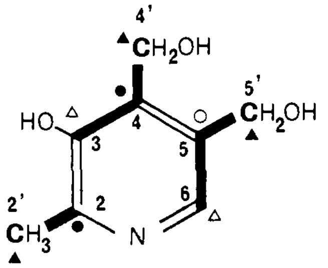

Figure 1. The distribution of label in pyridoxol. Sites of activity derived from [*1*-^{14}*C*]glycerol (triangles) (relative specific activity ~20%) and from [*2*-^{14}*C*]glycerol (circles) (relative specific activity ~33%), demonstrated by degradation (▲, ●) (Table I) or inferred (△, ○).

radiocarbon. The pattern of labeling observed within glycerol-derived pyridoxol (Figure 1) is exactly as predicted by, and therefore supports, the hypothesis outlined in Scheme I.

Table I. Observed and Predicted Distribution of Activity within Pyridoxol Derived from [^{14}*C*]Glycerol

Product (C atoms of pyridoxol)	Rel spec act. (%) (pyridoxol = 100) of the product derived from [*1*-^{14}C]Glycerol Obsd	[*1*-^{14}C]Glycerol Calcd	[*2*-^{14}*C*]Glycerol Obsd	[*2*-^{14}*C*]Glycerol Calcd
Pyridoxol (all)	100 ± 3	100	100 ± 3	100
Scheme II, sequence a				
3-*O*-Methylpyridoxol (**2**) (all)	99 ± 2	100		
Dicarboxylic acid (**3**) (all)	100 ± 3	100		
Monocarboxylic acid (**4**) (all but C-4′)	78 ± 2	80	103 ± 6	100
∴ C-4′	22 ± 2	20	0	0
Scheme III				
Phenylcarbinol (**6**) (all)	98 ± 2	100	99 ± 5	100
Benzoic acid (C-5′)	22 ± 1	20	0.5 ± 0.2	0
Scheme II, sequence b				
Acetic acid (C-2′,2)	22 ± 1	20	35 ± 1	33
Methylamine (C-2′)	18 ± 1	20	2.4 ± 0.4	0
Scheme II, sequence c				
2,4-Dimethylpyridine derivative **5** (all)	98 ± 1	100	101 ± 4	100
Acetic acid (C-2′,4′,2,4)	22 ± 1	20	32 ± 1	33
Methylamine (C-2′,4′)	19 ± 1	20		

A further experiment, with [*1*-^{14}*C*]glucose (0.5 mCi; Amersham/Searle) as the sole carbon source, was intended to throw light on the mode of incorporation of triose phosphate. Glycolytic breakdown of [*1*-^{14}*C*]glucose leads to *in situ* formation of [*1*-^{14}*C*]dihydroxyacetone 1-phosphate and thence of [*3*-^{14}*C*]D-glyceraldehyde 3-phosphate. According to Scheme I, label from the latter should enter C-5′ and, *via* pyruvate and acetaldehyde, C-2′ of pyridoxol. Activity from the former might be found either at C-3 or at C-4′, depending on the mode of the postulated combination of acetaldehyde with phosphodihydroxyacetone, leading to the intermediacy of the 3-phosphate or the 1-phosphate, respectively, of 5-deoxy-D-xylulose.

Decarboxylation of the dicarboxylic acid (**3**) obtained from the [^{14}*C*]glucose-derived pyridoxol gave the monocarboxylic acid (**4**) containing only 60% of the total activity (Table II), demonstrating the presence of label at C-4′. This result is consistent with the latter of the two alternatives, *i.e.*, condensation of acetaldehyde and phosphodihydroxyacetone to form the 1-phosphate of 5-deoxy-D-xylose,[5] as shown in Scheme I.

Table II. Partial Degradation of Pyridoxol Derived from [*1*-^{14}*C*]Glucose

Product (C atoms of pyridoxol)	Rel spec act.
Scheme II, sequence a	
3-*O*-Methylpyridoxol (**2**) (all)	100 ± 4
Dicarboxylic acid (**3**) (all)	100 ± 5
Monocarboxylic acid (**4**) (all but C-4′)	62 ± 3
∴ C-4′	38 ± 4

In a fourth experiment, the role of serine in the biosynthesis of pyridoxol[6] was explored. Pyridoxol, isolated from a culture which had been incubated with [*3*-^{14}*C*]DL-serine (0.2 mCi; Amersham/Searle), on Kuhn–Roth oxidation yielded acetate (C-2′,2), containing almost the entire activity of the intact vitamin (Table III).

