

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

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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

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with electronic orbital motion and the nuclear magnetic dipole and (iii) Fermi contact term, which arises because of the electron and nuclear spin. The theory of these coupling schemes was originally formulated by Ramsey (1953). Of the three contributions to nuclear spin-spin coupling listed above, the Fermi contact term is always predominant, particularly when protons are involved. Hence most of the attempts in this direction will normally be based on this term only. In the present study also, we restrict ourselves to calculating this term only.

## 2. Theoretical formulation

The isotropic nuclear spin-spin coupling constants between the protonic nuclei are calculated using molecular orbital wave functions generated within the limits of INDO level approximation which are self-consistent to the presence of Fermi contact interaction between the nuclear and electronic spin. The basic reason for preferring INDO method to widely used CNDO (complete neglect of differential overlap) method is that the retention of the monoatomic differential overlap integrals at least in one centre terms in the INDO scheme helps to reproduce the spin polarization effects much better. As mentioned earlier, Pople's parameters (Pople and Beveridge 1970) are used for atoms C, H and Cl, while for Br, parameters given by Hase and Schweig (1973) and for I, parameters introduced by Galasso (1974) are used. In the present method of calculation, a perturbation of magnitude

$$h_A = (8\pi/3)\beta_e\mu_A\phi_s^2(A) \quad (1)$$

is added to the diagonal element representing the valence  $s$ -orbital of atom  $A$  of the core hamiltonian for electrons with  $\alpha$ -spin and an equal amount is subtracted from the corresponding element of the core hamiltonian associated with electrons of  $\beta$ -spin. Here  $\beta_e$  is Bohr magneton,  $\mu_A$  is the magnetic moment of nucleus  $A$  and  $\phi_s^2(A)$  is the density at the nucleus of the valence  $s$ -orbital of atom  $A$ . The usual nuclear spin-spin coupling constant between atoms  $A$  and  $B$  is given by

$$J_{AB} = (\hbar/2\pi)\gamma_A\gamma_B K_{AB}, \quad (2)$$

where  $\gamma_A$  and  $\gamma_B$  are the nuclear gyromagnetic ratios for the two nuclei  $A$  and  $B$  respectively and  $\hbar = h/2\pi$ ,  $h$  is the well known Planck's constant.  $K_{AB}$  is the reduced isotropic coupling constant between atoms  $A$  and  $B$  which is related to the interaction energy of the two nuclear spins and the product of their magnetic moments according to the following equation

$$E_{int} = K_{AB}\mu_A\mu_B. \quad (3)$$

With the perturbation given in (1), the coupling constant between the nuclei  $A$  and  $B$  is given by

$$J_{AB} = h(4\beta_e/3)^2\gamma_A\gamma_B\phi_s^2(A)\phi_s^2(B)\left\{\frac{\partial}{\partial h_A}[\rho_{s_B}(h_A)]\right\}_{h_A=0} \quad (4)$$

where  $\rho_{s_B}(h_A)$  is the diagonal element of spin density matrix corresponding to  $s$ -orbital centred on nucleus  $B$  due to the perturbation  $h_A$  introduced at the nucleus  $A$ . On

introducing the details of the method of finite differences (Pople *et al* 1966), (4) reduces to

$$J_{AB} = h(4\beta_e/3)^2 \gamma_A \gamma_B \phi_s^2(A) \phi_s^2(B) \left( \frac{\rho_{s_B}(h_A)}{h_A} \right). \quad (5)$$

Equation (5) is the basis of our method of calculating isotropic nuclear spin coupling constants. To carry out detailed calculation using (5), proper values for the perturbation  $h_A$  and other computational parameters should be chosen so that the mathematical error involved in using the finite difference formula (5) instead of the actual formula (4) is a minimum. A range of values from 0.001 a.u. to 0.01 a.u. are chosen for perturbation and all these values are tried by introducing them on either  $A$  or  $B$  at a time and finding the spin density matrix element corresponding to the valence  $s$ -orbital of the unperturbed nucleus. That value of the perturbation, for which the discrepancy in the abovesaid equivalent calculations is minimum, is taken for calculating the factor  $\rho_{s_B}(h_A)/h_A$ . Since the spin density matrix elements must be known as accurately as possible, the energy criterion for the convergence of the SCF procedure is modified and the termination of the iterative calculation is invoked when the root mean square difference between two successive (NXN) density matrices

$$\left\{ \sum_{\mu, \nu}^N (\rho_{\mu\nu} - \rho'_{\mu\nu})^2 \right\}^{1/2} / N$$

is less than a specific quantity  $\Delta$ , the value of which is a reasonable estimate of the error  $\delta\rho$  involved in the calculation of spin density matrix elements. Though this procedure takes much longer time for convergence than that based on energy criterion, 25 cycles of iteration were found to give consistent results in the calculation of proton-proton coupling constant with accuracy up to two significant places. All computations were carried out on IBM 370/155 machine.

