# Conformational Studies of Normal, Medium, and Large Ring Diametric Cycloalkanediones and Their Ethylene Ketal Derivatives

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Even-membered diametric cycloalkanediones and corresponding bis-ketals having from 6 to 20 ring atoms have been studied by determination of dipole moments, by infrared spectroscopy of solid and solution, and by calorimetry of the melting process. Up to and including the 14-membered ring in both series, the solution has a single main conformer, which except in the case of cyclohexane-1,4-dione and cyclodecane-1,6-dione, is the same as in the solid. Also for the 16-membered rings the crystal conformer may be dominant in solution. In large rings the carbonyl group prefers to be $\beta$ to corner atoms, whereas the ketal group prefers corner positions.

In a preceding paper * we have described the properties of macrocyclic diametric diketones where the positions of the carbonyl groups on the ring conformation were more or less defined by the presence of *gem*-dimethyl groups confined by their bulk to certain positions. In this paper we shall describe the dielectric, spectroscopic, and calorimetric properties of corresponding unsubstituted diketones (I) in order to find out whether or not the carbonyl group has a preference for certain positions on the ring skeleton. As medium rings are also available in this series, these have been included, as has cyclohexane-1,4-dione, the only member which has been extensively studied before.

Since the torsional barrier in the CC ring-bonds adjacent to the carbonyl group is much lower than in saturated hydrocarbons [1] and might be expected to introduce a disturbing "flexibility" by partial eclipsing, it was desired to convert the carbonyl group to a derivative with an equally well-defined dipole geometry but having higher torsional barriers in adjacent CC ring bonds. Attempts to prepare bis-geminal difluorides by reaction with $SF_4$ failed in most of these cases; products containing two fluorine atoms and an oxygen bridge were formed in medium rings, fluoroolefins in larger rings. Although the *gem*-dialkoxy group would be unsuitable since the direction

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of its dipole would be ill-defined, a cyclic ethylene ketal might have a better defined dipole if the five-membered ring is close to planar, or even if it is present in a non-planar half-chair conformation with the spiro-atom in the preferred isoclinal[2] position. The bis-ketals (II) could all be prepared and their properties examined by the same methods.

$$O = C \underset{(CH_2)_n}{\overset{(CH_2)_n}{<}} C = O \qquad \underset{\overset{|}{CH_2} - O}{\overset{CH_2 - O}{|}} \underset{C}{\overset{(CH_2)_n}{<}} \underset{(CH_2)_n}{\overset{C}{>}} \underset{O - CH_2}{\overset{O - CH_2}{\overset{|}{|}}}$$

I, $n = 2 - 9$                  II, $n = 2 - 9$

## SYNTHETIC ASPECTS

The *cycloalkanediones* (I) with 14 and more ring atoms were obtained by cyclization of either diesters, dinitriles, or bis-acid-chlorides, following described procedures. No *in vitro* synthesis had been published for cyclododecane-1,7-dione, only a transannular bio-oxidation of cyclododecanol to cyclododecanol-7-one and subsequent chromic acid oxidation.[3] Attempts to cyclize 7-oxo-tridecanedioic acid diethyl ester, protected as the ethylene ketal, failed. Finally, a particular method was developed[4] using cyclododeca-1,5,9-triene as a starting material. Both this diketone and the well-known cyclodecane-1,6-dione were sensitive substances undergoing transannular condensation on active alumina. Cyclooctane-1,5-dione, prepared by direct oxidation of *cis*-cyclooctane-1,5-diol, was on the other hand perfectly stable.

The *bis-ketals* (II) were obtained by routine methods from the diketones, except in the case of cyclodecane-1,6-dione, which underwent transannular condensation under the reaction conditions. This bis-ketal was therefore prepared by catalytic hydrogenation of the bis-ketal of *cis,cis*-cyclodeca-3,8-diene-1,6-dione.[5] The bis-ketal of cyclooctane-1,5-dione was unstable undergoing partial hydrolysis to the mono-ketal.

