

# Chapter 13

## Theoretical Studies on the Structure and Spectroscopic Properties of 2,4-D (2,4-Diclorofenoxiacetic Acid)

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### ABSTRACT

*The 2,4-dichlorophenoxyacetic acid (2,4-D) is applied to and recovered from the leaf surfaces of garden bean and corn plants. This paper examines the theoretical study of the 2,4-D IR and UV spectra as well as the determination of its optimized molecular structure. Theoretical calculations are performed at the density functional theory (DFT) levels. The different structural and electronic effects determining the molecular stability of the conformers are discussed in a comparative fashion. The optimized geometry was calculated via the B3LYP method with 6-311G(d,p) and 6-311++G(d,p) basis sets and the FT-IR spectra was calculated by the density functional B3LYP method with the 6-311++G(d,p) basis set. The scaled theoretical wavenumbers show good agreement with the experimental values. A detailed interpretation of the infrared spectra of 2,4-D is reported.*

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## INTRODUCTION

There has been a great interest in aryloxyacetic acids as potential plant growth regulators (Cremllyn, 1979; Martin, 1973). In 1942, Zimmerman and Hitchcock showed that certain chlorinated phenoxyacetic acids, such as 2,4-dichlorophenoxyacetic acid (2,4-D), were more active than the natural growth hormone indole-3-acetic acid (IAA), and that they were not rapidly metabolized in the plant (Green, 1974). Consequently, 2,4-D could be externally applied to cause abnormal growth and the death of the plant since it is not internally regulated like IAA. The herbicidal phenoxyacetic acids were found to be much more active against broad-leaved weeds (dicotyledons) than against cereals and grasses (monocotyledons). Despite its vital importance, the selectivity of these compounds it was not clearly understood (Crafts, 1961; Crafts & Robins, 1962; Audus, 1964; Galston et al., 1980; Gruzdyev et al., 1983). Phenoxy acid herbicides show moderate toxicity but some chlorinated metabolites can be toxic to human and aquatic organisms (Bovey & Young, 1980). It was reported they can cause soft tissue carcinoma in man (Vineis et al., 1986; Lynge, 1985) and show embryotoxicity in animals (Hood et al., 1979).

It has also been established that 2,4-D strongly affects the synthesis of RNA. Therefore, it is probable that the herbicides first affect the nucleic acids and then, through them the biosynthesis process. 2,4-D noticeably affects the photosynthesis process; first of all the photolytic activity of chloroplast and photosynthetic phosphorylation (Gruzdyev et al., 1983).

The knowledge of pesticide levels in surface waters and groundwater has become a topic of great social concern because of its possible impact on health and the environment. This creates the need of their persistence in it, as well as their decomposition products formed in the water (Baradon & Frixione, 1982; Bacher & Gibson, 1988).

The physiological activity of phenoxyacetic acid increases when a halogen atom such as fluorine or chlorine is introduced into the aromatic portion of the molecule. The position of the halogen is crucial for this activity: for instance, activity decreases among the dichlorosubstituted phenoxyacetic acid derivatives in the order of 2,4-D > 2,5- > 3,4- > 3,5- > 2,6-. When an aliphatic group is substituted by one hydrogen atom on the ring, the activity of the compound increases insignificantly (Gruzdyev et al., 1983; Turker, 2000).

In order to show a high activity, the molecule must generally possess either the -COOH group or a group that is easily converted to it within the plant tissues (Cremllyn, 1979; Gruzdyev et al., 1983).

As far as the ring substitution-activity relationship is concerned it has been argued that the existence of one free ortho position is an essential requirement for activity, but there are some very active compounds, such as 2,4-dichloro-6-fluorophenoxyacetic acid, where all the ortho positions are substituted. There is therefore some uncertainty regarding the importance of specific nuclear positions on growth regulating properties. However, at least one nuclear position must be unsubstituted (Turker, 2000). The observations of herbicides causing contortions of leaf stalks and stumpiness of the roots require some theoretical explanation.

As a first step in the theoretical study it is necessary to analyse the electronic properties, conformational and spectroscopic properties of each pesticide or agrochemical utilized. The dimensional nature of tetrahedral carbon molecule provides spatial orientations of the organic compounds that result in a group of molecules stoichiometrically identical but spatially different from each other.

In the present study, 2,4D (2,4-dichloro-phenoxyacetic acid) was theoretically analysed via the DFT\_B3LYP method with the aim of clarifying the structure-activity relationship. This study

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