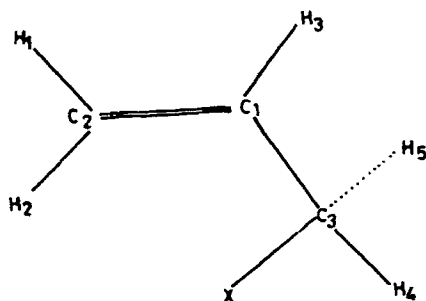
For generating the geometry of the systems chosen, only tetrahedral and trigonal bond angles along with the bond lengths taken from the compilation volume of Sutton (1965) are used. The valence  $s$ -orbital densities used in this work are reproduced in table 1 (Pople *et al* 1966; Goodman and Raynor 1970).

### 3. Results and discussion

The isotropic nuclear spin-spin coupling constants between the olefinic protons and the allylic protons are calculated for different conformers obtained when the allylic group atoms namely  $C_3$ ,  $H_4$ ,  $H_5$  and  $X$  are rotated as a whole about the  $C_1-C_3$  bond (figure 1) through  $40^\circ$  every time. The conformer with which the calculations are started is the one given in figure 1, in which the atoms  $C_1$ ,  $C_2$ ,  $C_3$ ,  $H_1$ ,  $H_2$ ,  $X$ , and  $H_3$  are in the plane of the paper and the atoms  $H_4$  and  $H_5$  are respectively above and below the plane of the paper. The torsional angle corresponding to this conformation is taken as zero. The mean values of the coupling constants thus calculated are given in tables 2 and 3. The coupling constants between the olefinic protons and the substituent halogen are also found in the same way and given in

**Table 1.** Valence  $s$ -orbital densities at the site of the nucleus ( $a_0^{-3}$ ).

Atom	$\phi_s^2(0)$
Hydrogen	0.3724
Fluorine	21.3126
Chlorine	10.662
Bromine	19.335
Iodine	22.836

**Figure 1.** *S-cis*-3 monosubstituted propene.**Table 2.** Coupling constants for the olefinic protons ( $J$ /Hz). (Experimental values are given in the parenthesis).

Molecule	$J_{12}$	$J_{23}$	$J_{13}$
3-Fluoropropene	4.77(1.54)	24.71(17.21)	9.84(10.64)
3-Chloropropene	4.23(1.26)	22.48(16.88)	9.58(10.12)
3-Bromopropene	4.27(1.25)	21.67(16.77)	8.8 ( 9.92)
3-Iodopropene	4.1 (1.24)	21.84(16.49)	9.22( 9.68)

table 4. The results obtained are based on the semi-empirical INDO method, using only valence  $s$  and  $p$  functions ( $sp$  basis) centred on each atom in the molecule.

An absolute maximum in the calculated values occurs in the all-*trans* arrangement of the coupled protons, a conclusion which was already drawn from calculations based on valence bond theory and experimental findings (Bothner-By *et al* 1965, 1966; Ewing and Parry 1970; Govil 1967). Of the three olefinic protonic coupling constants, the geminal  $H-H$  constant  $J_{12}$  appears to be overestimated in the present calculation. The reason might be that since the protons 1 and 2 form almost covalent bonds with the carbon atom  $C_2$ , with local electron densities almost equal to 1 (which is evident from Mulliken population analysis), their valence  $s$ -orbital densities  $s^2(0)$  should be lower than the one (0.3724), we have used in our calculation i.e. we might have to use the value corresponding to free hydrogen atom, to get better agreement with the experimental data. Generally positive values are obtained for trigonal  $H-C-H$  groups, a fact which is true in the present study as well. Vicinal  $H-H$  constants both for *trans* and *cis* forms are also well reproduced, though the *trans* coupling constants  $J_{23}$  are

