A Force Field for Conformational Energy Calculations on Ester Group Containing Polymers

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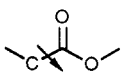
ABSTRACT: A force field suitable for conformational energy calculations on aliphatic hydrocarbon polymers containing ester groups in the main chain or as side groups is presented. It has been parameterized against a data base of model small molecule esters that includes structural, rotational barrier, and vibrational spectroscopy results. The force field also contains bond polarizabilities and moment parameters for representing dipole moments and electrostatic energies by the mutual induction polarization model.

The ester group is an important functionality in polymer chemistry. It occurs in a number of important polymers both as a main-chain constituent and as a side group. In work in our laboratory investigating the relation between side group relaxations and conformational energies in methyl acrylate/ethylene[1] and vinyl acetate/ethylene[2] copolymers and also in investigating the packing in crystalline aliphatic polyesters,[3] it became appropriate to parameterize a conformational energy force field that includes ester groups. In keeping with the spirit of "molecular mechanics", where the force field should be parameterized against molecular structural information on the bond types and groups encountered in projected applications, but not including that on the molecules of application themselves, data on model small or nonpolymeric molecules are best used. Although the available information from a base of appropriate molecules is not large, it appears to be adequate for the purpose.

Two features of the description of ester energetics will be kept especially in mind. One is the representation of the energetics of rotation about the two possible bonds connecting the ester group to its substituents (**1** and **2**). One or the other (methyl acrylates, vinyl acetates, etc.)



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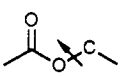

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or both (aliphatic polyesters) of these bonds could represent the incorporation into polymer structures.

The other feature is the representation of polar or electrostatic effects. Inclusion of polarity by means of point dipoles or fixed charges is straightforward. However the question of treating the interactions between polar groups is not. An effective dielectric constant for mediating the interactions has often been invoked. Since the dielectric constant is a macroscopic concept and the amount and kind of intervening matter between a pair of dipoles or charges can vary considerably, from none at all to many atoms, this is not a very satisfying approach. Fortunately this difficulty can be circumvented by a calculation of the microscopic equivalent of the dielectric constant, the internal electric field.[4,5] This requires placement, in addition to the permanent dipoles, of polarizability centers in each bond. The permanent dipole moments induce moments in other bonds, and these can in turn induce further moments. The problem is linear and the electric field at each bond is easily solved for. The molecular dipole moment is then just the sum of permanent and fixed moments, and the electrostatic energy is the energy of interaction of the permanent moments with the electric field of all the other moments, permanent and induced. Parameterizing this model requires determination of bond moments and bond polarizabilities from a data base of molecular moments and polarizabilities. This has been undertaken here for the ester group.

Parameter Development

The parameters were developed as an extension of the force field reported recently for hydrocarbons and ethers.[6] However in the present extension no nondiagonal force constants (stretch–stretch and stretch–bend interactions etc.) were introduced. The nonbonded functions reported in that work were used here also. No discrimination between valence types within a given atom is invoked: doubly bonded oxygen and carbon have the same nonbonded parameters as singly bonded. The parameterization was carried out against a data base of five esters. These are methyl formate, ethyl formate, methyl acetate, ethyl acetate, and methyl propionate.

Valence Force Constants. The ester group itself is planar and fairly stiff with respect to torsional distortion about the $C(sp^2)$–O bond.[7] Thus this bond is not highly crucial to representing ester conformations. There are experimental values of this torsional fundamental in methyl formate,[8–10] and also quantum mechanical calculations of the barrier have been made.[7] More important is the representation of the energetics of rotation about the bonds attaching to the ester group. For the ester–substituent bond, $-O-C(sp^3)-$, the $-O-CH_3$ barriers in both methyl formate[11] and methyl acetate[12] are known. The gauche/trans barrier in ethyl formate[13] and the gauche/trans conformational energy difference in ethyl formate[13] and ethyl acetate[14] have been measured. At the other attaching bond, $-C(sp^3)-C(sp^2)-$, the $CH_3-C(sp^2)$ methyl torsional barrier in methyl acetate is known.[12,15] A value for the gauche/trans energy difference in methyl propionate is available.[16]

