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Construction of Nonequivalent Hybrids in Hydrocarbon Polymers: Polybutadiene, Polyisoprene, and Related Systems

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Received October 11, 1973

ABSTRACT: Nonequivalent hybrid orbitals are constructed for a series of hydrocarbon polymers using bond overlaps as a criterion for the estimate of the relative contributions of s and p orbitals. A suitably weighted sum of bond overlaps is maximized according to the procedure initially developed by, Coulson, Randić, and others.[2] The following systems have been investigated: polyethylene (I), 1,4-polybutadiene (II), 2-methyl-1,4-polybutadiene (III), 2,3-dimethyl-1,4-polybutadiene (IV), polypropylene (V), 1,4-polyisoprene (VI), 1,2-polyisoprene (VII), and 3,4-polyisoprene (VIII). It is found that for a given carbon atom small deviations from the idealized hybrid forms sp^3, sp^2, and sp exist. The magnitude of these deviations is determined by the structural groups bonding to the carbon atom in question. It is shown that although only small changes accompany similar structural groups, such changes correspond to known variations in bond properties. Taken cumulatively these small variations may become important in long-chain systems. The problems associated with orientational isomerization are considered in polypropylene where the calculations have been performed for a head to tail and head to head-tail to tail sequences of the repeating monomer unit. An interesting correlation between the calculated hybrid forms and spin-spin coupling constants is discussed.

The application of theoretical methods to studies of hybridization in macromolecules is a subject which has received relatively little attention by comparison with efforts directed at smaller molecules. The reason is that most quantum chemical methods are laborious and expensive when applied to a relatively large system—if such an application indeed is possible. In this paper we consider hybridization in some common hydrocarbon polymers by a simple and reliable method which has already found widespread application in smaller systems[2f] but which has not previously been applied to polymers. The model abandons the usual description of carbon atoms bonding in terms of sets of equivalent hybrids: tetrahedral sp^3, trigonal sp^2, and digonal sp. It considers more general hybrids of an sp^n type, where n is not restricted to integers and may take any positive value. The particular values reported here are based on a criterion of maximum overlapping,[3] modified in order to take into account differences in various bond types.[4] It is important to recognize that the usual description in terms of sp^3, sp^2, or sp hybrids implies that the carbon atom in question is substituted by four, three, or two *equivalent* groups—a condition which is not generally realized in real hydrocarbon molecules. It has been demonstrated[2f] that the hybrids constructed by the method adopted here provide surprisingly precise and accurate predictions regarding bond properties. The quantitative agreement between various calculated quantities and correlated experimental data justifies a further extension and application of the model. Here we apply the method to polymers.

The purpose of the calculation is to provide a description of the differences between similar bonds in related compounds. The description may not only be qualitatively correct but also quantitative. One may at first be surprised that such a simple approach provides a useful basis for the discussion of molecular properties, but it is not unusual for empirical and semiempirical methods to provide a useful simulation of bonding through a judicious choice of empirical parameters. A theoretically more satisfactory treatment suitable for application to large systems will probably not occur in the immediate future. This is particularly true for all-electron SCF *ab initio* computations. Such calculations have in fact been recently reported for an infinite polyenic chain[5] which while indicating that *ab initio* calculations of the electronic structure of polymers is feasible, does not alter the fact that their extention to more complicated polymers is far from being in sight. Semiempirical calculations of intermediate complexity, such as various MO schemes based on partial or complete neglect of many center integrals, are applicable to systems such as those considered in this paper, and some calculations have been reported. However, their reliability is doubtful especially when applied to systems for which there exists only limited experimental data needed for parametrization. For instance a recent application of the CNDO/2 method to a discussion of the optical properties of polyethylene and its various conformers gave an excessive excitation energy.[6] One remedy for this is to readjust some of the CNDO parameters,[6] but such reparametrization often results in poor predictions of molecular geometry.[7]

