Theoret. chim. Acta (Berl.) 1, 302—307 (1963)

Institute of Physical Chemistry, University of Padua, Italy

Molecular Orbital Study of Hyperfine Splitting Constants in Ethyl and Cyclohexadienyl Radicals

By

PIERLUIGI NORDIO, MARIA V. PAVAN and GIOVANNI GIACOMETTI

Hyperconjugated models are used for a m.o. calculation of proton h.f.s. constants in Ethyl and Cyclohexadienyl radicals. A slightly modified Pariser-Parr-Pople SCF method is employed including extensive configuration interaction. The calculated spin densities for the hyperconjugated protons are in good agreement with experiment.

Zur Berechnung von Protonenhyperfeinstrukturkonstanten von Äthyl- und Cyclohexadienyl-Radikalen werden Modelle mit Hyperkonjugation verwendet. Die Rechnung gründet sich auf eine leicht modifizierte Pariser-Parr-Pople-Methode einschließlich ausgedehnter Konfigurationswechselwirkung. Die berechneten Spin-Dichten für die hyperkonjugierten Protonen stimmen mit experimentell ermittelten Werten gut überein.

Des modèles tenant compte à la hyperconjugaison sont usés pour le calcul des constantes de structure hyperfine protonique des radicaux éthyl et cyclohexadiényl. Le calcul se base sur une méthode Pariser-Parr-Pople un peu modifiée et comprenant une interaction de configurations extensive. Les densités de spin calculées pour les protons hyperconjugués sont en bon accord avec des valeurs expérimentales.

The hyperfine structure in electron spin resonance spectra arising from methyl group protons has been considered strong direct evidence of the formal operation of a hyperconjugation mechanism.

The case of π electron radicals and ions containing CH_3 groups has been treated using the simple Hückel procedure for hyperconjugated models [*1, 2*], or the valence bond method [*11, 12*]. Both treatments give rather good account of the experimental unpaired spin density on the methyl protons but the formal responsability of hyperconjugation in determining the phenomenon is still to be settled.

It seemed desirable to investigate further this point on the ground of more elaborate and less empirical theoretical methods.

More so in view of the fact that in some instances such extensions as introduction of configuration interaction in the m.o. calculations may change quite significantly the pattern of the spin densities from the one deduced by more simple calculations.

On the other hand it is surprising that the cases of radicals containing a possibly hyperconjugated methylene group, such as cyclohexadienyl [*7*], formyl imino radical [*3*], pyracene ion [*4,5*] etc. have not been taken into much consideration in spite of their very specific configuration and their unusually high coupling constants for the methylene protons.

It is our purpose in this paper to show that in fact formal hyperconjugation treated by a fairly complete m.o. method such as the Pariser-Parr-Pople (P.P.P.)

ASMO-CI maintains its leading role in accounting for hyperfine structure constants in ethyl and cyclohexadienyl radicals which we choose as typical examples of conjugated methyl and methylene systems.

Analogous calculations on the formylimino radical and other more complex systems are in progress.

Outline of the method

The method employed for both molecules is a configuration interaction procedure similar to the one already used for NH_3^+ radical [*9*].

Owing to the much more complex nature of the systems the simplifications of Pariser-Parr-Pople were adopted throughout and the *SCF* orbitals to be used for configuration interaction were taken as closed shell orbitals of a system containing one more electron than the actual radicals.

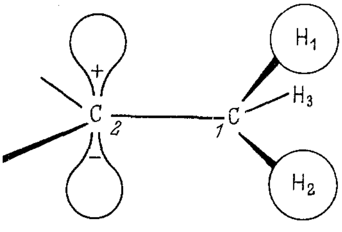

Fig. 1

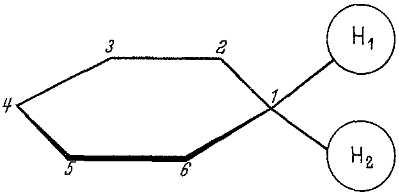

Fig. 2

Ethyl radical (Fig. 1) is treated as a three orbital system: $2p_z$ of C_2, $2p_z$ of C_1 and the correct symmetry orbital over the 1*s* hydrogen functions of the methyl group.

Table 1

Integrals and "core" parameters used in calculations

$(pcpc \mid pcpc)$	11.08 eV
$(1s_h 1s_h \mid 1s_h 1s_h)$	12.848 eV
β_{12}	— 1.886 eV
β_{23}	— 2.365 eV
W_C	11.54 eV
W_H (ethyl)	9.63 eV
W_H' (cyclohex.)	9.12 eV

Cyclohexadienyl (Fig. 2) is treated in an analogous way as a seven orbital system: $2p_z$ of C_2 to C_6, $2p_z$ of C_1 and the symmetry orbital over the 1*s* hydrogen functions of the methylene group.

