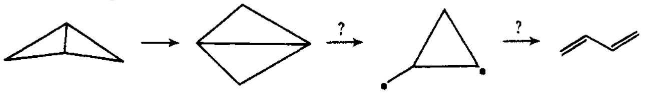
tically, there is probably a state of B_2 symmetry close in energy to the A_2 state.

From the rotational band contour analysis bicyclobutane was shown to undergo a distortion in the excited state breaking its C_{2v} ground state symmetry. The vibronic coupling involving b_1 vibrations along with a long progression involving the "ring-flapping" mode, ν_9, suggests that the excited species approaches planarity and is distorted in accord with b_1 symmetry. We should like to obtain an approximate geometry for the excited state based on the moments of inertia. The three moments allow only three geometrical variables. These were taken as the central C–C bond length, the change in the outside C–C bond lengths (which were assumed to be equal and opposite), and the dihedral angle between the two three-carbon planes. Local C_{2v} symmetry was assumed at the methylene groups with unchanged bond angles and lengths, and the C–C–H angle at the bridgehead also was assumed to be unchanged. Based on these assumptions, it was necessary to increase the dihedral angle to a value close to 180°. It was set at 180° and the other variables were adjusted. The best fit was found with the central C–C length = 1.647 Å and the outside C–C lengths = 1.778 and 1.218 Å. This gave as moments of inertia $A' = 0.567$ cm^{-1}, $B' = 0.338$ cm^{-1}, and $C' = 0.241$ cm^{-1}, which are in good agreement with the observed values, especially considering the uncertainty in the hydrogen positions. In summary, the experimental data suggest that the equilibrium geometry is planar, and that the molecule becomes "kite" shaped.



The sudden broadening of the vibrational bands at 48 431 cm^{-1} further suggests that the molecule may undergo a photochemical transformation at this energy. One obvious candidate would be a photochemical rearrangement to butadiene, and the observed deformation mode could lead to this product. The photochemical transformations which accompany this electronic transition are being examined.

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(1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-72-2239.

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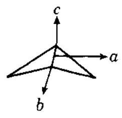
(6) A type "A" band implies polarization of the transition moment along the molecular *a* axis:



(cf. ref 11 for A, B, and C type band shapes for bicyclobutane).

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Ground States of Molecules. 33.[1] MINDO/3 Calculations of NMR Coupling Constants

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Abstract: MINDO/3 calculations of NMR coupling constants, using finite perturbation theory, for couplings between carbon, hydrogen, and nitrogen are in fair agreement with experiment but somewhat inferior to INDO. The orbital densities calculated by a nonlinear least-squares procedure are close to their theoretical values.

Now that NMR spectroscopy has grown into a major technique for determining molecular structures, the need for a corresponding theory of chemical shifts and coupling constants has become pressing. If such calculations could be carried out with sufficient accuracy and at reasonable cost, the results would be of major practical value in the identification of unknown molecules. However, while a number of approaches to this problem have been reported,[2] none as yet has proved satisfactory. Either the results are too inaccurate, or the calculations are limited by considerations of cost to very small molecules.

Recent work in these laboratories has led to the development of a semiempirical SCF-MO method (MINDO/3[3]) which has met with remarkable success in a number of connections. Although it was parametrized solely to fit the energies and geometries of molecules, it has also given surprisingly good results for a variety of other molecular properties.[4] We therefore decided to see whether the same would be true for calculations of NMR coupling constants partly in the hope that the results might be accurate enough for such calculations to be of practical value and partly to see how well MINDO/3 would cope with yet another molecular property.

This paper reports calculations of coupling constants between carbon, hydrogen, and nitrogen in a variety of organic molecules.

Procedure

The MINDO/3 method has been described in detail.[3] The calculations reported here were carried out using the standard parameters.[3] The geometry of each molecule was first determined by minimizing the energy with respect to all geometrical variables.[3] The calculations of coupling constants were then

Table I. Calculated (MINDO/3 and INDO[9a,b]) NMR Coupling Constants (Hz) (Undetermined Signs Are Given as (±))