Despite its unpromising appearance the situation is not this discouraging. Of course, one can carry just so far a simple approach in which one constructs a set of *nonequivalent* hybrids but, on the other hand, this procedure provides both a reliable and internally consistent description of atomic environments. This is achieved not only at minimal computational cost[8] but also by utilizing only a few empirical parameters which have not been selected for the particular molecules in question but which have been used in *all* hydrocarbon molecules.[9] In this connection empirical and semiempirical methods should only be judged by their success in correlating different experimental quantities and by their prediction of differences of one particular property from one compound to the next in a series of structurally related systems. The maximum overlap method is very successful in predicting such systematic trends even when the structural differences between one compound and the next in such series are very small. Numerous correlations between the calculated hybridization parameters and the relevant molecular property as measured experimentally[2f,10] gives support to the method. This includes correlations with spin-spin coupling constants,[11,21] vibrational stretching frequencies,[13] proton chemical shifts and proton acidities, bond energies,[9] and bond lengths.[12] However, such experimental data for hydrocarbon polymers are lacking, except perhaps for nmr data. So, much of the predictive potential of the maximum overlap method can not yet be fully exploited. A tabulation of the results for half-a-dozen systems when the accompanying discussion refers to most of them with only a sentence in the text may appear to some as a bad idea. This is however not a sign that there is little of value in the tables, but rather that there is little experimental data currently available for comparison. The tabulated data are nevertheless of interest when close comparisons are made between the calculated parameters of similar structural units in different molecules. Of course, such comparisons are not going to show dramatic variations in the computed quantities—which would then contradict the supposition of similarity of such structural groups. A change for example in bond overlap of 0.005 corresponds to a change in CC distance of approximately[14] 0.006 Å. The detection of such a change may frequently be beyond the currently possible experimental means. To insist on the significance of a prediction on such a fine level for an *individual* bond may well be unjustified, but to assert that such predictions are totally meaningless when considering *relative* changes in bonds when their immediate environment is somewhat altered would be equally unjustified. The ability to predict small pertubations due to minor differences between nearest neighbors in a structurally related series is in fact an asset of the maximum overlap method. Such small changes have been found to be due to structural differences and cannot therefore be dismissed as not significant. For an illustration one may consult the calculations of hybrids in small rings where a systematic increase in bond overlap could be traced to the nature of the substitutents at the carbons forming the bond.[15]

Outline of the Method

The method has been described in the literature[16] including presentation of a worked example. Essentially, the hybrid s-p content is not assumed prescribed, but is varied for all atoms until parameters are found which maximize a suitable weighted sum of bond overlaps

$$W = \sum_{\substack{\text{all CC} \\ \text{bonds}}} k_{CC} S_{CC} + \sum_{\substack{\text{all CH} \\ \text{bonds}}} k_{CH} S_{CH}$$

The quantities S_{CC} and S_{CH} are bond overlap integrals corresponding to CC and CH bonds. The weighting procedure, suggested initially by Coulson,[4] accounts for the fact that equal bond overlaps in different kinds of bonds correspond to different bond energies. So in fact the above criterion for the maximum no longer present a *spatial* criterion but an *energy* criterion, though of a special form which is related to the former. The distinction however is important not only from a conceptual point of view but also as the source of substantial improvement in the quality of the results and their predictive ability.

The actual calculations are preformed as follows. One selects a molecular geometry and the basis atomic orbitals. We adopted for CC and CH bond lengths values which take into account the variations of the immediate environments, *i.e.*, values which follow from a classification of bonds into various sp^m-sp^n bond types.[17] For atomic orbitals we use double ζ functions.[18] For convenience the basic overlap integrals have been tabulated.[19] All the hybrids of a same atom are constrained by orthogonality conditions

$$a_i a_j + b_i b_j \cos \theta_{ij} = \delta_{ij}$$

where a and b are the coefficients of the 2s and 2p orbitals involved related to the hybrid parameter n of the sp^n notation by: $n = (b/a)^2$. Initially assumed values for the hybrid exponents n_i are systematically varied in the range of interest and prescribed accuracy. In practice one can start with the idealized hybrids, namely sp^3, sp^2, and sp, and limit the accuracy in computed n values to 0.001. Thus when the input hybrids and optimal hybrids which maximize the weighted sum of bond overlaps differ by 0.001 or less the search is discontinued.