## CONFORMATIONS OF CYCLIC DIKETONES

The dipole moments and melting parameters for the simple cyclic diketones (I) are presented in Table 1 and compared graphically with the corresponding data for tetrakis(*gem*-dimethyl) substituted compounds in Figs. 1 and 2. The strong alternation of the dipole moment above and below the statistical average value of $2.7 \text{ D} \times \sqrt{2} = 3.8 \text{ D}$ immediately suggests that these rings have very strong conformational preferences. Furthermore, since the series having 8, 12, 16, and 20 ring atoms have high dipole moments, the carbonyl groups must be parallel and do not therefore occupy corner-like positions where the molecular dipole moment would have been cancelled. On the other hand, the less marked alternation for the largest rings, as compared with the *gem*-dimethyl substituted rings, suggests that the former are either less homogeneous conformationally or less rigid than the latter. The high entropy
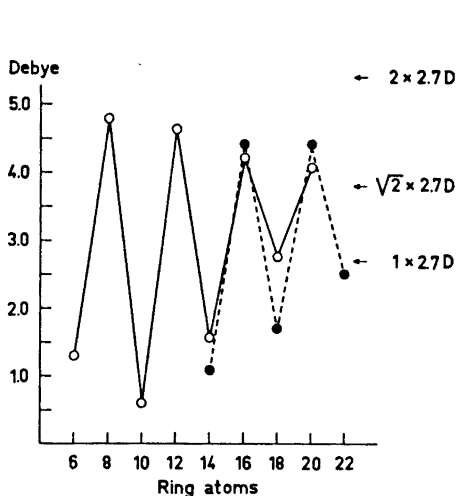
Fig. 1. Dipole moments in benzene solution at 25° of cycloalkanediones (I) (open circles) and of the octamethylcyclo-alkanediones described in the preceding paper (filled circles).
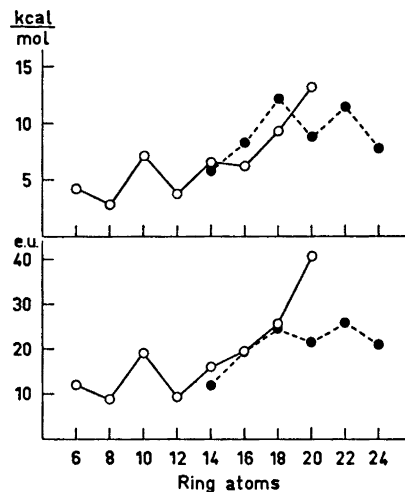
Fig. 2. Summed enthalpies (top) and entropies (bottom) of melting and transition for cycloalkanediones (I) (open circles) and of the octamethylcycloalkanediones described in the preceding paper (filled circles).

of melting and the observed complex infrared spectrum of the solution as compared with the solid (Table 1) give support for the conclusion that the 18- and 20-membered cyclic diketones are conformer mixtures in melt and solution. In view of the great number of possible ring conformations and dispositions of the carbonyl groups on them,[6] no further discussion of conformational candidates seems justified for these two cases.

The 14- and 16-membered rings on the other hand have only one possible diamond-lattice ring skeleton,[6] so that here the problem might be limited to choosing positions for the carbonyl groups. The observed similarity of the values of the dipole moment and the melting entropy with those for the *gem*-dimethyl substituted derivatives suggests conformational homogeneity, but this is only supported by identity of the infrared spectra in solid and solutions [7] in the case of *cyclotetradecane-1,8-dione* (Table 1). For this ring we then have to choose between the three possible dispositions of the carbonyl groups given in Fig. 3, since corner positions have already been excluded, and to seek a reason why one of these is favoured over the two others. It is immediately seen that the number of repulsive *gauche* methylene interactions,[6] which are eight in cyclotetradecane, have been reduced to four in conformations *a* and *b*, but only to six in *c*. In order to further choose between *a* and *b*, we have to postulate that between a carbonyl group *β* and a hydrogen *α* to the same corner atom there is a stabilizing interaction which is not found between a carbonyl group *α* and a hydrogen *β* to the same corner atom, the oxygen-hydrogen distance being much shorter in the former case (2.1 Å against 3.2 Å).

