bonds this shortening amounts to 7-8%, for CC bonds 6%, and for the CH bond 3%.

In Table 2 the length of the acetylenic bond is compared with the length of other triple bonds. In addition, each of the triple bonds is compared with double and single bonds between the same elements. Here it is more difficult to recognize a clear trend since different nuclei and charges are involved, and a direct relationship between bond length and bond strength is no longer valid. A better comparison is possible between thermochemical bond energies (Table 3).

The most striking feature of the thermochemical data in Table 3 is the extreme strength of the triple bond in the nitrogen molecule (and in carbon monoxide), particularly in view of the weakness of the double and single bonds between two

TABLE 1

Bond Lengths (in angstroms) of Simple Alkynes Compared with Bond Lengths of Corresponding Cyanides, Alkenes, and Alkanes (3)

R	R <sup>1</sup>	RC≡N (4)		RC≡CR <sup>1</sup>			RCH=CH <sub>2</sub>		RCH <sub>2</sub> —CH <sub>3</sub>	
		C—R	C≡N	C—R	C—R <sup>1</sup>	C≡C	C—R	C=C	C—R	C—C
H	H	1.063	1.155	1.059	1.059	1.205	1.084	1.332	1.093	1.534
CH <sub>3</sub>	H	1.460	1.158	1.459	1.056	1.207	1.501	1.336 (5)	1.54	1.54
F	H	1.262	1.159	1.279	1.053	1.198 (4)	1.347	1.329 (6)	1.375	1.540
Cl	H	1.631	1.159	1.637	1.055	1.204 (4)	1.740	1.327	1.777	1.551
Br	H	1.789	1.158	(1.80)	(1.06)	(1.20)	1.891	1.34	1.940	1.550
I	H	1.994	1.159	1.988	1.055	1.203 (7)	2.092	1.34	2.139	1.54 (8)
CH <sub>3</sub>	CH <sub>3</sub>			1.46	1.46	1.21				
Cl	CH <sub>3</sub>			1.637	1.458	1.207				
Br	CH <sub>3</sub>			1.793	1.460	1.207				
I	CH <sub>3</sub>			1.991	1.459	1.207				
Cl	Cl			1.64	1.64	1.195				
Br	Br			(1.80)	(1.80)	(1.20)				
I	I			(2.03)	(2.03)	(1.18)				

nitrogen atoms. This situation, contrasting so sharply with that of the carbon-carbon bonds, represents a standing challenge to bonding theory (11). It may here be useful to point out that from the immense strength of triple bonds it does not follow that the bond cannot tolerate elongation. On the contrary, the triple bond in, for example, the nitrogen molecule is surprisingly elastic and will oscillate between a closest distance of 0.89 Å and a longest distance of 1.52 Å by the expenditure of only half its dissociation energy (12). This corresponds to the excitation of 19 quanta of the ground-state stretching vibration.

The force constants for the stretching of bonds and the deformation of bond angles of a molecule can be calculated from the knowledge of all its fundamental vibration frequencies if these can be safely assigned by the combined use of infrared and Raman spectroscopy. Although the significance of calculated force constants for complex molecules may be questioned because the choice of force

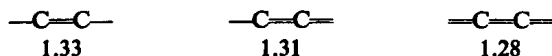
field has to be quite arbitrary, they can be informative for simple molecules, in particular the linear acetylenes. In fact, in acetylene itself and terminal acetylenes the extensive mechanical coupling between the stretching of the triple bond and the stretching of the adjacent CH bond makes the concept of group vibrations invalid (see Section V.B). A direct comparison of triple-bond stretching frequencies will therefore lead to erroneous conclusions if it is assumed that the highest frequency necessarily corresponds to the strongest bond. The only sensible

TABLE 2

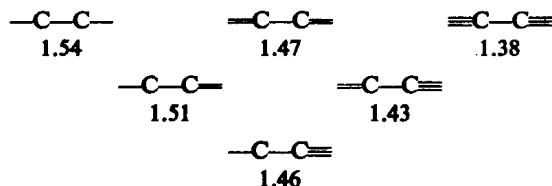
Lengths of Various Triple Bonds (in angstroms) Compared with Lengths of Corresponding Double and Single Bonds (3)

