On the d-Orbital Influence in INDO Calculations of NMR and ESR Parameters of Sulphur Heterocyclics

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Comparative calculations by the self-consistent perturbed INDO method on thiophene and by the unrestricted HF INDO method on the 2-thenyl radical show that satisfactory reproduction of nuclear spin coupling constants and hyperfine coupling constants for sulphur heterocyclics can be obtained by considering the sp interaction only.

1. Introduction

The INDO method [1] has proved to be reasonably successful in reproducing signs, magnitudes and trends of important magnetic resonance parameters such as hyperfine coupling constants (hcc's) and nuclear spin coupling constants (nscc's) of first-row radicals [2] and molecules [3].

Since a large amount of spectroscopic data on sulphur-containing conjugated compounds is available for theoretical investigations, it has been considered worthwhile to examine whether the enlargement of the basis set by including 3d orbitals within the framework of the INDO method is required to obtain satisfactory predictions of ESR and NMR parameters of such compounds. In order to assess the sensitivity of the results to d-orbital participation, three different INDO calculations have been performed on representative systems usign both the "restricted" sp and the "extended" spd basis set and different atomic parameters and orbital exponents. In particular, the test relative to the nscc's has been performed on thiophene, while the test relative to the hcc's has been performed on 2-thenyl radical since experimental information about the thiophene anion radical is until now not available.

2. Computational Details

The INDO method has been described fully elsewhere [1] and so only the features of particular relevance to the present treatment of sulphur-containing compounds are reported below.

The nscc's have been evaluated using the SCF finite perturbation technique developed by Blizzard and Santry [4] within the framework of the INDO method. The hcc's have been calculated from the spin densities based on the unrestricted Hartree-Fock INDO wavefunction assuming the proportionality constant suggested by Pople et alias [2].

The experimental structure [5] has been used for thiophene, while for 2-thenyl radical an idealized geometry has been built by connecting the geometry of thiophene with a standard geometrical model for the methylene group ($C-CH_2$ 1.40 Å, $C-H$ 1.08 Å, HCH 120°).

2.1. *Method INDO-SS*

This is the original INDO method extended to systems containing second-row atoms using the parametrisation [orbital electronegativities $\frac{1}{2}(I+A)$ and atomic parameters $\beta_A{}^0$] proposed by Santry and Seagl [6]. Slater-type orbitals (STO's) and exponents are used.

The core integral U_d of sulphur in the assumed configuration $s^2\,p^3\,d^1$ has been found semiempirically [1] from the relation:

$$-\tfrac{1}{2}\,(I+A)_d = U_d + \tfrac{11}{2}F^0 - \tfrac{1}{5}G^2 - \tfrac{1}{5} \cdot [G^1 + \tfrac{9}{14}G^3] - \tfrac{1}{63}[F^2+F^4]\,,$$

where the F^k and G^k are Slater-Condon integrals.

All the F^0 integrals have been assumed equal to γ_{AA} (the monocentric coulomb integral calculated with s-orbitals), while the F^2 and G^1 integrals have been given "spectroscopic" values taken from Hinze [7]:

$$F^2 = F^2(pp) = F^2(dd) = G^2(sd) = F_s{}^2(pp)\,,$$
$$G^1 = G^1(sp) = G^1(pd) = G_s{}^1(sp)\,.$$

The two remaining Slater-Condon integrals involving d-orbitals of sulphur, not obtainable semiempirically due to lack of atomic spectral data, have been estimated by scaling the corresponding theoretical values by a factor which is obtained as the

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ratio of the "spectroscopic" to the theoretical values for the integrals F^2 and G^1:

$$F_s^4(\mathrm{dd}) = F_t^4(\mathrm{dd}) F_s^2(\mathrm{pp}) / F_t^2(\mathrm{pp}) \, ,$$
$$G_s^3(\mathrm{pd}) = G_t^3(\mathrm{pd}) G_s^1(\mathrm{sp}) / G_t^1(\mathrm{sp}) \, .$$

2.2. *Method INDO-S*

This method differs from the previous one only in that the parameters given by Santry[8] are assigned to sulphur and the hamiltonian matrix element H_{ij} is calculated with the formula[8] $H_{ij} = S_{ij} \beta_S^d$ if either i or j are 3d orbitals centred on sulphur, where β_S^d is a parameter specifically for the 3d functions of sulphur.

2.3. *Method INDO-B*

This method has been developed from the original INDO method by giving different exponents to the s, p, and d orbitals. Slater-type orbitals with Burns[9] exponents (BTO's) have been adopted. The orbital electronegativities and the atomic parameters have been taken from Santry and Segal[6].

The following relation between the orbital electronegativity and the core integral U_d of sulphur holds now:

$$-\tfrac{1}{2}\,(I+A)_d = U_d + 2\,F^0(\mathrm{sd}) + 3\,F^0(\mathrm{pd}) + \tfrac{1}{2}F^0(\mathrm{dd}) - \tfrac{1}{5}\,G^2(\mathrm{sd}) - \tfrac{1}{5}\,[G^1(\mathrm{pd}) + \tfrac{9}{14}\,G^3(\mathrm{pd})] - \tfrac{1}{63} \cdot [F^2(\mathrm{dd}) + F^4(\mathrm{dd})] \, .$$

