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Molecular Orbital Study of Proton Hyperfine Splitting Constants in H_2CN Radical

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A hyperconjugated model is used to calculate the proton h. f. s. constants in H_2CN radical by the m. o. method. Agreement with experiment is excellent. A comparison between various approximations employed gives strong evidence of the importance of configuration interaction in such calculations.

Mittels eines hyperkonjugierten Modells werden die Protonenhyperfeinstrukturkonstanten im H_2CN-Radikal nach der MO-Methode berechnet. Die Übereinstimmung mit dem Experiment ist ausgezeichnet. Der Vergleich verschiedener Näherungsmethoden beweist die Notwendigkeit, bei derartigen Rechnungen Konfigurationswechselwirkung einzuschließen.

A l'aide d'un modèle à hyperconjugaison, les constantes de structure hyperfine protonique du radical H_2CN ont été calculées par la méthode MO. L'accord avec l'expérience est excellent. Une comparaison entre les différentes approximations employées met en évidence l'importance de l'interaction de configuration dans de tels calculs.

The E. S. R. spectrum of a molecular fragment obtained by photolyzing HI in the presence of HCN at 4.2° K has been recently obtained by E. L. COCHRAN et al. [1].

The spectrum consists of a main triplet with splitting of 87.4 gauss each line being further split into a second triplet by approximately 11 gauss.

The spectrum has been assigned to the H_2CN radical, the large coupling constant being assumed to be due to the two equivalent protons and the smaller one to the nitrogen nucleus.

The exceptionally large proton coupling must be due to the fact that both hydrogens lie in the plane containing the direction of the nitrogen p orbital where the unpaired electron may be thought to be located in first approximation.

The situation is similar to the one occurring for example in the cyclohexadienyl radical where the large coupling constants of the methylene protons are in excellent agreement with what one predicts on the basis of a molecular orbital calculation on a hyperconjugated model of the molecule [5]. In this respect WHIFFEN [9] has recently pointed out that also a very simple perturbation procedure on such a model is in agreement with experiment. The perturbation procedure gives the splitting as

$$a = Q\,(\Sigma_i\, C_i)^2 \tag{1}$$

where the C_i are the coefficients of the singly occupied m.o. at the atoms attached to the CH_2 carbon. The theory however leaves the constant Q to be determined empirically and this value is going to be rather different in the various cases according to the nature of the X atom and the X-C bond in the X-CH_2 fragment.

Furthermore the limits of validity of (1) are still uncertain owing to the small number of experimental cases available where the same Q is reasonably expected. As a consequence, even though hyperconjugation seems accepted as a decisive mechanism for the explanation of methylene protons coupling constants, further calculations of the type used for cyclohexadienyl and ethyl radicals [*5*] seemed desirable both for the purpose of a less empirical checking of the available experimental results and as an indirect means of testing the general fitness of the perturbation treatment leading to (1).

In this paper we present the results of this sort of calculations obtained for the alleged H_2CN radical.

Outline of the calculation

The radical structure is assumed to be planar and of symmetry C_{2v}. The HCH angle is assumed to be 120°, the CH distance 1.09 Å and the CN distance 1.26 Å (equal to the bond length existing in dicyandiamide [*7*]) (Fig. 1).

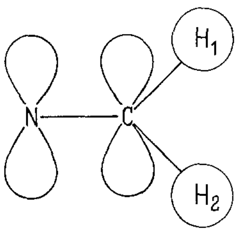

Fig. 1

The radical is treated as a three orbital system: a nitrogen $2p_z$ orbital (π_N), a carbon $2p_z$ orbital (π_c) and the correct symmetry orbital for the hydrogens (H).

The method of calculation of the molecular wave function is an extended configuration interaction (all monoexcited configurations are included) on the SCF molecular orbitals obtained for the positive ion (a closed shell structure) by the usual P.P.P. [*6*] procedure.

The same modifications adopted in ref. [*5*] were used and the same criteria employed for the choice of the parameters, collected in Tab 1.

The ionization potential for the hydrogen orbital has been taken slightly higher than in ref. [*5*] owing to the larger distance between the two nuclei supposed in the present case. The value of 10.8 eV is the one suggested by MULLIKEN in similar cases [*4*]. The following values of Slater exponents were found to give the fitting of the coulombic repulsion integrals at $r = 0$ to the I-A values: $\zeta_c = 1.04$, $\zeta_N = 1.22$, $\zeta_H = 0.756$. The β integrals are taken simply proportional to the overlap S on the basis of $\beta = -2.39$ eV for $S = 0.25$.

