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Conformational Characteristics of Poly(methyl vinyl ketone)s and of Simple Model Ketones

Ulrich W. Suter

Contribution from the Eidgenössische Technische Hochschule, Technisch-Chemisches Laboratorium, ETH-Zentrum, CH-8092 Zürich, Switzerland. Received April 2, 1979

Abstract: A semiempirical force field is constructed for the calculation of conformational potential energies of unstrained, acyclic, aliphatic aldehydes and ketones, taking solvent effects into consideration. Detailed conformational calculations for fitting and testing the necessary parameters are done with ethanal, propanal, 2-methylpropanal, propanone, 2-butanone, 2-pentanone, and 3-pentanone. The calculated results agree satisfactorily with available experimental data. Further calculations are carried out with the "monomer models" 3-methylbutanone, 2-methyl-3-pentanone, 2,4-dimethyl-3-pentanone, and 2,2,4-trimethyl-3-pentanone, and with the two compounds 4-methyl-2-pentanone and 4,4-dimethyl-2-pentanone. Conformational potential energy maps of meso and racemic dyads (i.e., of chain segments comprising two monomeric units) of poly(methyl vinyl ketone) are then computed. These results are incorporated into a rotational isomeric state scheme by integration in the appropriate limits of the intradyad backbone torsion angles and the torsion angles of the two side groups of the dyad. Two states at $\phi = 10$ and 110° are found to be suitable. The convenient procedure of only integrating over the backbone torsion angles (while adjusting the side groups so that the total energy of the dyad is minimal) is tested and it is found that this yields a rough approximation for this polymer. The first-order energy parameter E_η cannot be assigned a value with the results of the computations. Calculations of the unperturbed dimensions and of the vicinal proton-proton coupling constant in the backbone of isotactic poly(methyl vinyl ketone), and comparison with published experimental values, limits the feasible range for E_η to within ca. ±100 cal/mol. The assignments are tested further by calculating the dipole moment ratio of the atactic polymer. The theoretical results fit well with Guest, Matsuo, and Stockmayer's experimental data. The conformational characteristics of poly(methyl vinyl ketone) are satisfactorily represented by the conformational parameters $\eta = 0.7 \exp(+400/T)$, $\omega = 1.0 \exp(-900/T)$, $\omega' = 0.8 \exp(-1100/T)$, and $\omega'' = 0.8 \exp(-1400/T)$.

I. Introduction

Our interest in poly(vinyl ketone)s calls for a detailed conformational analysis. A prerequisite for this is a reliable set of conformational parameters that accurately describe the conformational potential energy surfaces of unstrained, acyclic, aliphatic ketones. A semiempirical force field is preferred rather than a quantum-mechanical approach, since a large number of single conformations of relatively large molecules or fragments of molecules must be considered, and since the reliability and accuracy of a well-parametrized force field is quite remarkable.[1] Several semiempirical force fields exist already that include carbonyl parameters.[2-9] However, these force fields are either not complete enough for our intentions[3,8] or they have serious shortcomings with respect to the task at hand: (1) most of them are parametrized to fit sets of vibrational data and contain force constants for bond length variation and bond angle deformation, parameters that probably can be included in the "hard" variables[10] for calculations of conformational equilibrium properties, and, if included in the calculations, would only increase the number of variables unnecessarily. Due to correlations between parameters one cannot simply reduce the number of variables. (2) The parameters of these force fields are often fitted so that conformations of *minimum* energy reproduce values obtained from experimental data that correspond to configurational *averages* over large domains of conformation space. While this is an expedient in the rapid evaluation of preferred conformations, it is not acceptable for a detailed analysis.[11] (3) These force fields do not contain simple means to account for neighbor effects in condensed media, but treat molecules as isolated units. For small molecules this is quite reasonable, but the interactions of "solvent" with individual groups or atoms become relevant in larger flexible molecules (i.e., when a considerable number of intramolecular distances become larger than 4-6 Å).[8,12]

A simple force field that works very satisfactorily, and that is devoid of the shortcomings (1) to (3) above, has been developed in Flory's group,[8,12,13] but intrinsic torsional potentials for rotations around bonds adjoining simple carbonyl functions were not included. We will therefore proceed to complete these potential-energy functions to include carbonyl groups. At first, we will analyze aldehydes rather than ketones, the class of immediate interest to us, because more detailed and accurate experimental investigations of simple aldehydes have been published. The principles established for aldehydes will then be applied to ketones, where the parameters only need to be adjusted somewhat to fit experimental data reliably. After comparison of the results obtained for low molecular weight ketones with experimental data we will proceed to the conformational analysis of poly(methyl vinyl ketone)s.

II. Basis for the Calculations

Bond lengths and bond angles are assumed to be "hard" variables[10] and to be fixed at the same values in all confor-

Table I. Geometrical Parameters

bond	bond length, Å
$C(sp^3)$—$C(sp^3)$	1.53
$C(sp^3)$—$C(sp^2)$	1.51
C=O	1.22
$C(sp^3)$—H	1.10
$C(sp^2)$—H	1.11

bond angle			angle, deg
on primary C	∠C—C—H		110
	∠H—C—H		108.9
on secondary C	∠C—C—C		114
	∠C—C—H		108.5
	∠H—C—H		108.5
on tertiary C	∠C—C—C		112
	∠C—C—H		106.8
on quaternary C	∠C—C—C		109.5
on carbonyl C	∠C—CO—C	ketones	116
	∠C—C=O	ketones	122
	∠C—CO—H	aldehydes	117.5
	∠C—C=O	aldehydes	124
	∠H—C=O	aldehydes	118.5

Table II. Parameters Used in Energy Calculations

atom or group	r_i^0, Å	α_i, Å^3	N_i
$C(sp^3)$	1.8	0.93	5
C(C=O)	1.8	1.23	5
CH_3	2.0	1.77	7
H	1.3	0.42	0.9
O(C=O)	1.6	0.84	7

in ketones in liquid phase: μ(C=O) = 2.75 D
($\pm$0.469 el charges)
$\epsilon = 3.5$

mations.[13] They are collected in Table I. Bond lengths and bond angles that apply to $C(sp^3)$-$C(sp^3)$ and $C(sp^3)$-H are taken from ref 12 and 13; angles were adjusted slightly so that all angles of the same type (e.g., all C-C-H angles) around one C atom are identical. Bond lengths for bonds adjoining C=O and for C=O itself as well as the angles between them are mean values of published experimental data, obtained by electron diffraction[14-16] or microwave spectroscopy,[17-20] on acetone,[14,17,18] 2-butanone,[15,19] acetaldehyde,[20] and 2-propanal.[16] All values in Table I are assumed to be reliable to within ca. 0.02 Å or ca. 1°.

The total conformational potential energy is assumed to consist of additive contributions from "intrinsic torsional potentials", V_{ir},[21] from "van der Waals" interactions between nonbonded atoms, V_{vdw} (subject to solvent effects), and from electrostatic interactions of permanent dipole moments, V_{coul} (dependent on the electric susceptibility of the solvent). For the intrinsic torsional potential of each C-C single bond a threefold potential with a barrier of 2.8 kcal/mol was chosen.[21] For single bonds adjoining C=O these potentials are not known and must be estimated by inspection of model compounds. Nonbonded interactions between atoms separated by more than two bonds were calculated on the basis of the Lennard-Jones 6-12 pair potential $V_{\mathrm{vdw},ij} = (a_{ij}/r_{ij}^{12}) - (c_{ij}/r_{ij}^{6})$. Atoms were treated individually except for methyl groups that were approximated by a larger spherical domain in most calculations. The London dispersion parameter c_{ij} was calculated according to the Slater-Kirkwood formula[22] using Ketelaar's values for the atom polarizabilities α_i and the "effective number of electrons" N_i.[21,23] The constants a_{ij} were assigned so as to minimize the pair potential $V_{\mathrm{vdw},ij}$ for a given pair of atoms when r_{ij} is set equal to the sum of the corresponding *adjusted* van der Waals radii r_i^0.[24,25] The values used[26] are given in Table II.

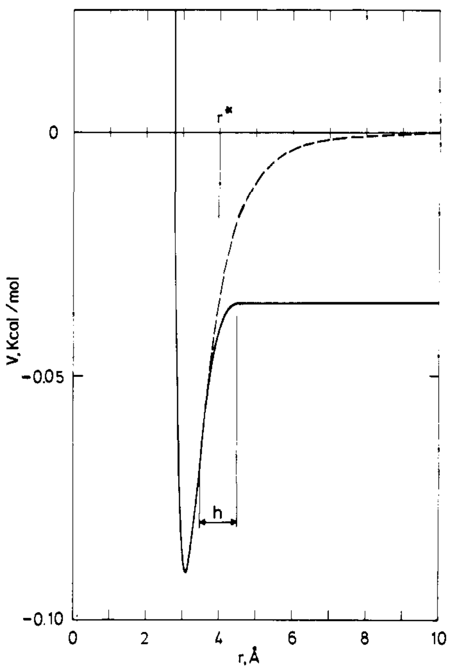


Figure 1. Nonbonded interactions for the pair C(carbonyl)/H. The solid line represents values calculated with $r^* = 4$ Å, $h = 1$ Å ("liquid phase"). The dashed line shows the unmodified 6-12 potential, corresponding to $r^* \to \infty$ ("gas phase").

Energies calculated with this 6-12 potential apply to isolated molecules, i.e., in the gas phase. For the liquid phase the potential overestimates the loss in attractive interactions when two atoms are moved apart once the separation is larger than a certain "critical distance", r^*. When the distance between two proximate atoms is increased, the energy of the system increases at first in "reality" as predicted by $V_{\mathrm{vdw},ij}$ above, but levels off for most pairs of atoms as soon as the separation is big enough for solvent molecules to be able to approach the newly exposed parts of the atoms and thus to compensate for the computed loss of attractive interactions. Brant and Flory[8] kept the pair potential constant at the value $V_{\mathrm{vdw},ij}(r^*)$, where $r^* = r_i^0 + r_j^0$, for all values $r_{ij} > r^*$; Yoon et al.[12,26] assumed a critical distance r^* of ca. 4-5 Å for all pairs of atoms to be appropriate. This latter procedure is simple and effective and has been used in various cases,[27-29] but it has the disadvantage that $\mathrm{d}V_{\mathrm{vdw},ij}/\mathrm{d}r_{ij}$ is discontinuous at r^* and $\mathrm{d}^2V_{\mathrm{vdw},ij}/\mathrm{d}r_{ij}^2$ has a singularity there. This has disastrous results in optimization schemes that use second derivatives. We therefore smooth the corner at r^* with a cubic polynomial in such a way that at the junction between the 6-12 function and the cubic polynomial and at the junction between the cubic polynomial and the constant potential (for $r_{ij} > r^*$) we have a continuous $\mathrm{d}V_{\mathrm{vdw},ij}/\mathrm{d}r_{ij}$. This is achieved by[30]

$$V_{\mathrm{vdw},ij} \begin{cases} = f_{6\text{-}12}(r_{ij}) & , r_{ij} \le r^* - h/2 \\ \left.\begin{array}{l} = f_{6\text{-}12}'(r_{\mathrm{l}})(r_{\mathrm{r}} - r_{ij})^2(r_{ij} - r_{\mathrm{l}})/h^2 \\ + f_{6\text{-}12}(r_{\mathrm{l}})(r_{\mathrm{r}} - r_{ij})^2[2(r_{ij} - r_{\mathrm{l}}) + h]/h^3 \\ + f_{6\text{-}12}(r_{\mathrm{r}})(r_{ij} - r_{\mathrm{l}})^2[2(r_{\mathrm{r}} - r_{ij}) + h]/h^3 \end{array}\right\} & , r^* - h/2 < r_{ij} < r^* + h/2 \\ = f_{6\text{-}12}(r^*) & , r_{ij} \ge r^* + h/2 \end{cases}$$

where $f_{6\text{-}12}(r_{ij}) = (a_{ij}/r_{ij}^{12}) - (c_{ij}/r_{ij}^{6})$ and $f_{6\text{-}12}' = \mathrm{d}f_{6\text{-}12}/\mathrm{d}r_{ij}$. $f_{6\text{-}12}(r_l)$ or $f_{6\text{-}12}'(r_l)$ is the corresponding value at the junction between 6-12 potential and cubic polynomial at $r_l = r^* - h/2$, and $f_{6\text{-}12}(r_r)$ applies to the junction between the cubic polynomial and the constant potential at $r_r = r^* + h/2$. All these values are constants for a given pair of atom types. Preliminary calculations have shown that a value of 1 Å for h, the range of r in which the cubic polynomial should apply, gives satisfactory results, and we set $h = 1$ Å for the rest of this work. An illustrative example for this three-piece potential is shown in Figure 1. In general, for calculations that have to be identified with gas-phase experiments we set r^* to infinity; for liquid-phase experiments we choose $r^* = 4$ Å.

Electrostatic interactions were assessed in the point-monopole approximation by assigning partial charges to atoms.[24,26] A value of 3.5 was chosen for the effective dielectric constant in liquid phases.[24,26] The effective dipole moment of aliphatic keto groups was taken to be 2.75 D as an average of literature values for several aliphatic ketones in solution.[31-37] Together with the bond length of 1.22 Å this corresponds to a point charge of ±0.469 elementary charges. In "gas-phase" calculations the values for the dipole moment as well as for the dielectric constant are altered,[35] but none of the experimental data for compounds with significant electrostatic interactions in this study refers to the gas phase. No interactions between carbonyls[38] were considered beyond the Coulombic term referred to above.

