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MOLECULAR MECHANICS CALCULATIONS (MM3) ON ALKYL IODIDES

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The MM3 force field has been extended to cover alkyl iodides. Structures, vibrational spectra and heats of formation have been well fitted to available experimental data. The experimental and *ab initio* conformational relationships are also satisfactorily reproduced

INTRODUCTION

There have been various force fields proposed for the treatment of organic halides.[1-3] Most of the early force fields were not based on adequate hydrocarbon force fields and were used only in connection with a small number of molecules or molecular types. Systematic studies of mono- and polyhalides within the framework of the MM2 force field[2,3] were reported more than 10 years ago. The derived MM2 force field reproduced the known structural and energetic relationships fairly well for fluoro-, chloro- and bromo-substituted alkanes. Over the past decade, new experimental results emerged and reliable *ab initio* results on structures and energies of the smaller alkyl halides became available. These developments now permit a new parameterization of the halides force field so that not only the structural and energetic relationships, but also the vibrational spectra can be satisfactorily fitted at the same time.

Table 1. Parameter set for alkyl iodides[a,b]

Stretching parameters:

Bond	K_S	l_0
1–14	2·15	2·166

Bending parameters:

Angle	K_b	θ_0
1–1–14	0·65	106·0 (type 1)
1–1–14	0·65	107·2 (type 2)
1–1–14	0·65	107·0 (type 3)
5–1–14	0·62	102.8 [types 1 and 2 (—CR_2— and —CRH—)]
5–1–14	0·62	107·8 [type 3 (—CH_2—)]
2–1–14	0·695	109·3

Torsional parameters:

Dihedral angle	V_1	V_2	V_3
1–1–1–14	−1·309	0·440	0·597
5–1–1–14	0·000	0·000	0·333
14–1–2–2	−0·700	−1·400	−1·400
14–1–2–5	0·000	0·160	0·090

Electronegativity parameters:

Bonds	Δl_0
5–1–1–14	−0·005
1–14–1–5	−0·009
1–14–1–2	0·009

Bohlmann effect parameter:

Bond	Parameter
1–14	+0·001

[a] All distances are in ångstroms, angles are in degrees, frequencies are in cm^{-1} (wavenumbers) and energies are in kcal mol^{-1} (1 kcal = 4·184 kJ), unless stated otherwise. Abbreviations used in all tables: str., stretch; def., deformation; sym, symmetric; asym, antisymmetric.

[b] Atom types: 1, saturated carbon; 2, alkene carbon; 5, hydrogen; 14, iodine.

The MM3 force field has been described for alkanes[4]

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and other compounds,[5] and is more accurate and useful than MM2 and other early force fields. This work is concerned with extending the MM3 force field to cover alkyl iodides. It should be pointed out that in some ways it is more difficult to parameterize the force field for iodides than for the other classes of organic halides. This is because there are fewer experimental data available on iodides and, unlike the other halides, owing to the large number of electrons in iodine, there have been reported only a few *ab initio* calculations on these compounds. Thus one has very limited information available. We have derived an MM3 parameter set for alkyl iodides in this work, and it seems that this set of parameters reproduced the available structural and vibrational data successfully to within the usual limitations of the MM3 force field. The parameters derived are presented in Table 1. Using these parameters, the calculated vibrational frequencies (Tables 2–8), molecular structures (Table 9), conformational energies (Tables 10 and 11), and heats of formation (Table 12) are compared with available experimental data.

RESULTS AND DISCUSSION

Vibrational spectra

The vibrational spectra of a few alkyl iodides have been studied experimentally. Complete assignments of all the normal modes are available in the literature for methyl iodide,[6] ethyl iodide,[7] isopropyl iodide,[8,9] *gauche*-1-propyl iodide,[10,11] *trans*-1-propyl iodide,[10,11] *tert*-butyl iodide[12] and 3-iodopropene.[13] As there have been

Table 2. Vibrational spectra of methyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
E	1	3027	3049	−22	C–H str.
	2	1404	1425	−21	HCH bend
	3	910	891	19	HCI bend
A_1	4	2918	2941	−23	C–H str.
	5	1269	1241	28	HCH bend
	6	525	523	2	C–I str.