Results

The polymers which we have chosen for investigation are: polyethylene (I), 1,4-polybutadiene (II), 2-methyl-1,4-polybutadiene (III), 2,3-dimethyl-1,4-polybutadiene (IV), polypropylene (V), 1,4-polyisoprene (VI), 1,2-polyisoprene (VII), and 3,4-polyisoprene (VIII). (Molecular skeletons and numbering of carbon atoms are shown in Table V.) In these molecules the following bond types arise: sp^3–sp^3 and sp^3–sp^2 for single C—C bonds and sp^2–sp^2 for double C=C bonds.[20] The C—H bonds are either tetrahedral or trigonal. The hybrid parameter n indicating their s-p composition and bond overlaps are shown in Table I for molecules I-IV and in Table II for monomer units of polymers VI-VII. Characteristic values for hybrids describing C—C single bonds are closely grouped around $sp^{3.06}$, $sp^{3.14}$, and $sp^{3.20}$ for methyne, methylene, and methyl carbons, respectively. The s-p content of quaternary carbons is little altered from the sp^3 form indicating approximate equivalence of the corresponding C-C bonds ($sp^{2.94}$–$sp^{3.02}$). In the case of hybrids involved in C=C double bonds the calculated s-p content is considerably different from the symmetrical sp^2 trigonal case indicating an inadequacy of the idealized model based on canonical hybridization. This is not surprising in view that the bonds involved are so different and the local trigonal symmetry absent. Hybrids participating in the formation of a C=C double bond increase their s content and the typical forms are close to $sp^{1.65}$. The increase in the s content is at the expense of the hybrids involved in formation of C—C single bonds, not from hybrids making a C—H bond if present, and the typical hybrids for C—C bonds are of the form: $sp^{2.25}$. These results are in accordance with the accumulated results of earlier applications on molecules having similar structural features.[21]

Table I
Calculated Maximum Overlap Hybrids and Bond Overlaps for Polyethylene (I), Polybutadienes (II–IV), and Polypropylene (V)[a]

Molecules	I	II	III	IV	V
CC Hybrids					
11	3.168				
12		3.126	3.126	3.126	3.167
21		2.266	2.228	2.226	3.080
22		1.662		1.634	
23			1.632	2.222	3.080
32			1.662	3.196	3.261
13			3.124		
31			2.226		
24			2.223		
42			3.196		
CH Hybrids					
1 H	2.845	2.882	2.882	2.882	2.846
2 H	2.143				2.779
3 H			2.143	2.939	2.920
4 H			2.939		
CC Bond Overlaps					
11	0.6494				
12		0.6727	0.6735	0.6735	0.6509
22		0.7679		0.7697	
23			0.7689	0.6724	0.6493
13			0.6727		
24			0.6724		
CH Bond Overlaps					
1 H	0.7212	0.7206	0.7206	0.7206	0.7212
2 H		0.7411			0.7224
3 H			0.7411	0.7196	0.7199
4 H			0.7196		

[a] The coefficient of 2s orbital a and the exponent n of the notation sp^n shown in the table are simply related: $n = (1 - a^2)/a^2$.

Molecular Geometries and Bond Overlaps. The maximum overlap method *assumes* a particular geometry for the system investigated. It may then appear that the method cannot discuss details of molecular geometries. The situation is similar however to that accompanying various π-electron calculations which also assume molecular geometry (usually by taking all CC bond lengths equal). Subsequent use of a bond order–bond length correlation allows one to predict changes implied by the theoretical model. The role of bond order is taken here by bond overlaps.[14] One can use the bond lengths predicted from a correlation between bond overlaps and bond lengths and repeat the calculations now assuming the geometry calculated in the first step as initial. This leads to an iterative procedure which will eventually result in internal consistency between the assumed and calculated bond lengths. Such a procedure has been outlined[14] and has been occasionally implemented.[12] Experience has however shown that *if* one adopts as the initial geometry a set of CC and CH bond lengths selected so to take into account variations in bond length due to an immediate environment, *i.e.*, if one distinguishes from the onset various sp^n–sp^m bond types,[17,22] one speeds up the covergence of the iterative procedure. This seems to be particularly true if no strained small rings are present, in which case the results of the first step in the calculations are frequently in approximate agreement with the assumed bond lengths. Accordingly here we have not adopted an iterative procedure.

The differences in bond overlaps are not only reflected in changes in bond length, but also in bond energy. For example, on the presumption that a chain is as strong as its weakest link, it is appropriate to give attention to the *relative* differences in various calculated bond properties, even if they are not large. For example, a difference in CC bond overlap of typical sp^3–sp^3 and sp^3–sp^2 bonds is about 0.015 (*cf.* 1,4-polyisoprene. Table II). If we adopt the relationship[9]