Entry No.	Molecule and coupling	MINDO/3	Exptl[cc]	Pople et al.[9a,b]
1[a]	Hydrogen H-H	285.80	278.2 ± 0.7	408.60
2[b]	Water H-O-H	−6.63	(+)7.2 ± 0.7	−8.07
3[c]	Methane H-C-H	−5.64	−12.4 ± 0.6	−6.13
4[d]	Ethylene H-C-H	3.24	2.5 ± 0.2	3.24
5[e]	Formaldehyde H-C-H	127.44	40.3 ± 0.1	31.86
6[f]	Ethylene H-C-C-H (cis)	8.81	11.7 ± 0.1	9.31
7[f]	Ethylene H-C-C-H (trans)	47.93	19.0 ± 0.1	25.15
8[d,g]	Acetylene H-C-C-H	42.06	9.6 ± 0.2	10.99
9[h]	Allene H-C-C-C-H	−33.17	(+)7.0 ± 0.1	−9.69
10[i]	Benzene H-C-C-H	23.86	7.54 ± 0.04	8.15
11[j]	Methane C-H	104.29	125 ± 1	122.92
12[d]	Ethane C-H	99.22	124.9 ± 0.3	122.12
13[d]	Ethylene C-H	132.92	156.4 ± 0.1	156.71
14[d]	Acetylene C-H	191.44	249.0 ± 0.3	232.65
15[k]	Benzene C-H	172.75	158.34 ± 0.18	140.29
16[d]	Ethane C-C	34.90	34.6 ± 0.3	41.45
17[d]	Ethylene C-C	77.62	67.6 ± 0.1	82.14
18[d]	Acetylene C-C	90.74	171.5 ± 0.2	163.75
19[d]	Ethane C-C-H	−4.91	−4.5 ± 0.3	−7.20
20[d]	Ethylene C-C-H	−19.51	−2.4 ± 0.15	−11.57
21[l]	Acetonitrile H-C-H	−11.42	−16.9 ± 0.3	−7.73
22[m]	Ammonium ion H-N-H	−9.65	−12.4	
23[h]	Allene C-H	160.78	168.2	155.50
24[n]	Formaldehyde C-H	126.17	172 ± 5	180.51
25[o]	Cyclopropane C-H	116.16	160.45 ± 0.1	
26[p]	Methylamine C-H	108.87	133.2 ± 0.2	129.92
27[q]	Acetonitrile C-H	99.76	136.0 ± 0.2	122.47
28[r]	Allene C-C	114.70	98.7 ± 0.3	108.5
29[s]	Benzene C-C	181.12	57.0	76.1
30[t]	Acetonitrile C-C	19.24	56.48 ± 0.08	76.7
31[u]	Cyclopropane C-C-H	−6.0	−2.6	
32[q]	Acetonitrile C-C-H	−14.0	−10.0 ± 0.2	
33[v]	Protonated acetonitrile H-N	132.84	136.0	
34[v]	Protonated hydrogen cyanide H-N	135.96	134.0	
35[v]	Protonated hydrogen cyanide H-C-N	2.89	19.0	
36[p]	Methylamine H-C-N	15.22	1.0 ± 0.2	
37[w]	Cyanide ion C-N	1.59	5.9	−1.3
38[q]	Acetonitrile C-N	−21.17	−17.5 ± 0.4	6.2
39[x]	Nitroethylene H-C-H	3.46	1.3	
40[x]	Acrylonitrile H-C-H	0.96	1.3	4.59
41[x]	Vinyl fluoride H-C-H	−4.57	−3.2	−3.2
42[x]	Nitroethylene H-C-C-H (cis)	8.74	7.6	6.93
43[x]	Acrylonitrile H-C-C-H (cis)	15.77	11.3	10.72
44[x]	Vinyl fluoride H-C-C-H (cis)	0.02	4.65	4.74
45[x]	Nitroethylene H-C-C-H (trans)	43.56	15.0	21.62
46[x]	Acrylonitrile H-C-C-H (trans)	51.59	18.2	26.05
47[x]	Vinyl fluoride H-C-C-H (trans)	42.76	14.6	20.73
48[y]	Vinyl fluoride C-H (carbon with F)	168.58	200.2	183.11
49[y]	Vinyl fluoride C-H (H trans to F)	128.44	162.2	162.36
50[v]	Protonated hydrogen cyanide C-H	223.0	320.0	278.43
51[z]	Methyl fluoride C-H	122.30	149.1	140.08
52[aa]	Fluoroformaldehyde C-H	431.85	267.0	244.77
53[aa]	Formic acid C-H	202.81	222.0	214.05
54[v]	Protonated acetonitrile C-C-H	−9.77	−10.4	
55[bb]	Dimethylformamide H-C-N (methyl)	1.60	1.1	
56[bb]	Dimethylformamide C-N (carbonyl)	15.76	13.4	
57[p]	Methylamine C-N	−4.96	+(7 + 1)	−4.6

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carried out using an unrestricted[5] version of the MINDO/3 program with this geometry.

The theory of NMR coupling constants has been developed in detail by Ramsey.[6] It now appears that the Fermi contact term is dominant, especially for proton–proton couplings; we have therefore used only this term.