The geometry of the two molecules is assumed as follows: valence angles of C_1 regular tetrahedral in both cases; $C_1 - C_2$ distances (and $C_1 - C_6$ for cyclohexadienyl) 1.48 Å; the other $C - C$ distances in cyclohexadienyl 1.39 Å and the other valence angles regular trigonal of 120°.

The values used for monocentric electron repulsion integrals, ionization potentials, and core integrals β are listed in Tab 1.

The parameters involving the hydrogen orbital require some comment.

The ionization potentials for the pseudo π-orbital

$$\psi_1 = (2 - 2\,S)^{-\frac{1}{2}} (1s_{h1} - 1s_{h2}) \qquad (1)$$

have been obtained by solving in the usual way the three or two electron problem for the pseudo-atoms H_3 or H_2.

In particular W_H (ethyl) has been taken as the energy of ψ_1 in the field of the three nuclei and the two other electrons described by the functions:

$$\psi_2 = (6 - 6\,S)^{-\frac{1}{2}}\,[1s_{h1} + 1s_{h2} - 2\,(1s_{h3})],$$

$$\psi_3 = (3 + 6\,S)^{-\frac{1}{2}}\,(1s_{h1} + 1s_{h2} + 1s_{h3}) \qquad (2)$$

One obtains, with random spins:

$$-W_H = e_1 = \langle \psi_1 \mid H^c \mid \psi_1 \rangle + (\psi_1\psi_1 \mid \psi_2\psi_2) - \frac{1}{2}(\psi_1\psi_2 \mid \psi_1\psi_2) + + (\psi_1\psi_1 \mid \psi_3\psi_3) - \frac{1}{2}(\psi_1\psi_3 \mid \psi_1\psi_3)$$

In analogy, for W_H' (cyclohexadienyl):

$$-W_H' = e_1' = \langle \psi_1 \mid H^{c'} \mid \psi_1 \rangle + (\psi_1\psi_1 \mid \psi_2'\psi_2') - \frac{1}{2}(\psi_1\psi_2' \mid \psi_1\psi_2')$$

with

$$\psi_2' = (2 + 2\,S)^{-\frac{1}{2}}\,(1s_{h1} + 1s_{h2}).$$

All integrals contained in the above expressions have been approximated by the Mulliken formula [*13*] and the ultimate integrals over atomic orbitals evaluated theoretically by using Preuss and Roothaan's tables [*14, 15*] of integrals for Slater functions with such exponents as to reproduce the value of 12.848 eV for the monocentric $(1s_h 1s_h \mid 1s_h 1s_h)$ found in the literature [*16*]. In the SCF calculation on the closed shell ions and in the configuration interaction on the actual radicals, the usual "zero differential overlap" approximation has been used but the following two slight modifications of the conventional P.P. procedure have been adopted:

a) Nuclear attraction integrals over atomic orbitals ψ_i of the type

$$\int \psi_i^*(1)\,H_\alpha(1)\,\psi_i(1)\,d\tau_1 \qquad (3)$$

arising from the core part of the hamiltonian ($H_\alpha(1)$ is the interaction potential between electron 1 and the "core" of nucleus α) have been considered explicitly instead of approximating them with the usual transformation into penetration and electron repulsion integrals. This makes easier to include penetration terms which are usually neglected in spectroscopic calculations but whose effect on the shape of the m.o.'s is difficult to estimate.

b) All integrals of type (3) and of the electronic repulsion type:

$$\int\int \psi_i^*(1)\,\psi_i(1)\,\frac{e^2}{r_{12}}\,\psi_j^*(2)\,\psi_j(2)\,d\tau_1\,d\tau_2 \qquad (4)$$

are calculated theoretically by choosing exponents of the Slater function with the same criterion stated above*. We consider this way of estimating integrals,

---

* In the cases where orbital ψ_1 appears, "zero differential overlap" is applied to such an orbital in "toto". The integrals of type $(p_z p_z \mid \psi_1\psi_1)$ reduce to $(p_z p_z \mid 1s_h 1s_h)$ following Mulliken approximation:

$$(p_z p_z \mid \psi_1\psi_1) = (2 - 2\,S)^{\frac{1}{2}}\,((p_z p_z \mid 1s_1 1s_1) - 2\,(p_z p_z \mid 1s_1 1s_2) + (p_z p_z \mid 1s_2 1s_2)) =$$

$$= (2 - 2\,S)^{\frac{1}{2}}\,[(p_z p_z \mid 1s_1 1s_1) - S\,((p_z p_z \mid 1s_1 1s_1) + + (p_z p_z \mid 1s_2 1s_2)) + (p_z p_z \mid 1s_2 1s_2)] =$$

$$= \frac{1}{2}\,((p_z p_z \mid 1s_1 1s_1) + (p_z p_z \mid 1s_2 1s_2)) = (p_z p_z \mid 1s_1 1s_1).$$

when possible without too much labour, as in the present case, more reasonable than the parabolic interpolation of PARISER and PARR, owing to the more realistic behaviour of the integrals for distances of the order of bond lenghts.