$$\Delta E_{CC} = 218.5 \Delta S_{CC}$$

which relates the change in the bond energy (E_{CC}) in kcal/mol to the change in calculated bond overlaps (S_{CC}) the difference in energy between the two bond types amounts to about 2.5 kcal/mol. This value is close to various empirical estimates (to the extent that they agree among themselves). Differences in bonds of the same type would be much smaller. For example in 1,2-polyisoprene (Table II) bonds C_1C_2 and C_2C_3 are both of the same type, but differ in the number of hydrogens attached to carbon. The difference in their CC bond overlaps is only 0.001 which corresponds to a slight enhancement (0.2 kcal/mol) of C—C bonds in C—CH_2 in comparison with C—C bond in C—CH_3. This difference of 0.2 kcal/mol may appear too small to be attributed any significance, but we shall show that such differences make sense and are not an artifact. Furthermore the small change in hybridization in the two sp^3–sp^2-type bonds of 1,2-polyisoprene (to be found also in other systems investigated) produces a change of 0.001 in C—C bond overlaps and causes similar differences in the corresponding C—H bond overlaps. These differences can be compared with the empirical bond energy estimated for such bonds. One such estimate is due to Bernstein[23] which we will quote: to -CH_3, CH_2, and CH Bernstein attributes the following C—H bond energies (all in kcal/mol): 98.46, 97.57, and 97.26, respectively. The differences between the individual types are quite small, being 0.9 and 0.3 kcal per mol. The results are quite close to the predictions of the maximum overlap method when a modified weighting procedure is adopted.[9] But if one wants to compare different kinds of C—H bonds, such as tetrahedral and trigonal C—H bonds

Table II
Calculated Maximum Overlap Hybrids and Bond Overlaps for Polyisoprenes Investigated

Molecules	VI	VII	VIII	VI	VII	VIII
CC Hybrids				Bond Overlaps		
12	3.134	3.112	3.112	0.6734	0.6586	0.6577
21	2.228	2.994	3.046			
23	1.632	2.992	3.076	0.7689	0.6575	0.6744
32	1.662	3.174	2.226			
34	2.266		1.630	0.6726		0.7679[a]
43	3.132		1.694			
14	3.102			0.6568		
41	3.132					
24		3.020			0.6744	
42		2.272				
25	2.223			0.6724		
52	3.196					
35			2.228			0.6723
53			3.196			
45		1.658			0.7671[a]	
54		1.692				
CH Hybrids				CH Bond Overlaps		
1 H	2.889	2.894	2.894	0.7205	0.7204	0.7204
2 H			2.841			0.7213
3 H	2.143	2.945		0.7411	0.7915	
4 H	2.889	2.143	2.181	0.7205	0.7411	0.7403
5 H	2.939	2.182	2.939	0.7197	0.7403	0.7196

[a] Only σ component of C=C double bond is shown. The contribution from π overlap is available from tables of overlaps (ref 19).

(*e.g.*, the two CH bonds in 1,4-polybutadiene, Table I), the accompanied difference in bond overlaps is larger, approximately 0.02, and the associated change in bond energies of the two types of C—H bonds amounts to 4.5 kcal/mol. Bernstein estimated for CH bond energy of the fragment (H)(H)C=C a value of 103.0 kcal/mol, and CH bond energy in methyl to have a value of 98.5 kcal/mol. The difference of the two empirical values is in full agreement with the above maximum overlap estimate.

Other examples of useful comparison between properties of different bonds and different molecules are possible. We will refrain from further elaboration of such more general conclusions. However, a particular discussion would be of interest when discussing polymers and polymer strength, as it pertains to changes in bond overlaps of the bonds forming the polymer backbone. An example is provided by 1,4-polybutadiene and its methyl-substituted derivatives III and IV (Table I). The repeating structure in these systems is a C=C double bond flanked by C—C single bonds. The differences between the individual polymers is solely due to the pertubation of the methyl substituents, which will alter the hybridization slightly. From Table I we see that each methyl substitution *increases* the C=C bond overlap by about 0.001, and a similar increase occurs in adjacent C—C bonds. The overall increase in CC bond overlaps of the backbone correspond to about 0.85 kcal/mol on going from 1,4-polybutadiene to dimethyl-substituted polybutadiene. The effect is additive, *i.e.*, the increase for the methyl substitution is half that found for dimethyl substitution. This is a comforting result, and in an agreement with experience, but it should be noticed that the maximum overlap procedure optimizes the weight sum of bonded overlaps without making provision to secure the simple additivity. That the contributions of the two methyl groups are to a high degree additive simply suggests that the major effects in rehybridization in encountered structural units are due to nearest-neighbor pertubations only.