[a] See footnote a, Table 1.
[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 22 cm^{-1} and the average deviation is −5 cm^{-1}.
[c] Ref. 6.

Table 3. Vibrational spectra of ethyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
A'	1	2988	2974	14	CH_3 asym str.
	2	2939	2974	−35	CH_2 sym str.
	3	2894	2919	−25	CH_3 sym str.
	4	1454	1450	4	CH_3 asym def. and CH_2 bend
	5	1434	1435	−1	CH_2 bend and CH_3 asym def.
	6	1370	1377	−7	CH_3 sym def. and C–C str.
	7	1253	1203	50	CH_2 wag.
	8	1004	1049	−45	CH_3 rock and CC str.
	9	968	950	18	CC str. and CH_3 rock
	10	513	498	15	C–I str. and CCI bend
	11	248	262	−14	CCI bend and C–I str.
A''	12	3000	3014	−14	CH_2 asym str.
	13	2988	2974	14	CH_3 asym str.
	14	1467	1450	17	CH_3 asym def.
	15	1150	1203	−53	CH_2 twist and CH_3 rock
	16	1004	998	6	CH_2 twist and CH_3 rock
	17	742	743	−1	CH_2 rock and CH_3 rock
	18	237	223	14	CH_3 torsion

[a] See footnote a, Table 1.
[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 25 cm^{-1} and the average deviation is −3 cm^{-1}.
[c] Ref. 7.

Table 4. Vibrational spectra of isopropyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
A'	1	2991	2978	13	Sym CH_3 str.
	2	2989	2961	28	Sym CH_3 str.
	3	2981	2925	56	CH str.
	4	2896	2882	14	Sym CH_3 str.
	5	1475	1468	7	Asym CH_3 bend
	6	1460	1458	2	Asym CH_3 bend
	7	1416	1389	27	Sym CH_3 bend
	8	1261	1210	51	Methine HCC bend
	9	1070	1153	−83	CH_3 rock/CC str./CCC and CCI bend
	10	1031	1020	11	CH_3 rock/methine HCC bend
	11	866	879	−13	CC str./CH_3 rock
	12	508	499	9	CCC and CCI bend/C–I str.
	13	393	398	−5	CCC and CCI bend
	14	257	269	−12	C–I str./CCC and CCI bend
	15	240	192	48	CH_3 torsion
A''	16	2989	2997	−8	Asym CH_3 str.
	17	2987	2934	53	Asym CH_3 str.
	18	2896	2890	6	Asym CH_3 str.
	19	1469	1468	1	Asym CH_3 bend
	20	1459	1459	0	Asym CH_3 bend
	21	1438	1389	49	Sym CH_3 bend
	22	1316	1321	−5	Methine HCC bend/CC str.
	23	1068	1113	−45	CC str./methine HCC bend
	24	967	937	30	CH_3 rock/CC str.
	25	943	925	18	CH_3 rock/methine HCC bend
	26	254	269	−15	CCC and CCI bend
	27	237	217	20	CH_3 torsion

[a] See footnote a, Table 1.

[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 32 cm^{-1} and the average deviation is 10 cm^{-1}.

[c] Ref. 9.

almost no complete experimental structural data reported, except for methyl iodide, ethyl iodide and 3-iodopropene, the available vibrational frequencies are important criteria in our parameterization. The parameterization was started with the MM3 hydrocarbon parameters, and the iodide parameters of the MM2 force field were added as an initial approximation. Needed parameters absent from the MM2 force field were first estimated with the parameter-estimation routine[14] in MM3. The various parameters were then adjusted to fit the available data insofar as possible. Tables 2–8 compare the calculated frequencies with the experimental assignments.

The root-mean-square (RMS) error between the calculated and experimental frequencies of methyl iodide (Table 2) is 22 cm^{-1}. When the electronegativity effect was not taken into account, the RMS error was 45 cm^{-1}. This difference is mainly due to the fact that the C–H stretching frequencies were systematically underestimated when the electronegativity and Bohlmann effects[15] were not considered. The modes that involve the C—I moiety are all very well reproduced. With the present parameters, the average error is −5 cm^{-1}, which indicates little systematic error.

For ethyl iodide, the RMS error between the calculated and experimental frequencies is 25 cm^{-1}, compared with the value of 35 cm^{-1} obtained without taking into account the electronegativity and Bohlmann effects.[15] The average error is now −3 cm^{-1}.