Nuclear spin coupling constants are second-order quantities which may be estimated either variationally[2,7,8] or by perturbation theory.[2] We have used the finite perturbation theory approach of Pople et al.[9] In this treatment the coupling constant K_{AB} between nuclei A and B is given by:

$$K_{AB} = \left(\frac{8\pi\beta}{3}\right)^2 s_A{}^2(0)s_B{}^2(0)\left(\frac{\rho s_A s_A(h_B)}{h_B}\right) \qquad (1)$$

where $s_A(0)$ and $s_B(0)$ are the values of the valence shell s AO's of atoms A and B respectively of the respective nuclei, and where the diagonal spin density matrix element $\rho s_A s_A$ is the electron spin density at the nucleus of atom A when a magnetic perturbation h_B is present at the nucleus of atom B. We used the value 0.027 eV for the finite perturbation h_B, and the spin densities were calculated to 10^{-8}.

The quantities K_{AB}, usually in cm^{-3}, are related to the experimental coupling constants J_{AB} (in Hz) by

$$J_{AB} = K_{AB}\gamma_A\gamma_B\hbar/2\pi \qquad (2)$$

where γ_A and γ_B are the gyromagnetic ratios for nuclei A and B, and $\hbar = h/2\pi$ (h is Planck's constant). The calculations were carried out using a computer program written by one of us (P.K.W.).

Since the AO's used in MINDO/3 are not clearly specified, the integrals involving them being calculated from parametric functions, it is logical to treat the $s_A{}^2(0)$ likewise as parameters. We accordingly calculated them for carbon ($s_C{}^2(0)$), hydrogen ($s_H{}^2(0)$), and nitrogen ($s_N{}^2(0)$) by a non-linear-least-squares fit, using a method developed by Weiner.[10]

Results and Discussion

Table I shows the coupling constants calculated for 57 miscellaneous compounds for which experimental data are available and which cover a wide variety of bonding situations. The quantities $s_C{}^2(0)$, $s_H{}^2(0)$, and $s_N{}^2(0)$ were found by a least-squares fit to the first 38 of these; the values found in this way are listed in Table II. Table I also shows experimental values for J_{AB} and the values calculated by Pople et al.[9a,b] where these are available. Table II compares our values for the s-orbital densities with those of Pople et al.[9a] and also with values derived from detailed ab initio calculations.[11] It should also be pointed out that our MINDO/3 results are based on geometries determined by minimizing the energy with respect to all geometrical variables whereas the INDO results were based on geometries deduced from standard bond lengths and angles. Since coupling constants are very sensitive to changes in geometry, calculations based on assumed geometries are of dubious validity.

Examination of Table I shows that while the general agreement of the MINDO/3 results with experiment is reasonable, there are large discrepancies in certain cases, e.g., the C–H couplings in HCN$^+$H and FCHO, and the C–C couplings in benzene and acetylene. There are also some systematic errors. Thus the *trans*-HCCH couplings in olefins are too large by 20–30 Hz while C–H couplings are too small by a comparable amount. In these cases the INDO results of Pople et al.,[9] while far from exact, are uniformly better.

It should, however, be noted that the MINDO/3 results refer to geometries calculated by minimizing the energy with respect to all geometrical variables, whereas the INDO ones were for "standard" geometries deduced from fixed values for bond lengths and angles. This distinction is important because coupling constants are sensitive to changes in geometry and because the ability of INDO to reproduce molecular geometries has been little tested. Since the MINDO/3 calculations (with complete geometry optimization) can be carried out quickly and easily for quite large molecules, using available programs, such calculations may be of practical value in assigning NMR spectra. Further studies of NH couplings might in particular prove useful in view of recent reports[12,13] concerning the dependence of ^{15}N–C–C–H couplings in peptides on their conformation. The MINDO/3 s-AO densities in Table II also agree better with the theoretical ones than do those of Pople et al.,[9a] a further encouraging result in view of the empirical way in which the MINDO/3 values were estimated.

Table II. MINDO/3 Calculated s Orbital Densities ($a_0{}^{-3}$)

Atom	$s^2(0)$ MINDO/3	$s^2(0)$ Pople et al.[9a]	$s^2(0)$ Theory[11]
H	0.2947	0.3724	0.3183
C	2.5583	4.0318	2.767
N	5.8181	6.9265	4.770

The relative success of INDO in this connection is not surprising in view of the fact that the parameters in it were chosen to make the calculated electron distributions agree as well as possible with those given by the Roothaan[14]–Hall[15] (RH; "ab initio SCF") method. Since the latter is known to give quite good estimates of electron distributions and related properties, one might reasonably expect INDO to do the same, given that both calculations were based on similar geometries. As one might equally have expected, INDO is unsatisfactory in most other applications, molecular energies in particular being very poorly reproduced.