A summary of the geometrical data based on the maximum overlap calculations is as follows: C—C single bonds of the sp^3-sp^3 type, having bond overlaps in the range 0.654–0.659 are associated with a range of C—C bond lengths from 1.534 to 1.530 Å. These values are somewhat smaller that the usually assumed C—C bond lengths of 1.545 Å. The sp^3-sp^2 bond lengths are also somewhat reduced relative to their usual values (1.513 Å as opposed to 1.520 Å).

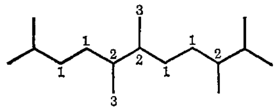
The changes in hybrid composition are also reflected in small deviations from the tetrahedral and trigonal bond angles characterizing local environments of appropriate symmetry (109°28′ and 120°, respectively). Although the changes in bond angles do not exceed a few degrees, for example, in polyethylene the CCC angle is decreased by 1.5°, the HCH angle being correspondingly increased, in polybutadiene and polyisoprene the reduction in the CCC angle is smaller, about 0.5°. The differences are larger at the trigonal carbon atoms which are characterized by larger changes in s-p content of their hybrids. Thus the angle (C)(C)C=C is calculated to be only 117° as a consequence of the drift of the s content to the hybrid involved in forming the C=C bond.

On the Calculations of the Strength of Polymers. Calculations of the strength of polymers and theoretical determinations of the elastic modulus, the breaking strength, and the breaking strain have been associated with electronic properties of polymers. Without going into the problem of distinguishing between intramolecular and intermolecular contributions the former aspect has received some theoretical attention,[24] and, for example, CNDO-type calculations have been made for polyethylene and polyethylene with side chains.[25] One of the results of such calculations is that increasing or decreasing the length of the side chain has very little effect on the elastic modulus. Such a conclusion is consistent with the general properties of the maximum overlap calculations which are based on the concept of localized orbitals. According to this approach, lengthening the side chain will have little effect on hybridization at the branching site, since hybridization depends primarily on nearest-neighbor interactions. However, there is one important difference between the conclusions drawn from CNDO calculations and ours. According to Boudreaux[25] the physical interpretation of the results of CNDO calculations on polyethylene and branched polyethylenes is that the presence of an additional carbon atom draws away some of those electrons participating in the backbone bonds, hence weaking them. Accordingly it seems appropriate to expect a reduction in strength of the backbone.[25] In contrast, the maximum overlap procedure shows that methyl substitution of the backbone increases the overlap of adjacent backbone bonds and hence strengthens them. This is interpreted as meaning that the replacement of a hydrogen by a carbon more closely approximates idealized sp^3 (or sp^2) hybridization in which all CC hybrids are similar. The s content is increased in all CC bonds, the increase resulting from the absence of C—H bonds which normally tend to have higher s content. This trend has been observed in numerous situations in the investigation of hybridization in hydrocarbons. Whenever bonds can attain higher s content, they will do so and rehybridization follows.[26,27] We are therefore justified in concluding from the hybridization model that branching of the polymer backbone, at least due to methyl and related alkyl substitutions, will strengthen the elastic modulus. However, if nonbonded interactions which are currently disregarded in the maximum overlap procedure should become important appropriate corrections will have to be made. We suspect that minor electronic migrations may have been exaggerated or inadequately treated in CNDO-type calculations and that this will become apparent in the future. Recent comparison of hybridization in a number of hydrocarbons[28] indicates substantial agreement in hybridization predicted by the two schemes, though the maximum overlap results are somewhat more consistent when hybrids in different molecules are compared.

Orientational Isomerization

Experimental evidence indicates that corresponding pairs of orientational isomers differ somewhat in their physical properties. Nmr spectroscopy[29] has proved particularly useful in deriving information about the sequential orientation of the monomer units, owing to the sensitivity of nuclear spin-spin couplings to the nuclear environment. Nmr has been used, for example, to determine the sequence characterizing the predominant configuration, meso or racemic, in vinyl polymers.[29] The monomer addition step may be random, *i.e.*, independent of the stereochemical configuration of the chain already formed. The accompanying statistics is Bernoullian. In other situations the monomer addition propagates such that orientation within the chain is influenced by the stereochemistry of the chain end, so that the addition constitutes a first-order Markov process. The theoretical study of systems and conditions leading to one or the other situation appears to be beyond the present capabilities of theoretical models, but the characterization of the polymer ends and the consequent differences in physical properties resulting from the orientation of the preceeding monomer unit may already be within reach of examination.[30] Here we examine such differences by the maximum overlap method, bearing in mind that even if they need not be decisive in regulating the generation of a polymer these differences may be helpful in drawing correlations between properties which depend on the structure and sequence of monomers.