As to the Slater-Condon parameters:

a) the theoretical values have been used for the F^0 integrals:

b) the "spectroscopic" values[7] have been given to $F^2(\mathrm{pp})$ and $G^1(\mathrm{sp})$;

c) "scaled" estimates of the other integrals have been obtained from the theoretical values with a criterion like that above mentioned:

$$F_s^2(\mathrm{dd}) = F_t^2(\mathrm{dd}) F_s^2(\mathrm{pp}) / F_t^2(\mathrm{pp}) \, ,$$
$$F_s^2(\mathrm{pd}) = F_t^2(\mathrm{pd}) F_s^2(\mathrm{pp}) / F_t^2(\mathrm{pp}) \, ,$$
$$G_s^1(\mathrm{pd}) = G_t^1(\mathrm{pd}) G_s^1(\mathrm{sp}) / G_t^1(\mathrm{sp}) \, ,$$
$$F_s^4(\mathrm{dd}) = F_t^4(\mathrm{dd}) F_s^2(\mathrm{dd}) / F_t^2(\mathrm{dd}) \, ,$$
$$G_s^2(\mathrm{sd}) = G_t^2(\mathrm{sd}) G_s^1(\mathrm{sp}) / G_t^1(\mathrm{sp}) \, ,$$
$$G_s^3(\mathrm{pd}) = G_t^3(\mathrm{pd}) G_s^1(\mathrm{pd}) / G_t^1(\mathrm{pd}) \, .$$

The monocentric coulomb integrals γ_{AA} have been taken as actual averages, weighted for the numbers of each integral that arises. Similarly, the two-centre coulomb integrals γ_{AB} have been determined as weighted averages. Finally, the resonance integrals H_{ij} have been computed from the relevant IP's[10] and overlap integrals *via* the Wolfsberg-Helmholz formula[11].

3. Results and Discussion

Nuclear spin coupling constants

Comparison of calculated nscc's with experimental values[12] is presented in Table 1. These results point to the following observations.

i) When the sp STO's are used (methods INDO-SS and INDO-S) all the nscc's are reproduced with the correct positive sign. As regards the vicinal couplings J_{23} and J_{34}, the internal order is reflected and the agreement between theory and experiment is fair. The reproduction of the long-range constants J_{24} and J_{25} is instead less good but a similar difficulty is encountered also for furan and pyrrole[13].

ii) The enlargement of the basis set by including 3d orbitals on sulphur causes a dramatic deterioration of the results in method INDO-SS and a slight improvement in method INDO-S. As a matter of fact, method INDO-SS gives the correct internal order of the nscc's but most of the values are grossly overestimated. Comparison of calculations using INDO-SS and INDO-S shows that the d-orbital participation is overemphasized by the Santry-Segal parametrisation while it is less important with the Santry parametrisation consistently with the minor role played by these orbitals in the bonding as shown by *ab-initio* calculations on thiophene[14].

iii) Method INDO-B with and without d-orbitals fails completely in accounting for the observation, yielding grossly underestimated coupling constants and in the case of the "restricted" basis set even one wrong sign.

Method	INDO-SS		INDO-S		INDO-B		Exp.[12]
Basis set	sp	spd	sp	spd	sp	spd	
J_{23}	4.23	7.85	4.07	4.41	2.75	1.51	4.90
J_{34}	3.18	3.42	3.51	3.51	1.94	1.41	3.50
J_{24}	2.22	2.81	2.33	2.38	−0.40	0.51	1.04
J_{25}	1.85	5.45	1.86	2.25	1.53	2.76	2.84

Table 1. Calculated and experimental proton-proton coupling constants (Hz) of thiophene.

Table 2. Calculated and experimental hyperfine coupling constants (G) of 2-thenyl radical.

Method	INDO-SS		INDO-S		INDO-B		Exp.[15]
Basis set	sp	spd	sp	spd	sp	spd	
H-3	− 8.58	− 6.52	− 9.15	− 9.10	− 6.53	− 5.50	8.26
H-4	3.36	3.48	3.66	3.85	4.64	3.24	1.62
H-5	− 6.64	− 4.52	− 6.96	− 6.87	− 7.16	− 4.31	7.89
CH_2	−14.25	−15.44	−13.68	−13.93	−14.67	−14.41	14.22
CH_2*	−13.80	−15.13	−13.38	−13.65	−14.04	−14.48	13.97

* Atom *trans* to sulphur.

Hyperfine coupling constants

The hcc's calculated by the individual methods and the experimental values are listed in Table 2. These data bring out the following points.

i) Methods INDO-SS and INDO-S employing the "restricted" basis set yield a satisfactory agreement with observation, only the H-4 splitting being overestimated. The agreement is slightly superior for the first method, which accounts quite well for the spectral inequivalence of the two methylene protons.

ii) The correlation provided by method INDO-B with sp basis set is less accurate than that obtained with methods INDO-SS and INDO-S. The internal order of the hcc's is not reflected.

iii) The inclusion of 3d orbitals does not bring about any remarkable difference in the results of method INDO-S; the correlation proves to be as good as that provided by the sp basis set. On the contrary, the effect of introducing 3d orbitals in methods INDO-SS and INDO-B is to give the protons distinctly different splittings with a comparatively poor agreement with experiment. These two methods lead indeed to larger spin-density in d-orbitals so that their polarizing effect on s-electrons of the hydrogens is overemphasized.

Conclusion

In the light of the foregoing results, the following conclusion emerges: Satisfactory predictions of nscc's and hcc's for sulphur-containing conjugated molecules and radicals can be obtained using the original INDO method with the minimal basis set of sp STO's and with either the Santry-Segal or Santry parametrisation. Indeed, the inclusion of d polarization functions on sulphur has proved (at least at the present level of parametrisation and sophistication) not to improve the quality of the results obtained by the only sp interaction so much as to justify the increased programming work and computer time.

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