In molecular mechanics parameterizations, torsional energetics are the sum of the effects of inherent torsional potentials and the superposed nonbonded functions. In the case of the $-O-C(sp^3)-$ and $-C(sp^3)-C(sp^2)-$ bonds, the barriers to rotation are rather low and it was found for methyl torsions, $CH_3-C(sp^2)$ and CH_3-O, the nonbonded functions alone, without an intrinsic barrier function, gave a good description of the barriers. However this was not the case with respect to the gauche/trans energy differences in ethyl formate and acetate, i.e. the $C(sp^2)-O-C-C$ bond. Thus a combination 3-fold and 2-fold barrier was devised for this bond that gave a rep-

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Table I
Bond Stretching and Bending Parameters[a]

type	k	R^0 or Θ^0
H-CD	5.08	1.09
CD-C	5.1	1.50
CD-O	5.2	1.33
CD-OD	9.5	1.22
C-C-CD	= C-C-C[b]	
H-C-CD	= H-C-C[b]	
H-CD-OD	0.80	2.0700
H-CD-O	0.50	2.0700
C-CD-O	1.7	1.9286
C-CD-OD	1.0	2.1642
OD-CD-O	1.0	2.0944
CD-O-C	0.70	1.91063
C-CD-O···OD*[c]	0.36	0.0
H-CD-O···OD*[c]	0.36	0.0

[a] For stretching, $V = (1/2)k(R - R^0)^2$; for bending, $V = (1/2)k(\theta - \Theta^0)^2$; units are such that energies are 10^{-18} J/molecule, R in Å, and angles in radians. C = sp^3 carbon, CD = sp^2 carbon, O = singly bonded oxygen, OD = doubly bonded oxygen. [b] Taken same as the indicated bend in ref 6 including stretch-stretch, stretch-bend, and tetrahedral carbon bend-bends. [c] Out-of-plane deformation of doubly bonded oxygen from the plane of the C-CD-O or H-CD-O atoms in the ester group.

Table II
Torsional Potential Parameters[a]

type	N-fold	V_0	ϕ_{max}
O-CD-C-H	3	0.0	0.0
OD-CD-C-H	3	0.0001	60.0
OD-CD-C-C	3	0.0060	60.0
OD-CD-C-C	1	0.014	180.0
O-CD-C-C	3, 1	0.0	0.0
OD-CD-O-C	2	0.10	90.0
C-CD-O-C	2	0.0	90.0
H-CD-O-C	2	0.0	90.0
CD-O-C-H	3	0.0001	0.0
CD-O-C-C	3	0.00095	0.0
CD-O-C-C	2	0.00281	0.0
CD-C-C-C	= C-C-C-C[b]		
CD-C-C-H	= C-C-C-H[b]		

[a] The torsional potential is $V = (1/2)V_0[1 + \cos N(\phi - \phi_{max})]$. Units of V_0 are 10^{-18} J/molecule (multiply by 602.5 to convert o kJ/mol); ϕ_{max}, the angle where the potential is maximum, is listed in degrees. A torsional potential is used about all of the bonds of the type indicated attached to the center two atoms. O-CD-C-H and OD-CD-C-H, for example, each have three terms in an acetate group. When there is more than one bond type about a torsion, for example, OD-CD-O-C and C-CD-O-C, only one was selected to carry the torsional potential. Thus the barrier constants for the redundant terms were set to zero. [b] Taken same as indicated torsion in ref 6. In the case of the methyl torsions, the 0.0001 values do not contribute significantly to the barrier and only serve to formally establish the possibility of an intrinsic barrier. The latter were found to be essentially zero by the fitting.

