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ON THE CONFORMATIONAL STRUCTURE OF CYCLOHEXADECANE, THE CORRESPONDING KETONE, THE 1,9-DIONE AND THE CORRESPONDING KETALS

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Abstract—The title compounds have been prepared, and their structures have been studied using molecular mechanics calculations, together with dipole moment measurements, and thermodynamic and spectroscopic data reported in the literature. It is concluded that the parent hydrocarbon exists to a very large extent in a "square" diamondoid conformation (D_{2d} symmetry). Other conformations (rectangular, nearly D_2, and puckered, D_{2d}) are considerably higher in energy. The ketone consists of a mixture of both square and rectangular conformations, with the CO group in several different positions. The monoethylene ketal exists primarily in a conformation which is square, with the ketal group on a corner. The diketone, diketal, and monoketal of the dione are considered in the light of the above, and conclusions are drawn regarding their conformations. The dipole moments of the difunctional compounds are in agreement with the conformational conclusions reached bv the calculations.

LARGE carbocyclic ring systems containing twelve or more ring members have been the subject of a great deal of investigation during the last ten years or so. When the general review appeared in the book "Conformational Analysis" in 1965,[1] the structure of cyclododecane was experimentally known, but for rings larger than this, no accurate structural data, from X-ray work or otherwise, were available. Elementary considerations indicated that large rings would tend, in so far as possible, to have anti arrangements of the butane segments, with a minimum number of *gauche* arrangements to close the ring. For the highest symmetry the 12-membered ring would, looking down the 4-fold symmetry axis, be approximately square, and the 14-membered ring would necessarily be rectangular. Less symmetrical forms are also possible. The 16, 20, 24, etc membered rings would each in principle have the option of being square or rectangular. From very old X-ray work,[2] it was known that the 24- and 28-membered diketones showed unit cells which were long and thin, which indicated structures analogous to those found for aliphatic hydrocarbons. It seemed clear that sufficiently large rings would be rectangular, rather than square, since a large square has a big hole in the center, and lacks the van der Waals attraction between the opposite sides that can be obtained with the rectangular shape. But it was not clear how large the ring had to be before it would adopt this rectangular shape.

There was also available in 1965 information[1] on m.ps. and transition points for the cycloalkanes, which showed that the 12-membered ring was an ordinary crystal, in which rotation of the ring within the unit cell did not occur. The 16- and 18-membered rings showed transition points far below their m.ps., and this fact had at least two possible interpretations. One was that these large rings were approximately a disc, and at the transition temperature, rotation of the disc about the principle axis set in, but rotation about the other axes did not occur below the melting point. This also would have explained the anisotropy of the crystals which was observed. Alternatively, it was suggested that there existed a "lattice imperfection" which traveled around the ring (analogous to the pseudorotation in cyclopentane). Or, possibly the imperfection (probably another conformation for the ring) was present in the lattice. It was also predicted that above about C_{20}, the interior hole of the disc would become too large and the van der Waals forces would collapse the molecule into two parallel straight chains.

Prior to that time[3] we had decided to investigate conformational properties of some large rings by preparing diketo derivatives, where the carbonyl groups were on opposite sides of the ring. Depending on the number of ring members, and on conformations, the keto groups on opposite sides of the ring would point in either the same direction, or in opposite directions, and measurement of the dipole moments of these compounds should yield information regarding the correctness of the general assumptions about conformations. In this paper we will discuss only the 16-membered ring.[4] The 1,9-dione of this ring was prepared by standard methods,[5] and its dipole moment was measured in benzene solution,[6] and found to have the value of 4.28 D. Since the monoketone has a dipole moment[6] of 2.48 D., it would seem that in the main the dipoles are oriented parallel, rather than antiparallel, but the observed number is certainly not twice the value for the monoketone (4.96), so clearly we have not only this conformation in solution, but a significant amount of something else. In 1972 Dale *et al.*[7] published the results of an investigation of many large ring diones, including this particular one. Their qualitative conclusions were substantially the same as ours.