MINDO/3, on the other hand, was parametrized to fit experimental heats of formation and geometries of molecules. It might therefore seem surprising that it should reproduce a totally unrelated property as well as it does NMR coupling constants. Studies of other molecular properties have, however, shown that MINDO/3 is usually much more successful than it has proved here. This is the case not only for heats of formation[3] and molecular geometries[3] (for which MINDO/3 was parametrized) but also for dipole moments,[3] first ionization energies,[3] electric polarizabilities[16] and hyperpolarizabilities,[17] nuclear quadrupole coupling constants,[18] ESCA chemical shifts,[19] molecular vibration frequencies[20] and isotopic shifts,[21] entropies and entropies of activation,[22] specific heats,[22] kinetic isotope effects,[22] and the electronic band structure of polymers.[23] In each of these connections MINDO/3 has proved superior to any previous semiempirical procedure, whereas each of the competing treatments is not only inferior but also limited to specific properties and/or types of molecules. The surprising feature of the results reported here is therefore not the relative success of MINDO/3 but rather its relative *lack* of success. This is the first area where it has failed to give results that are useful and reliable in a quantitative sense.

The explanation probably lies in a basic difference between NMR coupling constants and the other properties listed above.[3,16-23] While the latter depend on the electron distribution in the valence shell regions of the atoms in a given molecule, NMR coupling constants are controlled by the Fermi contact term and hence by the s-electron densities at the nuclei. In an LCAO–MO treatment where a single function is used for each AO, the electron density at the nucleus of a given atom is directly related to the electron density in its valence shell region. It is, however, well known that RH calculations are greatly improved by the use of linear combinations of two or more functions to represent each AO (multiple ζ basis sets). In such a treatment, the electron density at the nucleus depends not only on the electron distribution in the valence shell region but also on the relative contributions of the corresponding suborbital functions to each AO, in particular to each s AO. The latter factor is neglected in all current semiempirical SCF-MO treatments (including MINDO/3) since they all use minimum basis sets. It is therefore not surprising that MINDO/3 reproduces all the "chemical" properties that depend on the valence shell electron distribution but is much less successful for NMR coupling constants. This argument suggests that attempts to calculate the latter accurately by any LCAO-MO procedure are doomed to failure unless a multiple ζ basis set is used. To attempt this in a semiempirical treatment would raise obvious and formidable problems.

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Some Symmetry Considerations Concerning the Role of Atomic d Orbitals in Chemical Bonds: Discussion and Some Calculational Examples

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Abstract: The problem of the necessity for the inclusion of d orbitals in a computational basis set is discussed, with emphasis placed on the symmetry of the system under consideration. The distinction between qualitative and quantitative necessity for such inclusion is drawn on the basis of symmetry and illustrative examples, both computational and conceptual, for several simple systems are presented.

I. Introduction

Since the classic work of Pauling,[1] there have been many papers dealing with participation of orbital basis functions of atomic d-like character in molecular orbitals[2-42] for systems containing nontransition elements. The current literature contains papers in which the relative merits of inclusion or omission of atomic d orbitals in an LCAO basis set are debated.[43] Unfortunately, the question as generally stated is not precise, and consequently it is impossible to answer in any meaningful way. It is the purpose of this paper to restate the basic question, to relate this to the problem of chemical bonding, to present some heuristically helpful examples, and to develop guidelines for the desirability of including such basis functions in a quantum chemical calculation or explanation.

The addition of any linearly independent function to a basis set will result in a wave function which is better, variationally, than a wave function in the smaller basis. Thus the addition of 4f functions will improve a calculation on H_2, although 4f functions on an H atom are physically unimportant. One would like to understand the role of these higher angular momentum functions in orbital bases. Much misunderstanding comes from the idea that d functions (abstract mathematical constructs) can contribute to, or participate in, a chemical bond, an idea rooted in too close adherence to the simple minimal basis LCAO approximation. In LCAO theory the inclusion of higher angular momentum orbitals can be required or justified by appeals to arguments of orbital population, energy lowering, or improvement in computed one-electron properties. This works because the prescription for choosing a basis is well defined: one Slater-type orbital (STO) per occupied atomic orbital in the constituent atoms. In this situation, the addition of any basis orbital means the addition of an orbital of the next higher angular momentum, as lower angular momentum functions have already been saturated in the scheme. Since *any* basis orbital thus included will contribute to all the one-electron wave functions it is allowed to by symmetry, the added function will have a nonzero population. The result always is lowering