The value of β_{CH} is in this way larger than the one used in [*5*] in consequence again of the larger HCH angle implying a larger group overlap. In any case preliminary calculations have shown that small differences in the choice of β values do not affect greatly the results.

Table 1

Integrals and "core" parameters used in the calculation for H_2CN

$(\pi_N \pi_N \vert \pi_N \pi_N)$	12.98	eV
$(\pi_c \pi_c \vert \pi_c \pi_c)$	11.08	eV
$(1s_H 1s_H \vert 1s_H 1s_H)$	12.86	eV
I_N	13.84	eV
I_c	11.54	eV
I_H*	10.80	eV
β_{CN}*	— 3.74	eV
β_{CH}*	— 4.78	eV

* See text.

A few calculations with different methods seemed desirable in order to compare the results. Calculations have been made for this purpose by the LONGUET-HIGGINS and POPLE method [*2*] and by the perturbation treatment due to McLACHLAN [*3*] applied to the LONGUET-HIGGINS-POPLE wave functions. The effect on the resulting wave functions of neglecting nuclear attraction integrals has also been investigated.

Results and discussion

Most of the calculations were made with the aid of the Elea 6001 computer of the Padua University.

The results of the various calculations are reported in Tab. 2. Spin densities ϱ_H calculated by the various methods are shown together with the corresponding coupling constants a_H obtained from the relation:

$$a_H = \varrho_H Q_H$$

with

$$Q_H = \frac{8\pi}{3} g_H \beta_H \frac{(1s_{H_1} - 1s_{H_2})^2}{(2-2S)}$$

whose value is 319 gauss in the present case.

Inspection of the results shows, as already anticipated, that the model is adequate for explaining the proton coupling in this molecule.

The simple Hückel procedure whose result has been included for comparison purposes gives the poorest agreement. The complete configuration interaction wave function (based on closed shell *SCF* orbitals) gives excellent agreement with the experimental value showing once more the almost absolute necessity of including configuration interaction in spin density calculations.

Table 2

Method *	ϱ_H	a_H
Hückel[a]	.200	63.8
Longuet-Higgins[b]	.312	99.5
McLachlan[b]	.280	89.5
Closed Shell SCF[b]	.312	99.5
C.I.[b]	.267	85.2
Longuet-Higgins[c]	.335	107.1
McLachlan[c]	.302	96.3
Closed Shell SCF[c]	.306	97.8
C.I.[c]	.270	86.1
Experimental		87.4

* See text

[a] Parameters used: $\beta_{CH} = 2\,\beta_{CN}$; $\alpha_H = \alpha_C - 0.5\,\beta_{CN}$; $\alpha_N = \alpha_C + 0.5\,\beta_{CN}$

[b] Without Nuclear Attraction Integrals

[c] With Nuclear Attraction Integrals

The Longuet-Higgins wave function,even if corrected by the McLachlan perturbation, brings into the result the somewhat artificial way in which it is constructed, in so far as the more rigorous calculation including nuclear attraction integrals gives a worse agreement. In the complete *C.I.* calculation, instead, the introduction of nuclear attraction integrals produces a certain improvement even if not very significant.

The above calculation is not suitable to predict an absolute value for the nitrogen atom coupling constant for which a treatment considering also 2*s* and 1*s* electrons should be made.

The semiempirical procedure of using the calculated ϱ_N together with an appropriate Q in a McConnell's type relationship can however be employed. One could try for example the equation employed by Rieger and Fraenkel [*8*] for the nitrile anion systems:

$$a_N = (P^N + Q^N_{NC})\,\varrho_N + Q^N_{CN}\,\varrho_C \tag{2}$$

where for the nitrile systems:

$$P^N + Q^N_{NC} = \pm\,(23.1 \pm 1.4)\text{ gauss}$$

and

$$Q^N_{CN} = \mp\,(6.8 \pm 2.2)\text{ gauss},$$

fitted for use with McLachlan type spin densities. In our results ϱ_N and ϱ_C are respectively 0.77, —0.04 from the complete *C.I.* calculation; and 0.73, 0.007

from the McLachlan perturbation. The resulting values of a_N are around 17 gauss, more than 50% off the experimental value. Considering however that the empirical constants in (2) were obtained for nitrile systems and that the experimental splitting is not very accurate indeed [1], one feels that the mentioned assignement of the coupling constant to nitrogen is justified.

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