Table III. Partial Degradation of Pyridoxol Derived from [*3*-^{14}*C*]Serine

Product (C atoms of pyridoxol)	Rel spec act.
Pyridoxol (all)	100 ± 3
Scheme II, sequence b	
Acetic acid (C-2′,2)	92 ± 4
Scheme II, sequence c	
2,4-Dimethylpyridine derivative **5** (all)	100 ± 5
Acetic acid (C-2′,4′,2,4)	63 ± 3

Since this is the labeling pattern which was observed when pyruvate serves as the precursor of pyridoxol,[2] and since conversion of serine into pyruvate, a well-documented catabolic reaction,[7,8] is irreversible,[9] it follows that incorporation of serine into pyridoxol takes place *via* pyruvic acid.

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A Pseudo-Atom–Molecular Orbital Approach to Substituent Effects in Organic Compounds. I. Spin–Spin Coupling in Substituted Methanes[1]

Sir:

We report here a promising new approach to representing trends of substituent effects in organic

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Table I. Effect of Changing Atomic Parameters of Pseudo-Atom X in MO Calculations of Spin–Spin Coupling for CH_3–X

X parameter set					$P_{\mu\mu}$ values for X							
Set no.	$^1/_2(I + A)_{2s}$	$^1/_2(I + A)_{2p}$	β^0 [a]	ξ [b]	2s	$2p_x$	$2p_y$	$2p_z$	J_{CH}	$P_{1s2s}{}^2$	J_{54}	J_{53}
1	39.00	13.00	−47.00	3.000	1.9280	0.0629	0.0629	1.7478	146.79	0.2942	6.845	6.845
2	35.50	12.00	−43.00	2.800	1.9142	0.0815	0.0815	1.6894	143.83	0.2898	−1.195	−1.195
3	32.27	11.08	−39.00	2.600	1.8993	0.1044	0.1044	1.6241	140.36	0.2845	−3.808	−3.808
4	25.39	9.111	−31.00	2.275	1.8666	0.1349	0.1349	1.5176	133.95	0.2746	−5.816	−5.816
5	16.60	6.30	−23.00	1.780	1.7952	0.1932	0.1932	1.3436	118.73	0.2511	−6.750	−6.750
6	14.05	5.572	−21.0[c]	1.625[c]	1.7650	0.2404	0.0693	1.3389	118.65	0.2435	−7.124	9.221

[a] Values in electron volts. [b] Slater's exponents. [c] For the $2p_y$ orbital the values −47.00 and 3.00 were used for β^0 and ξ, respectively, in this parameter set.

compounds in molecular orbital calculations. This approach, called the *pseudo-atom* approach, is applied here to the description of the HH and CH spin–spin coupling constants in substituted methanes.

Qualitative theories dealing with substituent effects on the J_{CH} values in substituted methanes have focused on the hybridization of carbon in relation to the "effective electronegativity" of substituents,[2,3] on the role of s-orbital density at the nucleus,[4,5] and on electronic excitation energies.[6,7]

Qualitative interpretations of geminal H–H coupling constants ($^2J_{HH}$) in substituted methanes have been based on discussions of hyperconjugation[8,9] and inductive effects.[9]

Recent calculations using the finite perturbation–INDO approach[10] have accounted qualitatively for the established experimental trends of J_{CH} and $^2J_{HH}$ in substituted methanes,[11,12] success with the former depending upon the exclusion of $-I^-$ substituents[13] from calculations.