Other pertinent information has become available in more recent years. First, the structure of 1,1,9,9-tetramethylcyclohexadecane has been determined by X-ray crystallography, and it is a large square.[8] The Me groups may influence the equilibrium between the square and the rectangle, but such influence should be small. The Me's fit best in corner positions, but in this particular molecule either of these conformations can position both sets of Me's at the corners. It is also clear now that still larger rings will in general be conformational mixtures in solution, containing significant amounts of conformations

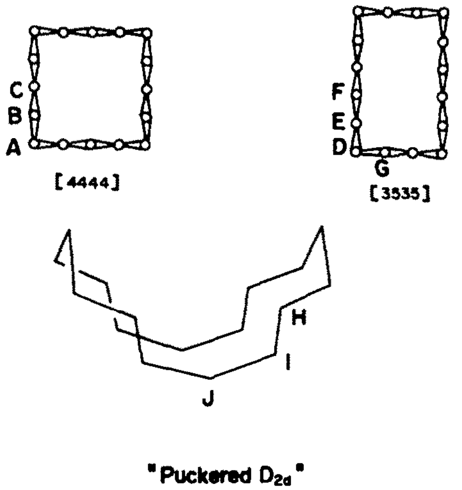

Fig. 1. The [4444] square D_{2d} conformation, [3535] rectangular almost D_2 conformation and the puckered D_{2d} conformation, with positions for substitution shown (see text).

other than the most stable one.[9] It has been suggested that this kind of disorder is present in cyclohexadecane and persists in the high temperature crystalline phase.[7]

We have applied molecular mechanics calculations (using MM2[10]) to the question of the possible conformations of cyclohexadecane, and the corresponding monoketone, the 1,9-dione, and the corresponding ethylene ketals, with the view of reaching some conclusions about the conformations of these compounds, and general conclusions regarding the structures of large rings. If we assume that large rings are indeed parallel chains, joined by end segments, the question is first, what is the length of the end segment? And second, what is the minimum ring size at which this kind of structure is observed? If we can answer these questions, then it would seem that the most stable structures of the cycloalkanes containing 4*n* carbons (above some minimum value for *n* yet to be determined) will all be known. In cyclododecane, the end segment contains four carbons. But this molecule is, according to our definition, significantly strained (12.81 kcal/mol).[11] The 16-membered ring has a choice of four carbon end segments, which leaves six carbon side pieces for the rectangle ((3535) in the Dale nomenclature[9]), or a square with five carbon segments all around (4444). (Fig. 1) The latter, although it has a calculated inherent strain[11] of 6.06 kcal/mol, is indicated by the present calculations to be favored over the (3535) conformation by 3.5 kcal/mol. This result should be valid in the gas phase, and a good approximation in an indifferent solvent. Anet and Cheng[12] recently reported similar calculations (using Boyd's Program)[13] and obtained a value of 1.9 kcal/mol for the energy difference. Our calculated geometries are similar to theirs,[21] which makes the size of the discrepancy between these calculated energy values surprising. An NMR study[12] showed no detectable amount of the rectangular conformation at about −100°. The IR spectrum of the molecule in solution is similar to that in the high temperature solid, and it is sharper in the low temperature solid. It is not certain why the IR peaks are broad at high temperatures and sharp at low temperatures, although a conformational mixture has been suggested as one possibility. The presence of a significant amount of one or more higher energy conformations seems improbable to us from the above calculations. It is also expected that there will be additional, less symmetrical conformations present, but probably these will be even higher in energy,[12] and we have not studied them.

A different interpretation for the broadening of the IR bands in the high temperature crystalline phase of cyclohexadecane (large librational motions) was suggested by Anet and Cheng.[12] When we calculate the heat of formation of cyclododecane, and smaller cyclic systems, values are obtained which agree well with experiment on the assumption that the potential wells in which the molecules lie are at least 7 kcal/mol or so in height. If the potential well is more shallow, as it is in the normal alkanes (about 4 kcal/mol), then the well becomes broader, and the torsional levels more closely spaced, and the heat of formation at 25° is increased by population of those excited torsional levels. Neglect of any special treatment of the torsional levels for cyclododecane leads us to a calculated heat of formation that is slightly too positive (−53.87 kcal/mol calculated, −55.03 ± 0.54, Cox and Pilcher,[14] but the latter value contains an estimated heat of vaporization and may be substantially in error). This agreement indicates that the molecule indeed lies in a fairly deep well, and is more like cyclohexane than it is like n-hexane in this regard. This is confirmed by low temperature studies of Anet,[15] which show the barrier to conversion of this conformation to others to be 7.9 kcal/mol.