The RMS errors between the calculated and available experimental frequencies of isopropyl iodide, *gauche*-1-propyl iodide, *trans*-1-propyl iodide and *tert*-butyl iodide are slightly larger than those of methyl and ethyl iodides. However, they are comparable to the results of most other classes of saturated molecules studied with MM3 (*ca* 35 cm^{-1}). Additionally, the experimental assignments for the larger molecules tend to be less reliable. Thus the spectra of methyl and ethyl iodides were given higher weight in our assignment of the force field parameters.

The complete assignment of the normal modes of *gauche*-3-iodopropene was published recently.[13] The RMS error between the frequencies calculated by the MM3 force field and the experimental assignments is

Table 5. Vibrational spectra of *gauche*-1-propyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
A	1	2997	3000	−3	Asym CH str. (C–CH_2–I)
	2	2978	2967	11	Sym CH str. (C–CH_2–I)
	3	2968	2967	1	Asym C–H str. (CH_3)
	4	2941	2967	−26	Asym C–H str. (CH_3)
	5	2937	2938	−1	Asym CH str. (C–CH_2–C)
	6	2893	2876	17	Sym CH str. (CH_3)
	7	2877	2846	31	Sym CH str. (C–CH_2–C)
	8	1480	1458	22	Asym CH_3 bend/CH_2 bend
	9	1468	1458	10	Asym CH_3 bend
	10	1462	1435	27	Asym CH_3 bend/CH_2 bend
	11	1447	1427	20	CH_2 bend (C–CH_2–I)
	12	1403	1382	21	CH_3 sym bend/CC str.
	13	1375	1340	35	CH_2 wag. (C–CH_2–C)/CC str.
	14	1282	1276	6	CH_2 twist (C–CH_2–C)
	15	1229	1194	35	CH_2 twist (C–CH_2–I)
	16	1170	1148	22	CH_2 wag (C–CH_2–I)
	17	1051	1076	−25	CC str./C–I str.
	18	1022	1020	2	CH_3 rock/CH_2 wag./CH_2 twist
	19	993	1012	−19	CH_2 twist/CH_2 wag.
	20	875	880	−5	CC str./CH_3 rock
	21	837	816	21	CH_2 rock/CH_3 rock
	22	736	764	−28	CH_2 rock/CH_3 rock
	23	513	505	8	C–I str./CCC and CCI bend
	24	385	355	30	CCC bend/C–I str.
	25	252	201	51	CCI bend/C–I str./CCC bend
	26	188	—	—	Torsion
	27	111	—	—	Torsion

[a] See footnote a, Table 1.

[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 23 cm^{-1} and the average deviation is 11 cm^{-1}.

[c] Ref. 11.

32 cm^{-1}. To calculate the vibrational frequencies of this molecule, the MM3 parameters derived from fitting the available data for the alkyl iodides were not altered. Additions were parameters for the bond angle 2–1–14 and for the torsion angles 14–1–2–2 and 14–1–2–5 (the numbers are the atom types used in MM3; see footnote b, Table 1). The latter were determined by fitting the *ab initio* torsional curves (see later). Also, an electronegativity parameter for the effect of a type 2 carbon (sp^2) on a C—I bond was needed to fit the observed moments of inertia for this molecule. We believe the present parameters are satisfactory.

For isopropyl iodide, it should be noted that the differences between the MM3 and experimental values of the two methyl torsional frequencies are 48 cm^{-1} (A' mode) and 20 cm^{-1} (A'' mode). These deviations are somewhat high because we need to compromise to fit the barrier of internal rotation of ethyl iodide. The latter is calculated too low by about 0·4 kcal mol^{-1} (MM3 3·10 kcal mol^{-1}, experiment 3·22–3·66 kcal mol^{-1}). The *ab initio* result is 3·6 kcal mol^{-1} (see Table 10).