Except where noted otherwise calculations are performed on grids with the necessary number of dimensions with a step size of 5°; this resolution proved to be sufficient for all results obtained. Integration over conformation space was always approximated by Simpson's rule.

Torsion angles are measured, according to the conventions used in polymer chemistry, from an "all-trans" position of the "main" carbon chain, and an angle has a negative sign when the bond in question and the adjoining "main-chain" bonds form a right-handed helix. To facilitate inspection of maps, we will draw a model with all angles set to zero beside each map. The symmetry of a molecular frame is necessarily reflected in the conformational energy map. This symmetry often allows elimination of large redundant parts of maps. In Figure 7, for instance, the pattern is defined by an area only 1/6 of the whole map; in Figure 9 1/4 of the map would suffice for a complete description. The symmetry also manifests itself in simple relations for the torsion angles, if the origin is well chosen. This is not the case here; the reference positions are chosen to conform to polymer conventions. Still, the symmetry of the molecular frame is apparent from the complete map. In Figure 9, for instance, a shift of the origin to the point ca. (−60, −60°), where two orthogonal mirror lines cross, both with an inclination of 45°, gives a system with the relations $(\phi_1', \phi_2') = (\phi_2', \phi_1') = (-\phi_1', -\phi_2') = (-\phi_2', -\phi_1')$.

III. Simple Aldehydes

Ethanal. Kilb, Lin, and Wilson found that in the preferred conformation of ethanal a C—H bond is syn periplanar with C=O ("eclipses" C=O).[20] The threefold barrier to rotation is 1.17 kcal/mol.[20,39] Ab initio calculations[40,41] are in perfect agreement with these results. The van der Waals potential alone is 0.05 kcal/mol higher in the eclipsed conformations than for the conformations where the C—H's are synclinal with C=O. Therefore, an intrinsic threefold torsional potential with a barrier height of 1.20 kcal/mol is required for agreement with experimental data. This is in harmony with the findings from ab initio calculations by Jorgensen and Allen,[40] that the ("attractive") torsional barrier in ethanal stems from a "weak covalent bond between O and the eclipsing H". We assume that this barrier shows little dependence on aliphatic substitution of the saturated C atom and we will use the same threefold potential for the higher aldehydes.

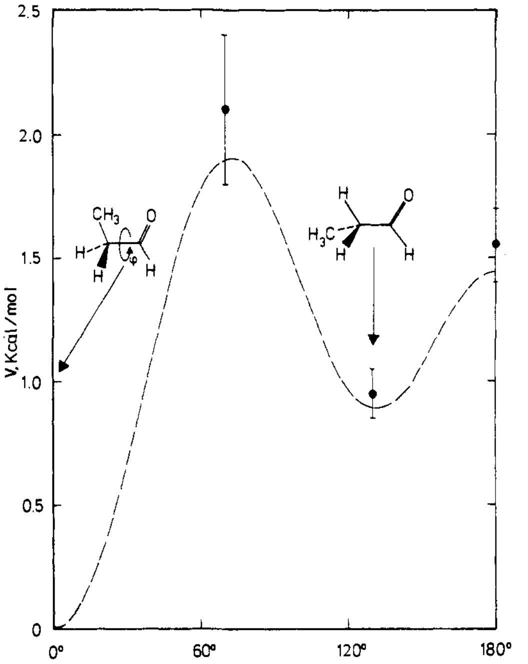


Figure 2. Potential energy of propanal as a function of the torsion angle around C—C=O. Points and error bars are taken from ref 45. Dashed line shows calculated potential with $V_1 = 1.1$, $V_2 = 1.8$, and $V_3 = 1.2$ kcal/mol.

Propanal. The rotamer of propanal of lowest energy has a structure in which the methyl group eclipses the carbonyl group (i.e., in which CH_3CH_2- is syn periplanar to C=O), as was first shown by Abraham and Pople and by Karabatsos and Hsi with measurements of the $^2J_{HH}$ NMR coupling constant in solution[42,43] and by Butcher and Wilson from microwave spectra in the gas phase.[44] The energy (or enthalpy) difference between the preferred conformation and the two less stable conformers with rotation angles displaced by ca. 120° (anticlinal) was estimated to be 0.8-1.0 kcal/mol.[42-44] In a more recent work Pickett and Scroggin analyzed the microwave spectrum and produced the complete potential function for the C—C=O bond.[45] These data are ideally suited for adjustment of potential parameters. The extrema of the experimentally determined potential curve together with the "expected uncertainty" [45] are plotted in Figure 2. The van der Waals potential alone would favor the anticlinal conformations by more than 1 kcal/mol over the syn periplanar one. Since the threefold torsional potential, taken from the analysis of ethanal above, has no effect on this comparison, we choose to employ one- and twofold intrinsic torsional potentials also. Indeed, a unique set can be found that brings calculated and experimental values to agreement within experimental error:

$$V_{ir}(\phi) = \sum_{n=1}^{3} V_n/2(1 - \cos n\phi)$$

when $V_1 = 1.1$ kcal/mol, $V_2 = 1.8$ kcal/mol, and $V_3 = 1.2$ kcal/mol. The calculated function is included in Figure 2.

The question arises as to whether the tendency for C—C rather than C—H to eclipse C=O is the same if more than one aliphatic residue is substituted on the C atom α to carbonyl, i.e., could not the onefold and twofold potentials simply be added for each substituent on that C atom.[46] The availability of experimental data on 2-methylpropanal makes a test of such a simple procedure possible.

2-Methylpropanal. Guillory and Bartell demonstrated in an electron diffraction study of gaseous 2-methylpropanal at −7 °C[16] that this compound is composed of ca. 90% of the ro-

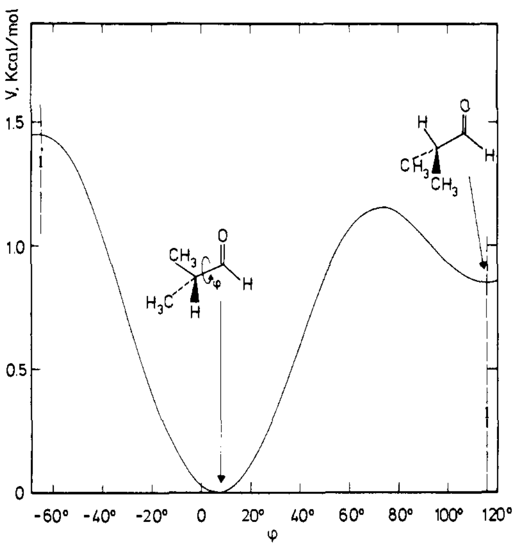


Figure 3. Calculated potential energy of 2-methylpropanal as a function of the torsional angle around C—C=O.

tamers with methyl groups eclipsing C=O and of ca. 10% of the rotamer with the C—H syn periplanar with C=O. Karabatsos and Hsi examined the ${}^2J_{HH}$ NMR coupling constant[43] (a less accurate technique) and found that in solution the methyl-eclipsing rotamers make up ca. 80% of the mixture. Figure 3 shows a curve calculated using one threefold potential and an additional onefold and twofold potential for each of the α-substituting C-C bonds.[47] Integration of $\exp(-V(\phi)/RT)$ over the domains of the troughs for a temperature of −7 °C yields a calculated population of 89.6% for the two methyl-eclipsing forms vs. the electron diffraction value of ca. 90%. This excellent agreement between calculated and experimental values induces us to use the simple additive scheme proposed above for branched carbonyl compounds. The barrier heights for the one-, two-, and threefold intrinsic torsional potentials are included in Table III.

At this point, it is worthwhile mentioning that this simple additive rule will not hold when the two α substituents are connected to form a cyclopropyl ring, e.g., in cyclopropylcarboxaldehyde, since in compounds of this type the two "2-methylpropanal" rotamers at ϕ = ca. 10 and ca. −135° (separated by a maximum of ca. 1.5 kcal/mol) merge into one single minimum.[38,48,49] Aldehydes with two α substituents that are part of a larger ring behave increasingly like 2-methylpropanal with increasing ring size.[43]

IV. Low Molecular Weight Ketones

Some Simple Ketones. Propanone (Dimethyl Ketone). For propanone the situation is similar to that in ethanal. Nelson and Pierce reported[18] that in the preferred conformations of propanone a C—H bond eclipses C=O in both methyl groups and that the threefold rotation barrier is 0.76 kcal/mol.[50] Ab initio calculations by Allinger and Hickey[41] produce the same preferred rotamer and the same order of magnitude for the barrier. The van der Waals interactions alone give a barrier height of ca. 0.52 kcal/mol and a preference for the same conformation found to be the most populated experimentally. Therefore, the intrinsic torsional potential necessary to bring the calculated barrier up to the microwave result[18] is threefold and has a barrier height of only ca. 0.25 kcal/mol. While one would anticipate that the threefold intrinsic torsional barrier would differ between aldehydes and ketones, it is nevertheless surprising that the difference should be that large, i.e., ca. 1 kcal/mol between propanone and ethanal. Courtien and Gounelle performed NMR experiments in nematic phase with fluoropropanone[51] (a molecule that is very similar to propanone in the spatial requirements of its atoms since F has a size similar to that of H) that indicate that the larger observed barrier is ca. three times as high as in propanone. Thus, the intrinsic torsional potential of a bond can indeed be altered appreciably by a small change in the environment of one of the adjoining atoms. Henceforth, a threefold potential with a barrier height of 0.25 kcal/mol will be used for all aliphatic ketones.

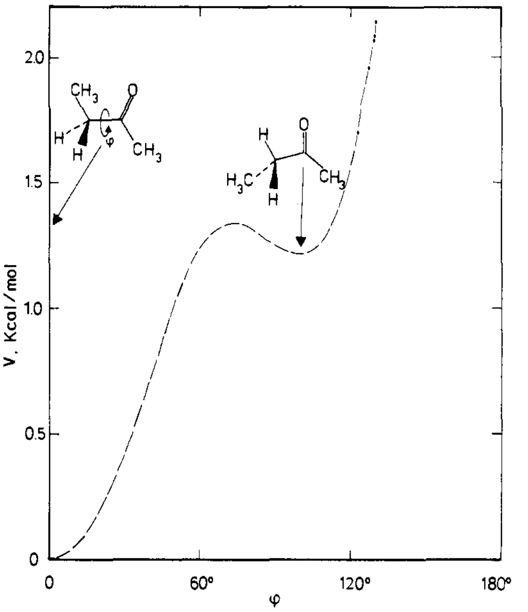


Figure 4. Calculated potential energy of 2-butanone as a function of the torsion angle around C—C=O.

Table III. Intrinsic Torsional Potentials

	$V_{ir}(\phi) = \sum_n 0.5V_n(1 - \cos n\phi)$			
	conformation	V_n, kcal/mol		
bond	with $\phi = 0$	$n = 1$	$n = 2$	$n = 3$
C(sp^3)—C(sp^3)	staggered			2.8
C(sp^3)—C(sp^2)	C—H or C—C syn-planar with C=O		(aldehydes) (ketones)	1.20 0.25
	for every C—C syn-planar with C=O	1.1 0.5	1.8 (aldehydes) 1.8 (ketones)	

2-Butanone (Methyl Ethyl Ketone). Stuart and Volkmann's suggestion, from an early Kerr-effect measurement in the gas phase,[52] that the methyl group eclipses C=O was later challenged on the basis of infrared data by Hirota et al.[53] With electron diffraction combined with infrared measurements in gas and liquid phase Shimanouchi et al.[54,55] obtained proof for the preponderance of the methyl-eclipsing conformation. The two rotamers with a torsion angle displaced by ca. 110° are higher in enthalpy by ca. 1.07 kcal/mol in the liquid phase.[54] The van der Waals contribution to the energy of the rotamers alone is minimal at ϕ = ca. 95°, however, and is ca. 0.93 kcal/mol higher for the trans conformation at ϕ = 0° (the methyl-eclipsing-methyl conformation at ϕ = 180° is disfavored by more than 3 kcal/mol). The tendency for the C—CH$_3$ to eclipse C=O must be attributed therefore to the intrinsic torsional potential, as in the case of propanal. If one integrates the (normalized) function $V(\phi)\exp(-V(\phi)/RT)$ over the conformational domains, i.e., if one calculates the average "energy" of the rotamers, one obtains with the "aldehyde" values for V_1 and V_2 a value of $\Delta\langle E\rangle$ = 1.39 kcal/mol between the trans and the gauche rotamers at 300 K. To obtain a value