Table III
Hybrids, Bond Overlaps, and Interhybrid Angles for Head to Head and Tail to Tail Orientation of the Repeating Unit in Polypropylene



Head to Head, Tail to Tail Polypropylene

Hybrid	*a*	*n*	Overlap	Interhybrid Angles (deg)	
11	0.4899	3.166	0.6495	C_1–C_1–C_2	108.40
12	0.4899	3.167	0.6511	C_1–C_2–C_2	109.03
21	0.4959	3.067		C_1–C_2–C_3	109.04
22	0.4926	3.121	0.6510	H–C_1–H	110.57
23	0.4960	3.065	0.6496	H–C_3–H	110.03
32	0.4844	3.262		C_2–C_3–H	108.91
1 H	0.5099	2.846	0.7212		
2 H	0.5152	2.767	0.7226		
3 H	0.5051	2.920	0.7199		

The effects of *structural* isomerizations are illustrated by the differences in calculated hybridization parameters of 1,4-polyisoprene, 1,2-polyisoprene, and 3,4-polyisoprene (Table II). Similar effects of *orientational* isomerization originate due to the relative orientations of subsequent monomer units in a head to head, tail to tail manner, $-(-{*}{*}-)_n-$, as opposed to a uniform head to tail arrangement, $-(-{*})_n-$. Polymerization in vinyl polymers such as the polyisoprenes or polybutadienes seldom proceeds in a purely head to tail orientation.[31] The changes in the hybridization are of the same order of magnitude as in structural isomerization and may be too small to be experimentally detected. However, even small alternations in a monomer unit may become important in a long-chain system. We have selected for examination one of the simplest polymers with an unsymmetrical repeating unit, polypropylene. The terminal carbon atoms in this case have approximately sp^3 hybridization and the differences resulting from reversing the monomer orientation will be small, but if we can detect such small perturbations in this case the method will presumably be even more useful when the terminal atoms show larger differences in their environment.

Instead of one single bond along the chain (C_1—C_2) characteristic of the head to tail arrangement, the head to head isomerization in polypropylene leads to three distinguishable C—C single bonds. The hybrids, bond overlaps, and bond angles are given in Table III. The smallest overlap is that of C_1—C_1 which is reduced by an amount of 0.0015 and corresponds to a bond energy reduction of 0.3 kcal/mol. Changes in bond energy of such magnitude have been already found and appear reasonable. The finding indicates a weaking of the chain at the C_1—C_1 junction. Differences in other bond overlaps are smaller, but even these may have a cumulative effect and can possibly be indirectly detected when the actual physical properties are examined.

Correlations between Hybridization Parameters and Nmr Spin-Spin Coupling Constants

As mentioned earlier several experimental quantities have been found to be strongly correlated with the calculated hybridization parameters[2] including CH and CC bond lengths, CH acidities, CH ir stretching frequencies, and, to a limited extent, proton chemical shifts. The most significant correlations, however, are those between the spin-spin coupling constants of directly bound nuclei and the s orbital composition of their respective hybrids. For CH coupling constants Muller and Pritchard found the following experimental relationship[32]

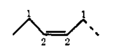
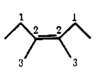
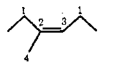
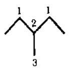
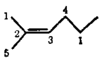
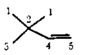
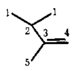
$$J(^{13}\mathrm{C}—\mathrm{H}) = 500a^2$$

Table IV
Experimental and Calculated Spin-Spin Coupling Constants $J(^{13}C—^{13}C)$ for Several C—C Single and C═C Double Bonds in Smaller Hydrocarbons

Molecule	Expt	Ref	INDO	Ref	Max, Overlap	Ref
		C—C Single Bonds				
Ethane	34.6	*a*	41.5	*b*	33.1	*e*
Propane	33.0 ± 2	*b*	42.1	*b*	33.1	
Propylene	41.8	*c*	55.3	*c*	46.6	
Isobutene	41.9	*c*	53.2	*c*	46.4	
Butadiene	53.7	*d*			61.2	
		C═C Double Bonds				
Ethylene	67.6	*a*			85.6	
Butadiene	68.8	*d*			84.5	
Propylene	70.4	*b*	79.4	*c*	85.4	
Isobutene	72.6	*b*	81.5	*c*	86.4	

[a] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **264,** 385 (1962). [b] V. J. Batruska and G. E. Maciel, *J. Magn. Resonance*, **5,** 211 (1971). [c] V. J. Batruska and G. E. Maciel, *J. Magn. Resonance*, **7,** 36 (1972). [d] G. E. Maciel, J. W. McIver, N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92,** 11 (1970). [e] M. Randić, Tables of Maximum Overlap Hybrids (to be published), a sample available on request.

