Theoret. chim. Acta (Berl.) 20, 292—298 (1971)

Relationes

INDO–MO Calculations of Hyperfine Splitting Constants for Pyridine Anions

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Received August 17, 1970

INDO–MO Calculations have been carried out on the anions of a variety of pyridine derivatives for which e.s.r. data have recently become available. The method gives reasonable results for proton hyperfine splitting constants but calculated nitrogen splitting constants are considerably larger than the experimental values. Some π-only calculations are included for the pyridine anion. All methods overestimate the spin density at the nitrogen atom. The orbital populations and excess charges for the pyridine molecule are not in agreement with those of an *ab initio* calculation.

1. Introduction

Pople *et al.* [1] have recently shown that the INDO (intermediate neglect of differential overlap) semi-empirical all valence electrons molecular orbital method [2] can successfully correlate the hyperfine splitting constants of a wide range of paramagnetic radicals and ions. However, their work only included one pyridine derivative, namely 4-cyano pyridine. Since the completion of their work, the e.s.r. spectra of the anions of a wide variety of pyridine derivatives have been observed both in this laboratory [3] and elsewhere [4]. We, therefore, considered that it would be worthwhile to examine the application of the INDO – MO method to these species.

2. Method and Results

Calculations were performed using the Fortran program of Dobosh [5] which carries out INDO calculations on open shell molecules using the unrestricted Hartree-Fock method of Pople and Nesbet [6]. Iteration proceeded until the energy changed by less than 10^{-6} a. u. Preliminary calculations with a modified version of Segal's program [7] indicated that slightly different results can be obtained depending on whether self-consistency in the energy or in the bond order matrices is used as the criterion of convergence. In view of the fact that the calculated spin densities in *s*-orbitals are small, especially for fluorine atoms, we feel that the criterion for self-consistency should be stated.

The anions considered are listed in Table 1 along with the results and experimental values for the hyperfine splitting constants. We did not consider methoxy pyridines because free rotation about two carbon-oxygen bonds makes the choice of a reasonable geometry impossible. It was not thought feasible to include pyridine dicarboxylic acids because further expansion of the basis set would make the computing time on the facilities available prohibitively long. Following Buick *et al.* [3] we assumed the carboxylate anions to have a double negative charge. The *N*-protonated species was also considered in the case of pyridine-2-carboxylic acid.

The experimental geometry of the ring of the pyridine molecule [8] was used and the C−H bond length was taken to be 1.08 Å for ring hydrogens. A C–C distance of 1.52 Å and a C−H distance of 1.09 Å were taken for the methyl group. For the carboxyl and nitro groups the following bond lengths and angles were taken: −C−O 1.23 Å, $\widehat{\mathrm{OCO}}$ 122°, C−C 1.53 Å; N−O 1.21 Å, $\widehat{\mathrm{ONO}}$ 124°, N−C 1.48 Å. The C−F bond length in 2−fluoro pyridine was assumed to be 1.30 Å. Bonds to the ring atoms were assumed to bisect the ring angles.

Two different configurations were taken for the monomethyl derivatives. In the first ('staggered') the methyl group was oriented so that one hydrogen was above the plane of the ring and the other two symmetrically below. In the 'eclipsed' configuration, one hydrogen was in the plane of the ring and the other two symetrically above and below the plane. The methyl hydrogen splitting constants reported in the Table 1 are the averages of the three individual values. This is a crude way of taking into account the free rotation of the methyl group. Since there was very little difference between the results for the two configurations, only the 'staggered' configuration was used for the dimethyl derivatives.

Table 1. *Calculated and experimental hyperfine splitting constants for anions of pyridine derivatives*

	Position	Calculated (gauss)		Experimental (gauss)	Reference
Pyridine	N	8.02		6.31	[a]
	2	− 3.75		3.55	
	3	0.36		0.79	
	4	− 8.75		9.63	
2-fluoropyridine	N	7.17		4.82	[b]
	F	−13.95		7.12	
	3	− 1.57		1.07[e]	
	4	− 8.99		8.31	
	5	1.94		3.67	
	6	− 5.92		4.62[e]	
		staggered	eclipsed		
2-Methyl pyridine	N	8.08	8.06	5.64	[a]
	Me	6.07	5.87	2.34	
	3	1.95	1.51	1.56	
	4	−8.21	−8.23	9.53	
	5	−0.42	−0.39	<0.1	
	6	−2.90	−2.93	4.39	
3-Methyl pyridine	N	7.81	7.77	6.34	[a]
	2	−2.70	−2.54	4.07	
	Me	0.88	1.18	0.45	
	4	−9.14	−9.14	9.61	
	5	0.66	0.70	1.35	
	6	−4.20	−4.25	2.68	

Table 1 (continued)