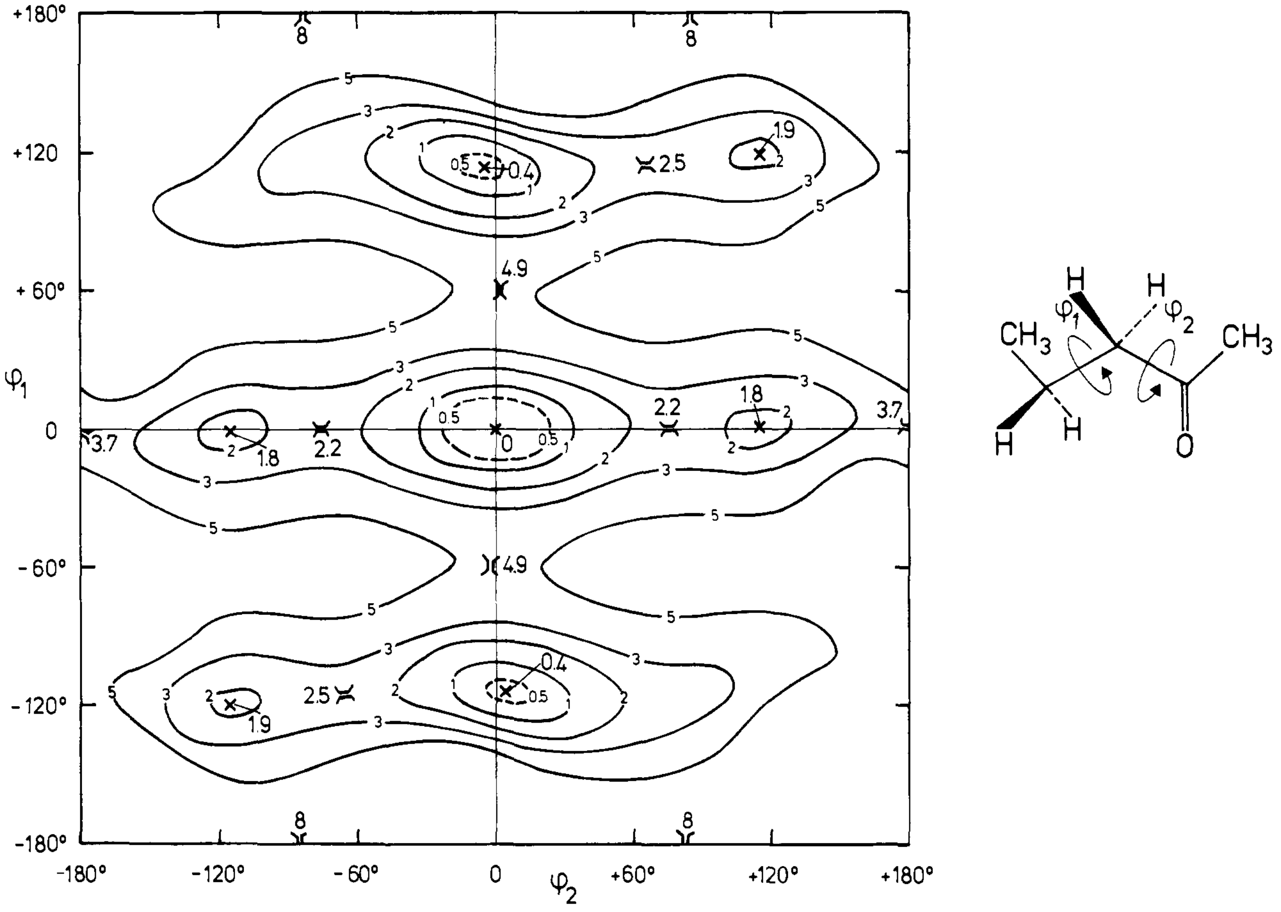


Figure 5. Calculated potential energy of 2-pentanone as a function of the torsion angles ϕ_1 and ϕ_2. The conformation with $\phi_1 = \phi_2 = 0$ is drawn at the right. Contours are drawn with respect to the absolute minimum at $\phi_1 = \phi_2 = 0$ (tt) with intervals of 1 kcal/mol, and are based on energies calculated on a grid with 5° step width. X denotes minima, ⋈ denotes cols between troughs.

equal to the experimental one of 1.07 kcal/mol it is requisite to choose values for V_1 and V_2 that satisfy the relation $V_1 = 3.7 - 1.8V_2$; for $V_1 > 1.3$ kcal/mol or $V_1 < 0.3$ kcal/mol no minimum is found for the anticlinal rotameter. The average torsion angle of this rotamer is obtained by integrating the (normalized) function $\phi \exp(-V(\phi)/RT)$ and the results can be summarized by the relation $\langle\phi\rangle = 87 + 7V_2$; the units are degrees when V_2 is given in kcal/mol. The experimental value for $\langle\phi\rangle$ is ca. 110°,[54] and we choose the values $V_1 = 0.5$ and $V_2 = 1.8$ kcal/mol that give a $\Delta\langle E\rangle = 1.07$ kcal/mol and $\langle\phi\rangle = 100°$, somewhat arbitrarily assigning the same value to V_2 as for aldehydes. The complete potential is drawn in Figure 4. The values for V_1, V_2, and V_3 used in ketones are collected in Table III. The set of parameters necessary for the calculation of conformational potentials is now complete (Tables I–III).

2-Pentanone and 3-Pentanone. A number of years ago Stuart and Volkmann[52] measured the Kerr constant in gas phase and they concluded that the keto group was eclipsed by C–C bonds in the favored conformations of these molecules. These interpretations were rejected subsequently by several authors (1) on the grounds that more than one conformation of comparable energy seemed to exist for both molecules as revealed by temperature dependence of infrared spectra,[53,56] and (2) from the intuitive concept that these eclipsing conformations, especially for 2-pentanone, should be disfavored for steric reasons.[53,56-58] A later Kerr-effect study of 2-pentanone in solution by Aroney, Izsak, and LeFevre[57] seemed to discredit the older results in gas phase,[52] but the analysis was limited to a single conformer at a time, mixtures of different conformations being excluded from consideration. Shimanouchi, Abe, and Mikami's detailed infrared and microwave study[54] of 2-pentanone and 3-pentanone as well as of 2-butanone in solid, liquid, and gas phase evidenced the presence of several rotamers and the preponderance of the one where C—C eclipses C═O in each case.

The calculated conformational potential maps for the two pentanones are plotted in Figures 5 and 6. The 2-pentanone map illustrates the ease with which rotation around a C—C═O bond takes place compared to a rotation around an aliphatic C—C bond, since the barriers of ϕ_1 are all at least 4.5 kcal/mol, while the barriers of ϕ_2 are mostly of the order of magnitude of 2 kcal/mol. This phenomenon produces a map for 3-pentanone that contains unusually large areas of low energy (ca. 30% of the total area lies below the 1 kcal/mol contour). In the case of 2-pentanone all traditional conformational domains are troughs separated by cols, except in the areas where the g^+g^- and g^-g^+ rotamers would be situated. In the case of 3-pentanone the regions where the g^+g^+ and g^-g^- rotamers are expected are additional exceptions, since a col is located in the middle of these domains. In general it is not desirable to locate rotamers in such areas, but we will do this for the purpose of a comparison with the experimental results[54] that were obtained by assuming rotational isomeric states at the "classical" locations. In Table IV we compare the experimentally obtained relative enthalpies of the rotamers with the average energies of the rotamers determined by integration of the (normalized) function $V(\phi_1, \phi_2) \exp[-V(\phi_1, \phi_2)/RT]$ over the ranges traditionally attributed to the rotational states t and g, i.e., −60 to +60° for t and +60 to +180° for g^+, or −60 to −180° for g^-. Also given are the calculated preexponential factors z_0 ("entropy factors") defined by

$$z_{|\phi|} = z_{0|\phi|} \exp(-\langle E\rangle_{|\phi|}/RT)$$

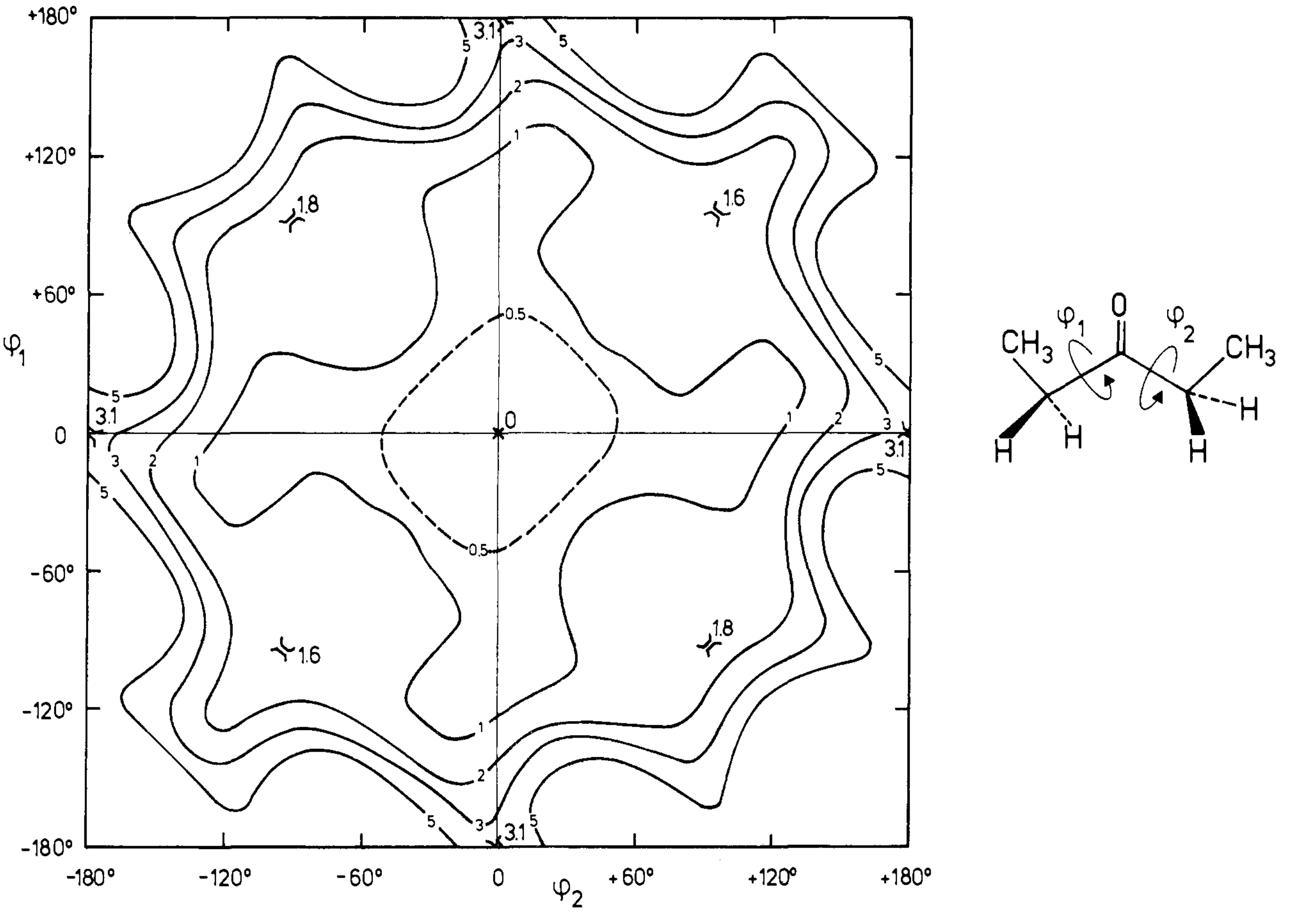


Figure 6. Calculated potential energy of 3-pentanone as a function of the torsion angles ϕ_1 and ϕ_2. For details see legend to Figure 5.

Table IV. Comparison between Experiment[a] (IR) and Theory for 2-Pentanone and 3-Pentanone at 300 K

	2-pentanone[b]			3-pentanone		
conformation	z_0	$\langle E \rangle$, kcal/mol	ΔH,[a] kcal/mol	z_0	$\langle E \rangle$, kcal/mol	ΔH,[a] kcal/mol
tt	1	0	0	1	0	0
gt	0.9	0.4	0.3 ± 0.2	1.4	0.7	1.0 ± 0.1
tg	1.1	1.7	1.3 ± 0.1			
g^+g^+ or g^-g^-	0.9	1.8	1.3 ± 0.1	0.9	1.5	~2
g^+g^- or g^-g^+	2.0	2.9	*c*	1.3	1.5	*c*

[a] Reference 54, from the temperature dependence of infrared spectra in the neat liquid. [b] The conformations of 2-pentanone are given with the first letter indicating the conformation of the aliphatic C-C bond; the second letter gives the state of C(sp^2)-C(sp^3). [c] These conformations were disregarded in the analysis of ref 54.

where $z_{\{\phi\}}$ is the partial conformational partition function $z_{\{\phi\}} = \int_{\{\phi\}} \exp(-E/RT)\, d\{\phi\}$ for the domain $\{\phi\}$. $\langle E \rangle$ is given relative to $\langle E \rangle = 0$ and z_0 is given relative to $z_0 = 1$, both for the tt conformer. Agreement between calculated $\langle E \rangle$ and experimental ΔH is reasonable, taking into consideration the combined inaccuracies in calculations and experiments. It is not as good for 3-pentanone as for 2-pentanone and we attribute this to the fact that in the evaluation of the experimental values the g^+g^- and the g^-g^+ conformers were not taken into consideration,[54] while in fact their populations are approximately equal to those of the g^+g^+ and g^-g^- domains. For 2-pentanone the corresponding assumption is more valid since g^+g^- has a computed $\langle E \rangle$ of almost 3 kcal/mol, which renders this conformation quite insignificant. The experiments support the assumptions underlying the calculations.

