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Conformational Analysis. 130. MM2. A Hydrocarbon Force Field Utilizing V_1 and V_2 Torsional Terms[1,2]

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Abstract: An improved force field for molecular mechanics calculations of the structures and energies of hydrocarbons is presented. The problem of simultaneously obtaining a sufficiently large gauche butane interaction energy while keeping the hydrogens small enough for good structural predictions was solved with the aid of onefold and twofold rotational barriers. The structural results are competitive with the best of currently available force fields, while the energy calculations are superior to any previously reported. For a list of 42 selected diverse types of hydrocarbons, the standard deviation between the calculated and experimental heats of formation is 0.42 kcal/mol, compared with an average reported experimental error for the same group of compounds of 0.40 kcal/mol.

It has been now amply demonstrated that force field calculations offer the method of choice for the determination of the structures and energies of molecules under many circumstances.[3-6] While many previously published force fields are very good, they do contain errors which are sufficiently large as to be worrisome to those wishing to utilize them to the fullest possible extent. While the organic chemist is primarily interested in compounds which contain functional groups, since the fundamental structure of organic molecules in general is hydrocarbon in character, a high degree of accuracy in the hydrocarbon part of the force field is crucial. "First generation" force fields showed that one could indeed calculate accurate structures and energies, although the fit to experiment was in some cases less good than one would desire. There has been some difficulty in ascertaining exactly where the force fields were in error, and in which cases the experimental data were less accurate than the probable errors indicated. This question is still not fully answerable but, clearly, more and better data have become available in the last several years. The best we can do is to utilize the existing data, and point out where we feel that there may be errors.

We will discuss herein three of the earlier force fields. These are our earlier force field MM1 (1973)[3] and the most recent force fields by Schleyer (EAS)[5b] and Bartell (MUB-2).[6]

For all of their usefulness and accuracy, these force fields contained various flaws which showed up in different ways. In an effort to minimize the discrepancy between calculations and experiment, the van der Waals characteristics of atoms were important quantities to be evaluated. In Figure 1 is shown a graph taken mainly from a recent paper by Bartell[6] in which the force exerted by a pair of atoms as a function of distance is plotted for several different force fields including MUB-2, EAS, and MM1. For present purposes we will define a "hard" atom as one for which the plot of the force vs. distance for the repulsive part of the curve shows a steep slope (as the dashed C/C line in the figure), and a "soft" atom as one where this slope is more gentle (as the solid line). We will also define a "bigger" atom as one where the line is slid farther to the right, and a "smaller" atom as one for which it is slid to the left. With this terminology, it is seen from the graph that in MM1 we used a hydrogen atom which was both rather hard and large compared to that used by Bartell (and other workers), while we used a carbon atom which was small. The "hardness" of our curves was determined by the Hill equation, which is known to fit well for interactions between rare gases.[7] There is no assurance that such curves are ideal for carbon and hydrogen atoms which are covalently bound. However, they seemed like a reasonable choice in the absence of definite information. Bartell, mainly on the basis of theory, chose a much softer hydrogen.[8] Most other workers have been inclined to follow Bartell's lead. Bartell's more recent choice (MUB-2) is based on theoretical calculations by Kochanski[9] on the H_2 molecule. His new hydrogen is larger but softer than the old one. In our early work[10] we noticed that we could not fit adequately to the axial-equatorial methylcyclohexane energy difference using Bartell's hydrogen, and varying the other parameters that it seemed one might reasonably vary. We therefore continued to use the hard Hill-type hydrogens. Bartell was less anxious to fit this energy difference, and felt he could do a better overall job with structure using soft hydrogens. In each case, the C/H interaction was taken to be the mean of the H/H and C/C interactions.

White has also pointed out in a recent paper that our hydrogens are too hard to explain certain data.[11] We too regard the cyclodecane case which he discusses as a key case, because of the data now available, and it will be discussed below. We

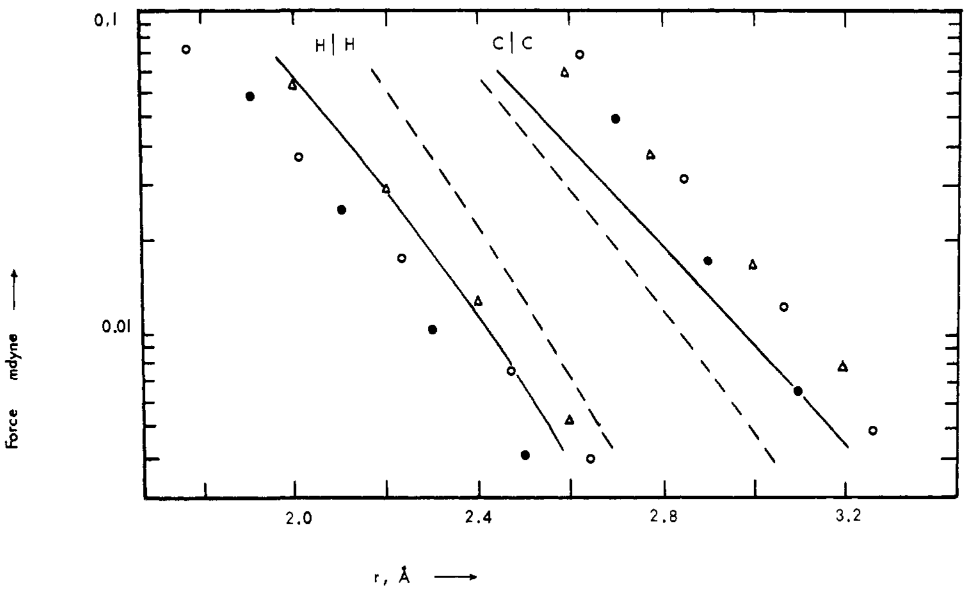

Figure 1. Calculated van der Waals forces for H/H and C/C interactions. The solid lines are current (MM2) values, the dashed lines are the 1973 (MM1) values. The triangles, open, and filled circles are respectively from the EAS,[5b] MUB-2,[6] and Ermer-Lifson[39] force fields.

have been aware of the problem for some years, but until recently, however, no solution to the problem acceptable to us was evident.