*Table 1.* Physical properties of cycloalkanediones (I).

| $n$ | Number of ring atoms | M.p. °C | $\Delta H_m$ (kcal/mol) | $\Delta S_m$ (e.u.) | Tr.p. °C | $\Delta H_{tr}$ (kcal/mol) | $\Delta S_{tr}$ (e.u.) | Dipole moment in benzene(D) | Infrared spectrum in $CS_2$-solution as compared with solid |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 6 | 75 | 2.40 | 6.9 | 49 | 1.47 | 4.6 | 1.34[a] | similar, but simpler (Fig. 10) |
|   |   |   |   |   | 66 | 0.23 | 0.7 |   |   |
| 3 | 8 | 68 | 2.85 | 8.4 |   |   |   | 4.81 | practically identical |
| 4 | 10 | 99 | 7.07 | 19.0 |   |   |   | 0.61 | sharp, but entirely different (Fig. 7) |
| 5 | 12 | 132 | 3.77 | 9.3 |   |   |   | 4.65 | sharp and identical |
| 6 | 14 | 144 | 6.58 | 15.8 |   |   |   | 1.59 | rel. sharp and practically identical |
| 7 | 16 | 78 | 1.92 | 5.6 | 28 | 4.29 | 14.2 | 4.21[b] | similar to solid above 28°; broader than solid at 5°. |
| 8 | 18 | 98 | 6.46 | 17.4 | 86 | 2.83 | 7.9 | 2.77[c] | very different, broad abs. regions |
| 9 | 20 | 54 | 13.16 | 40.3 |   |   |   | 4.07 | very different, broad abs. regions |

[a] Reported 1.30 D.[14]  [b] Reported 4.28 D.[27]  [c] Reported 2.78 D.[27]

Conformer *a* has four such short distances, while conformer *b* has only two. The opposite situation, with the short distance being repulsive, can be excluded on the basis that a similar arrangement is preferred even in an open-chain aldehyde, 3-methylbutanal.[8] Our conclusion is therefore that cyclotetradecane-
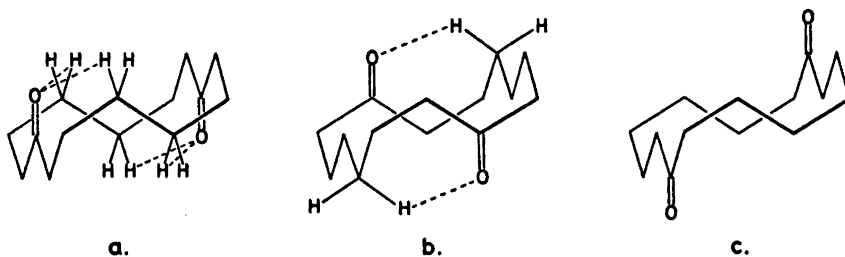


*Fig. 3.* Three of the four diamond-lattice conformations of cyclotetradecane-1,8-dione. Of the eight *gauche* H — H interactions four are eliminated in *a* and *b*, two in *c*. Of attractive H — O interactions there are four in *a*, two in *b*, and none in *c*.
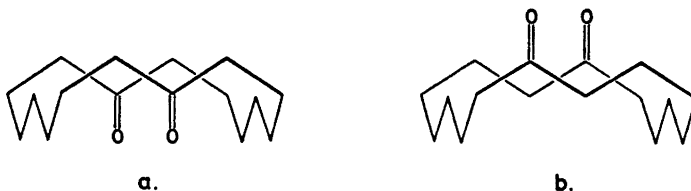


*Fig. 4.* Two of the three diamond-lattice conformations of cyclohexadecane-1,9-dione. Of the eight *gauche* H — H interactions four are eliminated in *a*, two in *b*. Of attractive H — O interactions there are four in *a*, and none in *b*.