4-Methyl-2-pentanone and 4,4-Dimethyl-2-pentanone. These two compounds play a somewhat decisive role in conformational potential calculations of ketones. For the first one (isobutyl methyl ketone) three different "best" conformations were found by Dubois from a quantum-mechanical calculation and from two different empirical force fields.[5] Our calculations favor conformations with a C—C bond eclipsing C═O, as does one of the empirical ("Allinger's") force fields,[4,5] and we estimate the minimum of the "second best" conformation (with C—H eclipsing C═O) to be 1 kcal/mol higher in energy than the minimum of the "best" one. The second compound (neopentyl methyl ketone), in our estimation, also exhibits a favored conformational minimum with C—C eclipsing C═O, but the "second best" minimum (ca. 1 kcal/mol higher in energy) is one in which C═O does *not* eclipse a bond on the neopentyl radical side, but rather is "bisecting", i.e., is synclinal with an angle of ca. 60°. This seems to be the least "crowded" ketone[5] that has a "bisecting" conformation of reasonably low energy, a deduction reached earlier by Dubois[5] from an analysis of infrared spectra. Again, this substantiates our calculations.

Isopropyl Ketones. The isopropyl ketones are especially important as monomer models of poly(vinyl ketones). The four simplest homologues of this series, 3-methylbutanone (methyl

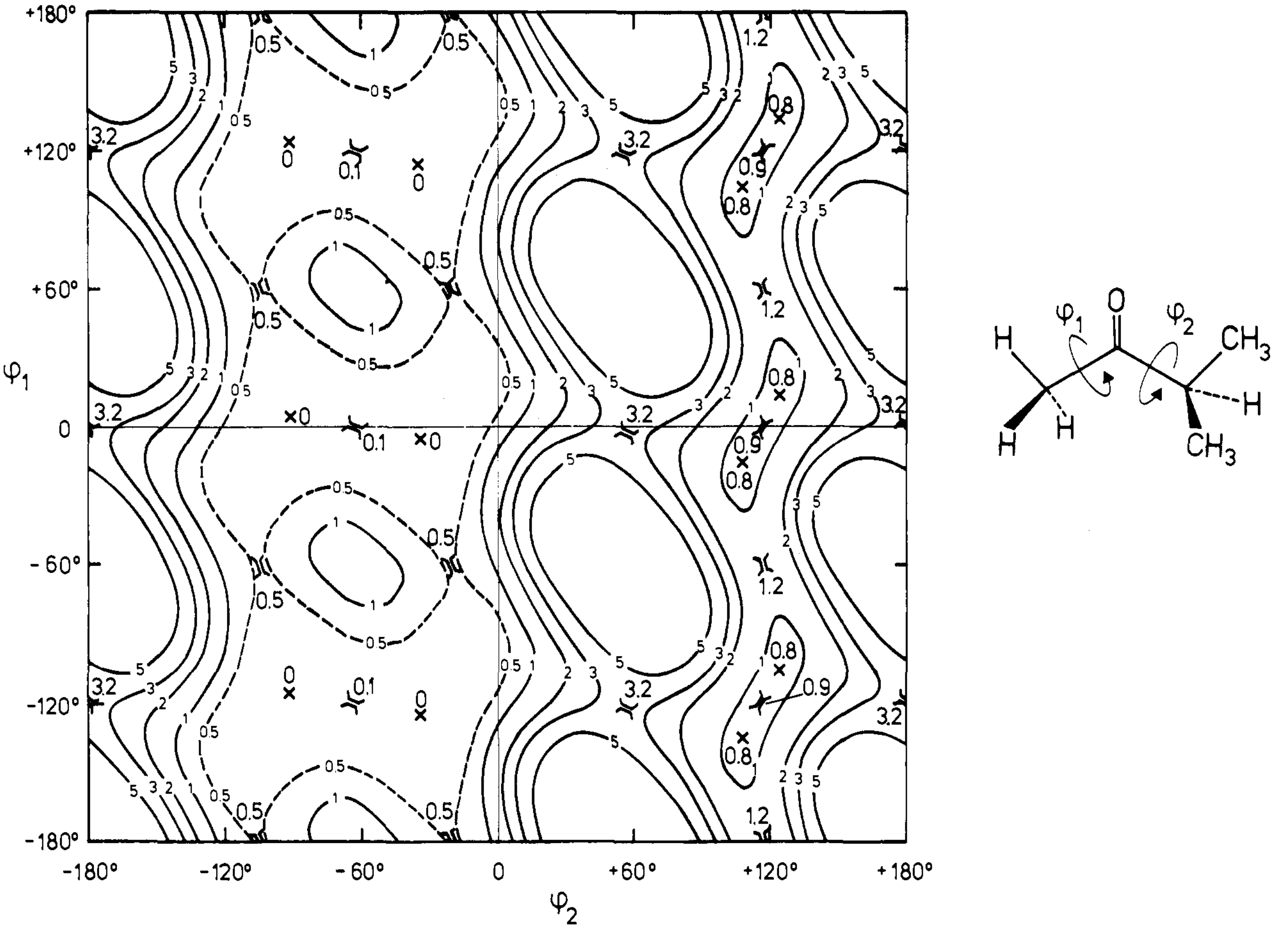


Figure 7. Calculated potential energy of 3-methylbutanone as a function of the torsion angles ϕ_1 and ϕ_2. For details see legend to Figure 5.

isopropyl ketone), 2-methyl-3-pentanone (ethyl isopropyl ketone), 2,4-dimethyl-3-pentanone (diisopropyl ketone), and 2,2,4-trimethyl-3-pentanone (*tert*-butyl isopropyl ketone), were considered in detail. The calculated potential energy maps are reproduced in Figures 7-10.

3-Methylbutanone (Methyl Isopropyl Ketone), Figure 7. Rotation about the methyl residue is almost as easy as in propanone. About the isopropyl group the rotation goes through similar stages as in 2-methylpropanal (Figure 3) and the conformation where C—H is eclipsing C=O (ϕ_2 = ca. 120°) is of similar energy. The col between the two conformations of lowest energy, however, is lowered to 0.1 kcal/mol. This originates in the differences in the intrinsic rotational potentials for aldehydes and ketones, as deduced above. As a result the isopropyl residue has a considerable rotational freedom and can assume values within a continuous range of ca. +70 to −70° about the minimum, while the potential energy never rises more than 0.5 kcal/mol above the absolute minimum. At room temperature the isopropyl group can assume any value in this range with approximately equal probability. Correlation between the two rotation angles is small, but large enough to be visible in the local C_2 symmetry of the troughs.

2-Methyl-3-pentanone (Ethyl Isopropyl Ketone), Figure 8. The map is superposable onto the previous one in the portions where the ethyl group is ca. anti periplanar to the C—C=O bond of the isopropyl residue (ϕ_1 = ca. 0°). Rotation of the ethyl residue by ca. 120° raises the potential by ca. 1 kcal/mol, if the isopropyl residue is allowed to relax to minimize the total potential. When the isopropyl group is forced into a conformation with C—H eclipsing C=O, the possibility of relaxation is small and only one trough remains at ϕ_2 = ca. +120°. The remarkable conformational freedom around the keto group in the neighborhood of the preferred conformation is the same as in 3-methylbutanone above, however.

2,4-Dimethyl-3-pentanone (Diisopropyl Ketone), Figure 9. The trend to restrict the conformation space available to the molecule continues with the new methyl substitution. The two symmetric lowest minima are separated by a sizable barrier of ca. 0.5 kcal/mol (compared to ca. 0.1 kcal/mol above) and they are somewhat reduced in width. The greatest change, however, occurs for the conformations where one C—H eclipses C=O. Here the trough is narrow and centered on a position where the other isopropyl group is "bisecting" C=O (i.e., C—H is anti periplanar to C=O), since for other positions the methyl groups would overlap excessively. Still, these less favored conformations have minima at only ca. 1 kcal/mol above the absolute minimum.

2,2,4-Trimethyl-3-pentanone (*tert*-Butyl Isopropyl Ketone), Figure 10. Here the situation in all potential troughs is about the same as in the two less favored conformations of 2,4-dimethyl-3-pentanone (Figure 9). The isopropyl group "bisects" C=O while the *tert*-butyl group "eclipses" it. The troughs are narrow. For an increase in energy over the minimum of 1 kcal/mol, ϕ_2 can assume values within a continuous range of +25 to −25° about the minimum position only; for ϕ_1 the range is even only +15 to −15°. The degeneracy in ϕ_2 being disregarded, this is a conformationally rigid compound.

Comparing the four isopropyl ketones, one notices the drastic decrease in conformation space available to the molecules with increasing degree of substitution. As a consequence, the conformational partition function $Z = \int_{\{\phi\}} \exp(-E/RT)\, d\{\phi\}$ over all of conformation space (E being measured relative to the absolute minimum in the molecule) decreases drastically. $Z^{1/2}/2\pi$ (a number between 0 and 1) at 300 K is 0.45 for 2-

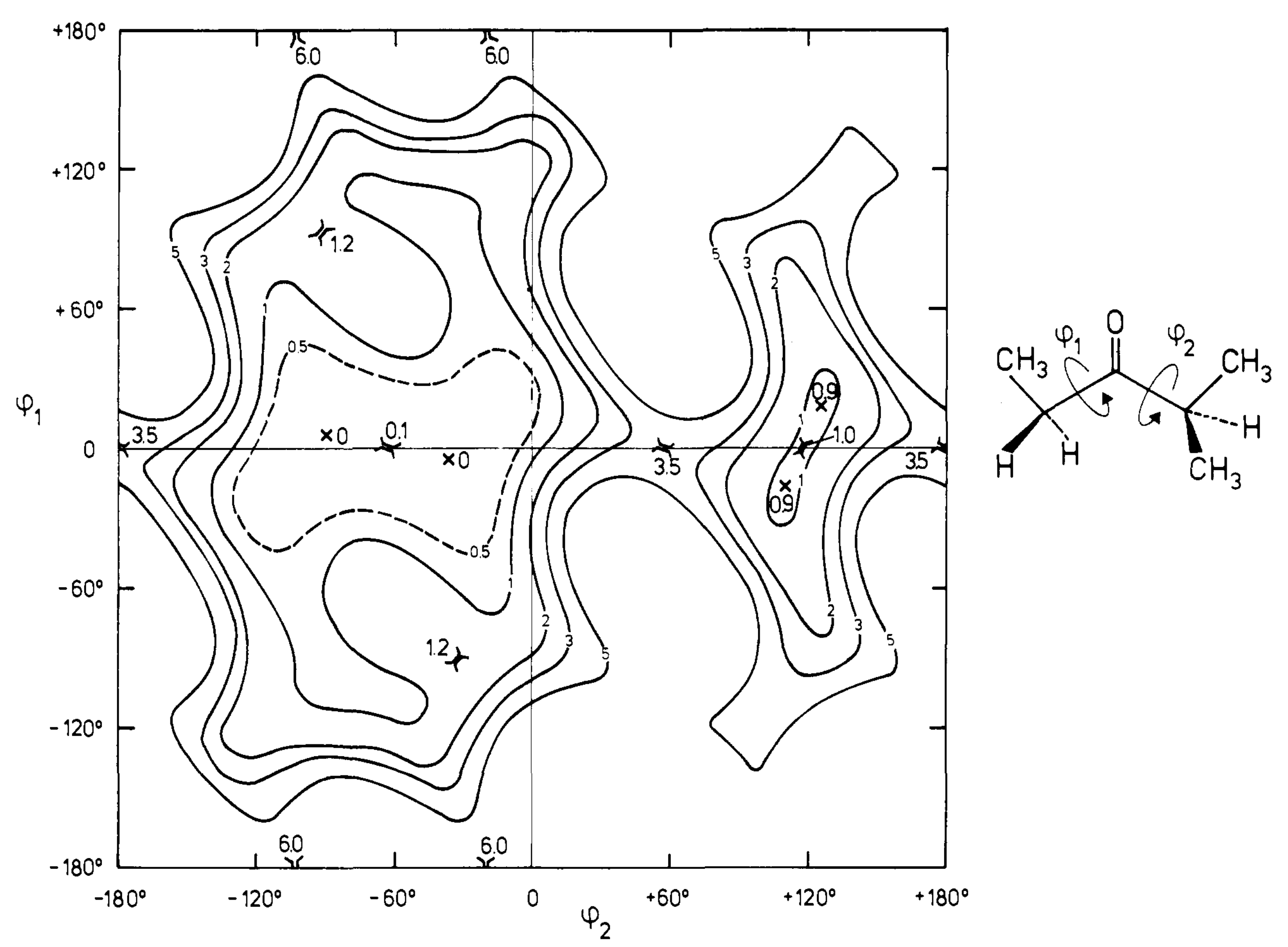
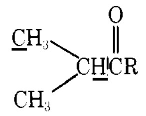


Figure 8. Calculated potential energy of 2-methyl-3-pentanone as a function of the torsion angles ϕ_1 and ϕ_2. For details see legend to Figure 5.

