Theor Chim Acta (1995) 92: 61–65

Theoretica
Chimica Acta

MBOHO calculations of phosphorus–carbon nuclear spin–spin coupling constants

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Received August 15, 1994/Final revision received December 10, 1994/Accepted December 10, 1994

Summary. The novel generalized correlation of the nuclear spin–spin coupling constants with the atomic hybrids and net charges is employed to give a new relationship for calculating the directly bonded phosphorus–carbon coupling constants by use of the maximum bond order hybrid orbital procedure together with the extended Hückel molecular orbital calculation. The calculated coupling constants of phosphorus–carbon are all in good agreement with the experimental data, which shows that the new relationship obtained in the present paper is quite satisfactory for calculation of the phosphorus–carbon coupling constants.

Key words: NMR – Nuclear spin coupling constant – Maximum bond order hybrid orbital – Phosphorus-carbon coupling – Net atomic charge

1. Introduction

There has been an extensive amount of interest in the measurement and interpretation of nuclear spin–spin coupling constants between directly bonded atoms [1–20]. Much of this interest has centered upon coupling between carbon and another atom, and the proposed relationships between the coupling constants and bond hybridization parameters [5]. On the assumption of the dominance of the Fermi contact mechanism, such relationships were predicted from the valence bond [6, 7] and molecular orbital [7, 8] approximation of Ramsey's formulation [13], using the average excitation approximation. It has been shown that such relationships are available in the calculation and interpretation of the C–H and C–C coupling constants as these couplings are mainly controlled by the Fermi contact term [5–12]. For the couplings between phosphorus and another atom,

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The project was supported by the National Natural Science Foundation of China and the Excellent University Teacher's Foundation of State Education Commission of China

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in 1977 Cray and Albright et al. proposed a relationship [21] between the ${}^1J_{P-X}$ values and s characters of the hybrids:

$$J_{P-X} = a(\%s)_P(\%s)_X/(1 + S^2_{P-X}) + b, \tag{1}$$

where a and b are constants, $(\%s)_P$ and $(\%s)_X$ the percent s-character on phosphorus and atom X, respectively, and S_{P-X} the overlap integral for the P–X bond. In many cases, however, these simple concepts fail to rationalize experimental one bond P–X coupling constants [21]. It has been shown that other spin–spin coupling mechanisms, i.e. orbital and spin-dipolar terms, may also contribute significantly to the coupling constant, particularly to ${}^1J_{P-C}$ of trivalent phosphorus compounds [21].

In our preceding paper [22], based on a further theoretical analysis of the second-order perturbation formula for the configuration interaction calculation of nuclear spin–spin coupling constants derived by Ramsey, a novel generalized relationship, which includes the contributions of not only the hybrid orbitals, but also the net atomic charges, has been introduced to calculate the coupling constants:

$$\begin{aligned} J_{AB} = {}& k_{AB}(\%s)_A(\%s)_B + k_A(\%s)_A Q_A + k_B(\%s)_B Q_B + l_A(\%s)_A \\ & + l_B(\%s)_B + l_{AB}, \end{aligned} \tag{2}$$

where Q_A and Q_B are the net charges of atoms A and B, respectively. The second and third terms on the right-hand side of Eq. (2) are the contribution of the ionic character of the A–B bond. This novel generalized relationship has been employed to elucidate the C–H, C–C, C–N and C–F couplings successfully [22, 23]. These satisfactory results inspire us to study the P–C coupling constants by use of the novel generalized relationship and the maximum bond order hybrid orbital (MBOHO) procedure [24] together with the extended Hückel molecular orbital (EHMO) [25] calculation.

2. Calculation method

Let $A = (|a_1\rangle|a_2\rangle \ldots |a_m\rangle)$ and $B = (|b_1\rangle|b_2 \ldots |b_n\rangle)$ be orthonormal atomic orbital basis sets on atoms A and B. The corresponding two sets of orthonormal hybrid orbitals G on atom A and H on atom B are expressed in

$$G = AT, \tag{3}$$

$$H = BU, \tag{4}$$

where T and U are unitary matrices of order m and n, respectively. According to the MBOHO method proposed in the previous paper [24], the MBOHOs and the corresponding maximum bond orders can be obtained simultaneously from the diagonalization of matrix PP^+:

$$(PP^+)T = TM_1^2, \tag{5}$$

where matrix P is the two center part of the density matrix of A and B over the basis of the orthonormal atomic orbitals and can be obtained from a molecular orbital calculation. Matrix M_1 is diagonal, and its diagonal elements are formed from the positive square roots of eigenvalues of matrix PP^+. The maximum bond order P_{AB} can be evaluated by the formula:

$$P_{AB} = \mathrm{Tr}\, M_1. \tag{6}$$

The detail procedure of the basic MBOHO method was described in the previous paper [24].

For a given molecule, before the MBOHO calculation we must determine molecular geometry and calculate the corresponding density matrix. As we know, the MNDO method presented by Dewar et al. [26] is qualified for geometry optimization of the molecules containing phosphorus atom even if the *d* orbitals are not included in the calculation. However, the density matrix obtained from the MNDO calculation without *d* orbitals cannot be used to construct the MBOHOs containing hybridization of *d* orbitals. In this paper, we use the MNDO method to optimize geometries of all the molecules studied, and because the *d* orbitals are not involved in our MNDO calculations, the optimized geometries are employed to perform the EHMO calculation involving *d* orbitals of phosphorus.

