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^{13}C-H Coupling Constants and Maximum Overlap Orbitals in Some Three-Membered Heterocyclic Compounds

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The criterion of maximum total overlap, modified to permit inclusion of ionic structures, has been employed to determine the hybridized bonding orbitals for ethyleneimine, ethylene oxide, ethylene sulfide, and cyclopropane. ^{13}C-H coupling parameters obtained from the NMR spectra of these compounds, which are linear functions of s-character in the appropriate carbon orbitals, served as experimental criteria for adjusting ionic content. The results appear reasonable as judged by calculated HCH angles and the order of heteroatom electronegativities.

Le critère de recouvrement maximum total, modifié pour permettre l'inclusion de structures ioniques, a été utilisé pour déterminer les orbitales hybrides de l'éthylèneimine, l'oxide d'éthylène, le sulfure d'éthylène et le cyclopropane. Les paramètres de couplage ^{13}C-H obtenus des spectres RNM de ces composés, qui sont des fonctions linéaires du caractère s des orbitaux de carbone correspondants, servaient de critère expérimental pour l'ajustage du contenu ionique. Le calcul des angles HCH et l'ordre des électronégativités des hétéroatomes conduisent à conclure que les résultants sont raisonnables.

Das Kriterium maximaler Überlappung wurde in einer Modifikation, die den Einschluß ionischer Strukturen gestattet, zur Bestimmung der Hybridzustände von Äthylenimin, Äthylenoxyd, Äthylensulfid und Cyclopropan herangezogen. Die ^{13}CH-Kopplungskonstanten der NMR-Spektren, die linear vom s-Charakter der entsprechenden Kohlenstoffzustände abhängen, dienten als experimentelles Kriterium für die Bestimmung der Anteils an ionischen Strukturen. Nach den berechneten HCH-Winkeln sowie der Reihenfolge der Elektronegativitäten der Heteroatome zu schließen, scheinen die Ergebnisse befriedigend zu sein.

Introduction

The criterion of maximum total overlap provides a basis for determining a suitable set of hybridized bonding orbitals which is intuitively appealing but without a satisfactory theoretical basis. Nevertheless, several recent developments tend to encourage continued interest in this simple method for approximating the electronic structures of molecules.

As was shown by Coulson and Goodwin [*3*], the maximum overlap orbitals (MOO) for the lower cycloalkanes predict geometrical properties which are essentially the same as those emerging from the earlier rigorous treatment of Coulson and Moffitt. Veillard and del Re have studied cyclopropane and cyclobutane in a similar manner and have pointed out that the fractional s-character of the orbitals so obtained agrees rather well with that predicted from the values of the ^{13}C-H coupling constants provided by NMR spectra [*12*].

This parameter, J (^{13}C-H), is of particular relevance in assessing MOO functions. As has been shown by Muller and Pritchard [*7*] and Shoolery [*11*], the following relation holds to a good approximation for ^{13}C directly bonded to H:

$$J\,(^{13}\text{C-H}) = 500\,\alpha^2 \tag{1}$$

where α is the coefficient of the *s*-component in the carbon orbital. Insofar as this relation is valid, Eqn. (1) provides a direct experimental basis for evaluating MOO functions.

The MOO method in conjunction with Eqn. (1) has recently been applied to all of the halomethanes for which J-values were available, with apparently good results [*6*]. In these molecules the halogen (X) orbital was hybridized to the extent indicated by the appropriate nuclear quadrupole coupling constants [*4*] and the ionic character (C^+X^-) was adjusted to provide agreement with experimental values of J. The ionic contents required for the series turned out to be in generally good agreement with the corresponding values inferred from the nuclear quadrupole data.

This study has now been extended to a series of simple three-membered heterocyclic compounds (ethyleneimine, ethylene oxide, and ethylene sulfide, with cyclopropane included for completeness), for which, unlike the case of the halomethanes, no independent criteria of the heteroatom hybridization are available. The results indicate that with the inclusion of what appear to be sensible amounts of ionic structure, the MOO functions can be adjusted to provide agreement between experimental and calculated values of J (C^{13}-H). These results and the methods used are discussed in some detail.