	Position	Calculated (gauss)		Experimental (gauss)	Reference
4-Methyl pyridine	N	7.67	7.67	5.67	a
	2	−2.94	−2.94	3.68	
	3	−0.35	−0.35	0.058	
	Me	14.27	14.26	11.31	
3,5-Dimethylpyridine	N	7.71		6.40	a
	2	−3.14		3.18	
	Me	0.28		1.06	
	4	−9.51		8.85	
2,6-Dimethyl pyridine	N	8.23		4.86	a
	Me	4.30		3.16	
	3	0.85		0.71	
	4	−8.10		9.29	
2,3-Dimethyl pyridine	N	8.04		5.78	
	2(Me)	4.24		2.89	a
	3(Me)	−1.36		0.46	
	4	−8.73		8.66	
	5	0.07		0.82	
	6	−3.36		2.89	
		N-protonated			
Pyridine-2-carboxylic acid	N	5.66	7.83	4.1	a
	3	2.36	0.57		
	4	−8.75	−8.08	5.5	
	5	3.79	−1.31		
	6	−7.05	−1.42	4.1	
	H(N)	−9.48			
Pyridine-3-carboxylic acid	N	7.78		1.64	a
	2	−2.88		1.09	
	4	−8.42		7.28	
	5	1.93		0.47	
	6	−5.61		8.83	
Pyridine-4-carboxylic acid	N	8.07		5.51	a
	2	−4.38		1.96	
	3	0.86		1.96	
3-Nitropyridine	N(ring)	−1.54		1.31	c
	2	−2.78		3.19[f]	
	4	−3.39		3.68[f]	
	5	1.79		1.07[f]	
	6	−3.03		4.52[f]	
	$N(NO_2)$	8.87		9.04	
4-Nitro pyridine	N(ring)	3.89		2.55	d
	2	1.19		3.00[f]	
	3	−3.28		0.53[f]	
	$N(NO_2)$	6.10		8.72	

[a] Buick, A. R., Kemp, T. J., Neal, G. T., Stone, T. J.: J. chem. Soc. (London) A **1969**, 1610.

[b] Buick, A. R., Kemp, T. J., Neal, G. T., Stone, T. J.: J. chem. Soc. (London) A **1969**, 666.

[c] Cottrell, P. T., Rieger, P. H.: Molecular Physics **12**, 149 (1967).

[d] Itoh, M., Okamoto, T., Nagakura, S.: Bull. chem. Soc. Japan **36**, 1665 (1963).

[e] Not distinguished.

[f] Assigned on basis of MO-Calculations.

3. Discussion

In general the calculated proton hyperfine splitting constants are in reasonable agreement with the experimental values. The standard deviation is 1.53 compared with 7.29 in the work of Pople *et al.* [1]. The agreement is much poorer for nitrogen coupling constants, the calculated constants being considerably larger than the observed values in almost all cases. The standard deviation is 2.50 compared with the value of 2.34 obtained by Pople *et al.* [1]. However, inspection of the results of Pople *et al.* shows that for aromatic systems containing nitrogen the calculated coupling constants are generally larger than the observed values. The calculated fluorine coupling constant in 2-fluoropyridine is in poor agreement with the experimental value. However, the experimental value is relatively small compared with those considered by Pople *et al.* [1]. The spin density in the 2*s* orbital of fluorine is small (using the experimental coupling constant and the proportionality constant of Pople *et al.* gives an 'experimental' spin density of 0.00016) and is understandably not well reproduced theoretically.

The results for pyridine-2-carboxylic acid do not give conclusive evidence supporting either the unprotonated species or the protonated species.

The small differences between the results for the 'staggered' and the 'eclipsed' configurations for the monomethyl pyridines suggest that taking the average of the three proton splitting constants in the 'staggered' configuration makes reasonable allowance for the free rotation of the methyl group.

It is worthwhile considering why the agreement for nitrogen splitting constants is poor. The work of Pople *et al.* [1] included 29 nitrogen splitting constants. This work considers a further 15 constants and thus significantly increases the total number to be considered. Therefore, it seems to us that the least squares determination of the proportionality constant relating spin density and hyperfine splitting constant should be repeated with the larger sample now available. This work is in progress.

A possible reason for the poor agreement is that the paramaterization of the INDO method is such that the π-electron spin densities are not in good agreement with the experimental values. The calculated π-electron spin densities for the pyridine anion are given in Table 2 along with the experimental values of Buick *et al.* [3] and the values they obtained from Hückel and McLachlan calculations. The INDO method clearly puts too much spin density on the nitrogen atom suggesting that the parameterization is not optimum.

