Theoret. chim. Acta (Berl.) 23, 259—265 (1971)

Applications of the INDO Method to Some Radicals Containing Second Row Elements

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Received May 26, 1971

The INDO molecular orbital method has been extended to allow for the inclusion of second row atoms. Equilibrium geometries have been calculated for several radicals containing Si and Cl and their hyperfine coupling constants compared with results from ESR experiments. The calculations give chlorine hyperfine splittings in organic radicals in good agreement with recently reported experimental values.

Die INDO Molekularorbital-Methode wurde so erweitert, daß sie auch auf Atome der 2. Periode anwendbar ist. Es wurden die Gleichgewichtsgeometrien für einige Si und Cl enthaltende Radikale berechnet. Die ebenfalls errechneten Hyperfeinkopplungs-Konstanten werden mit Resultaten aus ESR Experimenten verglichen. Für organische Radikale erhält man Chlor-Hyperfein-Aufspaltungen in guter Übereinstimmung mit neueren experimentellen Werten.

1. Introduction

The INDO (intermediate neglect of differential overlap) technique was developed by Pople and his coworkers [1] as an approximate method for calculating single determinant wavefunctions involving all the valence electrons of a molecule. They formulated the method for an unrestricted wavefunction with different spatial orbitals for electrons of different spin and it forms a convenient means of estimating ESR hyperfine coupling constants [2] and also molecular geometries [3]. Since the original investigations [1–4] the method has been widely used for assigning hyperfine splittings [5] but we are not aware of any applications to radicals containing second row atoms. The CNDO method was extended to second row elements by Santry and Segal [6, 7]; values of the extra parameters needed for INDO calculations are suggested in this paper together the results of calculations on a number of radicals.

2. Parameterization

The diagonal elements of the H matrix in the INDO approximation are evaluated [1] in terms of ionization potentials, I, electron affinities, A, one centre coulomb integrals γ and the Slater-Condon parameters, F^2 and G^1. The two centre elements $H_{\mu\nu}$ require values of the semiempirical parameters β_A^0 which have been obtained for CNDO theory by fitting the calculations to *ab initio* results on small systems [6]. The electron interaction integrals can be determined from the Slater-Condon parameters [8].

In the present work the values of the Slater-Condon parameters for both first and second row elements were those of Hinze and Jaffe [9]. Values for F and Cl were obtained by extrapolation across the periodic table. Coulomb and

Table 1. *Parameters used in* INDO *calculations (energies in* eV*)*

Atom	ζ	F^0	G^1	F^2	$\frac{1}{2}(I+A)_s$	$\frac{1}{2}(I+A)_p$	$-U_{ss}$	$-U_{pp}$	$-\beta^0$
C	1.625	16.059	6.897	4.509	14.051	5.572	67.384	58.938	21.0
N	1.95	19.271	8.957	6.459	19.316	7.275	100.811	89.717	25.0
O	2.275	22.483	11.814	6.902	25.390	9.111	140.186	126.897	31.0
F	2.60	25.695	13.388	8.058	32.272	11.08	187.017	170.734	39.0
Si	1.383	9.7122	4.812	2.262	9.0	4.5	40.988	36.617	8.5
P	1.60	11.236	1.048	2.947	11.2	5.2	61.151	54.823	10.0
S	1.816	12.76	3.075	4.537	13.0	6.4	80.874	74.285	11.5
Cl	2.033	15.01	2.864	5.277	16.0	7.0	110.94	101.711	12.2

overlap integrals were evaluated in a basis of valence shell Slater orbitals using exponents determined by Slater's rules ($\zeta_H = 1.2$). We have not attempted to allow for valence shell expansion by including 3*d* orbitals in the basis set. The full choice of parameters for both first and second row elements are given in Table 1. The values of $1/2(I+A)$ and β^0 for second row elements are those of Santry [6]. The notation is the same as used by Pople [1], U_{ss} and U_{pp} being diagonal elements of the atomic core matrix. The values for first row elements differ slightly from those used previously [1, 4].

The calculations were performed using a program written for the University of Sussex ICL 1905 computer. In each cycle of the SCF procedure the F matrices for α and β spin were set up and diagonalised using the eigenvectors from the previous cycle. The process was repeated until consecutive α and β density matrices both differed by less than 10^{-5} in each of their elements.

