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Relationes

Uncoupled Hartree-Fock Calculations of the Ring Current Properties of some Heterocyclics

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It is shown that uncoupled Hartree-Fock perturbation theory may be successfully applied to the determination of the ring current properties of heterocyclics.

Introduction

Uncoupled Hartree-Fock perturbation theory (UPT) has recently been applied to the calculation of the ring current contributions to both the diamagnetic susceptibility of, and the proton chemical shifts in conjugated hydrocarbons [1, 2]. One of the prime motives for that work was to demonstrate that UPT results approximate those obtained using the computationally more complicated coupled approach (CPT) [3, 4]. It was found that this was true if and only if certain correction terms were added to the UPT results. The geometric approximation (GA), which hitherto had only been applied to polarizability calculations [5], seemed indispensable as an aid to the correct prediction of these terms. More recently [6], by applying a procedure first developed by Feenberg and Goldhammer, the use of the GA has been justified.

It is, therefore, with some confidence that we have applied the UPT plus GA technique to investigate the role played by ring currents in a few selected heterocyclics. The molecules we have chosen have already been analysed by Hall, Hardisson and Jackman in 1962 [4]. The problem of choosing a suitable set of semi-empirical parameters to be used in the Pariser-Parr-Pople model of the molecule has never been fully resolved. The hope was expressed in Ref. [4] that a comparison of theoretical and experimental results for the magnetic properties of heterocyclics might prove valuable in establishing the size of certain parameters. For this reason, the CPT calculations were performed using different parameter sets. However, this hope was never fully realized, mainly due to the fact the experimental results describing the ring current effects were more qualitative than quantitative. It was not our object, then, to apply UPT using the parameters of Ref. [4] but, rather, to choose what appears to be a reasonably consistent parameterization and to demonstrate that UPT then gives results in accord with the qualitative observations of the experimentalist (however, a few test programs were run using parameters from Ref. [4] in order to ensure that our results did indeed approximate those obtained in that paper).

Results and Discussion

The following molecules were considered: – pyridene (A), pyrimidene (B), *S*-triazine (C), 1-methyl-2-pyridone (D), 1-methyl-4-pyridone (E), 1-methyl-2-cyclopentadienyl-1,2-dihydropyridene (F) and 1-methyl-4-cyclopentadienyl-1,2-dihydropyridene (G). Nomenclature and numbering are given in Fig. 1. For the purposes of the calculation an $\rangle N{-}CH_3$ group is represented as a pyrrole type nitrogen and written $\ddot{N}$ to signify that it contributes two electrons to the π system. A pyridene type nitrogen is correspondingly written as $\dot{N}$. All rings were taken to be regular polygons with sides equal to 1.4 Å, and the C–H bond distance was fixed at 1.08 Å.

In order to conform with the choice of parameters in previous calculations [1, 2] the following were fixed: $\beta_{CC} = -2.39$ eV, $I_C = 11.42$ eV, $E_C = 0.58$ eV and the two-electron γ integrals were found using the method of Mataga and Nishimoto [7]. Values consistent with these for the ionization potentials and electron affinities of $\ddot{N}$, $\dot{N}$ and O were then obtained from Pritchard and Skinner [8]. $\beta_{C\dot{N}}$ was fixed at -2.576 eV [9] and $\beta_{C\ddot{N}}$ at -2.45 eV [10]. It then remains to find a suitable value for β_{CO}. Brown and Heffernan [11] have found a value for this parameter which is spectroscopically consistent with their VESCF method. Comparing this with their other β parameters (e.g. Ref. [12]) it was decided to fix β_{CO} at -2.90 eV and the C=O bond distance at 1.23 Å, A full parameter list appears in Table 1.

Having decided on the parameterization, the SCF matrix can be built up in the usual way and the calculation for finding the diamagnetic susceptibility and chemical shifts proceeds as described in [1] and [2].

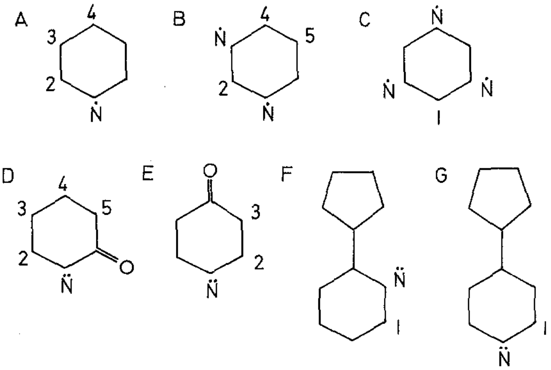

Fig. 1. Molecular labelling

Table 1. *Parameters of the calculation*[a]

Atom X	β_{CX}	I_X	E_X
C	−2.39	11.42	0.58
$\dot{N}$	−2.576	14.49	1.58
$\ddot{N}$	−2.45	27.50	13.79
O	−2.90	17.28	2.70

[a] Values quoted are in eV.
I denotes ionization potential and *E* denotes electron affinity.