Progress stopped momentarily at this point, because utilizing the parameters then regarded as available, it did not appear possible to fit simultaneously to the structural data as well as one would like, and also fit to the methylcyclohexane energy difference. Schleyer resolved this problem, at least temporarily, by introducing a new independent variable parameter, namely, the C/H van der Waals interaction.[12] Instead of taking this to be the mean of the H/H and C/C interactions, it was varied independently. Since the energy of an axial methyl on cyclohexane depends not only on the H/H interaction, but in part on the difference between the H/H and the C/H interactions, by making the latter sufficiently small, one can achieve the desired result without making the former particularly large. Schleyer's force field accomplished exactly this.[12] It gave fairly good results, comparable in general with our 1973 field, the biggest objection to it being an intuitive one and not anything that is obviously in error. Subsequently, both Bartell[13] and we[14] independently realized that there are available other key parameters in current force fields which had not previously been utilized. These are the V_1 and V_2 terms in the torsional potentials. While such terms cancel out exactly in the torsion of a symmetrical molecule such as ethane, they do not necessarily cancel out in a less symmetrical molecule such as butane. Suitable adjustment of these terms will permit one to choose a soft or small hydrogen and a resulting force field which will give good molecular geometries, the correct methylcyclohexane energy difference, and at the same time keep the C/H interaction near the mean where intuition indicates it should be.

For the last few years we have been trying to locate the defects in our 1973 force field, and experimenting with other possible force fields which might be used to correct those defects. With the aid of the V_1 and V_2 terms discussed above, it is possible to make a significant improvement relative to the 1973 force field. By adjusting other parameters, but without introducing those new torsional terms, we found that we could make some improvements, but they were not very substantial. However, we feel that the new torsional terms can correct in a net sense most of the error present in our 1973 force field, and accordingly are presenting here our new force field (1977) for hydrocarbons, which we will call MM2. We want to point out that not only does this force field do a better job for hydrocarbons, but of equal importance, it will also do a better job for many kinds of functionally substituted molecules. While it will take us quite some time to fully explore the impact of this new force field on functionalized molecules, it is clear that some of the previous difficulties (for example, in halides[15] and ethers[16]) which could be alleviated by having hydrogens that were softer will now automatically be improved.

In Figure 1 are also shown the curves for carbon and hydrogen which we have arrived at in the present work. Looking at hydrogen first, it can be seen that our hydrogen is both smaller and softer now than in 1973. It is in the general range of softness now advocated by most other workers. While it is possible to fit the methylcyclohexane energy difference with the aid of the additional torsional terms for a wide range of hydrogen softness, there are also other problems that must be considered.

One of the things we wanted to continue to fit approximately was the crystal spacing and the heat of sublimation of the *n*-hexane crystal.[1,10,17] These depend upon a balance between long-range and short-range van der Waals interactions, but they put some definite limits on the amount of variation permissible in the van der Waals functions. The current force field calculates an A spacing for the hexane crystal of 4.18 Å (from a 2 × 2 × 2 block of molecules) (exptl 4.18 Å) and a heat of sublimation of 11.0 kcal/mol (from a 7 × 7 × 7 block) (exptl 12.15 kcal/mol). The experimental values are for low temperatures and not exactly comparable with the calculated (room temperature) values, so that we judge the agreement to be adequate.

Our 1973 force field did not fit the structure of diamond at all well. We did not regard this as a *major* problem, as diamond is a somewhat special case. On the other hand, it is also a limit toward which we want organic molecules to tend as their C/H ratio becomes high. We therefore adjusted upwards our carbon size so as to fit better the structure of diamond (see latter).

It was found that we could not use the mean of the carbon and hydrogen values for the C/H interaction, because the relatively great C/H interactions caused more branched molecules to stretch out their bond lengths too much, and the spread in bond lengths along the series ethane, propane, isobutane, and neopentane became too large. We accordingly reduced the C/H interaction energy somewhat below the mean value, but not nearly as much as Schleyer found necessary when he did not incorporate the V_1 and V_2 terms (see Figure 1).

When all of the above were done, it was possible to fit simultaneously reasonably well the hexane crystal data, the bond lengths of the series ethane–neopentane, as well as the energy difference between the conformers of methylcyclohexane and the bond length of diamond. Thus all of these "boundary conditions" could be adequately met.

We then turned to the compounds listed in Table I. We want to fit as well as possible the heats of formation of these compounds, in addition to the structural information outlined above. Finally, we want to examine a number of specific points where we noticed discrepancies between calculation and experiment in our 1973 force field. These items will be discussed one by one. The entire force field was then adjusted to simultaneously optimize in so far as possible, according to our judgement, all of these items.

Besides the items already mentioned above, other significant problems with our 1973 force field included the structure of cyclobutane (degree of pucker), the relative energies of cyclopentane and cyclohexane, the structure of cyclodecane, the geometry and energy of the adamantane ring system, the structures of di- and tri-*tert*-butylmethane, the heats of formation of perhydroquinacene and dodecahedrane, and finally, the overall fit of heats of formation of a broad range of organic molecules.