For cyclohexadecane, the situation is markedly different. If the heat of formation is calculated neglecting these torsional motions as previously, and compared with experiment, the respective values are −83.65 and −76.83 ± 0.43 kcal/mol. The complete disagreement, assuming the experimental value is reliable, indicates that the calculated value must be significantly increased by addition of one or more terms. One possibility in principle would be the presence of large numbers of excited conformations, but the discussion above appears to rule out this possibility. The only other possibility apparent to us is that the torsional potential wells are very broad in this molecule, as with open chains, rather than as with the smaller rings. If this is correct, treating the torsional part of the molecule as we treat open chains, we would add $16 \times 0.36 = 5.76$ kcal/mol to the heat of formation, bringing it's value to −77.89. The agreement is now reasonable. Thus our conclusion is that this molecule has broad torsional wells, similar to those found in an open chain. The different parts of the molecule act rather independently, and are deformed by neighboring molecules in solution or in the high-temperature solid and liquid phases, and this leads to the observed bands in the IR spectrum. In the low temperature crystalline phase, apparently the lattice forces compress the molecule sufficiently to give narrow, well-defined torsional potential wells, in which the vibrational levels are more widely spaced, so the excited levels are less populated, which then sharpens the spectrum. There is no definite evidence for the presence of any other conformation, in solution or in the high temperature solid. While such an additional conformation might lead to broader bands, it really should lead to the appearance of new and different bands, which are not observed. Finally, the broad torsional potential wells are expected in conjunction with low barriers to interconversion. The observed barrier is 6.7 kcal,[12] which is in fact below our 7 kcal value where the effect is expected. (It is clearly

Table 1. Conformational data for cyclohexadecane systems[b]

System	Item	Steric Energy	ΔE	σ	dl[a]	-TΔS	ΔG	Mol %	μ
Hydrocarbon									
	Square	16.57	0	4	No	0	0	99.6	0
	Rect.	20.00	3.43	4		-0.41	3.02	0.4	0
	Puckered	23.90	7.33	4	No	0	7.33	—	0
Ketone									
	Square								
	A	15.39	0.78	2		+0.41	1.19	9.0	
	B	14.61	0	1		0	0	64.8	
	C	14.92	0.31	1	No	+0.41	0.72	19.2	
	Rect.								
	D	19.10	4.49	1		0	—	—	2.48
	E	17.58	2.97	1		0	—	0.7	
	F	17.34	2.73	1		0	—	1.0	
	G	16.09	1.48	1		0	1.48	5.3	
Ketal									
	Square								
	A'	34.22	0	1		0	0	75	1.32
	B'	34.87	0.65	1		0	0.65	25	0.82
	C'	39.52	5.30	1		--	--		
	Rect.								
	D'	37.65	3.43	1					
	E'	38.83	4.61	1					
	F'	39.80	5.58	1					
	G'	41.01	6.79	1					
Diketone									
	Square								
	AA	14.49	2.15	4		+0.41	2.46	--	0.50
	BB	13.01	0.67	2		0	0.67	21.5	4.14
	CC	13.37	1.03	2	No	+0.41	1.44	11.7	4.15
	Rect.								
	DD	18.46	6.12	2		--	--	--	--
	EE	15.23	2.89	2		--	--	--	--
	FF	14.77	2.43	2		--	--	--	--
	GG	12.34	0.00	2		0	0.00	66.8	4.18
	Pucker								
	HH	19.53	7.19	2		--	--	--	3.90
	II	20.92	8.58	2		0	--	--	3.56
	JJ	21.68	9.34	2	No	+0.41	--	--	4.38
Ketone-Ketal									
	Square								
	AA'	33.05	0.14	1		0	0.14	45	3.28
	BB'	32.91	0	1		0		55	1.97
Diketal									
	Square								
	A' A'	--	0	4		0	0	82	1.37
	B' B'	--	1.30	2		-0.41	0.89	18	1.16

[a] Each structure is a dl mixture unless otherwise indicated.

[b] Energies are in kcal/mol.

somewhat fortuitous that the rather small difference in the barriers between the 12- and 16-membered rings happens to straddle our 7 kcal value, but the "broad" and "narrow" torsional potentials none the less do seem like a reasonable interpretation of the facts.)

Next we examined cyclohexadecanone. There are quite a few conformations that one needs to consider. The ring can be square, in which case there are three positions for the CO group (giving the three conformations *A*, with the carbonyl on the corner, *B*, with the CO adjacent to the corner, and *C*, with the CO in the middle of the side of the ring. There are also four conformations in which the ring is rectangular, *D*, *E* and *F*, where the CO group is positioned along the longer side of the ring and the terminology is as before, and also a fourth conformation *G*, where the CO is adjacent to the corner of the ring on the short ring side. The calculations indicate that several of these conformations differ in energy by relatively small amounts (Table 1). Conformation *B* is the lowest in energy, but the compound should exist at room temperature as a conformational mixture containing substantial amounts of other conformations.