Table 2. *Ring current properties of molecules A-G*

Molecule	Proton	Susceptibility Absolute[a]	Susceptibility Ratio[c]	Chemical shift Absolute[b]	Chemical shift Ratio[d]
A	2	31.5	1.01	2.52	1.01
	3			2.52	1.01
	4			2.52	1.01
B	2	31.2	1.00	2.50	1.00
	3			2.50	1.00
	5			2.50	1.00
C	1	30.9	0.99	2.42	0.97
D	2	11.4	0.36	0.85	0.34
	3			0.79	0.32
	4			0.72	0.29
	5			0.84	0.34
E	2	10.3	0.33	0.61	0.24
	3			0.66	0.26
F	1	18.5	0.59	0.83	0.33
G	1	16.4	0.53	0.49	0.20

[a] Units of -10^{-6} cgs emu.
[b] Units of (-1) ppm.
[c] Benzene value equals 31.2 [1].
[d] Benzene value equals 2.50 [2].

The results are displayed in Table 2. Elvidge and Jackman [13] have predicted that the "aromaticity" of molecule *D* should be 0.35 ± 0.05 (this term being defined as an ability, relative to benzene, of being able to sustain an induced ring current). They have also shown [4] that the ring current contributions in the 2-series (*D* and *F*) should be greater than in the corresponding 4-series (*E* and *G*), and, further, that the contribution to the chemical shift in *D* should be approximately equal to that in F for the protons α to nitrogen. It is seen that these predictions are completely confirmed in the present calculations.

Results for molecules *A*, *B* and *C* are also included and we may note that, in the case of pyridene, the theory predicts a slightly larger ring current than for benzene. However, this is not to be taken as being significant since a change in the carbon-nitrogen resonance integral can easily be made to produce a value lower than that for benzene (e.g. $\beta_{C\dot{N}} = \beta_{CC} = -2.39$ eV gives a ratio to benzene for the chemical shifts in pyridene equal to 0.98).

We may note that, in the case of the susceptibilities, the results are those calculated at the centre of charge of the particular molecule. Values were also obtained with the origin at other positions but, as in [1], it was found that the results were independent of the choice of origin as long as the GA was used to calculate the correction terms.

It has been shown [2, 14] that ring current susceptibility and shielding values for hydrocarbons can be well approximated by applying a scaling factor $\lambda \Omega$ 0.5 to the results obtained using the Hückel method. However, it is well known that the latter is not reliable when applied to heterocyclics. Ref. [4] gives a detailed account of the shortcomings of the Hückel approach in molecules *D–G* and it is evident that there is little hope of being able to set up a general formula to obtain a suitable λ for any given molecule while still retaining the basic simplicity of the Hückel approach. Nevertheless, one might expect that a simple λ-technique would possibly emerge if one applied the Hückel procedure using the SCF. matrix as the zero order hamiltonian. Let us suppose then that we require, say, the ring current contribution to the susceptibility of molecules F and G. These being isomeric, we would expect to be able to use approximately equal λ values in the two cases. However, this method gives values 0.96 and 0.74 ($\times -10^{-6}$ cgs emu) respectively. The corresponding λ values would then have to be 0.61 and 0.72.

It would seem then that satisfactory results may only be achieved by using a complete SCF approach and that, at least in the case of heterocyclics, short cuts via the Hückel formalism should be avoided.

In recent years, a great deal of attention has been given to finding theoretical estimates for what may be described as the local contributions to proton shielding (e.g. [15] and the references contained therein). It would seem, however, from the arbitrary nature of some of the current procedures, that there is still some way to go before we can claim to have a complete picture of the processes involved. For this reason it is not the purpose of this note to attempt to correlate the theoretical and experimental results in an absolute sense.

Conclusions

In calculations of the ring current contributions to the magnetic properties of heterocyclics we have shown that uncoupled Hartree-Fock perturbation theory using the geometric approximation, while being much easier to apply than the corresponding coupled theory, yields results which are no less accurate. Further, the use of any form of Hückel theory should be avoided in this particular case.

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