The final force field parameter set is given in Table II. The full details of the method are well known,[3-6] and will not be given here. Differences between MM1 and MM2 (other than numerical values for parameters) include writing the torsional energy term in the form

$$E_\omega = \frac{V_1}{2}(1 + \cos\omega) + \frac{V_2}{2}(1 - \cos 2\omega) + \frac{V_3}{2}(1 + \cos 3\omega)$$

where ω is always measured from 0 to 180°. The bending energy is given by

$$E_\theta = k(\delta\theta)^2 + k'(\delta\theta)^6$$

where the k' term is small, and its effect is insignificant unless $\delta\theta$ exceeds 20°.

Finally, the best value for the torsion-bend interaction coefficient was found to be very small, and it was decided to omit this interaction completely from the calculation.

We might also comment here on the length of C–H bonds. Our 1973 and earlier force fields were calibrated to fit microwave C–H bond lengths, which are generally about 0.01 Å shorter than electron diffraction bond lengths. The current force field is calibrated to fit electron diffraction bond lengths, since the rest of the structure is also being fit to on that basis. It makes little difference in our calculations which are fit to, because the significant interaction of the hydrogen with the rest of the molecule comes from a van der Waals interaction, and this is not centered at the hydrogen nucleus but at an arbitrary point which is moved along the bond a little bit toward the attached carbon.[3,18] As long as the position of the van der Waals interaction is held constant, the nucleus itself can be slid in or out, and the outcome of the calculations is not affected; only the C–H bond length is changed. The result with our current force field is similar to that described previously by Bartell.[6] Namely, the C–H bond lengths increase with increasing methylation at the attached carbon. For the primary hydrogens in methane and ethane, and the secondary and tertiary hydrogens in propane and isobutane, respectively, the bond lengths which are calculated are 1.113, 1.115, 1.117, and 1.119 Å, respectively. These trends are similar to the experimental measurements. The range of the variation is smaller with our force field than with Bartell's, but all of our values are within the range of experimental error of the reported values, except for methane. After this work was completed, it was realized that if we were to shorten the bond length of a C–H bond by 0.003 Å, this discrepancy could be reduced. Since these C–H bond lengths are quite decoupled from the rest of the calculations, this small improvement did not seem worth the effort, and was not made.

Table I. Heats of Formation (Gas, 25 °C)

Calcd	Exptl	Calcd–Exptl	Compd
−17.97	−17.89	−0.08	Methane
−19.39	−20.24	0.85	Ethane
−24.77	−24.82	0.05	Propane
−29.87	−30.15	0.28	Butane
−34.94	−35.00	0.06	Pentane
−40.03	−39.96	−0.07	Hexane
−45.11	−44.89	−0.22	Heptane
−50.20	−49.82	−0.38	Octane
−32.17	−32.15	−0.02	Isobutane
−36.48	−36.92	0.44	Isopentane
−42.48	−42.49	0.01	2,3-Dimethylbutane
−40.55	−40.27	−0.28	Neopentane
−53.66	−53.95	0.29	Hexamethylethane
−48.81	−48.95	0.14	2,2,3,-Trimethylbutane
−59.05	−58.16	−0.89	Di-*tert*-butylmethane
−54.89	−55.77	0.88	3,3-Diethylpentane
6.31	6.38	−0.07	Cyclobutane
−18.27	−18.30	0.03	Cyclopentane
−29.53	−29.43	−0.10	Cyclohexane
−27.88	−28.22	0.34	Cycloheptane
−29.51	−29.73	0.22	Cyclooctane
−36.99	−36.88	−0.11	Cyclodecane
−36.94	−36.99	0.05	Methylcyclohexane
−43.37	−43.26	−0.11	1,1-Dimethylcyclohexane
−43.31	−42.99	−0.32	1(e),2(e)-Dimethylcyclohexane
−41.69	−41.13	−0.56	1(a),2(e)-Dimethylcyclohexane
−12.85	−12.40	−0.45	Norbornane
148.84	148.70	0.14	Cubane
−5.74	−6.39	0.65	Bicyclo[4.2.0]octane
−22.77	−23.75	0.98	Bicyclo[2.2.2]octane
−22.77	−22.30	−0.47	*cis*-Bicyclo[3.3.0]octane
−15.73	−15.90	0.17	*trans*-Bicyclo[3.3.0]octane
−30.46	−30.41	−0.05	*cis*-Hydrindane
−31.63	−31.45	−0.18	*trans*-Hydrindane
−41.03	−40.45	−0.58	*cis*-Decalin
−43.76	−43.54	−0.22	*trans*-Decalin
−58.10	−58.12	0.02	*trans-syn-trans*-Perhydroanthracene
−52.02	−52.73	0.71	*trans-anti-trans*-Perhydroanthracene
−20.73	−20.54	−0.19	Protoadamantane
−31.55	−31.76	0.21	Adamantane
−40.25	−40.57	0.32	1-Methyladamantane
−66.46	−67.15	0.69	Tetramethyladamantane
	Av dev 0.40	Std dev 0.42	

Diamond. As mentioned above, this bond length is something toward which organic molecules tend in one limit, and it is a number we would like to calculate more accurately. MUB-2 gives a good value for the diamond bond length. Our calculated bond length for diamond is now 1.541 Å, compared with the 1973 value of 1.523 Å and the experimental value of 1.544 Å.[19] Making the carbon larger or harder than our MM2 values would improve the diamond in the 1977 field; however, the molecule bicyclo[2.2.2]octane also needs to be considered. The bridgehead carbons here are very close together, and three other pairs of carbons quite close too, which contributes quite a bit of repulsion energy (3.3 kcal/mol) to the heat of formation. The heat of formation of this compound is already calculated too high (by 0.98 kcal/mol, Table I). Any improvement in the bond length of diamond would, in our force field,

Table II. Force-Field Parameters for MM2[d]