If we look at the Dale figure for the (4444) conformation (Fig. 1) and realize that the bulk of the instability of this conformation comes from repulsion between hydrogens on the same side of the interior of the ring (for example, if we numbered the carbons 1, 2, 3, ... beginning with *A*, and going in the direction of *B*, *C*, ..., the interior hydrogens on carbons 2 and 15 so interact), then it's clear that if we replace the pair of hydrogens on either of these carbons, we will remove the repulsion. Since the interior hydrogen on C15 interacts not only with the interior hydrogen on C2, but also with the one on C12, it would seem that replacing the hydrogens on C15 would lower the energy more than replacing the hydrogens on C2. Calculations show this is not the case. More careful examination of the figure (or of a model) shows why this is true. C2 is up above the mean plane of the ring, and when the hydrogens are replaced by a CO oxygen, this oxygen is far up above the ring, and does not have any repulsion with the hydrogen remaining at C15. But, if we replace the hydrogens at C15 with the CO, since C15 is down lower, near the mean plane of the ring, the CO oxygen is now in a position to interact with the interior hydrogen on C2. Thus, substitution of a CO at a position of type C only exchanges the repulsion between two hydrogens for a repulsion between an oxygen and a hydrogen, whereas substitution at a position of type *B*, while it affects only half as many interactions, does completely eliminate them. It is also worth pointing out that a CO at position *C* has the oxygen eclipsed by two carbons, the most favorable arrangement. A CO at position *B* has the oxygen eclipsed on one side by carbon but on the other side by hydrogen, which is less favorable. Nonetheless, substitution at position *B* is favored, although not by a very large amount.

The measured dipole moment of the compound was 2.48 D. This value, which is similar to that reported by Dale,[7] is significantly less than that observed[16] for acetone (2.86 D), or cyclohexanone (3.08 D). This relatively small value can be understood in terms of the induced moments which arise in the C–C bonds.[17] Since the latter are missing for the bonds beyond Me in acetone, the acetone value can be considered as the starting point. If we attach Me's around in the *gauche* position (as in cyclohexanone), the induced moments in the C–C bonds are in the same directions as the principle moment, and hence augment the latter value. But if the methylene groups are attached, say as in 3-pentanone, with the carbon skeleton in the all-anti conformation, then the induced moments in the C–C bonds oppose the principle moment, and hence reduce the observed value.

Consequently a smaller moment is expected for conformations *B* and *C*, while a larger one is expected for conformation *A*. The small value obtained experimentally is consistent with conformations in which *B* and *C* together strongly predominate over *A*.

The ethylene ketal of cyclohexadecanone was prepared, and its dipole moment had the value 1.05 ± 0.11 D. This compound has available to it the same types of conformations described above, (here called *A′* – *G′*) although here there is a greater spread in energy between the different conformations. The most stable conformation is calculated to be *A′*, in contrast with the parent ketone itself. This can be qualitatively understood on the basis that in going from the hydrocarbon to the ketone, one is removing a hydrogen. Thus, putting the ketone at any position other than on a corner will relieve some repulsion from the interior of the ring. The corner position therefore is the least favorable with the ketone, and the differences are relatively small between conformations *B* and *C*.

For the ketal, on the other hand, a relatively small hydrogen inside of the hydrocarbon ring would be replaced by a much larger oxygen, so that the conformations which are best for the ketone are poorest for the ketal. The corner position (*A*) enables both of the oxygens to be external to the ring, and this is preferred. Interestingly, it turns out that the calculated dipole moments are quite different, depending on whether the conformation is *A′*, *B′*, or *C′*. The reason for this is that the dioxolane ring can adopt either a half-chair (C_2) or an envelope (C_s) conformation, as these are rather similar in energy. If the dioxolane ring is attached to a corner *A′*, it prefers the C_s conformation, which has a substantial dipole moment (1.32 D), while if it is in the *B′* or *C′* conformation, the steric pressures from the neighboring methylene groups force it to adopt the C_2 conformation, and here the dipole moment is smaller (0.82 D).