$\text{—C}\equiv\text{C—}$ 1.21	$\text{—}\overset{+}{\text{C}}\equiv\text{N—}$ 1.17	$\text{—C}\equiv\text{N}$ 1.16	$\text{—}\overset{+}{\text{C}}\equiv\text{O}$ 1.13	$\text{N}\equiv\text{N}$ 1.09		
$[\text{C}\equiv\text{C}]^{2-}$ 1.20 (CaC <sub>2</sub> )	$[\text{C}\equiv\text{N}]^-$ 1.15			$[\text{N}\equiv\text{N—}]^+$ 1.10 (8b)	$[\text{N}\equiv\text{O}]^+$ 1.06	
$\text{>C=C<}^a$ 1.33	$\text{>C=N<}$ 1.29	$\text{>C=O}$ 1.22	$\text{>N=N<}$ 1.26	$\text{>N=O}$ 1.21	$\text{O=O}$ 1.21	
$\text{>C—C<}^b$ 1.54	$\text{>C—N<}$ 1.47	$\text{>C—O<}$ 1.43	$\text{>N—N<}$ 1.45	$\text{>N—O<}$ 1.37	$\text{>O—O<}$ 1.48	

<sup>a</sup> Strictly, the C=C bond length depends on whether the carbon atoms that are linked together are further engaged in single or double bonds:



<sup>b</sup> Strictly, the C—C bond length depends on whether the carbon atoms that are linked together are further engaged in single, double, or triple bonds:



thing to do is to compare calculated stretching force constants. These have been compiled in Table 4. In accordance with the constancy of the triple-bond length in substituted acetylenes (and nitriles), the stretching force constant also remains fairly unchanged with substitution and is roughly three times larger than that of the C—C single bond and about one and a half times larger than that of the C=C double bond. Similarly, the single bond adjacent to the triple bond has a somewhat larger stretching force constant than the corresponding bond in alkenes and alkanes. A comparison of force constants of carbon-carbon bonds with those of other triple, double, and single bonds is given in Table 3. A rough propor-



tionality between stretching force constants and thermochemically derived bond energies is apparent. Carbon monoxide is an exception, but it should be emphasized that in diatomic molecules, although there is just one bond, the thermochemical energy of the molecule is not necessarily given by the bond energy alone. It is not only a question of how the bonding electrons interact with the two atomic nuclei, but also of how all the electrons interact with each other. The "resonance energy" of benzene constitutes an analogous situation; it is not reflected in the CC bond distance (3) or force constant (10).

Intuitively, one might have expected, since the strength of both the CC bond and the adjacent bond to the substituent increases when passing from the alkane

TABLE 3

Thermochemical Bond Energies (in kcal/mole) (9) and Spectroscopic Stretching Force Constants (in  $10^5$  dynes/cm) (2, 10) of Triple Bonds Compared with Values for Corresponding Double and Single Bonds

$\text{—C}\equiv\text{C—}$ 200 (15.9) <sup>a</sup>	$\text{—C}\equiv\text{N}$ 213 (17.3)	$\text{C}\equiv\text{O}$ 256 (18.6)	$\text{N}\equiv\text{N}$ 226 (22.2)	
$\text{>C=C<}$ 146 (10.8)	$\text{>C=N<}$ 147	$\text{>C=O}$ 177 (12.9)	$\text{>N=N<}$ 100	$\text{O=O}$ 119 (11.8)
$\text{>C—C<}$ 83 (4.3)	$\text{>C—N<}$ 73 (4.9)	$\text{>C—O<}$ 86	$\text{>N—N<}$ 39	$\text{>O—O<}$ 35
	$\text{C}\equiv\text{C—H}$ 121 (5.9)	$\text{C=C—H}$ 106 (5.1)	$\text{C—C—H}$ 103 (4.8)	

<sup>a</sup> Force constants in parentheses.

through the alkene and to the alkyne, that the resistance to angle deformation should also increase. The bending force constants given in Table 4 reveal, however, the startling fact that the reverse is true; it is much more easy to bend a substituent out of the (linear) equilibrium position of an acetylene than it is to bend a substituent on an olefinic or saturated carbon atom. It therefore seems likely (10) that it is the angular distance between the substituents attached to a common atom which determines the magnitude of the bending force constant; the crowding of four substituents around a saturated carbon atom results in a maximum resistance to angle deformation. Consistent with this picture is the smaller force constant for the out-of-plane deformation of olefins and aromatics than for the in-plane deformation (18, 19). Furthermore, in acetylene (20) the magnitude of successive quanta of the symmetrical bending vibration increases by about 1% (613, 618, and 624  $\text{cm}^{-1}$  for  $\text{C}_2\text{H}_2$ ; 511, 513, and 518  $\text{cm}^{-1}$  for  $\text{C}_2\text{D}_2$ ).