Stretching

$E_s = 71.94k_s\,(l - l_0)^2\,(1 - 2.00(l - l_0))$

where lengths are in Å, k_s is in mdyn/Å

Bond	k_{s-}	l_0
C–C	4.4	1.523
C–H	4.6	1.113

Bending

$E_\theta = 0.021914k_\theta(\theta - \theta_0)^2\,(1 + 7.0(10)^{-8}(\theta - \theta_0)^4)$

where θ is in deg, k_θ in mdyn/Å rad^2

Angle	k_θ	θ_0	Type[a]	k_θ (cyclobutane)[b]
C–C–C	0.45	109.5	1	0.34
	0.45	109.5	2	0.29
	0.45	109.5	3	0.34
C–C–H	0.36	109.4	1	
	0.36	109.4	2	
	0.36	110.0	3	
H–C–H	0.32	109.4	1	
	0.32	109.0	2	

Stretch–Bend

$E_{s\theta} = 2.51124k_{s\theta}(\theta - \theta_0)((l - l_0)_a + (l - l_0)_b)$

where bonds a and b are attached with an angle θ

Angle	$k_{s\theta}$
C–C–C	0.12
C–C–H	0.09
H–C–H	0.00

van der Waals

$E_v = \epsilon(2.90\,(10)^5 \exp(-12.50/P) - 2.25P^6)$

where P = sum of van der Waals radii (Σr^*) divided by the distance (r) between interacting centers. For carbon the interacting center is at the nucleus; for hydrogen it is 0.915 of the bond length out from carbon. Note that the van der Waals C|H distance is not (CC + H/H)/2.

Atom pair	Σr^*	ϵ
C|C	3.80	0.044
C|H	3.34	0.046
H|H	3.00	0.047

Torsion

$$E_\omega = \frac{V_1}{2}(1 + \cos\omega) + \frac{V_2}{2}(1 - \cos 2\omega) + \frac{V_3}{2}(1 + \cos 3\omega)$$

where *all* torsional angles ω are measured (0–180°) and included in the calculation

Atoms	V_1	V_2	V_3
C–C–C–C[c]	0.20	0.27	0.093
C–C–C–H	0.00	0.00	0.267
H–C–C–H	0.00	0.00	0.237

[a] Type refers to the substitution pattern at the central atom. For C–C–C, quaternary, tertiary, and secondary carbons are respectively types 1, 2, and 3. For C–C–H, tertiary, secondary, and primary carbons are respectively 1, 2, and 3. For H–C–H, secondary and primary carbons are 1 and 2. [b] For C–C–C angles within a four-membered (cyclobutane) ring, the special values shown are used for the bending force constant. All other bending parameters are the same as for open chains. [c] For C–C–C–C torsional angles within a cyclobutane ring, the V_3 constant is replaced by the value 1.533. All other torsional parameters are the same as for an open chain. Note that, in contrast to our 1973 force field,[3] here torsional interaction energies are calculated between *all* vicinal substituents. This is in accord with the usual practice of spectroscopists, so is done here. The parametrization can apparently be made equally good either way. [d] Energies are in kcal/mol.

Table III. Some Fundamental Data

Compd	Quantity	Exptl	1977	1973
Hexane crystal[a]	A, Å	4.18	(4.18)	(4.18)
	H_s, kcal/mol	12.15	(11.03)	(10.53)
Diamond	Bond length, Å	1.544	1.541	1.523
Ethane	Bond length, Å	1.534	1.532	1.533
Propane	Bond length, Å	1.532	1.534	1.534
Isobutane	Bond length, Å	1.535	1.537	1.537
Neopentane	Bond length, Å	1.539	1.541	1.540
Cyclohexane	Bond length, Å	1.536	1.536	1.534
Me_3CCMe_3	Bond length, Å	1.582	1.572	1.575
t-Bu_3CH	Bond length, Å	1.611	1.603	1.601
Cyclobutane	Bond length, Å	1.549	1.549	1.548
	β, deg	35	28	15
Methylcyclohexane	Ax–eq ΔE	1.75–1.95	1.78	1.58
Cyclodecane	H···H, Å transannular	1.91–1.98	2.00	2.15

[a] The calculated values are for a hypothetical crystal at room temperature, while the experimental values are for low temperatures. The crystal would expand on warming, so the calculated value for A should be larger than experimental, while the heat of sublimation (ΔH_s) should be smaller. If a bigger model crystal had been used in the calculation, the value calculated for A would have been smaller. The calculated ΔH_s was determined from a large enough crystal that no change would be expected here. For further discussion, see ref 17. The heat of sublimation is given by A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses", Wiley, New York, N.Y., 1968, p 475.

be accompanied by a worsening in the energy of bicyclo[2.2.2]-octane. We have accordingly settled on the parameter set given as the best compromise.