The calculated energies of the monoketals are as shown (Table 1). As expected *A′* is the most stable, but *B′* is not far behind. *C′*, on the other hand, has a very high energy. These energy differences can be rationalized as was done for the monoketone (with reference to Fig. 1). If the ketal unit is placed at position *A*, it is quite out of the way, and sterically favorable. If it is placed at position *B*, because the carbon here is up above the plane of the ring, the ketal unit tends also to be up above the plane of the molecule, and the steric interactions are not very serious. But if the ketal is placed at *C*, since the latter carbon is below the plane of the molecule, the internal oxygen atom is forced into an extremely unfavorable location, resulting in quite a higher energy.

If we take the compounds to be a conformational mixture of only *A′* and *B′*, which is a good approximation, allowing for the enthalpy and entropy differences, we calculate that the equilibrium mixture would consist of 75% *A′*, and 25% *B′*. The calculated moment for the monoketal is 1.20 D based on this ratio. This value is in reasonable agreement with that observed experimentally.

Let us now examine the 1,9-dione. Here we have dealt with three families of conformations: the square, the rectangle and the puckered forms. The latter systems are based on the X-ray structure reported for the 1,5,9,13-tetraazacyclohexadecane.[18] This conformation in the hydrocarbon has an extremely high steric energy relative to the (4444) form ($\Delta E = 7.33$ kcal/mol) due to the adverse torsion and bad van der Waals repulsions. Most of these problems remain in the diketone forms which are labeled *HH*, *II*, and *JJ*, corresponding to the three unique positions on the skeleton. In the square, the three forms are labeled *AA*, *BB* and *CC*; in the rectangle *DD*, *EE*, *FF* and *GG*. Inspection of models of these systems reveals that in the majority of the conformers the dipoles are parallel or additive, with moments expected near 4.96 D, assuming a moment of 2.48 D for the monoketone. Since the MM2 Program does not allow for the induction effects as previously mentioned, one might expect the calculated moments for the parallel carbonyl orientations (conformers *BB*, *CC*, *EE*, *FF*, *GG*, *JJ*) to be nearly 2×2.90 or 5.80. Indeed, we find MM2 values of about 5.8 D for these conformers. These values were corrected for induction by multiplying by the factor 2.48/2.91 (Table I). In conformers *AA* and *DD*, near zero moments are expected (and calculated), due to the opposition of the dipoles.

The calculated energies for the various conformations are given in Table I. The more important conformations of the dione are *BB*, *CC* and *GG*. A conformation like *AA*, with large opposing dipoles, would show an apparent dipole moment of about 0.5 D, from atomic polarization.[19] The others with the dipoles nearly parallel would be expected to show moments slightly reduced by 5–10% as a result of their vibrational motions, which would yield the values for the individual conformations as given in Table 1.

Using these dipole moments (Table 1) and the mole fractions calculated from the relative free energies (Table 1), the overall dipole moment of the compound is calculated as 4.17 D., compared with the experimental value of 4.28 D, and the agreement is reasonable. Our conclusion is that *GG* is the major conformation, together with *BB* and *CC* in that order. This is quite a different conclusion from that reached by Dale[7] (that *CC* would predominate), which was based only on qualitative reasoning, however.

In the (4444) conformation there are 8 unfavorable gauche H/H repulsions, 0.05 kcal each. In the 3535 form there are 4 similar repulsions, which are more serious, 0.59 kcal each. These geometries have been a result of each conformation minimizing its strain, so the total difference in strain (3.43 kcal) is larger than the remaining contributions to strain from this one kind of interaction (2.16 kcal).

Replacing a CH_2 group by a C═O in (4444) at *B* removes one unfavorable hydrogen–hydrogen interaction and reduces the strain energy by a total of 0.26 kcal/mol (Table 1). A similar replacement at *F* removes one H–H interaction and stabilizes the molecule by 0.96 kcal, while replacement at *G* also removes one interaction, but stabilizes the molecule by 2.21 kcal. So the best conformers (by 1.48 kcal) is with the ketone at *B* in the (4444). However, if another C═O group is added in the 9 position, while the square is further stabilized, placing the C═O in the (3535) conformation at position *E*, *F*, or *G* leads to an even greater stabilization, as a larger fraction of the severe gauche hydrogen repulsions are eliminated. In fact the rectangular conformation *GG* is calculated to be more stable than the square *BB* by 0.67 kcal/mol, and is predicted to be the predominent conformation.