Calculations

The covalent overlap function

$$S = f\,(a, b, c) \tag{2}$$

where a, b, c are the hybridization parameters, was formulated following the procedure of Coulson and Goodwin [*3*]. The structures employed for the cyclic compounds are listed in Tab. 1. Using local cartesian coordinates, as shown in Fig. 1., and employing symmetry, the orbitals shown in Tab. 2 were obtained.

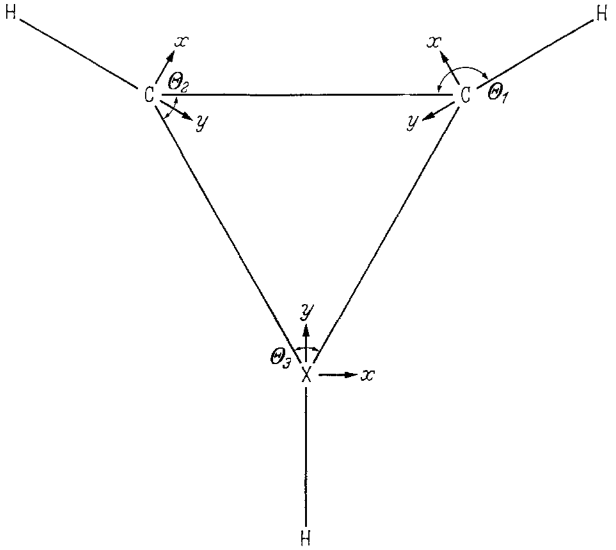

Fig. 1. Local cartesian coordinates for the three membered heterocyclic compounds

Table 1. *Bond lengths and bond angles for the three-membered ring compounds**

Molecule	R_{CC}	R_{CX}	R_{CH}	R_{XH}	Θ_1	Θ_2	Θ_3
Cyclopropane	1.534	1.534	1.085	1.085	150°	60°	60°
Ethyleneimine	1.480	1.488	1.083	1.000	159°25′	60°11′	59°38′
Ethylene oxide	1.472	1.436	1.082	–	159°25′	59°10′	61°40′
Ethylene sulfide ...	1.492	1.819	1.078	–	151°43′	57°06′	65°48′

* SUTTON, L. E., Editor, Interatomic Distances, The Chemical Society, London, 1958.

Table 2. *General bonding orbitals for the atoms in the three-membered ring compounds*

Nucleus	n	ψ_{ij}	ns	np_x	np_y	np_z
Carbon	2	ψ_{CX}	a	$-b(a^2+b^2)^{-1/2}$	$a(a^2+b^2)^{-1/2}(1-a^2-b^2)^{1/2}$	0
		ψ_{CC}	b	$a(a^2+b^2)^{-1/2}$	$b(a^2+b^2)^{-1/2}(1-a^2-b^2)^{1/2}$	0
		ψ_{CH}	$(2)^{-1/2}(1-a^2-b^2)^{1/2}$	0	$(2)^{-1/2}(a^2+b^2)^{1/2}$	$(2)^{-1/2}$
Nitrogen	2	ψ_{NC}	c	$(2)^{-1/2}$	$(2)^{-1/2}(1-2c^2)^{1/2}$	0
		ψ_{NH}	$(2)^{-1/2}(1-2c^2)^{1/2}$	0	$-c$	$(2)^{-1/2}$
		$\psi_{n.b.}$	$(2)^{-1/2}(1-2c^2)^{1/2}$	0	$-c$	$-(2)^{-1/2}$
Sulfur	3	ψ_{SC}	c	$(2)^{-1/2}$	$(2)^{-1/2}(1-2c^2)^{1/2}$	0
		$\psi_{n.b.}$	$(2)^{-1/2}(1-2c^2)^{1/2}$	0	$-c$	$(2)^{-1/2}$
Oxygen	2	ψ_{OC}	c	$(2)^{-1/2}$	$(2)^{1-/2}(1-2c^2)^{1/2}$	0
		$\psi_{n.b.}$	$(2)^{-1/2}(1-2c^2)^{1/2}$	0	$-c$	$(2)^{-1/2}$

The total overlap consists of a sum of integrals for each bond of the general form

$$S = 4\int \varphi_{CH\sigma}\,\varphi_{HC\sigma}\,dv + 2\int \varphi_{CX\sigma}\,\varphi_{XC\sigma}\,dv$$
$$+2\int \varphi_{CX\pi}\,\varphi_{XC\pi}\,dv + \int \varphi_{CC'\sigma}\,\varphi_{C'C\sigma}\,dv \quad (3)$$
$$+ \int \varphi_{CC'\pi}\,\varphi_{C'C\pi}\,dv + n\int \varphi_{XH\sigma}\,\varphi_{HX\sigma}\,dv$$

where $\varphi_{AB\sigma}$ and $\varphi_{AB\pi}$ are the components of ψ_{AB} parallel and perpendicular, respectively, to the bonding direction; and $n = 0, 1, 2$ for O or S, N, C, respectively.