***n*-Alkanes.** Next we may turn to the simple alkanes. In Table III are given the calculated bond lengths for ethane, propane, isobutane, neopentane, and cyclohexane, along with the best experimental values. The calculated trend is quite clear. Ethane has a shorter bond length than the others, and increasing branching leads to increasing bond length through the series to neopentane, although the differences between consecutive molecules is small. The experimental data show a good deal more scatter, but when experimental error is allowed for, appear to be consistent with this trend. The value for cyclohexane, 1.536 Å, is also consistent with recent experimental values (although it differs some from earlier values).[3] Thus, we feel that we can claim agreement with experiment as far as the bond lengths in simple hydrocarbons. For the bond angles, the situation is different. The most accurate extensive work on the bond angles of the simple normal alkanes is that of Bartell and Kohl.[20] Their conclusion was that the series from butane through *n*-heptane had bond angles for the trans conformations which averaged 112.65°, and for the overall average (all conformations), the value was 112.75°. Our 1977 force field gives values which deviate substantially from the former. For *n*-pentane, for example, the calculated values for the C–C–C angles are 111.8 and 112.0°. The other *n*-alkanes are similar in this regard. We were concerned for some time that these calculated angles are too small, but we were not able to devise any way to open them out without causing serious damage in other calculated structures or energies. We noted, however, that the calculated bond angle for gauche butane is 113.5°. For anti, the value is 111.8°. At room temperature the anti conformation predominates over the gauche by a factor of 2, so this would give an average bond angle for butane of 112.4°, in agreement with experiment. There is a certain amount of inaccuracy involved in extracting the two different experimental bond angles from the electron diffraction radial distribution function, and the average value is certainly more accurately known experimentally than are the two independent values for the gauche and anti conformations. Since we fit the average value well enough, we are consequently not overly concerned with the lack of accurate fit to the value for the anti conformation itself. The values calculated here for the individual conformations may in fact be more accurate than those deduced earlier from the electron diffraction measurements. One might ask if there are other measurements that can be used to furnish additional information here. Since the discrepancy in question is only 0.8°, crystallographic studies are rarely of the necessary accuracy. Further, the crystal packing forces could lead to distortions of this size, and so no information would appear to be available here in any case. The only other molecule which has been independently studied which can be looked at in this regard is propane.[21] Unfortunately, the experimental error (±1°) is such that it offers us no help in choosing between these alternatives. The microwave value, although accurate, refers to a somewhat different physical quantity, and again offers us no help.

With respect to bond lengths and bond angles in general, our fit to the available experimental data is, on the whole, quite similar to that found by Bartell with MUB-2. We will consequently not discuss this aspect of the results further, except for cases of special interest.

Methylcyclohexane. The energy of an axial methyl in methylcyclohexane was calculated to be 1.58 kcal/mol in 1973. While we regarded this value as somewhat low, it was a compromise with respect to other things, and it was much better than the MUB-1 (or the original MUB-2)[6] value of about 1.0 kcal/mol. The experimental value is 1.75 kcal/mol in solution and 1.95 kcal/mol in the gas phase. While we wish our calculations to be for isolated molecules generally speaking, in practice, much of the comparison that is done with energies is going to be in solution. We have, therefore, decided to err on the low side in this case, so that the numbers would be comparable with solution values (although still close enough for all practical purposes to the gas-phase numbers). Our 1977 force field therefore gives 1.78 kcal/mol for this energy difference.

Cyclobutane. With our 1973 force field the heat of formation of cyclobutane was correctly calculated,[3] but the structure was too flat, with a pucker of 7°. The experimental values for cyclobutanes[22] are generally in the range of 20-35°, with the latter being found for the parent. For cyclobutane itself, the barrier to planarity is about 1.5 kcal/mol[22] while our calculated value was only 0.12 kcal/mol.[3] Some pucker in cyclobutane was achieved earlier with the aid of a torsion-bend interaction term which was given a sign so that the planar cyclobutane ring tended to pucker.

In a Urey-Bradley field, one explicitly includes in the calculation the interaction between two atoms which are bound to a common atom. In a valence force field, this interaction is not included as such. Rather, a stretch-bend interaction term is included to give the same result in terms of geometry.[3] In trying to fit cyclobutane with the same force field used for rings of larger size, the following problem is evident.[23] In cyclopentane or any larger ring there is one carbon-carbon 1,3-interaction for each C-C-C bond angle. In cyclobutane there are only two such interactions, but four bond angles. In a Urey-Bradley treatment, this would hopefully be accounted for automatically, but in the valence force field treatment, something special has to be done if cyclobutane is to be treated along with rings of larger size. In MM1 we used a torsion-bend interaction term to try to get the four-membered ring to pucker. However, using the same functions as are used for larger rings, it was not possible to achieve an adequate amount of pucker and simultaneously keep the energy in the proper range (for any variation which was tried). The amount of torsion-bend interaction which was introduced also had some undesirable effects on our ability to correctly calculate other quantities of interest.

We did not wish to use the Urey-Bradley force field here now, because, except for the four-membered ring, everything already worked well. If we were to introduce 1,3-interaction terms, the whole force field would need to be reparametrized. Accordingly, we went back to an approach used earlier by us,[10] and also by Boyd,[23b] in which a four-membered ring is simply given a different parameter set (in part) from other rings. This is justified on the basis outlined above. The quantities which are assigned different values are the bending force constant for the C-C-C bond angle and the threefold torsional barrier for the C-C-C-C torsional angle. To decide when to use the special parameter set, the test is to observe whether or not the four carbon atoms in question are all present in the same cyclobutane ring. If they are present in the *same* cyclobutane ring, the special parameters are used. If even one of the atoms is outside of the cyclobutane ring (as would be the methyl group in methylcyclobutane, for example), then the ordinary constants are used. This is in accord with the idea that what we are really doing here is finding a way around the explicit inclusion of the 1,3-interactions.

Only three compounds which contain cyclobutane rings were initially included in developing the necessary constants. These were cyclobutane itself, cubane, and bicyclo[1.1.1]pentane. For the first two compounds, both structures and heats of formation are known. In addition, the barrier to inversion of cyclobutane is known. For the third compound, only the structure is known.

Parameters were chosen (Table II) so as to give a reasonable geometry for cyclobutane. The calculated bond length was long (1.549 Å) as is typically observed in cyclobutanes, and the angle of pucker (β) was 28.4°. The barrier to planarity was calculated as 0.9 kcal/mol. The reported values are 35° and 1.5 kcal/mol, respectively. However, these are spectroscopic quantities, which measure from the bottom of the potential curve, not from the thermally populated energy levels.[22] Accordingly, our numbers were chosen so as to better approximate the molecules near the zero-point vibrational level.