In order to gain intuitive insight into how empirically stated substitutent effects relate to MO theories, and to improve certain characteristics of the finite perturbation–INDO method, we have undertaken to see how well experimental trends can be simulated by altering pertinent atomic parameters in INDO.[14] Higher level approximations may ultimately be better capable of accounting for substituent effects in MO calculations. However, the valence-shell set of INDO is simple enough to retain most of the qualitative features of atomic orbitals that are customarily used by chemists in visualizing chemical problems. The parameters in INDO that can reasonably be varied in searching for agreement with experiment are: the exponents, ξ, of the STO's; the $^1/_2(I + A)$ values employed in the diagonal elements of the core-Hamiltonian matrix; the β^0 values involved in the empirical evaluation of off-diagonal core-Hamiltonian matrix elements; the core charges, Z, that represent the field due to the nuclei and inner-shell electrons; and the F and G values used to calculate Coulomb and one-center exchange integrals. Since variations in the F and G values for an atom (A) seem to have little effect on the values of calculated couplings between nuclei if neither nucleus belongs to atom A, or both are not attached to it, we did not include variations of F and G in this study.

Figure 1. The substituted methane system with X as the pseudo atom that represents a hypothetical substituent.

The system used here is the CH_3–X system shown in Figure 1, where X is the pseudo atom for which the parameter variations are carried out. The pseudo atom here was assigned a Z value of 4 and nominally allotted three valence electrons. Finite perturbation–INDO calculations were carried out as reported previously, except for the changes of INDO parameters described here. The results are given in Table I.

The calculated results in Table I cover ranges of J_{CH} and geminal J_{HH} values (J_{54} and J_{53}) that are not unlike those encountered with substituent effects on the corresponding experimental couplings. Furthermore, they exhibit some trends that might be expected on the basis of previously established empirical patterns. Thus, in progressing from parameter set 6 through set 1, the increasing values of P_{2s2s} and $P_{2p_zp_z}$, which represent 2s and $2p_z$ atomic densities of "pseudo atom" X, show the effect of inductive withdrawal that is empirically associated with increasing J_{CH} values. The computed J_{CH} values follow this trend, as do the calculated values of $P_{1s2s}{}^2$. The latter is related to the "per cent s character" in the CH bonds.

Inspection of the $P_{2p_x2p_x}$ and $P_{2p_y2p_y}$ values in the table, together with the corresponding values of J_{54} and J_{53}, shows the hyperconjugative effects that were described previously by Pople and Bothner-By and by Allred, Grant, and Goodlett, and established experimentally. Thus, in progressing from parameter set 5 through set 1, the density-matrix values indicate a hyperconjugative release from the pseudo atom to the CH_3 group. According to Pople and Bothner-By, this should produce an algebraic increase in J_{54} and J_{53}, and this increase is evident in the table. Of course,

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the prediction of a positive change in $^2J_{HH}$ is also associated with inductive withdrawal, so an additional comparison is needed. This is provided by cases 5 and 6. Comparison of cases 5 and 6 shows that the inductive differences are rather small. The value of J_{54} for set 6 is less than that for set 5, corresponding to the fact that the $P_{2p_z2p_z}$ value in 6 is larger than that for set 5. Similarly, the J_{53} value for set 6 is greater than that for 5, and this agrees with the fact that $P_{2p_y2p_y}$ is smaller in set 6 than for set 5. Thus the results in Table I convey a self-consistent picture of established patterns of experimental substituent effects.

Work is currently under way exploring further the use of the pseudo-atom approach in CH_3X and other systems to simulate common patterns of substituent effects with the aim of gaining insight into their fundamental nature.

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Phosphaundecaboranes

Sir:

During the last 3 years, several reports have appeared on the insertion of representative elements other than carbon into boron hydrides or carboranes. Boron hydrides containing sulfur,[1] nitrogen,[1] or phosphorus[2] and carboranes containing Be,[3] Al,[4] Ga,[5] Ge,[6] Sn,[6] Pb,[6] P,[7] As,[8] or Sb[8] have been reported. One polyhedral phosphaborane, $B_{11}H_{11}PC_6H_5$, was prepared in very low yield.[2] This communication is concerned with the preparation and some chemistry of 11-atom *nido*-phosphaboranes.