3. Calculation of Equilibrium Geometries

By studying variations in the total energy of a molecular system with nuclear configuration Pople has shown that the INDO method is quite successful in reproducing experimentally known bond angles and is reasonably satisfactory in correlating bond lengths [4]. In the present work the following procedure was adopted. An overdetermined set of energies for the radical at different nuclear configurations was generated and fitted to a general quadratic in the variables defining the geometry using a least squares procedure. The values of the variables corresponding to the minimum energy were then obtained either by differentiating this quadratic with respect to each variable and solving the resultant first order equations, or by using a numerical minimization procedure applied to the quadratic. These two procedures yield identical results for the minimum energy conformation if the surface is quadratic over the limits of the calculation. A check can be made by choosing alternative expansion points for generating the quadratic surface.

For small radicals of the form AX_2, AX_2Y, and AX_4 we assumed C_{2v} symmetry and for AX_3 systems C_{3v} symmetry. The latter condition would be too restrictive for systems with electronically degenerate ground states; indeed Olsen and Burnelle have used the INDO method to study Jahn-Teller distortions in the radicals NO_3 and CO_3^- [10]. However in the present work only systems with non-degenerate ground states have been investigated. A number of assumptions have been made about the geometries of larger systems for which a full optimisation of the structure would be too time consuming. In organic radicals C–H bond lengths were taken as 1.08 Å, the angles about sp^2 hybridised carbon were taken as 120° and about sp^3 carbon as 109.45°. For aromatic radicals it is sometimes possible to use π-electron first-order bond-fixation theory to define a geometry and we have described elsewhere the application of this technique to the benzyl radical [11].

4. Calculation of Nuclear Hyperfine Splittings

The isotropic nuclear hyperfine coupling constant is given [2] by:

$$a_N = \{(4\pi/3)\, g\beta\gamma_N h \langle S_z\rangle^{-1} |\phi_{SN}(r_N)|^2\}\, \varrho_{SNSN}, \tag{1}$$

where ϱ_{SNSN} is the unpaired electron density in the valence s orbital of atom N and $|\phi_{SN}(r_N)|^2$ is the density of the valence s orbital evaluated at the nucleus. The quantity in brackets in Eq. (1) is a constant for each type of magnetic nucleus. The value of $|\phi_{SN}(r_N)|^2$ is difficult to evaluate explicitly and is treated as a disposable parameter which can be determined from the linear relationship between experimental values of a_N and calculated spin densities.

Correlations for a large number of radicals containing first row elements were made by Pople [2]; more recently Hirst [12] has performed INDO calculations on several pyridine anions and has suggested a new scaling factor for ^{14}N splittings [13]. Since we have used different Slater-Condon parameters, it has been necessary to rederive the scaling factors and these are given in Table 2. There is no obvious advantage in our choice of parameters for first row elements except that they are taken from the same source [9] as those used for second row atoms. The number of data points is low for some of the nuclei and it is likely that improved scaling factors will emerge when more calculations are available.

As is well known a single determinant unrestricted wavefunction is not an eigenfunction of S^2. However annihilation of contaminating quartet states produces a better approximation to the doublet state wavefunction [14]. We have

Table 2. *Correlations between observed a_N and calculated ϱ_{SNSN}*

Nucleus	No. of data points	$(4\pi/3)\, g\beta\gamma_N h\langle S_z\rangle^{-1}\lvert\phi_{SN}(r_N)\rvert^2$	Std. dev.	Correlation coefficient	$\lvert\phi_{SN}(r_N)\rvert^2$ a.u.$^{-3}$
Preannihilation					
^{1}H	65	564.76	2.27	0.9794	0.354
^{14}N	7	315.45	3.26	0.8074	1.949
^{19}F	8	39303.5	16.84	0.9548	26.160
^{35}Cl	10	1216.0	1.95	0.9627	77.134
Postannihilation					
^{1}H	65	814.4	2.73	0.975	0.510
^{14}N	7	482.43	3.22	0.814	2.981
^{19}F	8	39152.8	18.26	0.932	26.06
^{35}Cl	10	1288.4	1.92	0.964	82.286

included a spin annihilation routine in our program and the results of correlations with annihilated spin densities are also given in Table 2. As was found by Beveridge and Dobosh [15] there are no significant differences between the correlations using pre- and postannihilation spin densities. The correlation for protons which involves the largest number of data points is better than reported previously [2, 15], probably because we have used optimised geometries whereas Pople *et al.* used standard geometries [2]. The results of INDO calculations on a series of radicals derived from acetylenes and nitriles [16] have been incorporated in the correlations together with data for some fluorobenzyl radicals [17].