For the core integral β_{CH} involving the orbitals on C_1 and the hydrogen pseudo π-orbital ψ_1 a value of 4.0 eV has been adopted.

The configuration interaction extends over the 4 monoexcited doublets of ethyl and the 14 ones of cyclohexadienyl having the symmetry of the ground state.

The SCF iteration and the diagonalization of the C.I. matrices have been made by electronic computer on the Elea 6002 of the University of Padua.

Results and discussion

The SCF m.o.'s for the closed shell negative ions are listed in Tab. 2 and 3. In Tab. 4 and 5 the resulting spin density matrices are reported together with the final spin densities on atomic orbitals.

The coupling constant of the methylene protons is given by

$$a_H = Q^{(H_2)}\,\varrho_H$$

where

$$Q^{(H_2)} = \frac{8\pi}{3}\,g_H\,\beta_H\,\frac{(1s_{h_1} - 1s_{h_2})^2}{(2 - 2\,S)}$$

which is 330 gauss taking normal hydrogen 1s functions.

Table 2

Ethyl Negative Ion SCF Molecular Orbitals

$$\varphi_1 = 0.2062\,p_1 + 0.7538\,p_2 + 0.6239\,\psi_1$$
$$\varphi_2 = 0.9154\,p_1 + 0.0766\,p_2 - 0.3951\,\psi_1$$
$$\varphi_3 = 0.3456\,p_1 - 0.6526\,p_2 + 0.6743\,\psi_1$$

Table 3. *Cyclohexadienyl Negative Ion SCF Molecular Orbitals*

$$\varphi_1 = 0.5094\,\psi_1 + 0.7312\,p_1 + 0.2647\,(p_2 + p_6) + 0.1597\,(p_3 + p_5) + 0.1216\,p_4$$
$$\varphi_2 = -0.2797\,\psi_1 - 0.2537\,p_1 + 0.2060\,(p_2 + p_6) + 0.4611\,(p_3 + p_5) + 0.5893\,p_4$$
$$\varphi_3 = 0.5113\,(p_2 - p_6) + 0.4885\,(p_3 - p_5)$$
$$\varphi_4 = -0.3616\,\psi_1 - 0.0360\,p_1 + 0.5220\,(p_2 + p_6) + 0.0103\,(p_3 + p_5) - 0.5682\,p_4$$
$$\varphi_5 = 0.4885\,(p_2 - p_6) - 0.5113\,(p_3 - p_5)$$
$$\varphi_6 = 0.5099\,\psi_1 - 0.3748\,p_1 - 0.1094\,(p_2 + p_6) + 0.4114\,(p_3 + p_5) - 0.4868\,p_4$$
$$\varphi_7 = 0.5210\,\psi_1 - 0.5091\,p_1 + 0.3211\,(p_2 + p_6) - 0.3041\,(p_3 + p_6) + 0.2795\,p_4$$

In the case of methyl protons a factor of 2/3 must be introduced to allow for equivalence of the three hydrogens due to supposed free rotation.

The results for h.f.c. of methyl and methylene protons are thus 21.6 gauss and 42.9 gauss for ethyl and cyclohexadienyl respectively in good agreement with the experimental values of 26.9 [6] and 50 ± 2 [7] gauss.

For the other protons the usual "spin polarization" model reproduces the experimental values of the h.f.c.'s (Tab. 6) by using $Q^{H}{}_{CH}$ values of 24.1 gauss, for ethyl and 27.7 for cyclohexadienyl both in the generally accepted range between 22.5 and 28 gauss.

Table 4

Ethyl Molecular Orbital Spin Density Matrix

0.0048	0.0135	0.0324
	0.9704	0.1627
		0.0248

Atomic Spin Densities

$\varrho_1 = 0.93$
$\varrho_2 = -0.03$
$\varrho_H = 0.10$

The only empirical parameter, not previously tested, used in our calculation is β_{CH} whose value is however in agreement with a rough evaluation by using MULLIKEN's magic formula.