The thirteen overlap integrals required were obtained by linear interpolation of published Slater overlap values [*8*] and are listed in Tab. 3. The maximum value of S was obtained by numerical methods, using an IBM 1620-II computer, and the values of a, b, and c appropriate to this maximum were determined. The corresponding orbitals are shown in Tab. 4 and Tab. 5 gives the interbond angles computed from these orbitals. The calculated covalent values of J (^{13}C-H), listed under J_0 in Tab. 6, were calculated from the expression $J_0 = 250\,(1-2a^2)$.

Ionic character ($CH_2C^+H_2X^-H_n$) was introduced by using the unnormalized wave function

$$\Psi = \psi_{cov} + 2\lambda\,\psi_{ionic} \quad (4)$$

where λ represents the ionic character per C-X bond. (There are two equivalent ionic structures, hence the use of 2λ in Eqn. (4)). The overlap integrals for the ionic structure (Tab. 3b) were computed using the previous covalent geometry, but with appropriate values of Z_{eff} for each atom as determined by Slater's rules [*5*]. Using the function (4) the calculated value of J (^{13}C-H) is

$$J_{\text{calc}} = \frac{J_0 + 2\lambda J_{01} + 2\lambda J_{02} + \lambda^2 J_{11} + 2\lambda^2 J_{12} + \lambda^2 J_{22}}{1 + 4\lambda + 4\lambda^2} \tag{5}$$

where J_0 is the covalent coupling constant; J_{11} is the coupling of neutral C in the ionic structure; J_{22} is that of C$^+$ in the ionic structure; J_{01} is the exchange term between covalent C and neutral C in the ionic structure; J_{02} is the exchange term between covalent C and C$^+$ in the ionic structure; and J_{12} is the exchange term between neutral C and C$^+$, both in the ionic structure.

J_{11} is determined solely by the s-character of C to H orbital in the ionic structure. J_{22} was calculated using the Z^3_{eff} dependence of the coupling as follows

$$J_{22} = \left(\frac{Z_{\text{eff}}}{Z_0}\right)^3 J'_{22} = \left(\frac{3.60}{3.25}\right)^3 J'_{22} = 1.359\, J'_{22} \tag{6}$$

where J'_{22} includes the s-character of the C$^+$ orbital but is not yet scaled for

Table 3a. *Slater overlap integrals for the covalent forms of the three-membered ring compounds**

Overlap Integral	Cyclopropane	Ethyleneimine	Ethylene sulfide	Ethylene oxide
$(1s_{\text{H}}, 2s_{\text{C}})$	.5715	.5765	.5751	.5732
$(1s_{\text{H}}, 2p\sigma_{\text{C}})$	.4644	.4649	.4658	.4651
$(2s_{\text{C}}, ns_{\text{X}})$	.3447	.3031	.2866	.2703
$(2s_{\text{C}}, np\sigma_{\text{X}})$	.3684	.2960	.3500	.2433
$(2p\sigma_{\text{C}}, ns_{\text{X}})$	.3684	.3635	.3019	.3538
$(2p\sigma_{\text{C}}, np\sigma_{\text{X}})$	.3298	.3102	.3281	.2814
$(2p\pi_{\text{C}}, np\pi_{\text{X}})$	.1952	.1609	.1521	.1386
$(2s_{\text{C}}, 2s_{\text{C}})$	.3447	,3682	.3625	.3717
$(2s_{\text{C}}, 2p\sigma_{\text{C}})$	.3684	.3860	.3818	.3885
$(2p\sigma_{\text{C}}, 2p\sigma_{\text{C}})$	.3298	.3320	.3320	.3320
$(2p\pi_{\text{C}}, 2p\pi_{\text{C}})$	.1952	.2136	.2090	.2163
$(ns_{\text{X}}, 1s_{\text{H}})$	.5715	.5502	–	–
$(np\sigma_{\text{X}}, 1s_{\text{H}})$	.4644	.4059	–	–

* Obtained by linear interpolation from Reference [*8*].