For cubane, the bond length calculated was 1.557 Å, slightly longer than reported. The heats of formation for both cubane and cyclobutane were in good agreement with the experimental values. Finally, bicyclo[1.1.1]pentane was, with the above parameters, found to have a too "squashed" geometry. The C-C-C angle at the methylene groups was less than 70° (observed 73.4°). This probably is best interpreted physically in terms of a van der Waals type repulsion between the bridgehead carbons, which would become very severe when the angles contracted this much, and which is not included in the calculations as so far described. In order to better fit the structure of this compound and still avoid explicit inclusion of 1,3-interactions, the bending function was changed from a pure quadratic function to a compound function which contained a very small 6th power term. This term has a negligible effect for bond angles as found in cyclobutane, cubane, and other less strained molecules, but becomes suddenly important when the angle gets to be less than about 80°. This compound, therefore, gives us a "one-point" parametrization, but this should be adequate down to angles of 70° or so, but of dubious validity below that. Unfortunately, the heat of formation of this compound has not been reported, so we are unable to ascertain the accuracy of this approximation as far as energy.

The only other compound containing a cyclobutane ring for which we could find the experimental heat of formation was bicyclo[4.2.0]octane. When the heat of formation was calculated using the parameter set developed above, the value differed from the experimental value by 0.65 kcal/mol. The probable error given for the experimental heat of formation is 0.65 kcal/mol, so the available data suggest that the cyclobutane ring is adequately handled in the present formulation.

Cyclopentane. We calculate that the C_2 and C_s forms have identical energies, as they should, so the molecule is a free pseudorotator. The bond lengths are calculated to be 1.534–1.540 Å, which are a little shorter than those obtained by electron diffraction.[24] The degree of pucker is near, but not quite as great as found experimentally[26] (q = 0.42 and 0.47, respectively). The planar form of cyclopentane is calculated to be 4.7 kcal above the energy minimum (exptl 5.2 kcal).[25,26] As discussed for cyclobutane, since these quantities are spectroscopic, the thermally averaged values should be more like the values here calculated. The heat of formation of cyclopentane is good, as are the heats of formation of cyclopentane rings fused to six-membered rings (hydrindanes), or other five-membered rings (bicyclo[3.3.0]octanes). On the other hand, perhydroquinacene has a calculated heat of formation which is definitely not in agreement with experiment. The calculated heat differs from the experimental by 2.38 kcal/mol,[27] which is considerably closer than we obtained with our 1973 force field (4.96 kcal/mol), but beyond the quoted experimental error limits (±0.86 kcal/mol). It is certainly possible that our calculated value here is in error. However, since the several cyclopentane derivatives mentioned have heats of formation which are well calculated, including the structurally very similar *cis*-bicyclo[3.3.0]octane, we believe that the problem here is an experimental one. This compound is related to the problem of dodecahedrane. The latter molecule was the only one for which there was a really large difference between the calculated heats of formation given by the MM1 and EAS force fields (−0.2 and 46.00 kcal/mol, respectively). The value calculated with the 1977 force field is between these, namely, 22.15 kcal/mol, and the difference here is the outstanding difference in the predictions of the EAS and MM2 force fields. In any case, we wish to point out that perhydroquinacene is not an especially good model for dodecahedrane. In the latter the individual five-membered rings are planar, while in the former they are highly puckered. (The overall structure is C_3. It is easy to misread McKervey[27] and think it is C_{3v}, but it is not.) Perhydroquinacene is closely related structurally to *cis*-bicyclo[3.3.0]octane, but not very closely to dodecahedrane.

Cyclohexane. The energy of the twist and boat forms are respectively 5.5 and 6.5 kcal/mol above that of the chair, which is in good agreement with the experimentally available facts.[3] The barrier to inversion, as one goes from the chair form, through a conformation in which four atoms lie in the same plane, and continues on to the twist form, is calculated to occur when the dihedral angle between the four atoms which go through the plane is about 13° out of the plane, on the side of the twist form. This is primarily a result of the fact that the other torsions are still increasing when the torsional energy of the eclipsed bond passes through a maximum at this planar conformation, and the maximum of total energy is not reached until somewhat later. Our calculated inversion barrier lies 10.5 kcal/mol above the chair form, in good agreement with the best reported experimental value (10.8 kcal/mol).[28]

Cyclodecane. The geometry of cyclodecane calculated in 1973 was reasonable with respect to the carbon skeleton (although the bond angles were on the average about $^1/_2$–1° too large), but there was an excessive amount of deformation due to the hydrogen–hydrogen repulsion in the interior. According to neutron diffraction work[29] (the results of which became available to us too late to help much in developing our 1973 force field) which located the hydrogens rather well, the closest transannular pairs are separated by distances which vary from 1.91 to 1.98 Å in crystallographically nonequivalent locations. MM1 put this separation at 2.15 Å, with most of the extra deformation required for the separation coming into the H–C–H bond angle (calcd 100.3°, exptl 105.7°). Because different ways of defining and measuring bond lengths (and angles) lead to somewhat different numbers when one considers molecules in which the vibrations are anharmonic, and hydrogen positions are especially difficult to define, we did not worry too much about an *exact* fit of this value. However, the discrepancy does seem to be excessive. With the force field described herein, the carbon–carbon–carbon angles tighten down somewhat, and the H–C–H angle is opened to 103.1°. The hydrogens are now calculated to be 2.00 Å apart, which we regard as close enough to experiment to be acceptable.