1,8-dione has the conformation shown in Fig. 3a, with exactly the same carbonyl positions as in the 3,3,6,6,10,10,13,13-octamethyl derivative.*

By the same arguments, *cyclohexadecane-1,9-dione* ought to have the square ring conformation shown in Fig. 4, and the carbonyl groups ought to be $\beta$ to two corner atoms as in $a$, rather than $\alpha$ to one corner atom as in $b$. Most likely, therefore, conformer $a$ is the low-temperature crystal conformer. Whether there are additional conformers present in the high-temperature solid, in the liquid, and in $CS_2$-solution, is hard to decide. The changes in the infrared spectrum consist mainly in broadening of the sharper bands of the low-temperature solid, and we therefore believe that the same conformation is preponderant but has become more "loosened". Cyclohexadecane itself, which most likely has the square conformation in the homogeneous low-temperature solid,[7] adopts other ring skeletons for the additional conformers present in solution. It therefore seems as if the carbonyl group interaction with methylene groups across corners does stabilize the square conformation $a$, and that this effect dominates over the flexibility expected initially in the ring bonds next to the carbonyl group. A similar and even stronger conformational stabilization has been noted when an ether function is $\beta$ to two corner atoms as in the case of 1,5,9,13-tetraoxacyclohexadecane.[7,10]

*Cyclododecane-1,7-dione* forms a transition to the medium rings, and if one assumes that the carbon skeleton is of the same square type preferred by the hydrocarbon [11] and that corner positions are avoided, then there is only the conformer shown in Fig. 5 to be expected. Each carbonyl group is then $\beta$ to

*Fig. 5.* Proposed conformation for cyclododecane-1,7-dione.
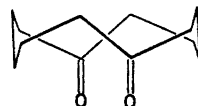


one corner atom, assumed to be stabilizing in larger rings, and it also replaces a $CH_2$-group having an intraannular hydrogen atom, assumed to be strain-releasing in medium rings.[11] The high observed dipole moment fits this conformation, and the invariant infrared spectrum shows that it is unique.

The assignment of conformation to *cyclodecane-1,6-dione* would then seem equally straightforward, particularly since in conformer $a$ of Fig. 6 the strongest
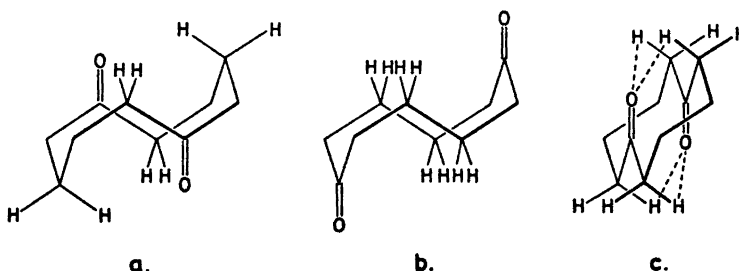


a.          b.          c.

*Fig. 6.* Possible conformations for cyclodecane-1,6-dione.

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* Dr. J. D. Schofield has pointed out to us that the empirically derived rule [9] that $\alpha$-hydrogen atoms tend to take up the two positions at 120° rather than the position eclipsing the carbonyl group, would also lead to a preference for conformer $a$ of Fig. 3.