In order to have a better fit to the C–H frequencies, we introduced not only an electronegativity effect but also a Bohlmann effect to the calculations, as was earlier found desirable when lone pairs were present.[15] The electronegativity effect changes the bond lengths of both the α- and β-C—H bonds (the latter 40% as much as the former). The Bohlmann effect changes only the bond length of the α-H. These bond length changes lead in turn to frequency changes.[15] The electronegativity effect and Bohlmann effect parameters were fixed at −0·005 and 0·001, respectively. These values minimize the differences between the experimental and MM3 C–H stretching frequencies. The negative value of the former indicates that the iodine is moderately electronegative, and the small value of the latter indicates very little delocalization of the lone pairs on iodine into the C–H antibonding orbitals, as expected because of the poor overlap.

Structures and moments of inertia

Complete experimental molecular structural parameters were reported for methyl iodide,[16] ethyl iodide[17] and *gauche*-3-iodopropene.[18,19] Microwave studies of

Table 6. Vibrational spectra of *trans*-1-propyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
A′	1	2968	2967	1	C–H sym str. (C–CH_2–I)
	2	2939	2967	−28	C–H asym str. (CH_3)
	3	2893	2876	17	C–H sym str. (CH_3)
	4	2874	2846	28	C–H sym str. (C–CH_2–C)
	5	1477	1458	19	CH_3 asym bend/CH_2 bend
	6	1454	1435	19	CH_2 bend(CCC)/CH_3 bend
	7	1438	1435	3	CH_2 bend (CCI)
	8	1389	1380	9	CH_3 sym bend/CC str.
	9	1362	1325	37	CH_2 wag. (CCC)/CC str.
	10	1239	1185	54	CH_2 wag. (CCI)
	11	1052	1090	−38	CC str./CH_3 and CH_2 rock
	12	989	1020	−31	CC str./CH_2 wag/CH_3 rock
	13	891	896	−5	CC str./CH_3 rock
	14	602	594	8	C–I str./CCC and CCI bend
	15	278	287	−9	CCC bend/CH_2 bend (CCC)
	16	196	201	−5	CCI bend/C–I str.
A″	17	3000	3000	0	C–H asym str. (C–CH_2–I)
	18	2970	2967	3	C–H asym str. (CH_3)
	19	2943	2938	5	C–H asym str. (C–CH_2–C)
	20	1456	1458	−2	CH_3 asym bend
	21	1234	1278	−44	CH_2 twist
	22	1161	1185	−24	CH_2 twist/CH_2 and CH_3 rock
	23	1023	1012	10	CH_2 twist/CH_2 rock
	24	851	819	32	CH_3 rock/CH_2 rock
	25	734	728	6	CH_2 rock
	26	229	—	—	Torsion
	27	109	—	—	Torsion

[a] See footnote a, Table 1.

[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 24 cm^{-1} and the average deviation is 3 cm^{-1}.

[c] Ref. 11.

several other molecules including isopropyl iodide,[20] *gauche*-1-propyl iodide,[21,22] *trans*-1-propyl iodide[21,22] and *tert*-butyl iodide[23] were also reported, but because of the large number of independent geometrical parameters in these molecules, complete structural determinations were not carried out. Some of the structural parameters of the C—I moiety were derived from the microwave spectra by assuming values for various geometrical parameters. So derived structural parameters are, of course, less reliable. The structural parameters calculated by the MM3 force field are compared with the available 'experimental' results and *ab initio* results in Table 9, including the moments of inertia. *Ab initio* calculations were performed using the TX90 program.[24] The energy minima with respect to nuclear coordinates were calculated by the simultaneous relaxation of all the geometric parameters using the gradient technique[25] with the geometry DIIS algorithm.[26] The basis set used was the 3–21G basis set for carbon and hydrogen atoms, and a Gaussian basis set consisting of 15 s-type, 11 p-type and 6 d-type functions for the iodine atom. This basis set was designed specifically for fourth-row main group elements.[27] It should be pointed out that owing to the large number of electrons in iodine, *ab initio* calculation at this level should not be considered as reliable as for hydrocarbon compounds. However, comparing the available experimental and *ab initio* structural parameters, it seems that structural features are reproduced adequately at this level of theory.

As is shown in Table 9, the structures of methyl iodide and ethyl iodide are well reproduced by the MM3 force field. The moments of inertia are also in good agreement with the experimental data. The largest deviation between the calculated and experimental moments of inertia was found for *gauche*-1-propyl iodide. The reason for these larger deviations is that we do not include the torsion–bend interaction in MM3, and it is expected to have some effect here. We believe that this set of CCCI (type 1–1–1–14) torsional parameters is reasonable, because it also fits the experimental axial–equatorial free energy difference for cyclohexyl iodide (see Table 11).