Table V. Selected Relative Chemical Shifts of Four Isopropyl Ketones. Comparison between Experiment and Theory



R	^{1}H Δδ, ppm this work[a]	Karabatsos et al.[c]	calcd	10^4dδ/dT, ppm/K exptl	calcd	^{13}C Δδ, ppm exptl[b]	calcd
$-CH_3$	0[d]	0	0	−5.7	−2.3	0[e]	0
$-C_2H_5$	0.02		0.01	−4.3	−1.8	+0.23	−0.06
$-i-C_3H_7$	0.19	0.20	0.04	−4.9	−1.0	+0.39	−0.22
$-t-C_4H_9$	0.54	0.55	0.09	−3.9	−0.2	+2.02	−0.51

[a] 90 MHz, ca. 20% (w/w) in $CDCl_3$, at 298 K. [b] 22.6 MHz, at 307 K, less than 1 m in $CDCl_3$ (concentrations below 1 m gave shifts independent of concentration). [c] Karabatsos, Sonnichsen, Hsi, and Fenoglio, ref 60; measurements in CCl_4. [d] δ 2.60 ppm relative to Me_4Si. [e] δ +18.16 ppm relative to Me_4Si.

methylbutanone, 0.28 for 2-methyl-3-pentanone, 0.23 for 2,4-dimethyl-3-pentanone, and 0.12 for 2,2,4-trimethyl-3-pentanone. Parallel to the decrease in Z is an increase in the calculated height of the cols.[59]

Karabatsos et al.[60] have interpreted the variation in the chemical shift of the protons α to C=O to be an indication of the variation in the conformational behavior in aliphatic, open-chain carbonyl compounds. Their calculations show that the chemical shift of these protons[60] varies mainly with the dihedral angle between C—H and C=O, and their published results, computed using the known magnetic anisotropy and electric dipole moment of the C=O group, can be conveniently condensed to the form

$$\sigma_H = +0.30 \cos \psi_H$$

where σ_H is the relative screening constant of the α proton (ppm) and ψ_H is the dihedral angle (measured from the syn periplanar position) between C—H and C=O. The amplitude of 0.3 ppm correlates reasonably well with the calculations of Fournier.[61] We have not found published experimental values for this amplitude. Chemical shifts and temperature coefficients were calculated by averaging cos ψ_H over all conformation space at different temperatures. The calculated results are compared with experiment in Table V. Even though the signs and the relative magnitudes of the chemical shift differences and their temperature coefficients are correctly estimated, the agreement between experiment and calculation is poor. Substitution in the second alkyl residue seems to influence the shift of the α proton in the isopropyl residue in ways other than through alteration of accessible conformation space.

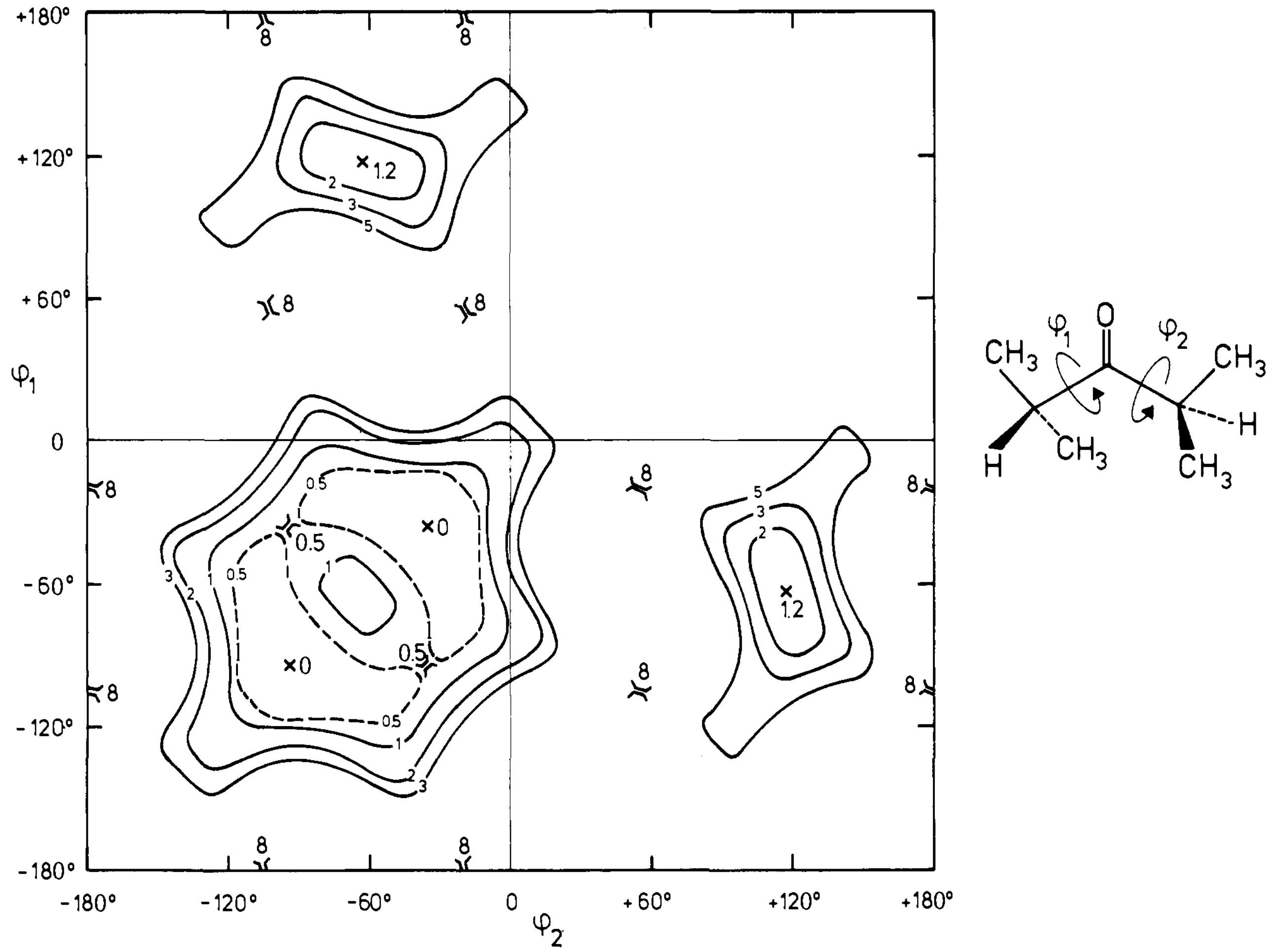


Figure 9. Calculated potential energy of 2,4-dimethyl-3-pentanone as a function of the torsion angles ϕ_1 and ϕ_2. For details see legend to Figure 5.

Nevertheless, NMR data do conform with the trends anticipated in our computations.

It is tempting to estimate the carbon-13 chemical shift differences of the methyl carbons in the isopropyl group in a similar fashion. We assume that the functional form of the dependence of the chemical shift difference on the dihedral angle is the same as for the above protons. The amplitude for the cos ψ function can be estimated from known shift differences in rigid ketones, given by Beierbeck, Saunders, and ApSimon,[62] and we obtain

$$\delta_C = -3.6 \cos \psi_C$$

where δ_C is the relative chemical shift of the α-methyl carbon in ppm, and ψ_C is the dihedral angle between C—CH_3 and C=O (measured from the syn periplanar position). The results obtained by averaging cos ψ_C over all conformations are compared with experimental data in Table V. There is no agreement between calculated and experimental shifts; even the sign of the prediction is wrong! This indicates that also in this case substitution in the second alkyl residue seems to influence the shift of the methyl groups in the isopropyl residue in ways other than through changes in the accessible regions of conformation space. These findings suggest that it is not always wise to use chemical shifts as conformational tools.

sec-Butyl Ketones. We have not carried out any calculations on *sec*-butyl ketones, but the results above for isopropyl ketones can assist in the interpretation of the experimental data available for *sec*-butyl ketones. The optically active (*S*)-4-methyl-3-hexanone (similar in structure to 2-methyl-3-pentanone above) was the object of a study by Lardicci, Salvadori, Botteghi, and Pino.[63] The authors found that the molecule's different optical activities in apolar and polar solvents and in the gas phase were indicative of appreciable conformational changes. They refrained from quantitative interpretation, since they deduced that intermolecular interactions play an important role as well. In two newer studies, Potapov, Dem'yanovich, and Zaitsev[64,65] investigated a series of optically active ketones in a variety of solvents and some of them over a large temperature range. Among the ketones studied are (*S*)-3-methyl-2-pentanone, (*S*)-4-methyl-3-hexanone, and (*S*)-2,4-dimethyl-3-hexanone,[66] that can be compared respectively with 3-methylbutanone, 2-methyl-3-pentanone, and 2,4-dimethyl-3-pentanone described above (Figures 7-9). They found, using the octant rule, that the *sec*-butyl residues assume two main conformations, those assigned to the rotation angles where C—CH_3 is eclipsing C=O and where C—C_2H_5 is eclipsing C=O. These two forms are approximately equally populated at room temperature in apolar and moderately polar solvents. In solvents like trifluoroacetic acid the form with C—CH_3 eclipsing C=O seems to predominate, presumably because association of solvent with the carbonyl group restricts the conformations around C—C_2H_5 more when it is eclipsing C=O than in the form where C—CH_3 eclipses C=O and C_2H_5 is far away from the keto group. In apolar and moderately polar solvents (where *sec*-butyl has two approximately equally populated conformations) one observes a trend with increasing size of the other residue that is correlated with the features of the maps in Figures 7-9. Upon going from the methyl ketone[64] to the ethyl ketone,[65] little change is seen, but the isopropyl ketone[65] shows some preference for the *sec*-butyl conformations with C—C_2H_5 eclipsing C=O. This is due to the fact that the C—C_2H_5 group overlaps with one of the

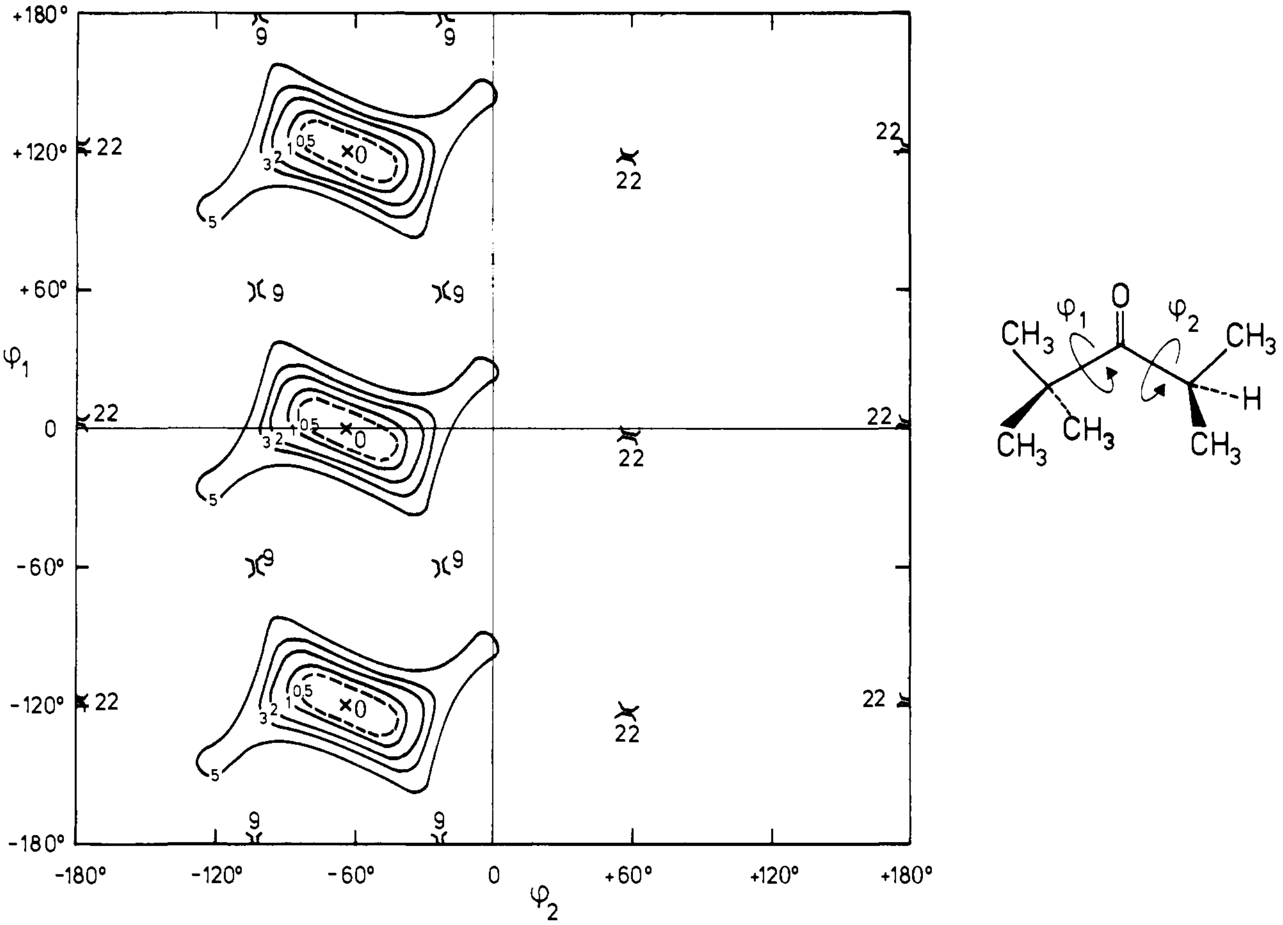


Figure 10. Calculated potential energy of 2,2,4-trimethyl-3-pentanone as a function of the torsion angles ϕ_1 and ϕ_2. For details see legend to Figure 5.

