THE STRUCTURE OF THE CYCLOOCTADECANE RING SYSTEM. 1,10-CYCLOOCTADECANEDIONE

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Abstract—The crystal structure of the title compound was determined by X-ray crystallography and solved by direct methods; the molecule has C_{2h} symmetry. The carbon atoms are arranged in a diamondoid lattice, but not of the rectangular type that might have been expected. The dipole moment for the conformation found in the crystal is zero, while the observed dipole moment of the compound in solution is 2.78 D. Molecular mechanics calculations were carried out on several of the large number of possible conformations. Of those studied, the conformation found in the crystal had the lowest energy.

Fairly thorough conformational analysis studies have been carried out on cycloalkane rings containing twelve or fewer members; as a class, these compounds and their simple derivatives can be regarded as being well understood in this respect.[1] It was predicted years ago[2] that very large rings would, because of attractive intramolecular van der Waals forces, exist preferentially in either the gas or crystal phase as structures containing two long parallel chains, joined by short end segments. It was also predicted[3] that these short end segments would consist of four carbon fragments, although very early work had been interpreted in terms of five carbon fragments.[4] To optimize the van der Waals attraction energy, two parallel side-by-side chains are needed. The only question is what length of end segment, considering also the bond angles necessary to turn the corners, will give the optimum distance apart of these two chains. This interpretation was concerned with the isolated molecule (gas phase). Recently a number of crystal structures have been carried out on rings containing 24,[5] 26[5] and 34[6] ring members, which have indeed been found to consist in the crystal of two long parallel chains, joined by four carbon end segments. In solution, such a conformation is probably of lowest enthalpy, but because of the van der Walls interactions of the molecule with solvent, one does not expect a very decisive margin here. Other conformations may well predominate for entropy reasons, perhaps decisively.

For rings containing between 13 and 23 members, while a considerable amount of data does exist,[1,7] the situation is much less clear. In the present work we have looked at the 1,10-diketo derivative of the 18-membered ring.[8] This ring system has been discussed previously by Dale and co-workers,[7,9,10] who have pointed out that there are four possible diamond-latice conformations.

For all the larger rings there are in general rectangular conformations possible. These are reasonably stable, because they consist of segments in which all the carbons are arranged in stable anti units, and there are four gauche-type corners. With certain numbers of carbon atoms, there may also be possible a square conformation where the sides happen to be equal in length. It is to be expected that for very large rings a rectangular conformation will be more stable than a square one, at least in the gas phase. This is because two long parallel chains will have a substantial van der Waals attraction between them, and this attraction will be greater if two of the end segments are short, so the two chains can lie close together, i.e. a rectangle. The square conformation would contain a large hole, and the resulting attractions would be less. In condensed phases, intermolecular interactions might be of sufficient importance to outweight this intramolecular interaction, although this seems unlikely. But for rings of intermediate sizes, such as in the present case, such a rectangular conformation will be reasonably stable. The four corners will necessarily exhibit considerable strain. On the other hand, a diamond-lattice conformation contains only gauche and anti conformations, with the former being only slightly strained relative to the latter. So it is not clear what one expects *a priori.*

In the present work we have determined the X-ray crystal structure of the title compound, and, at the same time, carried out molecular mechanics calculations to ascertain if the conformation found in the crystal is the most stable one for the isolated molecule. The structure found by crystallography has C_{2h} symmetry, and is also the most stable of those studied by molecular mechanics. A comparison of the two structures is given in Figure 1. The bond lengths are generally slightly longer as calculated by molecular mechanics, which is expected, since the calculated bond length is the average distance between atoms, whereas the crystallographic one relates to the distance between the average atomic positions, which is generally a slightly smaller number. The bond angles and dihedral angles are, generally speaking, in good agreement. Since torsional potentials are usually weak, the largest discrepancies are expected here. Only one discrepancy appears to be really significant, namely the one about the C-2–C-3 bond. The molecular mechanics value is considerably flatter (67°) than the X-ray value (74°). This may be due to crystal packing forces, or to the fact that the molecular mechanics value simply is not very good for this angle, because the torsional function about this particular kind of bond is not known from any direct measurement.