transannular hydrogen interactions of cyclodecane are relieved, and no other possible disposition of the carbonyl groups on the same skeleton, such as in *b*, can lead to a comparable tension release. Conformer *a* has also been shown [11] to be present in the crystal lattice. It therefore comes as a surprise that the infrared spectrum of the melt, and of solutions in $CS_2$ and $CCl_4$, is entirely different from that of the crystal (Fig. 7). The sharp bands of the crystal
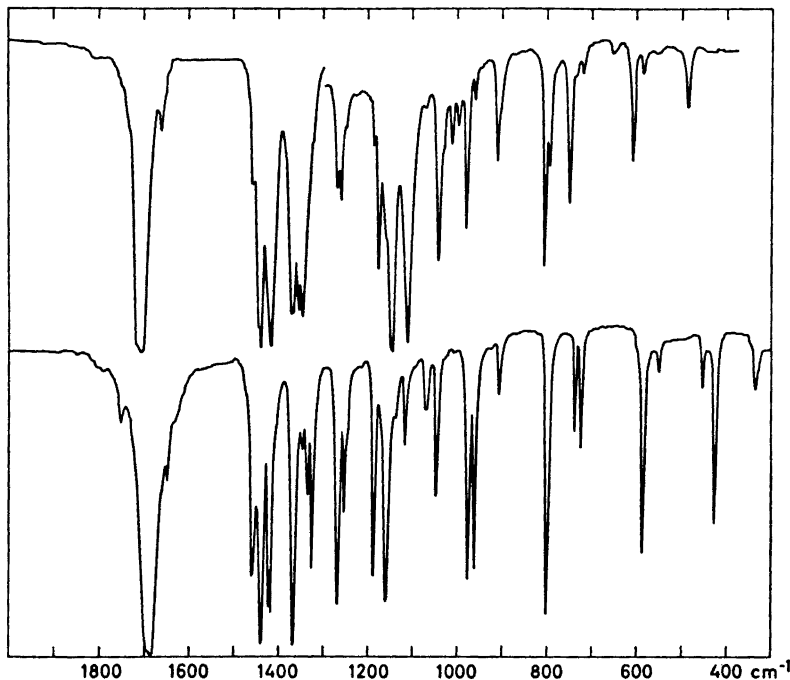


*Fig. 7.* Infrared spectra of cyclodecane-1,6-dione as solid in KBr (bottom), and as solution in $CCl_4$ above 1300 cm$^{-1}$, in $CS_2$ below 1300 cm$^{-1}$ (top).

have not broadened; they are present in low intensity corresponding to a few per cent, but have largely been replaced by a new set of sharp bands. A single new conformer has thus become dominant in solution. A second anomaly is the observed large value both of the enthalpy and the entropy of melting, which would indicate that strong packing forces favour the crystal conformer and keep the molecule rigid. The very low observed dipole moment suggests not only that the solution conformer is also centrosymmetric, but that the carbonyl groups are in close intramolecular association.* We propose that the conformation may be of type *c*, where the carbonyl – carbonyl distance can be adjusted to an optimum value without bond-angle strain, and where transannular $C-H\cdots O$ contacts (Fig. 6c) may be stabilizing.

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* A temperature variant NMR spectrum, coalescence temperature around − 90°, also indicates rigidity, but the coupling pattern of the low-temperature spectrum is too complex to give information about the geometry.

*Cyclooctane-1,5-dione* has the same conformation in solid and solution, as seen from the identical infrared spectra, and the line sharpness suggests that it is very well-defined.* The very large dipole moment restricts first of all the discussion to a limited number of non-centrosymmetric ring conformations,[2] and secondly to one way of placing the carbonyl groups on each of them. The three conformations shown in Fig. 8 seem the most likely candi-
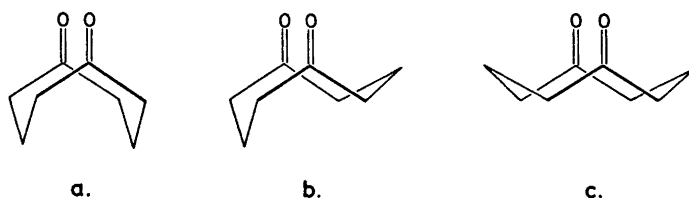


*Fig. 8.* Possible conformations for cyclooctane-1,5-dione.

dates. These have all the obvious motive for accepting carbonyl groups in the indicated positions that the most serious transannular hydrogen – hydrogen interaction of the hydrocarbon is eliminated.[11] The boat-boat (or saddle) *a* seems less likely than the others because it has a second transannular repulsion which is not improved, and the parallel carbonyl dipoles come too close. Of the remaining two conformations, the chair-chair (or stretched crown) *c* is better balanced energetically than the boat-chair *b*, since the four low-torsional-barrier bonds adjacent to the carbonyl groups fit into the four rather eclipsed positions, while the remaining four high-torsional-barrier bonds occupy the four staggered positions.[2] The energy may be further minimized by slightly moving the repelling dipoles away from each other towards a symmetric crown, or past each other towards a twist-chair-chair.