Table V
Calculated Spin-Spin Coupling Constants $J(^{13}C—^{13}C)$ for Polymers Investigated

			J (^{13}C—^{13}C)	
Molecule	Bond	Bond Type	Maksić, Eckert-Maksić, Randić (Hz)	Frei-Bernstein (Hz)
	Polyethylene			
	$C_1—C_1$	te–te	33.1	29.7
	1,4-Polybutadiene			
	$C_1—C_2$	te–tr	43.9	39.3
	$C_2—C_2$	tr–tr	82.4	77.8
	2,3-Dimethyl-1,4-polybutadiene			
	$C_1—C_2$	te–tr	44.5	39.8
	$C_2—C_3$	te–tr	43.8	39.1
	$C_2—C_2$	tr–tr	84.2	79.5
	2-Methyl-1,4-polybutadiene			
	$C_1—C_2$	te–tr	44.5	39.8
	$C_1—C_3$	te–tr	44.0	39.3
	$C_2—C_4$	te–tr	43.8	39.1
	$C_2—C_3$	tr–tr	83.3	78.7
	Polypropylene			
	$C_1—C_2$	te–te	34.0	30.4
	$C_2—C_3$	te–te	32.9	29.7
	1,4-Polyisoprene			
	$C_1—C_2$	te–tr	44.9	39.7
	$C_3—C_4$	te–tr	43.9	39.2
	$C_1—C_4$	te–te	33.8	30.7
	$C_2—C_5$	te–tr	43.8	39.1
	$C_2—C_3$	tr–tr	83.3	78.7
	1,2-Polyisoprene			
	$C_1—C_2$	te–te	35.1	31.6
	$C_2—C_3$	te–te	34.6	31.1
	$C_2—C_4$	te–tr	46.0	40.3
	$C_4—C_5$	tr–tr	81.6	77.0
	3,4-Polyisoprene			
	$C_1—C_2$	te–te	34.6	31.2
	$C_2—C_3$	te–tr	45.1	40.3
	$C_3—C_5$	te–tr	43.7	39.1
	$C_3—C_4$	tr–tr	82.4	77.8

where a is the coefficient of the s orbital in the hybrid ($\phi = (as) + (bp)$). Using this relation and the experimental coupling constant for the methyl group in isotactic polypropylene,[33] J = 124 Hz, one finds the corresponding CH hybrid to be sp$^{3.032}$. Alternatively, using the theoretical a value and deducing the coupling constant one obtains J = 127.5 Hz. A slightly better value (J = 126.3 Hz) results from the modified correlation in which changes of bond overlap with bond type are taken into account.[11,34]

We turn now to discuss the $J(^{13}C—^{13}C)$ values. Gutowsky and Juan[35] obtained from theoretical considerations a simple proportionality between the spin-spin coupling constant of directly bound nuclei and the s content of the two hybrids involved measured by $a_A{}^2$ and $a_B{}^2$

$$J_{AB} = \lambda a_A{}^2 a_B{}^2$$

An expression specifically for $^{13}C—^{13}C$ coupling was derived by Frei and Bernstein[36] and others.[11,34] Maximum overlap hybrids show satisfactory agreement with experiment where the Frei-Bernstein relationship is used. When the maximum overlap data are fitted by least squares to experiment the following more general relationship is obtained[34]

$$J(^{13}C—^{13}C)(\text{Hz}) = 1020.5 a_1{}^2 a_2{}^2/(1 + S_{CC}{}^2) - 8.2$$

The dependence on the bond overlap, S_{CC}, derives from the normalization of the bond wave function. This expression can be used for prediction of the $^{13}C—^{13}C$ spin coupling constants of the molecules considered here. Since, however, spin-spin data are not available for these polymers we give in Table IV the experimental constants for structurally similar systems: butadiene, propylene, and isobutene. For some of these molecules theoretical values based on INDO calculations are available (Table V, column 2). These are compared with our results (Table V, column 3).