Using the dihedral angle driver (MM2), the troublesome torsional angles were forced to the X-ray value of 74°. This caused the energy of the molecule to go up by 0.8 kcal/mole. (Since there are four identical angles of this kind, this amounts to only 0.2 kcal/mole per angle). This is a small enough increment that we are unable to decide if the error is more likely to be calculational, or from crystal packing, or from a combination of the two.
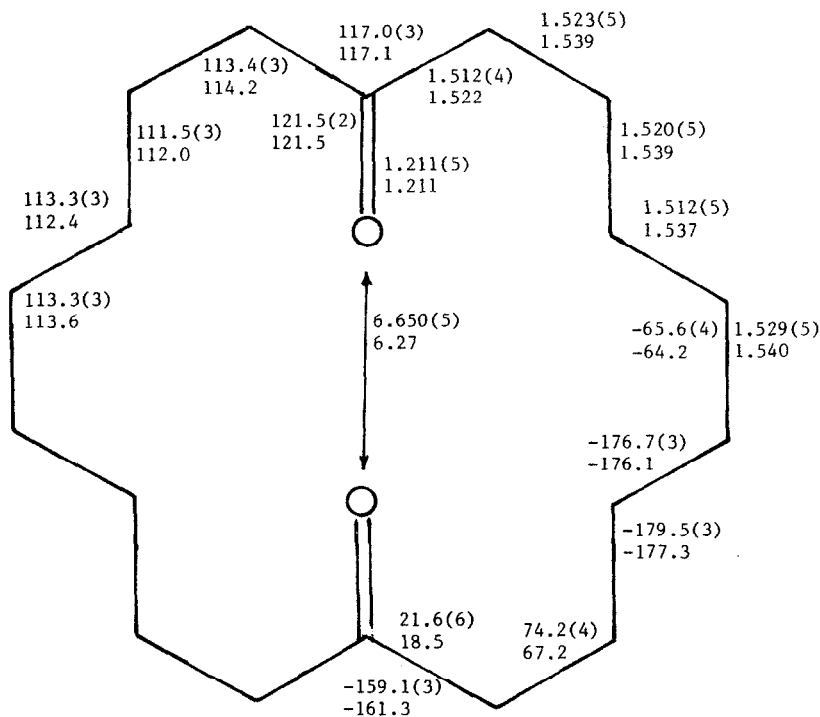
Fig. 1. Bond distances, bond angles and dihedral angles obtained from the X-ray structure (standard deviations in the last figure are given in parentheses, and experimental errors should be considered to be 2-3 times these values). The corresponding quantities from molecular mechanics (MM2) are given without error estimates.

In Figs. 2 and 3 are shown, respectively, a stereoscopic projection of the X-ray crystal structure, and the unit cell packing structure.

While the skeletal ring conformation can be any of the four discussed by Dale, or perhaps others, there are in each of the conformations various nonequivalent positions for the carbonyl groups. Many of these structures should be similar in energy, so that in solution, one would expect a complex conformational mixture. The dipole moment of the 1,10-dione is known to have the value 2.78 D.[8,11] Since cyclooctadecanone itself has a dipole moment of 2.47 D,[8] this suggests that there are about as many molecules in conformations with dipoles pointing in directions which add as there are conformations with dipoles pointing in directions such that they

subtract. However, each of the four favorable conformations have the dipole moments opposed, no matter what positions are chosen for the carbonyl groups. The simplest guess then, is that the expected net dipole moment should be zero. Since this is far from what is actually observed, the conformational situation is apparently more complex than the above considerations imply.