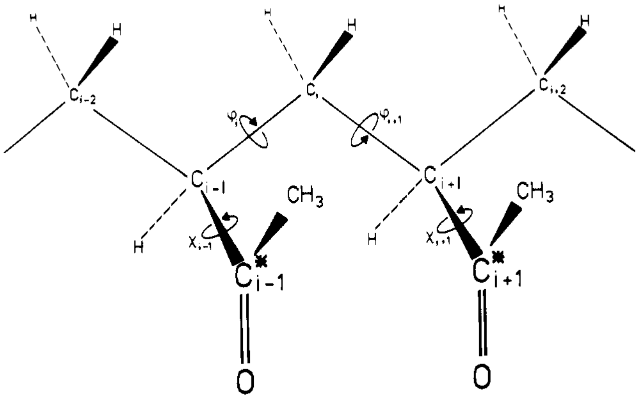


Figure 11. A meso dyad in |tt| conformation. All torsion angles are set to a value of zero.

methyl groups of the isopropyl residue in the conformation where C—CH_3 nearly eclipses C═O (compare Figure 9), while no such interaction occurs in the form where C—C_2H_5 eclipses C═O. This is also true when the isopropyl residue is replaced by a cyclohexyl group, since for the interactions of primary importance the only difference is the replacement of methyl by methylene, and indeed the CD spectra are almost superposable.[64,65]

V. Poly(methyl vinyl ketone)s [Poly(3-butenone-2), Poly(1-acetylethylene)]

Poly(methyl vinyl ketone) is the vinyl ketone polymer with the smallest possible side group. Inspection of the maps of its "monomer" model (Figure 7), and the maps of higher substituted analogues (Figures 8–10) shows that the side group enjoys an unusual conformational freedom, a freedom that is gradually lost with alkyl substitution on the methyl residue. Examination of molecular models suggests that the conformational characteristics of the polymers depend critically on the nature of the substituents of the keto group. We will consider here the case of extreme flexibility of the side group and hence of the least possible restrictions imposed on the main chain conformations.

Conformational Energies. A meso dyad in its |tt| conformation[67] is depicted in Figure 11. Angles χ for the side group rotations are measured from the position where C═O and the methine C—H in the main chain are syn periplanar. The main chain torsion angles are measured from the t conformations; according to standard procedures used in vinyl polymer analysis,[68] ϕ_{i+1} (Figure 11) in a meso dyad is measured in the left-handed sense, while the other ϕ's are measured as usual in the right-handed sense. Relative energies of meso and racemic dyads have been calculated as functions of the skeletal rotation angles ϕ_i and ϕ_{i+1}, values for the side-group torsion angles χ_{i-1} and χ_{i+1} being chosen to minimize the total energy of the dyad. For this minimization procedure a "quasi-Newton" method of Fletcher[69] was used. It was found to be both efficient and safe. In order to assure that the global minimum was found, minimization was performed four times for each pair of values of ϕ_i and ϕ_{i+1} with different starting values for χ_{i-1} and χ_{i+1}, namely, (0, 0°), (0, 180°), (180, 0°), and (180, 180°). The minimum found with the last set was in most cases the one with the lowest absolute energy. Solvent effects were taken into account as for the low molecular weight compounds above. Contour maps are shown in Figures 12 and 13. The portion of the maps in the "+−" quadrants are obtained from

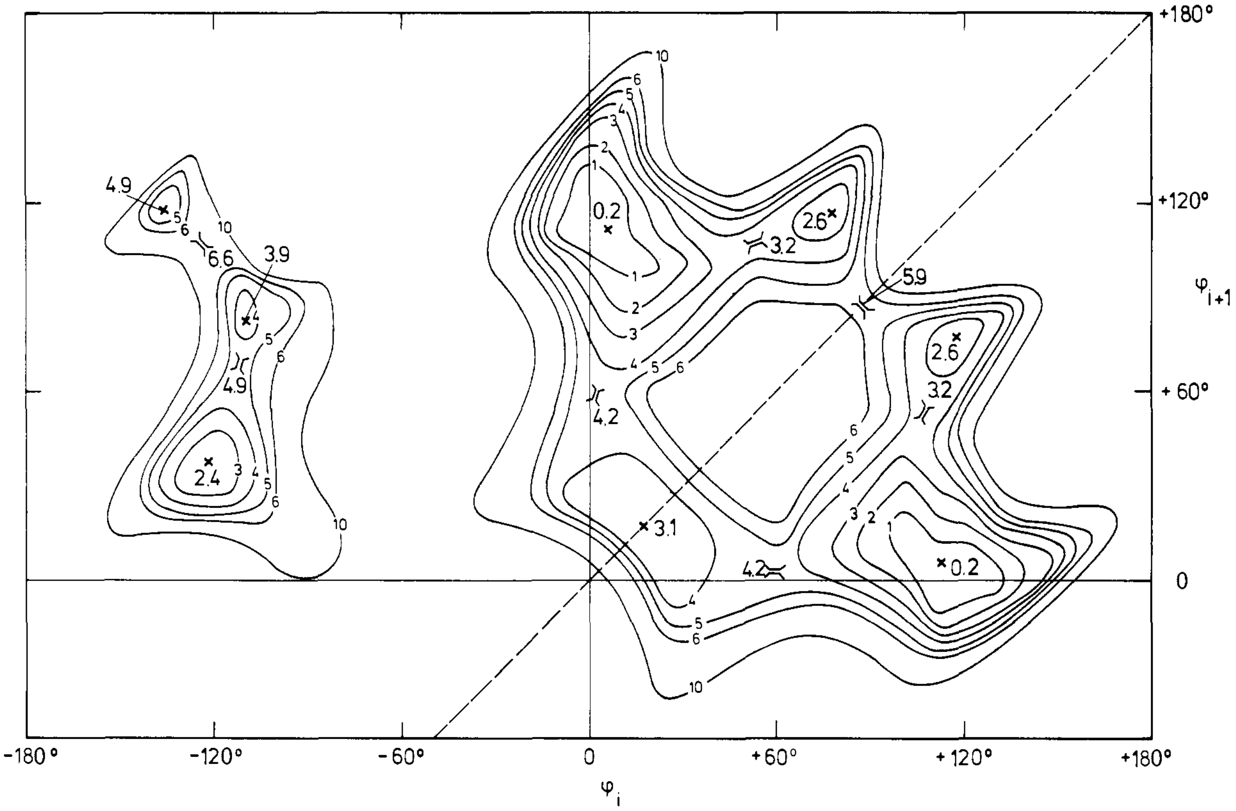


Figure 12. Potential energy contours for the skeletal rotational angles between two methine carbons in a meso dyad of poly(methyl vinyl ketone). Side group rotation angles are adjusted to minimize the energy for a given ϕ_i, ϕ_{i+1} pair. Minima are designated by ×, cols by)(. Indicated energies are in kcal/mol.

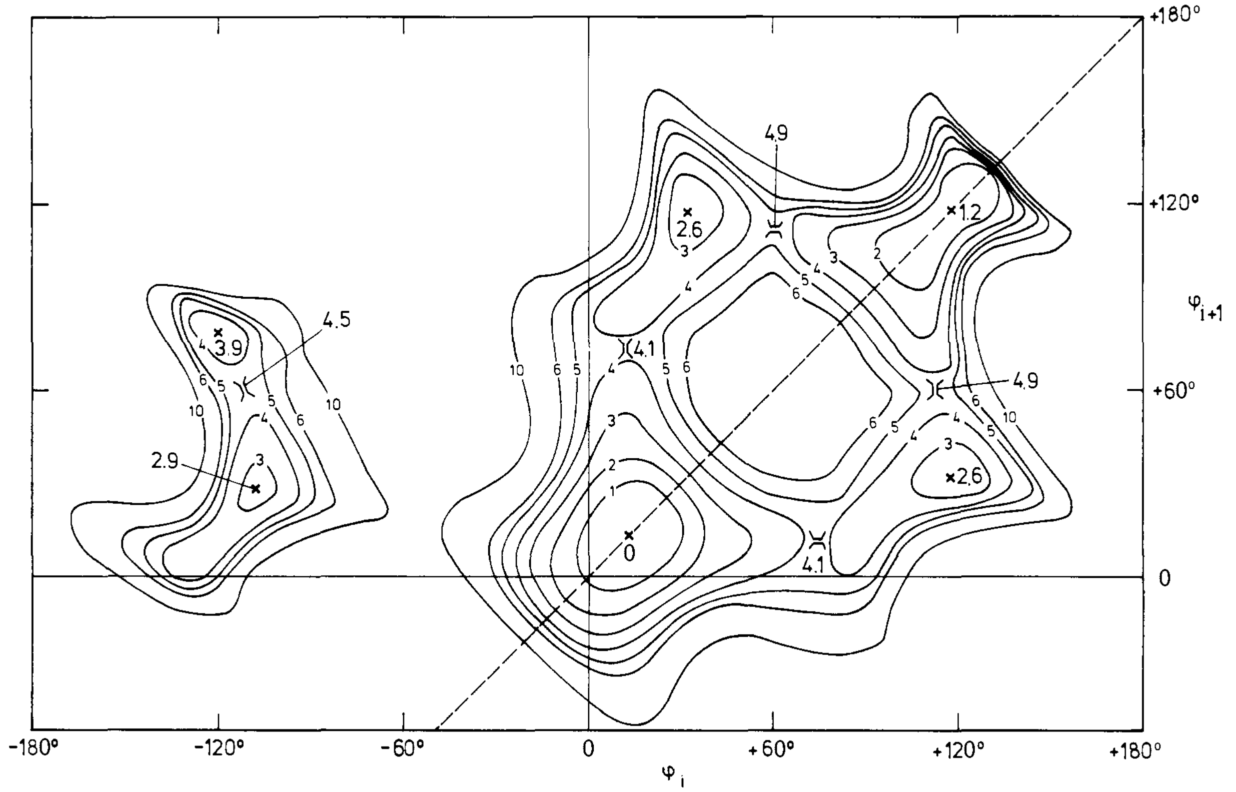


Figure 13. Potential energy contours for a racemic dyad of poly(methyl vinyl ketone).

"−+" by reflection at the dashed lines $\phi_i = \phi_{i+1}$. The "−−" quadrants contain no portions below 10 kcal/mol. All energies are given relative to the racemic |tt| minimum.

For the meso dyad, the features of the section in the "++" quadrant are similar to those observed in polypropylene[13] or polystyrene.[12] The major minima occur at ca. 10, 110 (|tg|) and ca. 110, 10° (|gt|). The |gg| domain is split into two troughs and the |tt| domain shows a single trough, as in the case of polystyrene, and these side minima are of rather high energy. The "−+" quadrant contains, rather unexpectedly,

Table VI. Conformational Averages for Dyad Conformations of Poly(methyl vinyl ketone) at 300 K

state		$E = E(\phi_i, \phi_{i+1}, \chi_{i-1}, \chi_{i+1})$				$E = E(\phi_i, \phi_{i+1} \mid \chi_{i-1}^{\min}, \chi_{i+1}^{\min})$			
		z^a	$\langle E \rangle^b$	α	$\langle \phi_i \rangle$, $\langle \phi_{i+1} \rangle$	z^a	$\langle E \rangle^b$	α	$\langle \phi_i \rangle$, $\langle \phi_{i+1} \rangle$
meso	$\lvert tt \rvert$	0.0076	2.77	0.8	21, 21	0.0064	3.07	1.1	21, 21
	$\lvert tg \rvert$	0.5482	0.57	1.4	8, 109	0.5922	0.24	0.9	9, 111
	$\lvert gg \rvert$	0.0085	3.35	2.3	92, 92	0.0137	2.70	1.3	94, 94
		(0.0042)			(70, 112)	(0.0068)			(78, 109)
	$\lvert \bar{g}t \rvert$	0.0008	3.73	0.4	−118, 34	0.0102	2.29	0.5	−123, 34
	$\lvert \bar{g}g \rvert$	0.0002	3.84	0.2	−110, 79	0.0009	3.75	0.5	−111, 86
racemic	$\lvert tt \rvert$	1	0	1	12, 12	1	0	1	13, 13
	$\lvert tg \rvert$	0.0087	2.90	1.1	31, 110	0.0138	2.65	1.2	29, 110
	$\lvert gg \rvert$	0.0941	2.03	2.8	105, 105	0.1333	1.18	1.0	113, 113
	$\lvert \bar{g}t \rvert$	0.0002	4.27	0.2	−108, 37	0.0072	2.81	0.8	−112, 26
	$\lvert \bar{g}g \rvert$	0.0003	4.18	0.3	−115, 73	0.0009	3.48	0.3	−118, 75

[a] z is expressed relative to $z = 1$ for the racemic $\lvert tt \rvert$ state. [b] $\langle E \rangle$ is expressed in kcal/mol relative to $\langle E \rangle = 0$ for the racemic $\lvert tt \rvert$ state. [c] Values are for the merged state; values in parentheses represent the individual troughs.

three minima with ϕ_i = ca. −120° and ϕ_{i+1} = ca. 40 ($\lvert \bar{g}t \rvert$), ca. 80, and ca. 120° (both $\lvert \bar{g}g \rvert$). The $\lvert \bar{g}t \rvert$ minimum is as low in energy as it is in the case of polypropylene. The reason for the relatively low energy of the $\bar{g}$ domains is apparent upon inspection of models. The fact that the side groups are able to assume any torsion angle within a wide range of values at practically no cost in energy, and that these side groups are rather flat and planar, makes it possible that by adjustment of side group rotation angles unusually low potential energies can be obtained. Also, the minimum in the $\lvert \bar{g}g \rvert$ domain at ϕ_i = ca. −140, ϕ_{i+1} = ca. 120° is possible only because the flat side group can adjust itself so that there is no excessive overlap if the methylene group (around C_{i+2}) approaches the side group substituted on C_{i-1}. The splitting into pairs of the $\lvert \bar{g}g \rvert$ as well as of the $\lvert gg \rvert$ minima reflects the alleviation of second-order steric repulsions brought about by minor adjustments in ϕ_i and ϕ_{i+1}.[12,13,21]

The conformational energy surface for the racemic dyad resembles in the "++" quadrant the map of polystyrene.[12] The major minima occur at ca. 10, 10 ($\lvert tt \rvert$) and at ca. 120, 120° ($\lvert gg \rvert$); the former is the conformation of lowest energy of both meso and racemic dyads, the latter is 1.2 kcal/mol higher. Remarkable is the unusually shaped trough in the $\lvert gg \rvert$ domain. The "−+" quadrant contains two minima at ca. −110, 30 and at ca. −120, 80°, similar in magnitude and location to the ones found for the meso dyad discussed above. A third minimum, corresponding to the second one in the $\lvert \bar{g}g \rvert$ domain of the meso dyad, is not present. This is due to the fact that in these $\lvert \bar{g}g \rvert$ conformations two methylene groups are juxtaposed (C_{i-2} and C_{i+2}). These groups occupy a more spherical volume than the flatter keto groups, and adjustment of side group torsion angles cannot substantially decrease the larger overlap; thus the total energy is raised above 10 kcal/mol in this domain.