Table 3b. *Slater overlap integrals for the ionic forms of the three-membered ring compounds**

Overlap Integral	Ethyleneimine	Ethylene sulfide	Ethylene oxide
$(1s_{\text{H}}, 2s_{\text{C}})$	.5727	.5752	.5732
$(1s_{\text{H}}, 2p\sigma_{\text{C}})$	.4649	.4658	.4651
$(2s_{\text{C}}, ns_{\text{X}^-})$	.3333	.3093	.2703
$(2p\sigma_{\text{C}}, ns_{\text{X}^-})$	.3765	.3028	.3538
$(2s_{\text{C}}, np\sigma_{\text{X}^-})$	.3401	.3839	.2434
$(2p\sigma_{\text{C}}, np\sigma_{\text{X}^-})$	.3235	.3309	.2814
$(2p\pi_{\text{C}}, np\pi_{\text{X}^-})$	.1858	.1673	.1387
$(2s_{\text{C}}, 2s_{\text{C}^+})$	.3320	.3266	.3356
$(2p\sigma_{\text{C}}, 2s\sigma_{\text{C}^+})$	.3782	.3732	.3811
$(2s_{\text{C}}, 2p\sigma_{\text{C}^+})$	.3361	.3319	.3387
$(2p\sigma_{\text{C}}, 2p\sigma_{\text{C}^+})$	.3226	.3213	.3232
$(2p\pi_{\text{C}}, 2p\pi_{\text{C}^+})$	.1846	.1805	.1874
$(1s_{\text{H}}, 2s_{\text{C}^+})$	.5358	.5384	.5363
$(1s_{\text{H}}, 2p\sigma_{\text{C}^+})$	.4221	.4233	.4223
$(1s_{\text{H}}, ns_{\text{X}^-})$	.5871	–	–
$(1s_{\text{H}}, np_{\text{X}^-})$	.4457	–	–

* Obtained by linear interpolation from Reference [*8*].

Table 4. *Calculated bonding orbitals for the covalent forms of the three-membered ring compounds*

Molecule	Atom	n	ψ_{ij}	μ*	ns	np_x	np_y	np_z
Cyclopropane	C	2	ψ_{CC}	2.0518	.4381	.7071	.5550	0
			ψ_{CH}	1.4988	.5550	0	−.4381	.7071
Ethyleneimine	C	2	ψ_{CC}	1.8575	.4740	.5944	.6495	0
			ψ_{CN}	2.6729	.3504	−.8041	.4802	0
			ψ_{CH}	1.4374	.5711	0	−.4169	.7071
	N	2	ψ_{NC}	1.8099	.4836	.7071	.5158	0
			ψ_{NH}	1.6609	.5158	0	−.4836	.7071
			$\psi_{n.\,b.}$	1.6609	.5158	0	−.4836	−.7071
Ethylene sulfide	C	2	ψ_{CC}	2.1165	.4272	.7003	.5719	0
			ψ_{CS}	2.1664	.4191	−.7139	.5610	0
			ψ_{CH}	1.4548	.5665	0	−.4232	.7071
	S	3	ψ_{SC}	1.5862	.5333	.7071	.4642	0
			$\psi_{n.\,b.}$	1.9081	.4642	0	−.5333	.7071
Ethylene oxide	C	2	ψ_{CC}	1.8572	.4741	.5734	.6682	0
			ψ_{CO}	2.8431	.3818	−.8193	.4676	0
			ψ_{CH}	1.4168	.5767	0	−.4092	.7071
	O		ψ_{OC}	1.3502	.5952	.7071	.3817	0
			$\psi_{n.\,b.}$	2.4210	.3818	0	−.5952	.7071

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* The coefficient of mixing from $\psi = a\,(s + \mu p)$.

Table 5. *Calculated angles in the covalent forms of the three-membered ring compounds*

Molecule	$< (\psi_{CC}, \overline{CC})$	$< (\psi_{CX}, \overline{CX})$	$< (\psi_{XC}, \overline{XC})$	$< (\psi_{CH}, \psi_{CH'})$	$<HCH_{exptl.}$ *
Cyclopropane	21°53′	21°53′	21°53′	116°38′	118°12′
Ethyleneimine** ..	21°53′	19°33′	24°4′	118°58′	116°41′
Ethylene sulfide ...	22°29′	23°1′	23°49′	118°24′	116°
Ethylene oxide	20°3′	21°49′	30°48′	119°14′	116°41′

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* See footnote Tab. 1.