Conformational energies

Molecular conformational energies calculated by MM2

Table 7. Vibrational spectra of *tert*-butyl iodide[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
E	1	2991	2970	21	CH_3 asym str.
	2	2989	2970	19	CH_3 asym str.
	3	2897	2890	7	CH_3 sym str.
	4	1480	1456	24	CH_3 asym def.
	5	1461	1456	5	CH_3 asym def.
	6	1431	1370	61	CH_3 sym def.
	7	1192	1230	−38	C–C str.
	8	977	1029	−52	CH_3 wag.
	9	921	928	−7	CH_3 wag.
	10	378	386	−8	Skeletal def.
	11	272	259	13	CH_3 torsion
	12	244	227	17	Skeletal def.
A_1	13	2990	2970	20	CH_3 asym str.
	14	2897	2890	7	CH_3 sym str.
	15	1473	1456	17	CH_3 asym def.
	16	1420	1370	50	CH_3 sym def.
	17	1130	1139	−9	C–C str.
	18	806	804	2	CH_3 wag.
	19	514	490	24	C–I str.
	20	245	259	−14	Skeletal def.
A_2	21	2988	—	—	C–H str.
	22	1470	—	—	CH_3 sym def.
	23	969	—	—	CH_3 wag.
	24	245	—	—	CH_3 torsion

[a] See footnote a, Table 1.

[b] The root-mean-square deviation (RMS) between the calculated and observed frequencies is 28 cm^{-1} and the average deviation is 7 cm^{-1}.

[c] Ref. 12.

Table 8. Vibrational spectra of 3-iodopropene[a,b]

Symmetry	Mode	MM3	Experimental[c]	Difference	Assignment
A	1	3017	3100	7	$=CH_2$ asym str.
	2	3041	3033	8	$-CH_2$ asym str.
	3	3010	3020	−10	$=CH$ str.
	4	3004	2990	14	$=CH_2$ sym str.
	5	2944	2976	−32	CH_2 sym str.
	6	1675	1643	32	C=C str.
	7	1480	1450	30	CH_2 def.
	8	1375	1404	−29	$=CH_2$ def.
	9	1260	1298	−38	$=CH$ bend
	10	1223	1197	26	CH_2 twist
	11	1147	1157	−10	CH_2 wag.
	12	1100	1059	41	$=CH_2$ wag.
	13	1071	993	78	CH bend
	14	973	938	35	$=CH_2$ rock
	15	952	925	27	C–C str.
	16	755	821	−66	CH_2 rock
	17	665	672	−7	$=CH_2$ twist
	18	512	502	10	C–I str.
	19	382	384	−2	CCC bend
	20	235	232	3	CCI bend
	21	106	95	11	Asym torsion

[a] See footnote a, Table 1.

[b] The mean deviation (RMS) between the calculated and observed frequencies is 32 cm^{-1} and the average deviation is 6 cm^{-1}.

[c] Ref. 13.

Table 9. Molecular structures and moments of inertia of alkyl iodides[a]