**Table 3.** Cisoid and transoid allylic coupling constants (J/Hz).

Molecule	Cisoid coupling constant				Transoid coupling constant			
	$J_{2,(4,5)}$ (0°)	$J_{2,(4,5)}$ (120°)	$\langle J_{2,(4,5)} \rangle_{ave}$	$J_{2,(4,5)}$ (Exptl.)	$J_{1,(4,5)}$ (0°)	$J_{1,(4,5)}$ (120°)	$\langle J_{1,(4,5)} \rangle_{ave}$	$J_{1,(4,5)}$ (Exptl.)
3-Fluoropropene	-2.30	-1.75	-2.22 <sup>a</sup>	-1.63	-1.66	-0.225	-1.56 <sup>a</sup>	-1.27
		-0.938	-1.68 <sup>b</sup>			-0.685	-0.876 <sup>b</sup>	
3-Chloropropene	-2.29	-1.505	-2.24	-1.42	-1.77	-0.211	-1.71 <sup>a</sup>	-0.93
		-0.832	-1.34			-0.725	-0.67 <sup>b</sup>	
3-Bromopropene	-2.34	-1.63	-2.34 <sup>a</sup>	-1.20	-1.63	-0.237	-1.63 <sup>a</sup>	-0.56
		-0.873	-1.3 <sup>b</sup>			-0.715	-0.52 <sup>b</sup>	
3-Iodopropene	-2.26	-1.52	-2.26 <sup>a</sup>	-1.06	-1.58	0.04	-1.58 <sup>a</sup>	-0.42
		-0.854	-1.19 <sup>b</sup>			-0.717	-0.4 <sup>b</sup>	

<sup>a</sup> Values obtained from energy consideration.

<sup>b</sup> Values obtained using population coefficients cited in Halmann *et al* (1966) and Bothner-By and Gunther (1962).

**Table 4.** Coupling constants for the olefinic protons and the substituent halogen atom (J/Hz). (Experimental values for 3-fluoropropene are given in the parenthesis).

Molecule	$J_{H_1,X}$	$J_{H_2,X}$	$J_{H_3,X}$
3-Fluoropropene	-0.699(-0.89)	-5.79(-4.32)	16.57(14.53)
3-Chloropropene	-0.17	-0.56	0.94
3-Bromopropene	-1.25	-2.86	3.48
3-Iodopropene	-0.76	-1.62	1.62

again overestimated. On the whole, the vicinal H-H coupling in the *cis* form seem to agree well with the experimental values, though the other two constants apart from reproducing the experimental trend qualitatively, are slightly overestimated. The figures for  $J_{12}$ ,  $J_{13}$  and  $J_{23}$  given in table 2 are the mean of the values corresponding to different conformers resulting from free rotation of the allyl group atoms (namely C<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub> and X) about the C<sub>1</sub>-C<sub>3</sub> bond. It is also found that the change in the orientation of the allyl group atoms does not affect the  $J_{12}$ ,  $J_{13}$  and  $J_{23}$  values much, as might be expected, and the large positive values for the coupling constants between the protons in *trans* arrangement can only be due to direct interaction between the bonds connecting the coupled nuclei (Meniwold *et al* 1961; Padwa *et al* 1968; Barfield and Karplus 1969).

The coupling between the protons on C<sub>3</sub> and the protons on C<sub>2</sub> and C<sub>1</sub> depends very much on the orientation of the allyl group with respect to C<sub>2</sub>=C<sub>1</sub> bond. In propene molecule itself, the methyl protons can assume all the possible equilibrium positions with equal probability and so the allylic coupling constants can be obtained

by averaging out the values corresponding to the equilibrium positions of the methyl protons (Barfield 1971). For 3-substituted propenes, rotamer populations will be unequal in general and one has to give proper weightage to each of them while averaging. Microwave studies on 3-substituted propenes have identified the existence of three minima in the potential curves for rotation about C—C single bond (Hirota 1962) and they are given in figure 2. Making a reasonable assumption that for a single isolated molecule, the coupling constant can be represented by taking weighted average of the characteristic *cis* and *gauche* coupling constants, we can write

$$J_{HX} = pJ_{HX}^c + (1 - p)J_{HX}^g \quad (6)$$

$$J_{HY} = pJ_{HY}^c + \left(\frac{1-p}{2}\right)[J_{HY}(120^\circ) + J_{HY}(240^\circ)], \quad (7)$$

