

Conformational analysis of allyl halides from the calculation of indirect spin-spin coupling

V SANTHANAM, J SOBHANADRI* and S SUBRAMANIAM†

Department of Physics, †Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras 600 036, India

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Abstract. A theoretical study on the conformation of allyl halides from the calculation of nuclear spin-spin coupling constants by adopting the finite perturbation theory (FPT), is carried out in terms of the self-consistent, semi-empirical INDO (intermediate neglect of differential overlap) approximation of molecular orbital theory. Results of the calculations performed using 's' and 'p' valence orbitals alone ('sp' basis) at INDO level approximation seem to replicate the experimental trend quite satisfactorily. Despite the overall agreement of the theoretical values with the experimental ones, the uncertainties in the INDO parametrization scheme lead to overestimation of certain coupling constants. The calculations also show that the orientation of the coupled protons with respect to the substituent halogen atom is an important factor to be considered.

Keywords. Indirect spin-spin coupling; allyl halides; SCF-MO-INDO method; finite perturbation theory.

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1. Introduction

Of all the methods most commonly used in the evaluation of nuclear spin-spin coupling constants, the calculations based on finite perturbation theory (FPT) (Pople *et al* 1966, 1968) is quite good in giving broad agreement with experimental values (Contreras *et al* 1980). A complete review of the present situation in this field is given by Kowalewski (1977) wherein the different methods in vogue and their applications in different directions are discussed. Several semi-empirical methods with different parametrization schemes (Dewar *et al* 1977 and Bingham *et al* 1975) were tried with this FPT method; but it was found that the INDO method with Pople's parameters (Pople and Beveridge 1970) seems to serve the purpose better in reproducing the experimental features.

In the present study, FPT-INDO method is used in carrying out the conformational analysis of allyl halides by calculating indirect spin-spin coupling constants between the various protonic nuclei involved. Basically there are three contributions to the electron-coupled interactions between nuclear spins in a molecule and they are (i) dipole-dipole interaction between the magnetic dipoles associated with electron spin and nuclear spin, (ii) orbital-dipole interaction between the magnetic field associated

*To whom correspondence should be addressed.