Methyl iodide	Experimental (MW)[b]	MM3	*Ab initio*
C—I	2·1358	2·1446	2·1956
C—H	1·084	1·1075	1·0759
HCI	107·47	109·53	107·56
Dipole moment	1·66	1·74	
Moments of inertia			
I_a	3·25859	3·2947 (1·10%)	3·1816
I_b, I_c	67·3743	68·1337 (1·11%)	70·5169
Ethyl iodide	**Experimental (MW)[d]**	**MM3**	***Ab initio***
C—I	2·151	2·1517	2·2068
C—C	1·521	1·5239	1·5296
C—C—I	111·62	112·02	112·13
CH$_2$			
C—H	1·086	1·1118	1·0768
H—C—I	104·83	105·00	105·16
H—C—C	109·85	112·69	112·09
CH$_3$			
CH$_s$	1·093	1·1131	1·0861
CH$_a$	1·093	1·1131	1·0817
CCH$_s$	108·6	111·05	108·96
CCH$_a$	110·8	111·85	111·11
H$_s$CH$_a$	109·32	107·12	108·48
H$_a$CH$_a$	107·93	107·65	108·62
Dipole moment	1·98	1·74	
Moments of inertia[c]			
I_a	17·3571	17·5075 (0·86%)	17·2839
I_b	169·6140	170·3126 (0·41%)	176·7520
I_c	180·7205	181·3025 (0·32%)	187·7954
Isopropyl iodide	**Experimental (MW)[e,f]**	**MM3**	***Ab initio***
C—I	2·144–2·223	2·1704	2·2190
C—C	1·538–1·498	1·5288	1·5309
C—C—C	111·5–116·1	112·27	112·18
C—C—I		109·82	
Dipole moment	1·97	1·70	
Moments of inertia[c]			
I_a	63·0002	63·5886 (0·93%)	62·8672
I_b	231·0732	232·9343 (0·37%)	240·8540
I_c	278·0465	280·0336 (0·71%)	287·6650
***gauche*-1-Propyl iodide**	**Experimental (MW)[f,g]**	**MM3**	***Ab initio***
C—I	2·196	2·1531	2·2100
CCI	114·08	114·06	113·49
CCCI	63·73	65·6	68·74
Dipole moment	1·64	1·74	
Moments of inertia[c]			
I_a	47·6975	47·7899 (0·19%)	47·4125
I_b	283·6531	287·5245 (1·35%)	297·464
I_c	313·0814	316·9256 (1·21%)	326·1450

(Continued)

Table 9 *Continued*

trans-1-Propyl iodide	Experimental (MW)[f,g]	MM3	*Ab initio*
C—I	2·206	2·1524	2·2059
CCI	110·5	112·21	112·47
CCCI	180	180·0	180·0
Dipole moment	1·70	1·74	
Moments of inertia[c]			
I_a	20·4517	20·6377 (0·90%)	20·2709
I_b	387·2015	390·2051 (0·77%)	400·1940
I_c	398·1334	401·0984 (0·74%)	411·1260

3-Iodopropene	Experimental (MW)[h]	Experimental (ED)[i]	MM3	*Ab initio*
C(1)—C(2)	1·348	1·348	1·3389	1·3167
C(1)—C(3)	1·493	1·478	1·5010	1·4920
C(1)—H(4)	1·080	1·081	1·1040	1·0740
C(2)—H(5)	1·080	1·081	1·1022	1·0725
C(2)—H(6)	1·080	1·081	1·1018	1·0740
C(3)—H(7)	1·095	1·081	1·1071	1·0771
C(3)—I(8)	2·189	2·186	2·1661	2·2211
C(3)—H(9)	1·095	1·081	1·1071	1·0765
C(2)—C(1)—C(3)	121·6	123·0	123·98	123·62
C(2)—C(1)—H(4)	120·0	120·0	119·11	120·49
C(1)—C(2)—H(5)	120·0	120·0	120·75	121·46
C(1)—C(2)—H(6)	120·0	120·0	121·21	122·05
H(5)—C(2)—H(6)	120·0	120·0	118·04	116·49
C(1)—C(3)—H(7)	107·0	110·6	112·44	112·47
C(1)—C(3)—I(8)	107·6	111·7	111·78	111·65
C(1)—C(3)—H(9)	107·0	110·6	113·43	112·66
H(7)—C(3)—I(8)	112·0	107·2	105·21	103·81
H(7)—C(3)—H(9)	111·0	109·5	108·76	110·27
I(8)—C(3)—H(9)	112·0	107·2	104·61	105·40
C(2)—C(1)—C(3)—I(8)	119·4	111·0	112·6	113·04
Dipole moment	1·60		1·74	
Moments of inertia[c]				
I_a	28·6576		28·9920 (1·15%)	28·5285
I_b	318·4480		322·2456 (1·18%)	328·3820
I_c	328·8074		332·3295 (1·18%)	338·6180

tert-Butyl iodide	Experimental (MW)[f,j]	MM3	*Ab initio*
C—I	2·190(5)	2·1918 (0·0018)	2·2297
Dipole moment	1·89	1·74	
Moments of inertia			
I_a[c]	—	112·6432	111·1859
I_b, I_c	323·8351	326·9680 (0·97%)	334·7089