These results indicate that the coupling constants obtained via the maximum overlap method are accurate for C—C single bonds. Those for C═C double bonds are about 10 Hz (1-1.5%) too large. A possible explanation for this discrepancy is that the maximum overlap procedure as applied here used the same k_{CC} scaling factor for both σ and π carbon overlaps. On the other hand, the INDO calculations[37] based on the approach of Pople, McIver, and Ostlund[38] give $J(^{13}C—^{13}C)$ constants which are about 10-15 Hz too large for both singly and doubly bound carbons. Thus, the maximum overlap hybrids appear as good if not better for predicting $^{13}C—^{13}C$ coupling constants than those based on the more elaborate INDO procedure. Of course, the maximum overlap method in its present form is applicable only to hydrocarbons while the INDO procedure has more general applicability and should not in any case be judged solely by its performance on such a small selection of molecules.

We believe the foregoing indicates the predictive potential of this procedure and justifies our presenting in Table IV theoretical $J(^{13}C—^{13}C)$ values for the polymers considered here. The results are similar to those of Table V and, in view of the preceding discussion, are expected to be accurate for C—C single bonds and about 10 Hz too large for C═C double bonds. Confirmation of these predictions awaits experiment and it will be particularly interesting to see whether small differences between the coupling constants of similar bond types will be detected.

Acknowledgments. We thank Professor J. Deutch and R. Silbey from the Massachusetts Institute of Technology for providing financial support for this work. We also thank Professor E. B. Wilson of Harvard University for partial support permitting completion of the work.

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(9) Recent considerations (M. Randić, to be published) of heats of atomization indicated an impressive agreement with experimental values for large number of mono olefins, of each bond kind, namely C—C, C—C, and C—H, are described by *two* parameters (*i.e.*, a linear relationship between bond overlap and bond energy, instead of frequently assumed proportionality). Calculated heats of atomization are with ±3 kcal/mol from the experimental values with a further improvement in sight.

(10) Only references to more recent work published after the review (ref 2f) on the subject will be given.

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(20) More correctly one should refer to these bond types as te–te, te–tr, and tr–tr, where *te* and *tr* stand for tetrahedral and trigonal, respectively, in order to avoid confusion by not actually implying sets of equivalent hybrids and allowing a variable *n* in sp^n.

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Polymer–Solvent Interactions from Gas–Liquid Chromatography with Capillary Columns

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Received December 26, 1973

ABSTRACT: To determine the effect of polymer-film thickness on thermodynamic properties, capillary columns and packed columns were used to measure polymer–solvent interactions. Experimental retention volumes at 50–175° are reported for several solvents with poly(isobutylene), poly(vinyl acetate), and poly(dimethylsiloxane). The capillary-column results are often strongly sensitive to gas flow rate, probably because of the large time required to attain equilibrium between solvent and a polymer film whose thickness is in the range 10^4–10^5 Å; in packed columns the film thickness is about two orders of magnitude smaller. When capillary-column data are extrapolated to zero flow rate, the retention volumes differ from those obtained with packed columns, sometimes by as much as 20%; this difference, however, decreases to 5% or less at higher temperatures. For poly(isobutylene) with benzene and with cyclohexane, Flory χ parameters obtained with capillary columns appear to be in better agreement with those obtained from static data than are those measured in packed columns. The results obtained in this work suggest that polymer–solvent interactions for a bulk polymer may be different from those for a thin polymer film adsorbed on a granular packing.

Gas–liquid chromatography (glc) shows much promise as a technique for rapid measurement of polymer–solvent interactions in highly concentrated polymer solutions. Several recent articles have discussed application of the method.[2–5] In all previous work, thermodynamic measurements for polymers with glc have been made exclusively in packed columns, where the polymer is coated onto a solid support. These columns are easy to prepare with an accurately known amount of polymer and, with a little experience, much data can be obtained rapidly. Their primary disadvantage is that the maximum attainable film thickness is only about 10^2 or 10^3 Å, which is the order of magnitude of the length of a polymer molecule. The important question therefore arises whether the polymer–solvent interactions in such a thin polymer film, adsorbed on a granular solid, are the same as those in a bulk polymer. It appears likely that the morphology, or the degree of order, in a thin film of polymer, adsorbed on a solid support, is different from those of a bulk polymer.

To determine the effect of polymer-film thickness on polymer–solvent interactions, we report here thermodynamic measurements with glc in capillary (open tubular) columns. These columns are prepared by coating the polymer onto the inside wall of a small-bore tube; no granular