5. Discussion of Results

a) Tetra-Atomic Radicals

We consider first calculations on some radicals of structure AX_3, the results of which are summarised in Table 3. For the methyl radical we find an essentially planar structure in accord with previous INDO calculations [24] which gave $\widehat{HCH} = 119.7°$ for a C–H bond length of 1.08 Å. A more recent calculation [25] using a minimum basis of Gaussian fitted Slater type orbitals (STO-3G [26]) gave $R_{CH} = 1.08$ and $\widehat{HCH} = 118.3°$ with an inversion barrier of 0.19 kcal.-mole^{-1}. Use of an extended basis set (4-31G [27]) gave a planar geometry with $R_{CH} = 1.07$. Our results for CF_3 are also similar to those reported previously [24] and support the pyramidal structure deduced from the ESR spectrum [19].

The geometry of the trichloromethyl radical is a subject of some current interest. From a matrix isolation study of its infra-red spectrum Andrews [28] inferred that the radical was non-planar. However a reinvestigation of the spectrum [29] failed to reveal the band at 674 cm^{-1} previously attributed to the non-degenerate stretching fundamental ν_1 which is infra-red inactive for a planar molecule. Milligan and his coworkers therefore concluded that a pyramidal C_{3v} structure was not established. Qualitative arguments based on electronegativity differences [30] suggest that the radical should be non-planar and a similar conclusion was reached in a recent discussion [31] of the bonding in CCl_3. Our calculations support the idea of a pyramidal structure and predict a Cl–C–Cl bond angle of 114.3° intermediate between those of CH_3 and CF_3. The lower electronegativity of chlorine and increased steric interactions would account for the fact that CCl_3 is less pyramidal than CF_3. We can also predict the ^{13}C coupling

Table 3. *Calculated equilibrium geometries, spin densities ϱ (postannihilation values in brackets) and experimental isotropic hyperfine coupling constants a for tetra-atomic radicals*

Radical	R_{AX}	$\widehat{XAX}$	ϱ_{ns}^{A}	$\lvert a_A \rvert$	ϱ_{ns}^{X}	$\lvert a_X \rvert$	Refs.
CH_3	1.11	119	0.069 (0.052)	38.5	−0.037 (−0.024)	23.0	[18]
CF_3	1.32	111	0.246 (0.249)	271.6	0.0031 (0.0031)	142.2	[19]
CCl_3	1.73	114.3	0.216 (0.219)	—	0.0037 (0.0041)	6.25	[20]
SiH_3	1.60	110	0.259 (0.256)	199	0.0047 (0.011)	7.84	[21]
$SiCl_3$	2.33	109.4	0.442 (0.450)	416	0.0055 (0.0058)	13.4	[22]
$CFCl_2$	1.75 (C–Cl)	116 ($Cl\widehat{C}Cl$)	0.238 (0.243)	—	0.0073 (0.0075)	10.5	[23]
	1.31 (C–F)	102 ($F\widehat{C}Cl$)			0.0017 (0.0017)	84.6	

constant of CCl_3 using calculated spin densities for carbon 2*s* orbitals and known values for CH_3 and CF_3. Averaging the results obtained before and after spin annihilation we estimate the splitting as 190 *G*. In a recent analysis of chlorine hyperfine splittings [32] it was assumed that CCl_3 is planar. However the chlorine coupling constant (6.25 *G*) is larger than for alkyl radicals with one or two chlorine substituents such as CH_3CCl_2 (4.2 *G*) [33] $CH_2(OH)CCl_2$ (4.1 *G*) and $CH_2(OH)CHCl$ (2.8 *G*) [23]. We believe this indicates that the deviation from planarity increases with the number of chlorine substituents thus paralleling the behaviour of the ^{19}F splittings in the fluoromethyl radicals [19, 24].

Support for this analysis comes from results for the radical $CFCl_2$. It was suggested previously [23] that the increased chlorine coupling constant of $CFCl_2$ indicated it is more pyramidal than CCl_3. This is in accord with the higher electronegativity of F compared with Cl and possibly reduced steric interactions. The INDO calculations also predict a more pyramidal structure for $CFCl_2$ and successfully account for the increase in chlorine splitting. Moreover the calculated ^{35}Cl and ^{19}F coupling constants for both radicals are in good agreement with experiment.