Calculation of the energies of conformations with various values for χ_{i-1} and χ_{i+1} but fixed values for ϕ_i and ϕ_{i+1}, not included here, shows that the acetyl side groups enjoy almost as much rotational freedom as in the monomer model (Figure 7) in the most preferred conformations, meso $\lvert tg \rvert$ and $\lvert gt \rvert$ and racemic $\lvert tt \rvert$ and $\lvert gg \rvert$. They prefer positions in which their individual C=O groups eclipse one of the backbone C—C bonds adjoining the methine C atom that carries them, and are rendered almost independent of each other. Electrostatic interactions are not relevant; their magnitudes remain below 0.2 kcal/mol in these conformations. The conformation space allowed for the side group torsion angles is much more restricted in the conformational domains with higher energies (with the exception of meso $\lvert gg \rvert$) since there one or both side groups are brought close to the other side group or to the methylene group at the opposite end of the dyad (Figure 11).

In the conformations where the two acetyl side groups are brought close to each other, i.e., meso $\lvert tt \rvert$ and racemic $\lvert \bar{g}t \rvert$ and $\lvert t\bar{g} \rvert$, we observe a coupling between the two torsion angles χ_{i-1} and χ_{i+1}. Fortunately, the energies of these minima are higher than 2.5 kcal/mol, so that these conformations are rare and the problem of the coupling of side-group conformations along the chain is rendered insignificant.

Direct experimental evidence for calculated energy maps is not easily found. For poly(methyl vinyl ketone) such a confirmation may be obtained from an experiment by Bullock, Cameron, and Smith.[70] With a spin-labeled, atactic poly(methyl vinyl ketone) (1 label/2800 monomeric units) in THF solution they measured the activation energy of the isotropic motion of the label and obtained an estimate of 3 kcal/mol for the "barrier to local conformational changes in the polymer" after taking into account the effects of solvent viscosity. Even though this is not a well-defined quantity, since it corresponds to some "segmental rotation", it nevertheless gives an order of magnitude estimate for the conformational barriers. We observe that the calculated barriers between the most populated domains, in the meso dyad as well as in the racemic dyad, are of the same order of magnitude as the experimental value (Figures 12 and 13).

Rotational Isomeric States and Statistical Weight Matrices. Incorporation of the results shown in Figures 12 and 13 in a rotational isomeric state scheme requires that every element of conformation space (ϕ_i, ϕ_{i+1}, χ_{i-1}, χ_{i+1}) for which the energy is not excessively high be allocated to one of the appropriately chosen states. Regions comprising all the elements of the conformation space assigned to a single state were defined so that their boundaries either enclose all elements in a trough for which $E < 6$ kcal/mol or they run along the ridge that passes through a col. At first the meso $\lvert gg \rvert$ domain was split into two regions along the line $\phi_i = \phi_{i+1}$; the two troughs in the meso $\lvert \bar{g}g \rvert$ domain were considered together, owing to the high energy of the one with the larger ϕ_{i+1}. The partition function z_ζ, the average energy $\langle E \rangle_\zeta$, and the average rotation angles $\langle \phi_k \rangle_\zeta$ for each rotational state ζ were calculated for temperatures of 300, 400, and 500 K according to

$$z_\zeta = \int_\zeta \int \int_0^{2\pi} \int_0^{2\pi} \exp(-E/RT)\, d\phi_i\, d\phi_{i+1}\, d\chi_{i-1}\, d\chi_{i+1}$$

$$\langle E \rangle_\zeta = z_\zeta^{-1} \int_\zeta \int \int_0^{2\pi} \int_0^{2\pi} E \times \exp(-E/RT)\, d\phi_i\, d\phi_{i+1}\, d\chi_{i-1}\, d\chi_{i+1}$$

$$\langle \phi_k \rangle_\zeta = z_\zeta^{-1} \int_\zeta \int \int_0^{2\pi} \int_0^{2\pi} \phi_k \times \exp(-E/RT)\, d\phi_i\, d\phi_{i+1}\, d\chi_{i-1}\, d\chi_{i+1},\ k = i, i+1$$

Integrations were performed on a grid with a step size of 10°. The results for a temperature of 300 K are reported in Table VI. Energies are given relative to $\langle E \rangle$ for the racemic |tt| state; partition functions are expressed as ratios with z of this state. Energies and angles are nearly independent of temperature, i.e., between 300 and 500 K, $\langle E \rangle$ varies by less than 0.2 kcal/mol and $\langle \phi_i \rangle$ by less than 4°, for states with $\langle E \rangle < 3$ kcal/mol.

If the dependence of E on $\chi_{i-1} - \chi_{i-1}{}^{\min}$ and on $\chi_{i+1} - \chi_{i+1}{}^{\min}$ were similar for all the principal states ($\chi^{\min}$ being the value of χ that minimizes E for a particular set of values of ϕ_i, ϕ_{i+1}), then integration over the four angles ϕ_i, ϕ_{i+1}, χ_{i-1}, and χ_{i+1} as carried out above could be approximated by integration over the two angles ϕ_i and ϕ_{i+1} only, if $E(\phi_i; \phi_{i+1}, \chi_{i-1}, \chi_{i+1})$ were replaced by $E(\phi_i, \phi_{i+1}|\chi_{i-1}{}^{\min}, \chi_{i+1}{}^{\min})$.[13] In our case this simplification cuts computation time to less than one-tenth of that required for the "complete" integration performed above. The results for integration over the same domains of ϕ_i, ϕ_{i+1} are also listed in Table VI. The numbers are as independent of temperature as the ones calculated before. The factor α_ζ is defined by[12]

$$z_\zeta = \alpha_\zeta \exp(-\langle E \rangle_\zeta / RT)$$

and measures the effective size of the domain ζ with respect to racemic |tt|. For the integration over two angles only, this affords a direct measure of the size of the troughs in Figures 12 and 13. For the most populated domains (without a $\bar{\text{g}}$ state) they are close to unity. For the integration over all four angles, including the side groups, however, α must also reflect the torsional freedom of the side groups. In the racemic |tt| state, for instance, the two acetyl groups enjoy a relatively large freedom of rotation, overlapping with each other only for certain torsion angles χ_{i-1} and χ_{i+1}. Changing one of the ϕ's to the g state relieves the acetyl groups from this small impediment, but hinders one of them in turn by a newly approaching methylene group. In the |gg| state, finally, both side groups are optimally free of obstructions. In the meso |tt| state, overlap of the acetyl groups is more severe than in the racemic |tt| conformation, but changing one of the bonds to the g state results in freer side groups than in the racemic dyad, since the methylene group that restrained a side group in racemic |tg| is farther away from it in meso |tg|. In the |gg| states, neither structure is going to be handicapped by obstructions from the main chain.

The "two-dimensional" potential function displayed in Figures 12 and 13 yields a rough approximation of the results computed by integrating the "complete" potential function over the four angles ϕ_i, ϕ_{i+1}, χ_{i-1}, and χ_{i+1}. The most conspicuous difference between results calculated with the two methods is the fact that, with integration over the "two-dimensional" potential, the population of the $\bar{\text{g}}$ states is overestimated by factors ranging from 3 to more than 30. This is due to the effect of the relatively crowded conformations on the conformational flexibility of the side group.

Table VII. Conformational Parameters from Energy Calculations[a]

	racemic |gg| ignored[b]	least-squares solution[b]
E_η	−0.57	−1.10
E_ω	2.21	1.32
$E_{\omega'}$	2.33	1.97
$E_{\omega''}$	2.77	2.94
η_0	0.70	0.58
ω_0	1.15	0.82
ω_0'	0.79	0.68
ω_0''	0.79	0.85

[a] Energies are in kcal/mol. [b] See text.

At 300 K the cumulated partition functions of all the $\bar{\text{g}}$ states together are less than 0.1% of the total of all states. At 400 K they still constitute less than 0.6% of the total. We therefore neglect these states and represent the results listed in Table VI by a rotational isomeric state scheme comprised of two states, t and g, corresponding to rotation angles of 10 and 110°. The corresponding statistical weight matrices for a meso and a racemic dyad are[12,68,71]

$$\mathbf{U}_{\mathrm{m}}'' = \begin{bmatrix} \eta^2\omega'' & \eta \\ \eta & \omega \end{bmatrix} \qquad \mathbf{U}_{\mathrm{r}}'' = \begin{bmatrix} \eta^2 & \eta\omega' \\ \eta\omega' & 1 \end{bmatrix}$$

where η is the first-order parameter expressing the statistical weight of the trans relative to the gauche state; second-order interactions are characterized by ω, ω', and ω'' for interactions between CH_2/CH_2, $CH_2/COCH_3$, and $COCH_3/COCH_3$, respectively. Interactions of first order for both bonds, i and $i + 1$, and "intradyad" second-order interactions are included in the matrices given above. The complementary matrix $\mathbf{U}'$ for the pair of bonds flanking the methine carbon in the chain must contain only the "interdyad" second-order interactions. These interactions are overriding for the g|g state, so that a value of zero is appropriate.[12,13] For other states no appreciable interactions occur. Hence, the matrix $\mathbf{U}'$ is given by

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix}$$

We let

$$\xi = \xi_0 \exp(-E_\xi/RT)$$

for each statistical weight ξ (ξ is η, ω, ω', or ω''). A satisfactory representation of the results of integration is obtained if we ignore the racemic |gg| state and solve the resulting four equations containing the appropriate combinations of the four unknown E_ξ's, as well as the four equations for the four unknown ξ_0's, once the E_ξ's are determined. Values for ξ_0 and E_ξ thus obtained are shown in Table VII under the label "racemic |gg| ignored". With these parameters the estimated partition function of the racemic |gg| state is too large by a factor of ca. 3 in light of the results from Table VI. Alternatively, the least-squares solutions of the complete set of five relations between each set of four unknowns can be calculated, through computation of the generalized inverse of the matrix of coefficients of these relations. Under the label "least-squares solution" the parameters thus obtained are also included in Table VII. With these parameters the racemic |gg| state is more equitably represented; however, the other most populated domains necessarily are accounted for to a lesser degree than in the previous calculations. The partition function for the meso |tg| state, the worst case, is underrepresented by a factor of ca. 2. Only three parameters are sensitive to the method of elaboration, namely, E_η, E_ω, and ω_0. The influence of the exact value of ω_0 is practically negligible, considering the large uncertainty in E_ω, and we set ω_0 equal to unity. We will represent henceforth the statistical weights by the rounded values

$$\eta = 0.7 \exp(-E_\eta/RT)$$

$$\omega = 1.0 \exp(-E_\omega/RT)$$

$$\omega' = 0.8 \exp(-1100/T)$$

$$\omega'' = 0.8 \exp(-1400/T)$$

where E_η and E_ω will be allowed to vary in the ranges inferred from the results in Table VII, i.e., $0.6 < -E_\eta < 1.2$ kcal/mol and $1.3 < E_\omega < 2.2$ kcal/mol.

Unperturbed Dimensions. Characteristic ratios $C_n = \langle r^2 \rangle_0 / nl^2$ were calculated using the well-known matrix generation technique.[12,72] The rotational states were taken at $\phi_t = 10°$ and $\phi_g = 110°$. The statistical weight parameters were assigned using the relations given above for a temperature of 300 K. Limiting values, C_∞, for stereoregular chains were

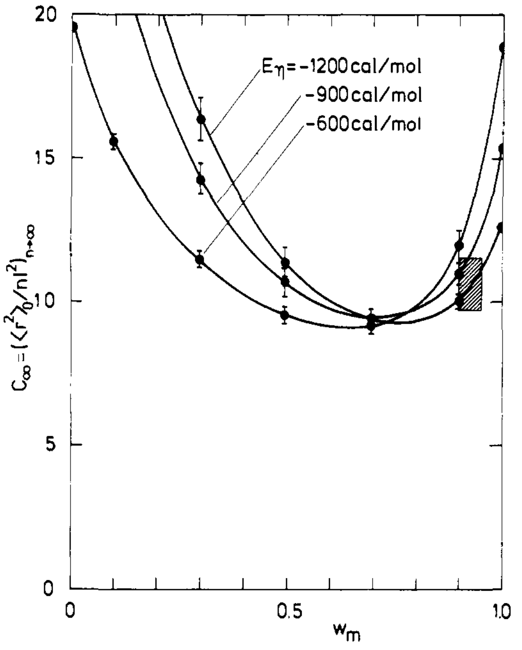


Figure 14. Characteristic ratio C_∞ for poly(methyl vinyl ketone) at 300 K for different stereochemical compositions, w_m being the probability of a meso placement. Values for stereoregular chains are exact; other values are averages from 30 Monte Carlo chains of 200 bonds each. Dots represent the averages; error bars indicate 2σ limits. The shaded rectangle represents the "experimentally feasible" area; see text for details.

obtained by linear extrapolation of C_n vs. $1/n$, where values of n up to 500 were used. Atactic chains were found to approach their limits within 100 monomeric units. In Figure 14 values of C_∞ for poly(methyl vinyl ketone) are plotted against the stereochemical composition for three values of E_η. The dyad statistics were assumed to be Bernoullian and dyad compositions are expressed as the probability for a meso placement: w_m. Calculations were made at intervals of 0.2 in w_m for 30 Monte Carlo chains at each value of w_m. Dots and error bars represent averages and 2σ limits; values for the stereoregular chains are exact. Calculations for different values of E_ω at each value for E_η reveal that C_∞ does not change appreciably with changes in E_ω (i.e., by less than 0.2).