For comparison we made some semi-empirical π-electron SCF calculations. From the variety of methods and parameters reported in the literature we selected two methods and two parameterization schemes. Firstly we used the unrestricted Hartree-Fock (U. H. F.) method of Pople and Nesbet [6] and also included the spin annihilation procedure of Amos and Snyder [9]. Spin annihilation was not included in the INDO calculations since Beveridge and Dobosh [18] concluded that the presence of contaminating spin components in the unrestricted wavefunction does not introduce any serious errors. We also used Adams and Lykos' [10] version of Roothaan's open shell SCF method (R. H. F.) [11] and included pseudo doubly excited configurations by the method of Hoijtink [12]. The calculations were made with QCPE program 77.1 [13]. We used the parameters

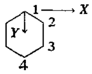
Table 2. *π-Electron spin densities for the pyridine anion*

Atom	N	2	3	4
INDO	0.463	0.087	−0.024	0.410
Expt[a]	0.226	0.150	0.033	0.408
Hückel[a]	0.258	0.143	0.059	0.338
McLachlan[a]	0.273	0.148	0.011	0.408
UHF	0.403	0.050	0.019	0.459
	(0.460)[b]	(0.072)	(−0.055)	(0.505)
UHF with spin annihilation	0.350	0.068	0.052	0.407
	(0.391)[b]	(0.073)	(0.019)	(0.425)
RHF	0.303	0.079	0.075	0.388
	(0.318)[b]	(0.071)	(0.068)	(0.404)
RHF with perturbation theory	0.358	0.056	0.047	0.437
	(0.382)[b]	(0.042)	(0.036)	(0.461)

[a] Buick, A. R., Kemp, T. J., Neal, G. T., Stone, T. J.: J. chem. Soc. (London) A **1969**, 1610.

[b] Using Mataga-Nishimoto integrals.

Table 3. *Orbital populations, excess charges and dipole moment for the pyridine molecule*



(a) *Orbital Populations*

Atom	2s	$2p_x$	$2p_y$	$2p_z$	1s
N	1.4873	1.0939	1.5339	1.0733	
C2	1.0407	0.8958	0.9509	0.9577	
C3	1.0410	0.9541	1.0011	1.0303	
C4	1.0363	1.0094	0.9351	0.9507	
H2					1.0445
H3					1.0116
H4					1.0245

(b) *Excess Charges*

	This work			Emsley[a]	Clementi[b]
Atom	σ	π	total	Total	Total
N	−0.1151	−0.0733	−0.1884	−0.3750	−0.2262
C2	+0.1126	+0.0423	+0.1549	+0.2149	−0.1097
C3	+0.0038	−0.0303	−0.0265	−0.0816	−0.2252
C4	+0.0192	+0.0493	+0.0685	+0.0518	−0.2024
H2	−0.0445			+0.00004	+0.2217
H3	−0.0116			+0.02186	+0.2171
H4	−0.0245			+0.01293	+0.2203

(c) *Dipole Moment*

Calculated	*Expt*[c]
2.087 D	2.2 D

[a] Emsley, J. W.: J. chem. Soc. (London) A **1968**, 1387.

[b] Clementi, E.: J. chem. Physics **46**, 4731 (1967).

[c] McLellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman 1963.

of Hinchcliffe *et al.* [14] and repeated the calculations using the Mataga-Nishimoto method [15] for calculating two electron repulsion integrals. The results are in Table 2. It can be seen that, in general, the π-electron methods also overestimate the spin density on the nitrogen atom. The best results are given by the RHF method without mixing in excited states by perturbation theory. The use of Mataga-Nishimoto integrals gives poorer results.

Although the INDO method is able to correlate successfully a wide range of hyperfine splitting constants, perhaps the calculated spin densities should be regarded with a certain amount of circumspection. It has been pointed out by Emsley [16] that for the pyridine molecule, although the CNDO/2 method gives good agreement with the experimental dipole moment, the orbital population and excess charges are not in agreement with those of the *ab initio* calculation of Clementi [17]. We have carried out an INDO calculation on pyridine and, as Table 3 shows, the results are very similar to these of Emsley [16]. In particular the hydrogen atom populations are very different from those of Clementi [17]. In view of the considerable discrepancy between the INDO populations and the *ab initio* populations for the closed shell species we feel that spin densities calculated by the INDO method should be treated with some reserve.

4. Conclusions

The INDO method successfully correlates the proton hyperfine splitting constants for the anions of a variety of pyridine derivatives. Agreement for the nitrogen splitting constants is less good. It is felt that in view of the fact that this work considerably augments that of Pople *et al.* [1], the factor relating spin density and hyperfine splitting constant should be recalculated.

The poor agreement may also be a consequence of the parameterization because the calculated π-electron spin density on the nitrogen atom is much larger than the experimental value.

Acknowledgements. The author wishes to thank Drs. Kemp and Stone for bringing this problem to his attention. He is grateful to the Science Research Council for the provision of computer time on the S. R. C. Atlas computer and to Mrs. A. Baker and Mr. M. Claringbold of the Atlas Computer Laboratory for their assistance with the computer programs.

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