** $< (\psi_{NH}, \text{plane}) = 124°22'$; $< (\overline{NH}, \text{plane}) = 112°$ (see footnote Tab. 1).

Table 6. *Calculated values of J* (^{13}C-H) *with the inclusion of ionic character in the* C-X *bonds for the three-membered ring compounds*

Molecule	J_{exptl}	J_0	λ^c	% I^d
Cyclopropane	161[a]	158.4	.000	.00
Ethyleneimine	168[b]	163.0	.080	6.93
Ethylene sulfide ...	170[b]	160.5	.191	13.84
Ethylene oxide	176[b]	166.3	.163	12.28

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a Reference [7].

b MORTIMER, F. S., J. Mol. Spec. 5, 199 (1960).

c The coefficient of mixing from $\Psi = \psi_{cov} + 2\,\lambda\,\psi_{ionic}$; adjusted to give agreement between J_{calc} and J_{exptl}.

d Per C-X bond.

Table 7. *Calculated bonding orbitals for the ionic forms of the three-membered ring compounds*

Molecule	Atom	n	ψ_{ij}	μ*	ns	np_x	np_y	np_z
Ethyleneimine	C	2	ψ_{CC^+}	1.9869	.4496	.6300	.6333	0
			ψ_{CN^-}	2.5531	.3647	−.7766	.5137	0
			ψ_{CH}	1.4170	.5766	0	−.4093	.7071
	C	2	ψ_{C^+C}	1.6981	.5074	.3613	.7822	0
			$\psi_{n.b.}$	4.9869	.1966	−.9324	.3031	0
			ψ_{C^+H}	1.3571	.5932	0	−.3848	.7071
	N$^-$	2	ψ_{N^-C}	1.4259	.5742	−.4143	.7062	0
			$\psi_{n.b.}$	3.6925	.2614	.9101	.3215	0
			ψ_{N^-H}	1.5240	.5486	0	−.4461	.7071
			$\psi_{n.b.}$	1.5240	.5486	0	−.4461	−.7071
Ethylene sulfide	C	2	ψ_{CC^+}	2.1063	.4289	.6894	.5838	0
			ψ_{CS^-}	2.2363	.4082	−.7244	.5555	0
			ψ_{CH}	1.4422	.5698	0	−.4187	.7071
	C	2	ψ_{C^+C}	1.7451	.4972	.4242	.7569	0
			$\psi_{n.b.}$	4.1757	.2329	.9056	−.3545	0
			ψ_{C^+H}	1.3649	.5910	0	−.3882	.7071
	S$^-$	3	ψ_{S^-C}	1.1480	.6568	−.4374	.6142	0
Ethylene oxide	C	2	ψ_{CC^+}	2.0018	.4469	.5855	.6764	0
			ψ_{CO^-}	2.9321	.3228	−.8106	.4886	0
			ψ_{CH}	1.3685	.5900	0	−.3882	.7071
	C	2	ψ_{C^+C}	1.6539	.5174	.3351	.7874	0
			$\psi_{n.b.}$	5.3538	.1836	−.9422	.2801	0
			ψ_{C^+H}	1.3650	.5910	0	−.3883	.7071
	O$^-$	2	ψ_{O^-C}	.8255	.7712	−.3986	.4964	0

* The coefficient of mixing from $\psi = a(s + \mu p)$.

increased Z. In order to estimate the cross terms we have assumed a geometric-mean relationship

$$J_{01} = (J_0 J_{11})^{\frac{1}{2}} \tag{7}$$

$$J_{02} = (J_0 J_{22})^{\frac{1}{2}} = (1.359\, J_0 J'_{22})^{\frac{1}{2}} \tag{8}$$

$$J_{12} = (J_{11} J_{22})^{\frac{1}{2}} = (1.359\, J_{11} J'_{22})^{\frac{1}{2}} \tag{9}$$

where the prime has the same significance as before.

