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The chemistry of  
**cyanates and their thio  
derivatives**

Part 1

*Edited by*

SAUL PATAI

*The Hebrew University, Jerusalem*

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1977

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## THE CHEMISTRY OF FUNCTIONAL GROUPS

*A series of advanced treatises under the general editorship of  
Professor Saul Patai*

- The chemistry of alkenes (2 volumes)
- The chemistry of the carbonyl group (2 volumes)
  - The chemistry of the ether linkage
  - The chemistry of the amino group
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- The chemistry of cyanates and their thio derivatives (2 parts)
- Supplement A: The chemistry of double-bonded functional groups (2 parts)

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## Foreword

The present volume, "The Chemistry of Cyanates and their Thio Derivatives" includes material on cyanates, isocyanates, thiocyanates and isothiocyanates as well as on isocyanate dihalides and on selenocyanates and related compounds. The volume is organized on the same general lines as the other volumes of "The Chemistry of Functional Groups" series, and which are described in the "Preface to the Series" appearing on the following pages.

For once, all the chapters included in the original plan of the volume materialized. Hence omissions, if any, this time are solely the responsibility of the Editor.

The chapters have been commissioned for this volume in the Spring of 1974, and were mostly delivered between March and August 1975. In most cases the literature coverage of the chapters is therefore roughly up to the Spring of 1975.

Jerusalem, June 1976

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 treated 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 'Ketenes' 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 Groups (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 (two parts)*
- The Chemistry of Cyanates and their Thio Derivatives (two parts)*
- Supplement A: The Chemistry of Double-Bonded Functional Groups (two parts)*

Titles in press:

- The Chemistry of the Diazonium and Diazo Groups*
- The Chemistry of the Carbon–Carbon Triple Bond*
- 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  $-\text{NH}_2$ ,  $-\text{OH}$ , and  $-\text{SH}$  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

# Electronic structure of the cyanato and thiocyanato groups—ground state and excited states†

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† This work was supported by the U.S. Energy Research and Development Administration—Division of Biomedical and Environmental Research—Physics and Technological Program and by the Deutsche Forschungsgemeinschaft.

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## I. INTRODUCTION

There are several ways in which one might treat the electronic structures of such functionals as the cyanato and thiocyanato groups. One might, for example, compile lists of experimental and computational data; or one might focus on discussions of high quality *ab initio* wavefunctions, such as those of McLean for the  $\text{NCS}^-$  ion<sup>1</sup>. Both of these approaches have merit. However, we have chosen a more limiting path. We will select and discuss those experimental techniques which bear on the general question of electronic structure, and we will utilize the information which these techniques provide in order to present a 'status report' on the electronic structure of some simple cyanates and thiocyanates (i.e., the anions  $\text{NCO}^-$  and  $\text{NCS}^-$ , some of their covalent and ionic metal salts, and their methyl and phenyl derivatives).



The theoretical framework will consist of a molecular orbital (MO) approach and will reduce, on occasion, to such a simple, but fundamental, level as Walsh's rules<sup>2</sup>. That is not to say that we will evade all *ab initio* results, forget about any configuration interaction effects, neglect spin-orbital mixings, etc.—indeed, we will not. Our intent is to remain simple, but when the proper interpretation of the phenomenon at hand demands theoretical complexity, we will not hesitate to use it.

The types of experimental data which we deem relevant to electronic properties include:

(i) Gas-phase structures as determined by electron diffraction and microwave spectroscopy. This information provides the minima of the total molecular energies with respect to the geometric coordinates.

(ii) ESCA (Electron Spectroscopy for Chemical Analysis) chemical shifts. Such data can be used to obtain atomic charges for an atom when the atom is part of a molecule.

(iii) Ultraviolet photoelectron spectra (PES). These spectra provide easy access to approximate valence MO energies.

(iv) X-ray emission spectra. The intensities of the individual bands in these spectra contain information on the shapes of valence molecular orbitals.

(v) Ultraviolet and visible absorption and emission spectroscopy. These techniques generate the set of excited state properties for valence as well as for Rydberg excitations (i.e., for  $V \leftarrow N$  as well as  $R \leftarrow N$  excited configurations).

The choices (i)–(v), not surprisingly, represent our own personal interests. We will endeavour to present a unified interpretation of these diverse experimental techniques, and to bring them to bear on the subject of the electronic structure of the cyanates and thiocyanates. We fear, however, that the principal result of our discussion will be the conclusion that a great deal of experimental work is still required even for these simple molecules enumerated above.

## II. GROUND STATE PROPERTIES

### A. Anions

#### 1. Molecular orbitals and geometry

Triatomic ABC species are linear (e.g., the 16 electron molecules,  $\text{CO}_2$ ,  $\text{N}_3^-$ ,  $\text{NO}_2^+$ ), bent (e.g., the 18 electron molecules,  $\text{NO}_2^-$ ,  $\text{O}_3$ ) or linear (e.g., the 22 electron molecules,  $\text{I}_3^-$ ,  $\text{XeF}_2$ ). Geometry seems to depend on the number of valence electrons.  $\text{NCO}^-$  and  $\text{NCS}^-$  contain 16 valence electrons and are isoelectronic with the linear species  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2^+$ ,  $\text{HgCl}_2$ ,  $\text{N}_3^-$ ,