A second problem that also has been long worrisome concerns the energetically favored structure for cyclodecane. Several cyclodecane derivatives have been studied crystallographically, and they all have the same conformation (except for special cases which would have to have methyl groups or other large groups in the interior of the ring).[30] This was not the conformation of minimum energy according to our 1973 field. Rather, another conformation was about 1 kcal lower in energy. It is, of course, possible that for the isolated and unsubstituted molecule, a different conformation predominates over what is found in substituted molecules in the crystals. But considering that several derivatives are now available, and all have the same conformation, this seems unlikely. Furthermore, a gas-phase electron diffraction study on the parent hydrocarbon, while less definitive than one would like, is also best interpreted in terms of the same conformation.[31] The 1977 force field gives the structure of lowest energy as the same one found experimentally.

Adamantane. Another problem in 1973 was the energies of adamantane derivatives. The observed bond length is 1.540 ± 0.002 Å whereas our calculated bond length was marginally acceptable, 1.535 Å. The energies of the adamantanes were, however, a real problem. The values reported in the literature for the heat of formation of adamantane scatter over some 2 kcal. The group of adamantane derivatives more recently studied by McKervey et al.[32] provide the bulk of the data available on these compounds. We are not, however, convinced that all of these numbers are as accurate as the probable errors attached to them indicate. We noted, however, that in MM2 when diamond was fit better with the larger carbon, the bond lengths in adamantane stretched out to a value in good agreement with experiment (1.538 Å), and in addition, most of the adamantane derivatives had their heats of formation calculated in good agreement with experiment as well. A few did not. While we do not know, we suspect that the heats of formation which are correctly calculated for adamantanes (and these adamantane values are given practically no weight in the least-squares fitting) are also experimentally correct. The places where disagreement occur, we feel, are not due to any error in the force field, but rather to experimental errors. We believe that this is the correct explanation, because it seems quite impossible to fit those values of the adamantanes which are in error by any reasonable parametrization of the force field that we have been able to device. Congressane and 1-methylcongressane form a pair which we feel illustrates the point. When a methyl group is substituted at the bridgehead of adamantane, the change in the heat of formation is 8.81 kcal/mol, and we calculate 8.75 kcal/mol. When the same substitution is made into congressane, the same change must occur, since the only difference between adamantane and congressane is at the other end of the molecule. However, while we calculate a very similar change (8.79 kcal/mol), the experimental values show a marked discrepancy (10.93 kcal/mol). The error would appear to be in the latter number.[33]

We have therefore decided to use a few adamantane values which do not affect much the outcome of the parametrization in fitting the force field. And these values are probably experimentally accurate. However, the values which we cannot fit we do not think are experimentally accurate, and unless convincing evidence is provided to the contrary, we will continue to believe that the force field here gives results more accurate than those experimental results which are in conflict with them.

Di- and Tri-*tert*-butylmethane. A few other compounds are worthy of mention. These include di- and tri-*tert*-butylmethane. For the former, we calculate a heat of formation which is somewhat too low. The heat of vaporization of the compound is not known experimentally, however. The estimate for it leads to the experimental heat of formation given in Table I (with some uncertainty). On the other hand, for 3,3-diethylpentane we calculate a heat of formation which is somewhat too high. The experimental value is an old one. Both of these compounds contain neo groupings, and it is not possible to improve significantly on the heat of formation of one without damaging the other, although either one alone could be fit well if we were certain about the experimental data. These compounds constitute two of our more serious errors in the heats of formation, but we were unable to improve them further. The most interesting feature of di-*tert*-butylmethane is the central C-C-C angle, which is opened very wide by the repulsions between the *tert*-butyl groups. Our calculated value is 124.2°, while the experimental value is reported[34] to be 125-128°. For tri-*tert*-butylmethane, the structure which we calculate is indeed highly distorted. Our calculated structure is not in exact agreement with the experimental structure,[35] but it is pretty close. Features of interest in this molecule include the central C-C bond lengths, which are unusually large. We calculated 1.603 Å (Bartell gives 1.611 Å). Also of interest is the large C-C-C central angle, for which we calculate the value of 116.7° (Bartell gives 116.0°).

Heats of Formation. In Table I is listed our set of compounds used to derive the parameters for the heats of formation. Some of these compounds have been discussed individually above. The set is a reasonably large one (42 compounds), which contains as much diverse, accurate data as we can locate in the literature. The normal hydrocarbons are included up to octane. Branched-chain hydrocarbons, isobutane, and a few similar compounds, come next, followed by increasingly branched compounds such as neopentane, hexamethylethane, 2,2,3-trimethylbutane, and 3,3-diethylpentane. Then come cyclic compounds, the parent rings from cyclobutane through cyclooctane, plus cyclodecane. Several methylated cyclohexanes are then included, and then a great many bi- and polycyclic systems. These include four-, five-, and six-membered rings in all sorts of combinations. Finally, some adamantane derivatives and other bridged ring systems are also included.

Compounds which were considered for inclusion in this table, but were specifically excluded here, were diamantane, perhydroquinacene, and 2-methyladamantane. These are compounds which would show sufficient deviation between the calculated and experimental values, while being quite closely related to other compounds in the basis set, that we feel the problem with them is experimental rather than calculational.

Heats of formation are calculated by fitting five parameters (Table IV) to the set of 42 compounds. These parameters are the C-C and C-H bonds, and iso, neo, and methyl units. As previously, the heat of formation is calculated from these quantities, plus 2.4 kcal/mol (to account for translation, rotation, and a correction to constant volume[3]) plus torsional terms, 0.36 kcal/mol for each bond about which there is a rotational barrier of less than 7 kcal/mol, excluding bands attached to methyl groups.[3] Thus, for propane the torsional term is zero; for butane it is 0.36 kcal/mol. For pentane or isohexane, it is 0.72 kcal/mol, etc. For ethane, the value is −0.36 kcal/mol.[3]

The outcome of the heat of formation fitting is very encouraging. For the 42 compounds in the basis set, the standard deviation between the calculated and experimental values is 0.42 kcal/mol. This compares with a value of 0.60 from our 1973 force field (MM1), and with a value of 0.40 kcal/mol for the average reported experimental error for the basis set. Schleyer[12] has reported an average error of 0.83 kcal/mol (for a slightly different sample) for the EAS force field.