Table I. Analytical Data

Compound	Calculated, % C	H	B	P	Mn	Mol wt	Found, % C	H	B	P	Mn	Mol wt[a]
$B_{10}H_{12}PC_6H_5$	31.58	7.51	47.40	13.57		228.2	31.62	7.51	45.46	13.54		235
$(CH_3)_4NB_{10}H_{11}PC_6H_5$	39.85	9.36	35.86	10.36		301.4	39.67	9.42	35.74	10.17		
$B_{10}H_{12}PCH_3$	7.23	9.10	65.04	18.63		166.2	7.23	9.28	64.60	17.93		166
$(CH_3)_4NB_{10}H_{11}PCH_3$	25.09	10.95	45.17	12.94		239.3	25.19	10.76		13.28		
$(CH_3)_4N(B_{10}H_{10}PC_6H_5)Mn(CO)_3$	35.53	6.19	24.62	7.05	12.50	439.3	35.04	6.53	24.40		12.28	

[a] Osmometric in benzene

Deprotonation of decaborane(14) in diethyl ether with sodium hydride and then slow addition of a diethyl ether solution of $C_6H_5PCl_2$ produce $B_{10}H_{12}PC_6H_5$ (I) in moderate yield. Unreacted decaborane is removed by sublimation and the residues are dissolved in aqueous ammonia and precipitated with tetramethylammonium chloride solution. The crude salt is dried, dissolved in acetonitrile, and passed through strongly acidic ion exchange resin. Sublimation produces pure I, mp 82–84°. The low-energy mass spectrum cuts off at *m/e* 230, corresponding to the parent ion $^{11}B_{10}{}^{1}H_{17}{}^{12}C_6{}^{31}P^+$. The ring protons appear in the proton nmr spectrum as a complex multiplet centered at −7.8 ppm. Doublets in the boron-11 nmr spectrum at 32.1 MHz are badly overlapped, but can be interpreted as the 1:1:2:2:2:2 pattern expected for C_s symmetry. This does not distinguish between 7-$B_{10}H_{12}PC_6H_5$ and 2-$B_{10}H_{12}PC_6H_5$.[9] Assuming, however, that the decaborane framework has not rearranged under the mild reaction conditions, 7-$B_{10}H_{12}PC_6H_5$ would be the product of simple phosphorus insertion.

Synthesis of 7-$B_{10}H_{12}PCH_3$ (II) (mp 86.5–88.5°) is carried out by the method cited above for I using CH_3PCl_2. The low-energy mass spectrum cuts off at *m/e* 168, corresponding to the parent ion $^{11}B_{10}{}^{1}H_{15}{}^{12}C^{31}P^+$. The proton nmr spectrum at 60 MHz consists of a doublet (J_{PCH} = 11 Hz) centered at −2.08 ppm, assigned to P–CH_3. Boron-11 nmr at 70.6 MHz shows six different types of boron in 1:1:2:2:2:2 distribution, strongly suggesting that this molecule possesses C_s symmetry.

For I and II, one bridging proton can be removed by weak base, such as aqueous ammonia, and both "extra" protons can be removed by strong base, such as NaH. Addition of aqueous tetramethylammonium chloride to aqueous ammonia solutions of I and II precipitates $[(CH_3)_4N]$7-$B_{10}H_{11}PC_6H_5$ (III) or $[(CH_3)_4N]$7-$B_{10}H_{11}PCH_3$ (IV), both of which are recrystallized from acetone–ethanol. A sharp singlet (12 H) and a broad multiplet (5 H) appear at −3.48 and −7.65 ppm, respectively, in the proton nmr spectrum of III. The proton nmr spectrum of IV consists of a sharp doublet (3 H, J_{PCH} = 9 Hz) at −1.60 ppm and a sharp singlet (12 H) at − 3.50 ppm. The boron-11 nmr spectrum of III at 32.1 MHz is very similar to that of the analogous thiaborane,[1] $B_{10}H_{11}S^-$.

By treating I in tetrahydrofuran with 2 equiv of NaH and 1 equiv of $BrMn(CO)_5$, moderate yields of $(B_{10}H_{10}PC_6H_5)Mn(CO)_3^-$ may be obtained. The pale yellow [λ_{max}, mμ (ϵ): 219 (23,000), 309 (sh, 1060), 340 (sh, 901)] tetramethylammonium salt of this metallocene

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