For the 1,9-cyclohexadecanedione diketal, the experimental dipole moment was 1.21 ± 0.02 D. For *A'A'* there are two possible conformations with the dioxolane rings individually in the C_s conformation. They can be arranged in such a way as to give a C_2 axis in place of what was a C_4 axis in the hydrocarbon, and this conformation has a dipole moment of zero (which would show an apparent dipole moment of about 0.5 D).

Alternatively, there is the conformation where the moments of the dioxolane rings are additive; the vector addition of the component moments for this form is 1.94 D. Thus a 50:50 mixture of the *A'A'* forms gives rise to a calculated net moment of 1.37 D for *A'A'*. In *B'B'*, this situation does not exist since the C_2 form of the dioxolane rings are preferred over the C_s forms due to steric hindrance. Thus, the individual moments of the dioxolane rings in *B'B'* point in approximately the same direction and give a calculated total moment of 1.16 D. By assuming a moment of 1.37 D for *A'A'* and 1.16 D for *BB'* (all other conformers are much higher in energy) we calculate a moment of 1.33 D for an 82:18 mixture of these forms. This value is in agreement with our observed value.

Next we can consider the monoketal of cyclohexadecanedione. Here it is difficult to make a qualitative predication as to what is to be expected. Conformations which are best for the ketone group are poorest for the ketal, so one might expect roughly equal amounts of each conformation. The conformation best for the ketone (*BB'*) in this case have the moments subtracting, rather than adding, their values. The conformation best for the ketal, on the other hand (*AA'*), has the moments adding. Only these two conformations (*AA'* and *BB'*) are expected to have relatively low energies. Of these, *BB'* is calculated to be of lower enthalpy by 0.13 kcal/mol, which should lead to a 55/45 mixture with *AA'*. The calculated dipole moments are respectively 1.97 and 3.28. The 55/45 mixture is therefore calculated to show a dipole moment of 2.64 D, while the experimental value is 2.78 D.

Our conclusions are that the square conformation predominates over the rectangular for most of the compounds considered here involving a cyclohexadecane ring system, and the energy difference is quite substantial. The ketal group prefers to be on a corner position, whereas a ketone group appears to prefer any position other than a corner. The various kinds of conformations which can result from a diketone, diketal, or monoketal monoketone have been predicted, and the calculated dipole moments in all cases agree reasonably well with those determined by experimental measurement. The calculated inherent strain energy for cyclohexadecane (the strain of the square conformation, neglecting that which results from the population of higher torsional levels, which in turn result from the floppiness of the molecule) is only 6.05 kcal/mol. It would seem that the larger rings of analogous possible structures (20, 24, 28, etc.), which in principle can exist in rectangular or square conformations, will not prefer rectangular conformations with *four* atoms at the ends, and the rest of the atoms the sides. Rather a conformation with at least five atoms at the end, and the rest of the atoms along the sides would appear to be preferable. Thus it would seem that the very large molecules that fall into this category will consist of two parallel chains with end segments containing at least five carbons.

EXPERIMENTAL

The dione was prepared by the ketene dimerization method, then converted to the ketal and diketal in standard ways.[7] The dipole moments were measured at 25° in benzene solution using standard methods.[20] Atomic polarization was neglected.

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University, Detroit, Michigan, in partial fulfillment for the degrees of Master of Science, 1964. A preliminary discussion of these results was given in Ref. 1, pp. 217–221.

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[10] MM2, a molecular mechanics program to be submitted to QCPE shortly. This program has been parameterized to deal with ketones and ethers (ketals) by S. Profeta, Jr., S. H-M. Chang and D. H. Glaser, unpublished work. Until such time as the QCPE program is available, the parameter set may be obtained upon request from the author (NLA).

[11] Strain can and has been defined in several different ways. The definition used here is the one we have used for some time, and it depends to some extent, on the force field used to calculate it. The numbers given in this discussion are what we call "inherent strain". This is strain which is contained in the conformation of lowest energy, not including that which results from wide amplitude torsional motions. For further discussion concerning this particular definition of strain, see N. L. Allinger, *Advances in Physical Organic Chemistry*. 13, 1 (1977).

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[21] A referee asked us to comment on our calculated structures. They are generally rather unexceptional. Bond lengths are all in the range typical for the bond type. The bond angles tend to be opened out somewhat wider than in simple compounds, especially in strained conformations. The C–C–C angles were 117–119° if the central carbon was a carbonyl carbon, and 112–118° when it was an sp^3 carbon.