"Crystalline" poly(methyl vinyl ketone), prepared by anionic initiators in toluene and similar solvents, is isotactic,[73-75] and the acetone-insoluble fractions can have meso dyad contents of 0.90[75] to 0.95.[74] Using Privalko's estimate for the unperturbed dimensions of "crystalline" poly(methyl vinyl ketone) in the bulk at ambient temperature[76,77] we calculate a value for C_∞ of 9.7-11.5. These limits combined with the limits obtained from the determination of dyad tacticities above comprise an "experimentally feasible" area included in Figure 14 as a shaded rectangle. Theoretical curves for $-E_\eta > 0.8$ kcal/mol pass through the rectangle. Values for E_η below -0.8 kcal/mol are consistent with experiment.

NMR Coupling Constants. Merle-Aubry, Merle, and Selegny[75] report experimental data for the vicinal coupling constants in the 220-MHz proton magnetic resonance spectra obtained for solutions of isotactic poly(methyl vinyl ketone) (ca. 90% meso dyads) at temperatures of 20, 40, and 60 °C. The quantity extracted directly from the spectra and readily calculated is the difference ΔJ between the conformationally averaged vicinal coupling constants for pairs of protons that are syn and anti, i.e., $\Delta J = \langle J_{\text{anti}}\rangle - \langle J_{\text{syn}}\rangle$.[26,29] Calculation is based on the assumption that the vicinal coupling constant J depends only on the dihedral angle between the two protons in question. For the special case of two states per bond at ϕ_t and $\phi_g = 120° - \phi_t$, the relation for the calculation of ΔJ reduces to[26]

$$\Delta J = \delta J_t(2p_t - 1)$$

where δJ_t is the difference between a pair of anti and syn protons when the connecting C-C bond is in the trans state, and p_t is the a priori probability[78] for this C-C bond to be in this state. For $\phi_t = 10°$, we assume $\delta J_t = 10$ Hz.[26] The a priori probability p_t was calculated according to standard methods[78] for a bond in a meso dyad embedded in the middle of an isotactic chain of 129 dyads. The calculated values for ΔJ increase for decreasing values of E_η, but are not sensitive to changes in E_ω (variation of E_ω between 1.3 and 2.2 kcal/mol causes ΔJ to vary by less than 0.1 Hz for all values of E_η considered).

The most accurate experimental value of Merle-Aubry, Merle, and Selegny[75] is the one at 60 °C, since the resolution is higher at this temperature than at 20 or 40 °C. It is

$$\Delta J_{\text{exp}} = 0.9\text{-}1.0 \text{ Hz}$$

The calculations for 60 °C can be reproduced to within 0.05 Hz by the linear relationship

$$\Delta J = 0.4 - 0.8E_\eta$$

where $0.4 < -E_\eta < 1.3$ kcal/mol, and ΔJ is obtained in hertz. Comparison between experiment and this linear equation suggests that $E_\eta = -0.7 \pm 0.2$ kcal/mol, assuming a possible experimental error of 0.1 Hz outside the stated limits. This range overlaps with the one deduced from experimental data on unperturbed dimensions above. A value of E_η = ca. -0.8 kcal/mol will satisfy both.

Dipole Moments. Guest, Matsuo, and Stockmayer[79] report a carefully determined value of 0.32 ± 0.01 for the dipole moment ratio, $D_\infty = (\langle\mu^2\rangle/x\mu_0{}^2)_{x\to\infty}$, of atactic (free radical initiated) poly(methyl vinyl ketone) in dioxane at 25 °C.

The calculations of D_∞ in poly(methyl vinyl ketone) are somewhat complicated by the flexibility of the side groups added to the fact that the main dipole moment of the monomeric unit, the one inherent to the carbonyl group, is not parallel to the axis of rotation of the side group. Correct treatment would start with the construction of a rotational isomeric state scheme in which the side groups can assume two different torsion angles in each state of the main chain bonds. This procedure has been elaborated by Abe[80] and Mattice,[81] but it necessarily introduces new parameters and is therefore not very promising. We have observed above that in the most preferred conformations the side groups assume with almost equal probability the two torsion angles in which the individual C=O groups eclipse one of the backbone C—C bonds joining the methine C atom that carries them. As a rough approximation we choose a single state with a torsion angle corresponding to a state exactly between the two preferred conformations, i.e., we set $\chi_{i-1} = \chi_{i+1} = 180°$. This represents a preaveraged side group state.

Dipole moment ratios, D_∞, were calculated using the well-established matrix generation technique.[72,82] Parameters were taken as in the calculations of the unperturbed dimensions above. The side-group dipole moment in the frame of reference of bond i (Figure 11) is 2.75 col (−0.23, 0.35, −0.91) D. Limiting values for stereoregular chains were obtained from a linear extrapolation of D_x vs. $1/x$. Atactic chains were found to be adequately represented by chains of 100 monomeric units.

In Figure 15 calculated values of D_∞ are plotted against w_m for various values of E_η. The calculations were made at intervals of 0.2 in w_m for 15 Monte Carlo chains at each value of w_m. Dots and error bars represent averages and 2σ limits; the values for the stereoregular chains are exact. Calculations for different values of E_ω at each value for E_η reveal that D_∞ does not change appreciably with changes in E_ω.

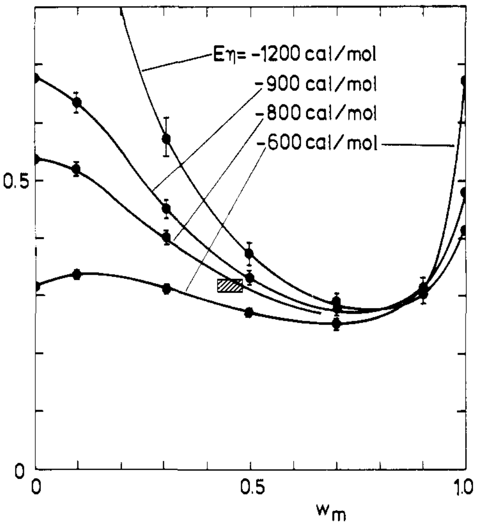


Figure 15. Dipole moment ratio D_∞ for poly(methyl vinyl ketone) at 300 K for different stereochemical compositions. Values for stereoregular chains are exact; other values are averages from 15 Monte Carlo chains of 200 bonds each. Dots represent the averages; error bars indicate 2σ limits. The shaded rectangle represents Guest, Matsuo, and Stockmayer's experimental data, ref 79.

Guest, Matsuo, and Stockmayer's value of $D_\infty = 0.32 \pm 0.01$,[79] combined with Allio and Pino's determination of the tacticity of free radical initiated poly(methyl vinyl ketone) that yielded a value for (m) = ca. 0.45,[74] defines, if we assume an accuracy of ±0.02 in (m), an "experimentally feasible" area represented in Figure 15 by a shaded rectangle. The calculated values for D_∞ change by almost 10% with a change in E_η of 10%. The fact that the theoretical curve for $E_\eta = -0.8$ kcal/mol passes through the shaded area indicates that our conformational parameters are well chosen.

Conformational Parameters for Poly(methyl vinyl ketone)s. The available experimental results suffice to assign a value to E_η. E_ω is still indeterminate, however, within the limits $1.3 < E_\omega < 2.2$ kcal/mol set by the conformational energy calculations. Comparison with results for other vinyl polymers indicates that E_ω, i.e. the second-order interaction corresponding to the pair CH_2/CH_2 separated by four bonds, is similar in magnitude for different polymers; in polypropylene, polystyrene, poly(methyl acrylate), and poly(vinyl acetate) it has values of 1.6–1.9, 2.0, 1.6, and 1.8 kcal/mol, respectively. We arbitrarily assign a tentative value of E_ω = ca. 1.8 kcal/mol, which is also in the center of the computed limits, and the expressions for the statistical weights are then

$$\eta = 0.7 \exp(+400/T)$$

$$\omega = 1.0 \exp(-900/T)$$

$$\omega' = 0.8 \exp(-1100/T)$$

$$\omega'' = 0.8 \exp(-1400/T)$$

which at 300 K give $\eta = 2.7$, $\omega = 0.05$, $\omega' = 0.02$, and $\omega'' = 0.008$.

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Flat-Band Potential of n-Type Semiconducting Molybdenum Disulfide by Cyclic Voltammetry of Two-Electron Reductants: Interface Energetics and the Sustained Photooxidation of Chloride

Lynn F. Schneemeyer and Mark S. Wrighton*

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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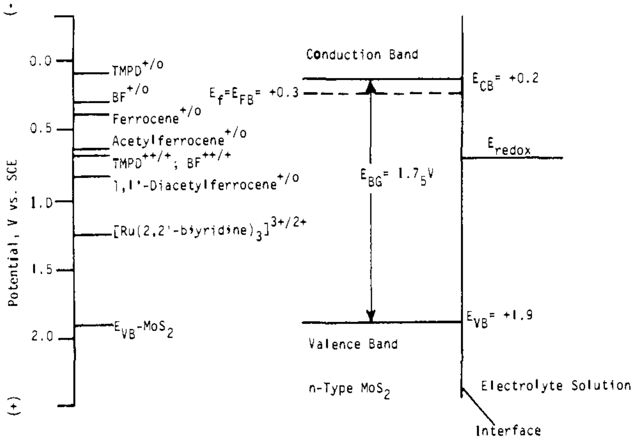
Abstract: Cyclic voltammetry has been used to locate the band edges of n-type MoS_2 in CH_3CN/ and EtOH/[*n*-$Bu_4N]ClO_4$ solutions. The crucial experiments concern the study of the cyclic voltammetry of biferrocene (BF) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) each of which has two, reversible, one-electron waves at Pt. At MoS_2, the first oxidation is reversible in the dark, whereas the second oxidation is observed only upon illumination of the MoS_2. The dark oxidation $BF \rightarrow BF^+$ and the photoanodic $BF^+ \rightarrow BF^{2+}$ are separated by only ~150 mV, allowing us to assign an uncommonly accurate flat-band potential of +0.30 + 0.05 V vs. SCE to MoS_2. This flat-band potential reveals that the valence band edge is at ca. +1.9 V vs. SCE showing that photooxidations workable at TiO_2 are thermodynamically possible at illuminated MoS_2 as well. As an example of the ruggedness of MoS_2, we demonstrate the ability to effect the sustained oxidation of Cl^- at illuminated n-type MoS_2. Conclusions from BF are fully supported by those from TMPD and one-electron systems ferrocene, acetylferrocene, 1,1'-diacetylferrocene, and $[Ru(2,2'\text{-bipyridine})_3]^{2+}$. Oxidation of $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ can be effected >0.5 V more negative than at Pt by illumination of MoS_2.

We wish to report an exceptionally well-defined flat-band potential, E_{FB}, for n-type semiconducting MoS_2 in nonaqueous electrolyte solution. The procedure used follows from that outlined by Bard and his co-workers[1-3] for locating energy levels of semiconductors relative to the potentials of various redox couples by cyclic voltammetry. Locating the energy levels for MoS_2 is useful since MoS_2 has attracted interest recently as a photoelectrode material with a small band gap, E_{BG} = 1.75 eV, and having unusual ruggedness with respect to photoanodic decomposition.[4] The material has a layered geometrical structure leading to an electronic (band) structure which is consistent with a lowest optical absorption associated with Mo d bands. Most other n-type semiconducting photoanodes that have been studied involve p-band materials.[5] The durability of the n-type MoS_2 photoelectrode has been associated with the fact that the electronic excitation does not involve a transition having $S^{2-} \rightarrow Mo(IV)$ charge-transfer character. In a material such as CdS, optical excitation involves considerable $S^{2-} \rightarrow Cd(II)$ charge transfer, and photoanodic decomposition is a typical result. Our measurements establish what reductants can be photooxidized by illumination of n-type MoS_2. Quite interestingly, we find that the uphill oxidation of Cl^- can be sustained by illumination of n-type MoS_2 in CH_3CN solvent.

Scheme I. Energy Levels of n-Type MoS_2 at the Flat-Band Potential $E_f = E_{FB}$ Relative to the Positions of Various Redox Couples in CH_3CN Solution



Results and Discussion

Determination of Flat-Band Potential of n-Type MoS_2.

Cyclic voltammetry has been used to locate the band edges for

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