Table III
Calculated and Experimental Conformational Energies and Barriers

compound	calc	exp	ref
methyl formate			
barrier (ester torsion), kJ/mol	58		
freq (ester torsion), cm^{-1}	313	325, 337, 341	8–10
barrier (methyl torsion), kJ/mol	4.6	4.9	11
methyl acetate			
barrier (ester torsion), kJ/mol	61		
barrier (acetate methyl torsion), kJ/mol	1.36	1.19	12, 15
barrier (methoxy methyl torsion), kJ/mol	4.5	5.1	12
$\Delta H_f°$, kcal/mol	−100.5	−97.9	23
methyl propionate			
gauche/trans energy Δ, kJ/mol	4.2	4.6 ± 1.2	16
$\Delta H_f°$, kcal/mol	−105.2	−105.3	23
ethyl formate			
gauche/trans energy Δ, kJ/mol	0.9	0.78 ± 0.25	13
trans/gauche barrier, kJ/mol	3.9	4.6 ± 1.0	13
gauche torsional angle, deg	83.6	85	13
ethyl acetate			
gauche/trans energy Δ, kJ/mol	0.8	1.3	14
trans/gauche hot bands, cm^{-1}	932/917	939/917	14
$\Delta H_f°$, kcal/mol	−105.2	−105.8, −106.6	23

resentation of the gauche/trans energy differences in ethyl formate and acetate: the torsional angle in gauche ethyl formate and the gauche/trans barrier in ethyl formate. The choice of the 2-fold barrier was occasioned by the gauche torsional angle being at ~85°,[13] and this barrier type is effective in accomplishing this. In the case of methyl propionate, the C-C-C(sp^2)-O bond, a multiple barrier function was necessary as well to represent the gauche/trans energy difference. Since no knowledge of the gauche torsional angle is available 3- and 1-fold functions were invoked. The latter type tends to leave the gauche torsional angle nearer to the 60° value than does a 2-fold term.

The stretching and bending constants in addition to those previously developed were parameterized against experimental vibrational assignments for methyl acetate[17] and methyl formate.[10,17] Since the number of frequencies available in these two compounds is not large, it was decided not to undertake the refinement of a set of force constants that included new nondiagonal valence interaction constants. We elected instead to make adjustments to the diagonal force constants of Hollenstein and Guenthard.[17] One difference was to explicitly introduce bending constants for both of the angles at the carbonyl oxygen double bond but to set them to the same value.

The force constants for stretching and bending are reported in Table I, and the torsional potential parameters are listed in Table II. The fits achieved for the key conformational quantities are shown in Table III. Table IV compares the calculated and experimental vibrational frequencies for methyl formate and methyl acetate. Since the omission of nondiagonal force constants can often lead to errors of 100–200 cm^{-1} in calculated frequencies, the fact that there are only two such instances in Table IV is pleasing. The calculated geometry of methyl acetate is shown in Figure 1. The barriers for rotation about the bond in 1 for methyl propionate and the one in 2 for ethyl formate are shown in Figures 2 and 3, respectively. For each of the points shown in the latter two figures the structures are energy minimized with respect to the other internal coordinates.

Polar Parameters. As indicated above, the mutual induction polarization model was used to represent the polar or electrostatic effects. In accomplishing this, a permanent intrinsic dipole moment is assigned to each polar bond and a polarizibility tensor, diagonal in the local bond coordinates, is assigned to all bonds.[4] The parameters to be determined, then, are, for each bond type, the permanent moment, the polarizability components parallel and perpendicular to the bond, and the location of the moment and polarizability center along the bond. In the present case there are three new bond types in addition to those previously determined.[6] These are the ester group C=O, C(sp^2)—O, and C(sp^3)—O bonds. The parameterization of the polarizability can proceed more or less independently of the permanent moments since the latter do not influence the polarizability. The experimental polarizabilities were calculated from opti-

Table IV
Calculated and Experimental Vibrational Frequencies[a]

methyl formate				methyl acetate			
A'		*A''*		*A'*		*A''*	
calc	exp	calc	exp	calc	exp	calc	exp
1760	1754	1486		1776	1769	1485	1462
1473	1465	1188		1477	1469	1453	1447
1440	1445	1122		1452	1440	1139	1160
1339	1371	313	341	1441	1437	1022	
1195	1207	159	130	1422	1372	601	603
1143	1168			1353	1246	164	
899	925			1148	1194	139	
632	767			1096	1058	74	
320	325			984	976		
				814	840		
				577	636		
				479	438		
				303	295		

[a] Experimental values are the assignment of ref 17.