Table 5. *Cyclohexadienyl Molecular Orbital Spin Density Matrix*

0.0012	0	—	0.0026	—	—0.0014	0.0324
	0.0107	—	—0.0019	—	—0.0910	0.0430
		0.0190	—	0.1339	—	—
			0.9359	—	0.0263	0.0382
				0.0190	—	—
					0.0095	—0.0030
						0.0047

Atomic spin densities

ϱ_H .... = 0.13
ϱ_1 .... = —.003
ϱ_2 (orto) .... = 0.36
ϱ_3 (meta) .... = —0.10
ϱ_4 (para) .... = 0.38

Table 6. *Coupling Constants of "Aromatic" Protons*

		exp.	calc.
Ethyl	a_2	22.38	fitted with $Q^H{}_{CH} = 24.1$
Cyclohexadienyl	a_2	10.6 ± 0.5	9.97
	a_3	2.6 ± 0.2	—2.77
	a_4	10.6 ± 0.5	10.53

The above results are indicating that the m.o. hyperconjugation model is still a very good description of the spin densities also at a more elaborate level. The difference between such a description and the McLachlan v.b. model in which mainly spin polarization occurs is not only formal in such that an experimental test would be possible in principle by measuring the ^{13}C c.c. of the methyl or methylene groups.

The v.b. treatment predicts in fact a high spin polarization of the carbon 2*s* electrons while the m.o. procedure does not take explicitly into account *s* type electrons. The effect can be however discussed as in fact has been done by Strauss and Fraenkel in their paper on ^{13}C splittings [*17*]. Their results seem to be more in agreement with the m.o. conclusions.

A further point in support of this idea can be found in the fact that systems of the type:

show a high ^{13}C c.c. for the methyl carbons, a zero c.c. for the quaternary carbon atoms [*8*, *10*] and a very small, if any, c.c. for the hydrogen atoms.

The French authors [*8*] have treated these systems by the v.b. method but are unable to justify the zero coupling to the quaternary carbon.

On the ground of our present results we feel that a hyperconjugation treatment where the pseudo π-orbital were constructed only from carbon orbitals would probably account for the very small coupling constant of the quaternary carbon which is now in the place of the methyl or methylene carbon of the systems treated in the present paper.

We thank the Italian National Research Council (Chemistry Committee, Research Group IV) for financial support. One of us (P.L.N.) thanks Sicedison S.p.A. for a grant.

Note added in proof: After this paper was already sent for publication a note by R. W. Fessenden and R. H. Schuler [J. chem. Physics **38**, 773 (1963)] appeared, containing new improved experimental values for cyclohexadienyl. The new results (a_{CH_2} = 47.70, a_2 = 8.99, a_3 = 2,65, a_4 = 13.04 gauss) are in slighty better agreement with the calculated values expecially in the sense that a_4 is correctly predicted to be higher than a_2.

References

[1] Bolton, J. R., A. Carrington and A. D. McLachlan: Mol. Physics **5**, 31 (1962).
[2] Chesnut, D. B.: J. chem. Physics **29**, 43 (1958).
[3] Cochran, E. L., F. G. Adrian and V. A. Bowers: J. chem. Physics **36**, 1938 (1962).
[4] De Boer, E., and E. L. Mackor: Mol. Physics **5**, 493 (1962).
[5] — — Proc. chem. Soc. **1963**, 23.
[6] Fessenden, R. W.: J. chem. Physics **37**, 747 (1962).
[7] Fisher, H.: J. chem. Physics **37**, 1094 (1962).
[8] Hirota, N., and S. I. Weissman: J. Amer. chem. Soc. **82**, 4424 (1960).
[9] Giacometti, G., and P. L. Nordio: Mol. Physics (1963) in press.
[10] Lemaire, H., A. Rassat and P. Servoz-Gavin: J. Chim. physique **59**, 1247 (1962).
[11] Lykos, P. G.: J. chem. Physics **32**, 625 (1960).
[12] McLachlan, A. D.: Mol. Physics **1**, 233 (1958).
[13] Mulliken, R. S.: J. Chim. physique **46**, 675 (1949).
[14] Preuss, H.: Integraltafeln zur Quantenchemie. Berlin-Göttingen-Heidelberg: Springer 1956.
[15] Roothaan, C. C. J.: Tables of two-center coulomb integrals between 1s, 2s and 2p orbitals (1955).
[16] Skinner, H. A., and H. O. Pritchard: Trans. Faraday Soc. **49**, 1254 (1953).
[17] Strauss, H. L., and G. K. Fraenkel: J. chem. Physics **35**, 1738 (1961).

(Received April 11, 1963)