To perform the MBOHO procedure on the density matrices obtained from the EHMO calculations, one has to obtain a density matrix in an orthogonalized basis. Let N be the number of atomic orbitals in a molecule. The standard density matrix of order $N \times N$ in the non-orthogonalized basis for the molecule is expressed as $P(N \times N)$. The density matrix $P'(N \times N)$ in Löwdin orthogonalized basis used in this work can be written as

$$P'(N \times N) = S^{1/2} P(N \times N) S^{1/2}. \tag{7}$$

Because we use Löwdin orthogonalized atomic orbital basis, the matrix P in Eq. (5) is formed from the submatrix of $P'(N \times N)$.

3. Results and conclusion

The calculated *s*-characters of the MBOHOs and the net atomic charges on the EHMO level for the phosphorus–carbon single bonds are listed in Table 1. By use of the least-squares process, we obtain:

$$\begin{aligned} J_{P-C} = {} & 0.108427\,(\%s)_P\,(\%s)_C + 4.6861(\%s)_P Q_P + 12.3901\,(\%s)_C Q_C \\ & - 5.4217\,(\%s)_P + 4.2608\,(\%s)_C - 88.61 \quad (\mathrm{Hz}) \end{aligned} \tag{8}$$

with the standard deviation 3.13 Hz. The concrete numerical results are also listed in Table 1.

A survey of the data listed in Table 1 reveals that the calculated phosphorus–carbon coupling constants by using Eq. (8) are all in good agreement with the experimental ones. They adequately reflect several important trends, e.g. ${}^1J_{P-C}$ values in the compounds $Et_{3-n}PCl_n$ ($n = 0 - 2$) increase with halogen substitution, which is in good agreement with the conclusion obtained by van Linthoudt et al. [27], and the negative values of ${}^1J_{P-C}$ in $Et_{3-n}P(t-Bu)_n$ ($n = 0 - 3$) increase with increasing n because of the widening of the C–P–C bond angle [21, 28]. Moreover, from our calculation we can get different ${}^1J_{P-C}$ values for the P–C bonds existing in different chemical environments. This is coincident with the chemical intuition. It follows that Eq. (8) obtained in the present report are quite satisfactory for calculation of the nuclear spin–spin coupling constants between directly bonded phosphorus and carbon atoms in trivalent and pentavalent

Table 1. The calculated *s*-characters of MBOHOs, net atomic charges and nuclear spin–spin coupling constants for P–C bonds

No.	Molecule	Bond	$(\%S)_P$	$(\%S)_C$	Q_P	Q_C	$^1J_{P-C}$ (Hz)		
							Eq. (8)	Expt.	Ref.
1	$(Me)_3P$	P–C (Me)	29.11	37.16	−0.186	−0.042	−15.51	−13.6	1
2	$(Et)_3P$	P–C (Et)	28.20	34.33	−0.246	0.025	−12.10	−13.9	1
3	$(Et)_2PCl$	P–C (Et)	28.47	34.59	−0.007	0.040	26.94	28.8	1
4	$EtPCl_2$	P–C (Et)	27.99	34.60	0.184	0.032	49.89	43.2	1
5	$(Et)_2P$(t-Bu)	P–C (Et)	30.42	34.62	−0.277	0.027	−19.79	−18.6	28
		P–C (t-Bu)	27.91	28.98	−0.277	0.132	−17.60	−15.4	28
6	EtP(t-Bu)$_2$	P–C (Et)	29.33	34.34	−0.306	0.018	−26.53	−30.1	28
		P–C (t-Bu)	27.89	28.32	0.306	0.142	−23.70	−23.6	28
7	P(t-Bu)$_3$	P–C (t-Bu)	29.53	28.67	−0.348	0.143	−32.11	−33.6	28
8	$MeP(O)(OMe)_2$	P–C (Me)	29.36	34.17	1.375	−0.131	140.30	142.2	1
9	$MeP(O)(OEt)_2$	P–C (Me)	29.29	34.12	1.377	−0.131	139.93	143.2	1
10	n-BuP(O)(OEt)$_2$	P–C (n-Bu)	28.98	32.69	1.357	−0.084	145.13	140.9	1
11	$HC{\equiv}CP(O)(OEt)_2$	P–C (C≡CH)	33.16	51.72	1.384	−0.091	294.66	294.0	1
12	$(MeC{\equiv}C)_3P$	P–C (C≡CMe)	31.50	48.21	−0.210	−0.115	11.01	+ 8.8	1
13	(n-Bu)$_2PC_6H_5$	P–C (C_6H_5)	29.79	35.03	−0.314	0.029	−18.99	−17.7	21
		P–C (n-Bu)	29.70	36.09	−0.314	0.018	−15.27	−13.4	21
14	$P(S)(CH_3)_3$	P–C (Me)	23.48	37.91	0.399	−0.065	55.52	56.1	21
15	(n-Bu)$_3$P	P–C (n-Bu)	28.30	34.63	−0.253	0.013	−15.75	−10.9	1
16	$F_4PC{\equiv}CH$	P–C (C≡CH)	33.36	53.73	2.295	−0.057	474.66	476.0	1
17	$(C_6H_5)_3P$	P–C (C_6H_5)	27.88	36.36	−0.355	0.020	−12.31	−12.5	1
18	$P(O)(OMe)_2$ $\vert$ $CH_2CHOHCH_2COPh$	P–C	28.95	32.80	1.360	−0.095	143.02	141.5	29

phosphorus compounds. This satisfactory relationship, Eq. (8), reveals that the Fermi contact mechanism plays a key role for the change of ${}^1J_{P-C}$ values, and that the contribution of the other mechanisms to ${}^1J_{P-C}$ values, which might be important, may be regarded as a constant included in the constant term, l_{PC}, of Eq. (2).

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