[a] See footnote a, Table 1.
[b] Ref. 16.
[c] Numbers in parentheses are differences between the MM3 and experimental results, expressed as a percentage. Since the MM3 values have r_g bond lengths and the experimental values are r_α, the former moments of inertia should be larger than the latter by about 0·5–1·0%.
[d] Ref. 17.
[e] Ref. 20.
[f] Structural parameters not listed in the table were fixed in the experimental work.
[g] Ref. 21.
[h] Ref. 18.
[i] Ref. 19.
[j] Ref. 23.

and MM3 are closely related to the torsional parameters. For monoiodoalkanes, there are only two kinds of torsional angles associated with the iodine (atom type 14): 1–1–1–14 and 5–1–1–14. In order to carry out calculations on *gauche*-3-iodopropene, torsional parameters for the 14–1–2–2 and 14–1–2–5 were also required. All of these torsional parameters were determined by fitting the MM3 calculations to *ab initio* torsional energy curves. The latter were calculated by fixing the torsional angles at 15° increments, while optimizing geometries with respect to the rest of the degrees of freedom. These calculations were carried out at the SCF level using the same basis set as for geometry optimizations. Although the basis set and *ab initio* level

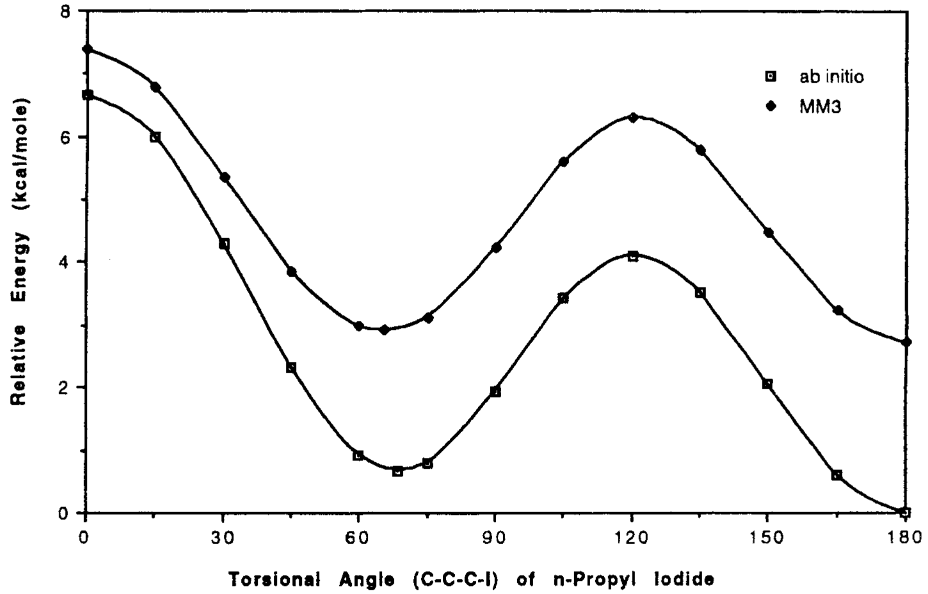

Figure 1. Relative energies as a function of torsional angle (C—C—C—I) of 1-propyl iodide

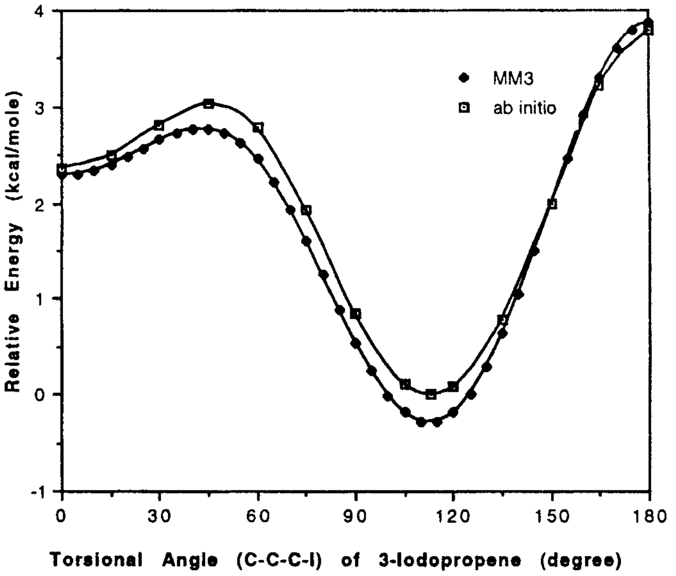

Figure 2. Relative energies as a function of torsional angle (C—C—C—I) of 3-iodopropene