After evaluating each of these terms and inserting them into Eqn. (5), λ was adjusted to obtain agreement with $J_{\text{exptl.}}$ and the fractional ionic character per C-X bond was determined as [2]

$$I = \lambda/(1 + 2\lambda)\ . \tag{10}$$

The MOO functions for the ionic structures are listed in Tab. 7. The values of λ and I obtained are shown in Tab. 6.

Discussion

As can be seen in Tab. 6, maximization of total overlap, using only the covalent structures, leads to coupling values (J_0) which are in all cases within 6% of the observed values. The amount of ionic structure (I) which must be included for exact agreement appears to be of a reasonable magnitude, and in the case of N and O follows the order expected from Pauling's electronegativity values [*9*]. The value of I for ethylene sulfide appears to be somewhat high. This may be due to some degree of participation of *d*-orbitals, not considered here, or it may reflect the fact that the orbital electronegativity is in this case larger than Pauling's value.

The calculated value of J_0 for cyclopropane is about 2.5 cps smaller than J_{exptl}. We find that exact agreement is obtained by including 2.59% ionic structure of the form $H^-C^+H\ (CH_2)_2$. Inclusion of these structures in the other three molecules would decrease the values of I shown in Tab. 6.

The calculated bonding orbitals are not parallel to the line joining the nuclei, as can be seen from Tab. 5. This is consistent with the results reported previously [*3*, *12*], which were presented as evidence for bent bonds in molecules of this type. The CH bonds are not expected to be bent, however. The angle between the C to H orbitals is in all cases within 2.2% of the experimental HCH angle.

The presence of non-bonding electrons in the heterocyclic molecules creates a problem that is absent in the MOO treatment of the cycloalkanes. In the latter, all valence shell electrons participate in bonding. This serves to restrain the tendency towards arbitrary hybridization of some bonds in order to maximize the overlap of the others. Lone-pair electrons contribute nothing to the total overlap function and are, so to speak, at the mercy of the bonding orbitals. Therefore, unless some constraint is incorporated, the MOO method may lead to totally unrealistic results where non-bonding electrons are involved. In the case of the halomethanes such a constraint was provided by using a constant fraction of *s*-character in the halogen orbitals, as inferred from analyses of nuclear quadrupole coupling data [*6*].

In the cyclic molecules studied here the fixed ring geometry appears to provide a fairly effective and realistic constraint. However, in the case of ethyleneimine this contraint alone was inadequate, since in addition some decision was required regarding the disposition of the two out-of-plane nitrogen orbitals, N-H and lone-pair. For example, if the hybridizations in these two orbitals were allowed to vary independently the resultant structure was found to be planar sp^2 with the lone-pair occupying a pure p_π orbital. If we restricted the lone-pair electrons to the *s*-orbital, the three bonding N orbitals were necessarily p^3. The final structure obtained was based on the condition that the N-H and lone-pair orbitals be alike. This assumption, arrived at after several trial calculations, was accepted only because it yielded an angle of inclination of the N-H bond reasonably near the experimental value. In the case of O and S, with two occupied non-bonding orbitals, we have no way of determining how realistic the non-bonding MOO functions are.

If the fixed ring geometry of the cyclic compounds with lone-pair electrons actually provides a constraint upon the overlap function of these molecules, then we should expect the MOO technique to yield unreasonable results when applied to molecules in which this constraint is not operative. Indeed, when we applied this technique to dimethyl ether and dimethyl sulfide, we obtained *sp*-hybridization of the oxygen and sulphur bonding orbitals if the geometries of the molecules were allowed to be dictated by the overlap function. Fixing the geometry at the experimental values led to more reasonable hybridizations of the bonding orbitals, but predicted angles between the bonding orbitals were greater than the angles between the lines joining the nuclei. Microwave evidence that this is actually the case for dimethyl ether has been presented elsewhere [*1*].

The foregoing remarks are not intended to disparage the MOO method. On the contrary, it is felt that the agreement obtained between the calculated and observed values of the ^{13}C-H coupling constants and HCH bond angles in this study is quite encouraging to further inquiry. The point stressed here is that the method might be improved if an additional constraint, reflecting the effects of rehybridizing the non-bonding electrons, were added to the original requirement that S_{total} be a maximum. PAULING has suggested the use of the *s-p* promotional energy for a rather similar purpose [*10*]. Such an approach, although it appears to neglect the compensating energy gained through rehybridization of the bonding orbitals, may provide a basis for the needed modification.

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