Table IV. Heat of Formation Parameters[3] for MM2 (kcal/mol)

	C-C	C-H	Iso	Neo	Methyl
Regular	−0.004	−3.205	0.078	−0.707	−1.510
Strainless	0.493	−3.125	−0.073	−1.120	−1.575

We believe that it is safe to conclude that the present force field (MM2) gives heats of formation to an accuracy which is competitive with experiment. It remains to be established in a few cases where there are discrepancies whether the experimental value is better than the calculated value, or vice versa.

Conclusions

Considering the various errors which occurred in structures calculated by our 1973 force field, these have all been reduced markedly, or entirely eliminated, in 1977 force field. Our overall heat of formation for a selected sample of 42 compounds (Table I), which was 0.60 with our 1973 force field, is now 0.42 kcal/mol, compared with an average reported experimental error of 0.40 kcal/mol. Various energies and energy differences which we wish to be able to calculate are now either satisfactory or very close to it, as have been discussed under specific examples above. We conclude that this 1977 force field (MM2) is a definite and substantial improvement over our 1973 force field for hydrocarbons MM1). The key improvements are the use of the V_2 torsional term, and the resulting smaller and softer hydrogens that then became possible. Extensions to functionally substituted organic molecules are underway and will be reported shortly.

Finally, some comments regarding the "gauche butane interaction" seem in order. While the original interpretation of this interaction was in terms of repulsions between the methyl groups,[14,36] and a subsequent interpretation was in terms of the gauche hydrogens,[37] we no longer believe that the situation is quite that simple. We are not prepared to say just what the physical reality of the situation is. The facts are that these two interpretations are physical models, which are more or less useful in understanding the observed phenomena. Neither of these models is at present as good as the third model (MM2) discussed in detail herein.[38] In this model, the repulsion between methyls and the repulsions between gauche hydrogens are both significant quantities. But to these quantities must also be added the effect of the V_1 and V_2 torsional terms. In our current model, all three of these effects contribute significantly to the gauche butane interaction.

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of van der Waals repulsion for a hydrogen atom to lie at the nucleus, in our 1973 force field we took that center to lie 7.5% of the distance in toward the carbon atom to which the hydrogen is attached. This shift of the repulsion center is based on work by Williams,[18] and has been justified elsewhere. In the cyclodecane molecule, the two pairs of hydrogens which are exerting the severe transannular repulsion come at one another almost head on. Thus, while the internuclear distance between them was 2.15 Å in our 1973 force field, the distance between repulsion centers was 2.25 Å. The repulsion was accordingly a whole lot less than implied in White's paper. When this orientation factor (which is referred to by Bartell as "foreshortening") is taken into account, our 1973 hydrogens were very nearly the same as Schleyer's, in their effective hardness to a head-on approach.

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On Geometries of First Triplet States of Linear Polyenes

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Abstract: A restricted open-shell Nesbet SCF ab initio minimal basis set description of the geometrical changes of the olefinic double bond in the first excited states of linear polyenes is in agreement with experimental evidence on cis-trans isomerization. The allylmethylene triplet form of *s-trans*-butadiene yields the lowest minimum in the first triplet energy surface. There are three close-lying triplet minima corresponding to different triplet forms of *trans,trans*-hexatriene, indicating that cis-trans isomerizations around the central and terminal double bond are competitive. In the first triplet state of the longer polyenes, geometrical changes should take place around the internal double bonds.

Introduction

The properties of the olefinic double bonds in the first excited states (triplet T_1 and singlet S_1) of polyenes have been the subject of numerous theoretical studies. Their motivation ranges from possible interpretation of the vibrational structure of ultraviolet spectra[1,2] to predictions about olefin cis-trans isomerization in photochemical reactions.[3-6] Correspondingly, the use of quantum chemical calculation methods ranges from very elaborate ab initio procedures[2] to semiempirical treatments.[3,4,6]

In this work we investigate the twisting and stretching motion of a linear polyene double bond in the first triplet states as well as, for comparison, in the first singlet excited states. These geometrical changes give rise to "biradicaloids" and particularly to diradicals which are assumed to account for the olefinic photoisomerization mechanism. We seek out the existence of possible minima in the lowest triplet hypersurface because a return through such "diradical" minima in T_1 should be responsible for cis-trans isomerization.

The SCF-minimal basis set STO-3G procedure,[7] using a restricted open-shell Nesbet Hartree-Fock operator and very limited configuration interaction[8] (3 × 3 for singlet and 2 × 2 for triplet states), was applied to all considered geometrical changes on hypersurfaces of the lowest excited states. This admittedly very simplified procedure is used because it mimics well the four-state diradical model,[9] and, therefore, the essential qualitative features of a diradical are reproduced in an acceptable manner.

On the other hand, this simple description, which uses a too limited basis set without diffuse functions and an extremely limited configuration interaction, is evidently inappropriate for determining the electronic structures of the excited states for the ground state and neighboring geometries. Also, the spectroscopic properties are poorly described because a proper simultaneous description of two electronic states is required for the determination of these properties. The inclusion of diffuse functions and an extension of configuration interaction can differently influence different states.[2] Therefore, a method with a minimal or slightly extended basis set can, in general, lead to uncertain predictions of excitation energies. Especially, the values for excitation energies $S_1 - S_0$ and energy differences $S_1 - T_1$ are usually too large because the diffuse func-