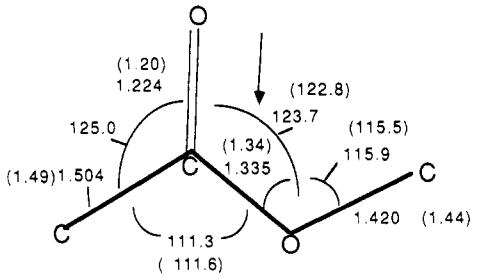

Figure 1. Calculated and experimental (in parentheses, from ref 24) molecular geometry of methyl acetate. The direction of the calculated dipole moment is shown by the arrow.

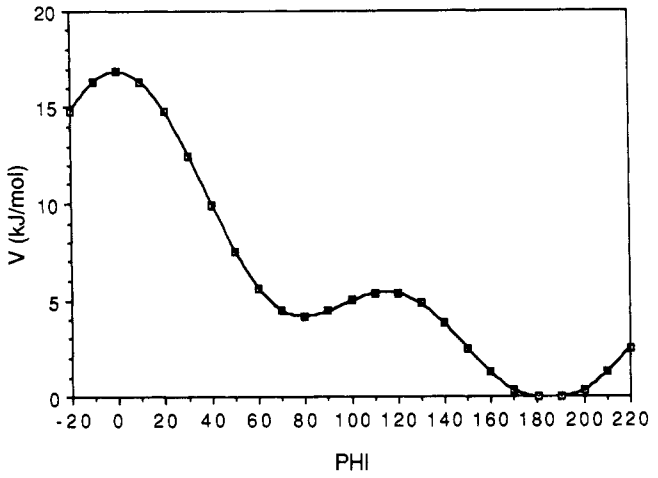

Figure 2. Calculated barrier to rotation about the CH_3–$C(sp^3)$–$C(sp^2)$–O bond in methyl propionate, 180° = trans planar structure of 1 in text.

cal frequency refractive indices and densities.[18] The experimental values of the dipole moments of all the molecules except methyl propionate are gas-phase measurements listed by Nelson et al.[19] The value for the latter is from solution and is given by Le Fevre.[20] The polar parameters determined are listed in Table V. The fits achieved for the ester data base are shown in Table VI. The mutual induction model is invoked after minimization in determining the electrostatic energy. During minimization to determine the molecular geometry, fixed atom charges are invoked.[4] In implementing fixed charges in minimization, charges of ±0.27e placed on the C and O atoms of the C=O bond and ±0.063e at the two C—O bonds in the ester group with the oxygen negative give the ester dipole moment.

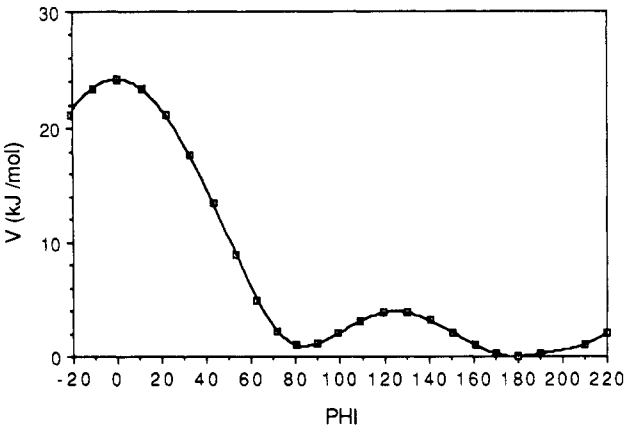

Figure 3. Calculated barrier to rotation about the $C(sp^2)$–O–$C(sp^3)$–CH_3 bond in ethyl formate.

Table V
Polar Bond Parameters for Ester Group[a]

bond	μ^0, D	$\alpha_\parallel$, Å^3	$\alpha_\perp$, Å^3	f
O–CD	0.92	0.26	0.26	0.5
OD–CD	1.79	1.320	0.622	0.2
O–C	0.90	0.295	0.295	0.5

[a] A permanent dipole of moment, μ^0, in the direction from the first atom to the second and a polarizability center ($\alpha_\parallel$, $\alpha_\perp$) are placed at a fractional distance, f, along the bond from the first atom to the second atom. These parameters are to be used with the C–C and C–H parameters of ref 6; the values for the ester C–O bond differ from the ether C–O bond in that reference only by the μ^0 value.