where  $p$  denotes respectively, in (6) and (7), the population of the rotational isomer in which the substituent halogen atom  $X$  and one of the allyl group hydrogen atoms  $Y$  ( $H_4$  or  $H_5$ ) eclipses the double bond. In fact in (6) also there are contributions from two *gauche* forms with the fractional coefficients each equal to  $(1-p)/2$ . Since the contributions are also the same, they are combined together and written as a single term with the fractional coefficient  $(1-p)$ . *Ab initio* calculation (Cadioli and Pincelli 1972) on 3-fluoropropene revealed the existence of two low energy conformers, with energy difference of 0.002 a.u., the lower energy conformer being the *cis* form (figure 1). Our earlier calculations (Santhanam and Sobhanadri 1985) using INDO semi-empirical SCF method with 'spd' basis set have also revealed the same trend with almost the same energy difference between the two stable conformers. Other 3-monosubstituted propenes show almost the same behaviour with varying energy difference between the two stable forms, with the *cis* form always assuming lowest energy. The population of the *cis* conformer in each system is found using Boltzmann's distribution and the calculated figures are given in table 5. If the allyl coupling constants are calculated using these population coefficients, it is found that the predominant contribution comes only from *cis* form in each case. On the other hand high resolution proton nmr spectral studies (Bothner-By and Gunther 1962) reveal that in allyl chloride, that conformer with the substituent halogen atom in the *gauche* position with respect to the trigonal carbon is slightly preferred and that this tendency increases in allyl bromide and allyl iodide. On calculating the coupling constants with the population coefficients as given by Bothner-By and Gunther (1962), the results seem to agree well with the experimental values and now the predominant contribution comes from

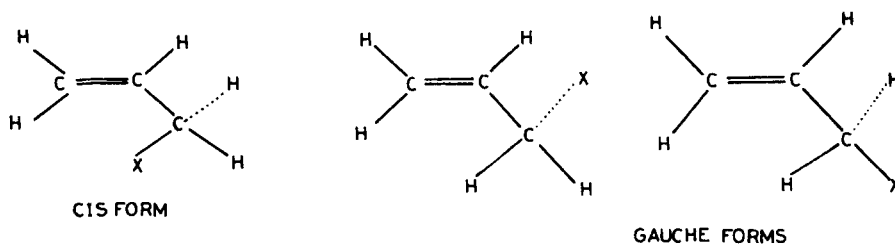


Figure 2. Energetically favoured rotamers in 3-monosubstituted propenes.

**Table 5.** Population coefficients for the *cis*-isomer.

Molecule	$n_A$	$n_B$
3-Fluoropropene	0.91	0.35
3-Chloropropene	0.96	0.22
3-Bromopropene	0.99	0.05
3-Iodopropene	0.99	0.0

$n_A$  – calculated values based on energy consideration using Boltzmann distribution.

$n_B$  – taken from reference (Bothner-By and Gunther 1962).

the *gauche* forms. Interestingly enough, almost all contribution to the coupling constants comes only from the *gauche* forms, in the case of allyl iodide. This is perhaps the reason why the profile of the energy *vs* torsional angle curve showed reverse trend when calculations were performed with *sp* basis set (Santhanam and Sobhanadri 1986). For e.g. in the case of allyl iodide, the *gauche* form assumed lower energy than the *cis* form, when calculations were carried out with only *s* and *p* valence atomic orbitals as the basis functions (*sp* basis) in the molecular orbital scheme. Also it was found that the calculated dipole moment values for different conformers with *spd* basis set showed marked disagreement with the experimental values, while values improved much when *sp* basis set is used. So the SCF-MO calculations performed at the INDO level approximation with *sp* basis set seem to support the experimental trend quite well for 3-monopropene derivatives with heavy atom substitution.

#### 4. Conclusion

Finite perturbation theory working within the framework of INDO semi-empirical molecular orbital theory provides a satisfactory picture of the long-range H–H coupling in 3-monosubstituted propenes. The findings in the present study confirms the earlier conclusions on the rotameric forms of the compounds based on microwave studies (Hirota 1962), gas-phase electron diffraction studies (Helene Schei and Quang Shen 1982) and proton magnetic resonance spectral studies (Bothner-By *et al* 1965, 1966). The preference of INDO to CNDO in the present study also proves the necessity of the retention of monoatomic differential overlap at least in one centre integrals which satisfactorily takes care of the direct and indirect mechanisms involved in nuclear spin coupling. However a very successful and adequate comparison of theoretical and experimental data as a function of conformation is possible if we realize the geometric relaxation during internal rotation and include the correlation effects. Such effects are not included in the present calculation and as such we cannot expect as good an agreement as might be hoped in so far as the numerical results are concerned. Yet another reason for getting poor agreement of the calculated coupling constants with the available experimental data is the overestimation of the substituent effects (Pople *et al* 1966, 1968) which can be reasonably related to the parametrization scheme in the INDO method.

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