We also obtain pyramidal structures for the silicon radicals SiH_3 and $SiCl_3$ in agreement with theoretical predictions [30] and ESR results [21, 22]. Earlier discussions of the shapes of the radicals $SiMe_nH_{3-n}$ [34, 35] were based upon a value of 266 *G* for the ^{29}Si coupling in SiH_3 [36] but it is now established [37] that the isotropic coupling is about 190 *G* [21]. This is very close to the results obtained for $SiMe_3$, $SiMe_2H$ and $SiMeH_2$ and suggests that the mean bond angles are insensitive to replacement of H by Me. It seems likely that the α–H coupling constants in all these radicals are positive [37], a conclusion supported by the INDO results for SiH_3. Averaging results obtained before and after spin annihilation, we estimate the proton splitting in SiH_3 to be 5.9 *G* in reasonable agreement with experiment but the calculated equilibrium geometry is more pyramidal than that deduced by Symons ($\widehat{HSiH} \sim 113–114°$) [37].

The non-planar geometry predicted for $SiCl_3$ is in agreement with matrix isolation studies of the infra-red spectrum [38] and ESR studies [22]. Large ^{29}Si splittings have also been found for the series of radicals Me_nSiCl_{3-n} [39] and it is clear that substitution of Cl for H or Me leads to successively more pyramidal structures. Our calculated equilibrium geometry is slightly more pyramidal than for SiH_3 but the difference is not as great as expected from the ^{29}Si splittings.

b) Organic Chloro-Radicals

Data has recently become available on the ^{35}Cl hyperfine coupling constants of several chloroalkyl radicals [23]. A feature of these results was the unusually large splitting found for 2-chloroethyl and it was suggested that the radical exists in an unsymmetrically bridged conformation with the chlorine atom eclipsing the odd electron orbital. The INDO results for some of these radicals are given in Table 4. For CH_2CH_2Cl and $CH(CH_2Cl)_2$ we adopted locked conformations with chlorine eclipsing the odd electron orbital, and took $R_{CH} = 1.08$, $R_{CC} = 1.536$, $R_{CCl} = 1.75$ Å, and regular trigonal and tetrahedral bond angles. The radical $CH_2C{\equiv}CCH_2Cl$ was taken as linear [16] with C–C bond lengths of 1.39, 1.22 and 1.46 Å, and free internal rotation of the CH_2Cl group.

Table 4. *Calculated and experimental hyperfine coupling constants (G) for some chlorine containing free radicals*

Radical	Nucleus	Experimental coupling constant	Calculated coupling constants preannihilation	Calculated coupling constants postannihilation	Refs.
$CFCl_2$	F	84.6	68.6	66.8	[23]
	Cl	10.5	8.9	9.7	
CCl_3	Cl	6.25	4.47	5.24	[20]
CH_2CH_2Cl	α-H	21.5	−20.2	−19.4	
	β-H	11.5	8.7	10.3	[23]
	Cl	17.4	19.6	19.4	
$CH(CH_2Cl)_2$	α-H	21.3	−18.7	−17.8	
	β-H	11.4	14.5	10.7	[23]
	Cl	14.2	13.2	13.0	
$CH_2C{\equiv}CCH_2Cl$	α-H	17.6	−18.8	−17.7	
	δ-H	9.7	11.2	12.4	[23]
	Cl	4.9	5.8	5.3	
$SiCl_3$	Cl	13.4	6.8	7.4	[22]

The results demonstrate that the INDO method reproduces ^{35}Cl coupling constants in good agreement with experiment and supports conclusions about molecular conformations drawn from ESR studies. Some improvement in the results might be expected if all the geometries were individually optimised but the level of agreement is sufficient for the calculations to be useful in interpreting experimental data.

6. Conclusions

The investigations of the INDO method reported in this paper suggest that it is likely to be useful for interpreting the ESR spectra of radicals containing second row atoms as has been amply demonstrated for first row elements [5]. We are currently studying the geometries and hyperfine coupling constants of radicals containing phosphorus and it will be interesting to see if reasonable results can be obtained without including 3*d* orbitals in the basis set. Recent *ab initio* SCF-MO calculations [40] suggest that this may not be the case and some extension of the present method may then be necessary. However the current parameterization seems to be adequate for calculations involving Si and Cl.

Acknowledgement. We thank the Rothermere Fellowship Trust for a fellowship to H.G.B. and Mr. M. F. Guest for assistance with the INDO program.

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