are perhaps not really adequate for a good description of alkyl iodides, owing to error cancellations, the calculated torsional energy curve should be reasonably reliable. Comparisons between the *ab initio* torsional energy curves and those obtained from the MM3 calculations are given in Figures 1 and 2. As can be seen, the MM3 force field satisfactorily reproduces the *ab initio* conformational energy relationships for these molecules, indicating that the MM3 torsional parameters are adequate.

There have been some experimental studies on the barrier to internal rotation in ethyl iodide. The result from our MM3 calculations is 3·10 kcal mol^{-1}, which is in good agreement with the *ab initio* value and the experimental results derived from Raman studies (Table 10).

We also calculated the energy difference between the axial and equatorial conformers of cyclohexyl iodide (Table 11). The experimental axial–equatorial free energy differences range from 0·43 to 0·47 kcal mol^{-1} (in solution). Our calculated result is 0.48 kcal mol^{-1}, in agreement with the experimental results.

Heats of formation

The heats of formation of alkyl iodides were calculated using the usual bond energy scheme.[32] The parameters to be fitted were the 1–14 bond energy and structural parameters for methyl iodide and secondary and tertiary iodides. The structural parameter for primary iodide is redundant and therefore was set equal to zero. Hence there are four parameters to be fitted. The gas-phase heats of formation for six alkyl monoiodides were available. The input and output data of the least-squares fitting of the heat parameters are given in Table 12. As there are few experimental data available, they are fitted very well, but the small RMS value is fortuitous.

Table 10. Barriers to internal rotation in ethyl iodide

	Experimental[a]	MM3	*Ab initio*
Energy (kcal mol^{-1})	3·22–3·66	3·10	3·60

[a] Ref. 28.

Table 12. Heats of formation for alkyl iodides[a,b]

Compound	$H_f(0)$ Calc.	Exptl	Difference (Calc. – Exptl)
Methyl iodide	3·29	3·29	0·00
Ethyl iodide	−2·06	−2·00	−0·06
Isopropyl iodide	−9·45	−10·00	0·55
n-Propyl iodide	−7·24	−7·30	0·06
tert-Butyl iodide	−17·60	−17·60	0·00
Cyclohexyl iodide	−12·76	−12·20	−0·56

C—I (1–14) = 13·290 MET. = 1·180
SEC. = −2·825 TER. = −7·010

[a] The standard deviation is 0·32 based on six equations.

[b] The parameters used in fitting the heats of formation are as follows (see Ref. 32 for details). The sum of heats is −13·77 kcal mol^{-1} for methyl iodide, −19·46 kcal mol^{-1} for ethyl iodide, −25·15 kcal mol^{-1} for isopropyl iodide, −26·19 kcal mol^{-1} for 1-propyl iodide, 30·83 kcal mol^{-1} for *tert*-butyl iodide and −35·81 kcal mol^{-1} for cyclohexyl iodide. The steric energy is 0·19 kcal mol^{-1} for methyl iodide; 1·71 kcal mol^{-1} for ethyl iodide, 2·84 kcal mol^{-1} for isopropyl iodide, 2·73 kcal mol^{-1} for 1-propyl iodide, 4·55 kcal mol^{-1} for *tert*-butyl iodide and 8·79 kcal mol^{-1} for cyclohexyl iodide. The POP and TORS contributions are zero for methyl iodide, ethyl iodide, isopropyl iodide and *tert*-butyl iodide, 0·11 and 0·42 for 1-propyl iodide and 0·14 and 1·26 for cyclohexyl iodide.

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Table 11. Axial–equatorial free energy differences for cyclohexyl iodide

	Experimental[a]	Experimental[b]	Experimental[c]	Calculated
Energy (kcal mol^{-1})	0·43	0·47	0·46	0·48

[a] Best values, 1967; see Ref. 29.

[b] PMR in CS2 experiment; see Ref. 30.

[c] Carbon-13 NMR data; see Ref. 31.

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