One might expect that the molecule will be very "floppy", and that substantial deformations on one side of the molecule can be carried out with essentially no effect on what occurs on the other side. As was discussed earlier,[12] this what is observed in the 16-membered ring, and presumably in larger rings. Evidence for such "floppiness" comes from the heat of formation in
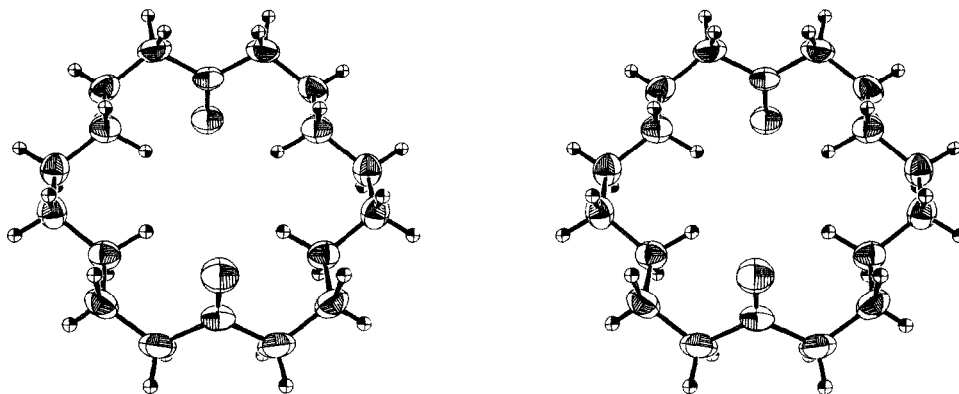

Fig. 2. A stereoscopic drawing of the X-ray crystal structure of 1,10-cyclooctadecanedione.
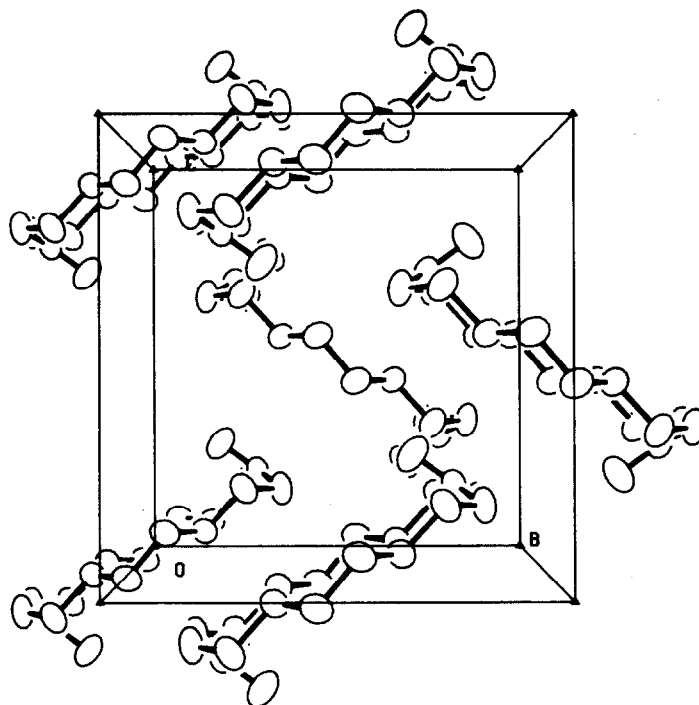
Fig. 3. The unit cell projection for 1,10-cyclooctadecanedione.

the case of the 16-membered ring. The heat of formation for the 18-membered ring has not been reported, but it seems safe to infer that a similar floppiness exists.

It is well-known that molecules which contain strong opposing dipoles separated by several bonds (p-dibromobiphenyl and its relatives are well-known examples)[13] show apparent dipole moments, as measured by polarization methods, of about 0.7 D. These apparent moments result from molecular vibration (atomic polarization). A similar result would be expected here, but because of the increased floppiness of the molecule, one might expect a somewhat larger observed dipole moment. Still, the value actually observed is so large that it makes one question this explanation. The following approach was therefore taken to try to determine if such an explanation is indeed reasonable. Beginning with the known structure for the diketone (C_{2h}), the dihedral angle about the carbonyl carbon–alpha carbon bond, which had a calculated dihedral angle of 19° in the ground state, was driven to higher and lower values in increments, using the dihedral angle driver. The energy was minimized for each of these dihedral angles in all other degrees of freedom, and the dipole moment was obtained. This permits one to estimate the energy change, and also the dipole moment variation with vibration.