Table VI
Data Fit for Polar Bond Parameters for Esters[a]

compound	μ_{calc}, D	μ_{exp}, D	α_{calc}, Å^3	α_{exp}, Å^3	method, ref
methyl formate	1.71	1.77			MW, 19
ethyl formate	1.79	1.93	6.70	7.06	V, 19
trans	1.86	1.98			MW, 13
gauche	1.70	1.81			MW, 13
methyl acetate	1.83	1.72	6.96	6.94	V, 19
ethyl acetate	1.91	1.78	8.84	8.83	V, 19
methyl propionate	1.72	1.75	8.81	8.79	S, 20

[a] Calculated and experimental dipole moments and polarizabilities. V = dielectric measurement in vapor phase, S = in solution; MW = microwave measurements (on individual conformers for ethyl formate). For ethyl acetate, ethyl formate, and methyl propionate, the calculated conformer values were Boltzmann averaged by using the calculated energy differences.

Heats of Formation. A group value for computing heats of formation was derived for the ester group, when connected to aliphatic carbon atoms, that is based on the formalism previously given[21] and utilizes the calculated enthalpy function. For ethyl acetate and methyl propionate the calculated heats of formation are conformationally averaged according to the procedure previously described.[22] In the notation of ref 21, E^*_I = 383.0 kcal/mol for the ester group and this is to be used with the other group values of that reference. The calculated and experimental[23] heats of formation are listed in Table III.

Discussion

It may be seen in Table III that an adequate job of representing the salient facts concerning the esters is accomplished. However, it is true that the available experimental information is not adequate to give a rigorous test of the generality of the force field. The proposition of a low gauche/trans barrier at the ester substituent bond,

$-O-C(sp^3)-$, and a small but appreciable gauche/trans energy difference is probably correct and rests on the barriers in both methyl and ethyl formate and the gauche/trans energy difference in both ethyl formate and ethyl acetate. The force field does not discriminate between the low but somewhat different experimental values for the gauche/trans energies in ethyl formate and ethyl acetate.

For the other attaching bond at the ester group, $C(sp^3)-C(sp^2)$, the situation is similar to the $-O-C(sp^3)-$ bond but the gauche/trans energy difference is higher. The information upon which the conclusion is based is less and embraces only the methyl rotation barrier in methyl acetate and the gauche/trans energy difference in methyl propionate.

The fit of the vibrational spectra (Table IV) is adequate especially considering that no nondiagonal valence interaction force constants beyond those already in the hydrocarbon field were invoked. As an interesting aside, it may be remarked that the gauche/trans energy difference in ethyl acetate is based experimentally[14] on the temperature dependence of the relative intensities of a pair of infrared bands at 939 and 917 cm^{-1}. The former is attributed to the low-energy, i.e. trans, conformation and the latter to the higher energy one, the gauche. The vibrational analysis here confirms this. A frequency of 932 cm^{-1} is calculated for an A′ species in the trans, and in the gauche the vibration is calculated as 917 cm^{-1}.

There is now a precision analysis of the molecular geometry of methyl acetate comparing electron diffraction and X-ray analyses.[24] Figure 1 compares the average of the two experimental methods with the calculated one, and it appears that the force field representation is satisfactory.

It may be seen in Table VI that the polar parameters result in an adequate fitting of the moments and average polarizabilities. The direction of the calculated moment for methyl acetate is shown in Figure 1 and is nearly parallel to the carbonyl bond. The dipole moments of the esters are to a first approximation characteristics of an ester group moment. Any nuances between the molecules due to inductive effects seem to be relatively minor. However it is interesting to note that in the case of ethyl formate the dipole moment of the individual conformers are available from the microwave measurement.[13] It may be seen that the calculated difference in moments between the conformers agrees rather well with the experimental values. In the polar model used here this arises as a difference in inductive effects in the substituent bonds.

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Registry No. Methyl formate, 107-31-3; methyl acetate, 79-20-9; methyl propionate, 554-12-1; ethyl formate, 109-94-4; ethyl acetate, 141-78-6.