Knowing the change in energy with the change in θ, the angle between the dipoles, we can estimate that a change in the former by 0.6 kcal/mole (RT) leads to a dipole moment of about 0.5 D, indicating that the observed dipole moment does not result from large amplitude motions alone. Rather, it is likely that some of the less symmetrical conformations, of which there are many, have sufficiently low energies to contribute appreciably to the conformational population in solution at room temperature, and thus lead to the observed dipole moment.

EXPERIMENTAL

1,10-Cyclooctadecanedione was prepared by dimerization of sebacyl chloride using triethylamine, following the procedure of Blomquist.[14] The compound was recrystallized from methanol or hexane and had m.p. 95–96°.

Crystal Structure Determination. All diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer using Cu $K\bar{a}$ radiation and a graphite monochromator. The orientation matrix and cell dimensions were determined from 15 accurately centered reflections. Pertinent crystallographic information is summarized in Tables 1 and 2.

Intensity data were corrected for Lorentz-polarization effects but not for absorption. In all, 642 unique nonzero reflections were used in the structural analysis. The structure was solved by the direct methods program MULTAN[18] (E's ≥ 1.5). The E map produced from phases with the highest ABSFOM value (1.91) revealed starting positions for the 6 unique nonhydrogen atoms. Refinement of these atomic positions and generation of a difference map gave starting positions for the 8 unique hydrogen

Table 1. Summary of crystallographic data

molecular formula	$C_{18}H_{32}O_2$
mulecular weight	280.45
linear absorption coeff.	5.18 cm^{-1} (Cu $K\bar{a}$)
ρ (calcd)	1.055 g/cm^3
space group	Cmca
cell dimensions	a = 17.663(5) Å
	b = 9.765(3) Å
	c = 10.233(3) Å
	z = 4
	V = 1765 Å^3
no. of reflections measd	1082
no. of unique reflections obsd	642
final R	0.068
R$_w$	0.074

Table 2. Positional coordinates and temperature factors for 1,10 cyclooctadecanedione

ATOM	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O_1	0.0	0.18192(34)	0.27466(36)	0.00504(14)	0.01386(39)	0.01701(49)	0.0	0.0	0.01254(73)
C_1	0.0	0.28252(37)	0.20548(41)	0.00444(17)	0.00876(39)	0.01056(44)	0.0	0.0	-0.00367(74)
C_2	0.07298(21)	0.34875(30)	0.16102(43)	0.00535(15)	0.00805(28)	0.01801(52)	-0.00195(35)	0.00259(44)	-0.00319(68)
C_3	0.14086(20)	0.25268(33)	0.16604(36)	0.00425(13)	0.01240(35)	0.01460(39)	-0.00394(40)	0.00005(39)	-0.00786(69)
C_4	0.13846(19)	0.14832(31)	0.05587(32)	0.00429(12)	0.01096(33)	0.00992(33)	-0.00047(34)	-0.00126(34)	-0.00229(57)
C_5	0.20451(19)	0.04987(35)	0.05758(34)	0.00349(11)	0.01495(40)	0.01082(36)	-0.00106(34)	-0.00112(33)	-0.00371(62)
H_{21}	0.0615(27)	0.3820(49)	0.0498(47)	7.3(12)					
H_{22}	0.0820(25)	0.4369(47)	0.2004(38)	6.1(11)					
H_{23}	0.1483(25)	0.1815(43)	0.2618(46)	6.1(10)					
H_{24}	0.1804(23)	0.3002(40)	0.1619(38)	4.5(9)					
H_{25}	0.0866(18)	0.0940(32)	0.0645(30)	2.4(6)					
H_{26}	0.1369(23)	0.1951(43)	-0.0201(42)	4.7(9)					
H_{27}	0.2057(19)	0.0110(33)	0.1480(36)	3.0(7)					
H_{28}	0.2509(24)	0.1019(40)	0.0698(37)	4.9(9)					

atoms. Full-matrix least-squares refinement with anisotropic temperature factors for the carbon and oxygen atoms, isotropic temperature factors for hydrogen atoms, and weights of $1/\sigma_F 0$ gave a final R of 0.068 ($R_w = 0.074$).

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