Finally, *cyclohexane-1,4-dione*, which would be expected to adopt a normal chair conformation (Fig. 9a) but is known [12] to be an unsymmetrical twist-boat *b* with an angle of 154° between the carbonyl groups in the lower solid phase, has definitely a different and simpler spectrum in $CS_2$ and $CCl_4$ solution [13] and in the melt (Fig. 10), and an intermediate spectrum in the upper solid phase. The observed apparent dipole moment [14] might well be due to a large atomic polarization, since by a different technique, the electric deflection of a molecular beam, the dipole moment is found [15] to be zero. This might all have been taken as a proof for the chair conformation if the infrared spectral differences were not too marginal to support a change from a twist-boat to
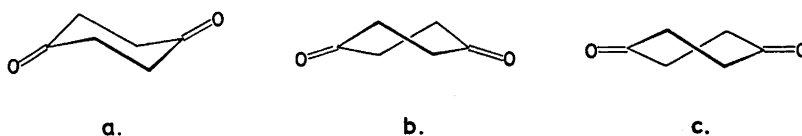


*Fig. 9.* Possible conformations for cyclohexane-1,4-dione.

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* Again, the NMR spectrum, coalescence temperature around − 120°, supports rigidity but gives no detailed information.
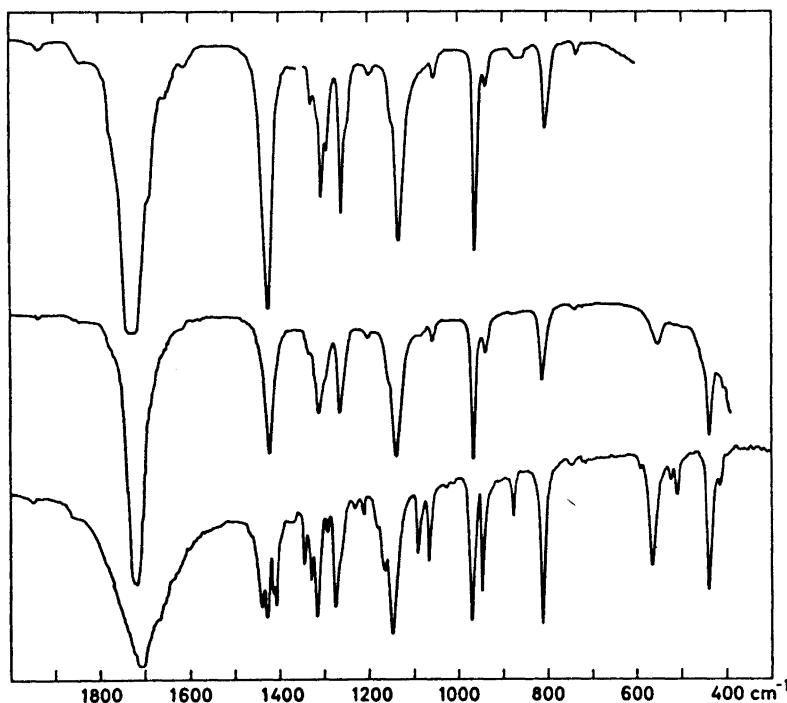
*Fig. 10.* Infrared spectra of cyclohexane-1,4-dione as solid in KBr at 20° (bottom), as melt (middle), and as solution in $CCl_4$ above 1350 cm$^{-1}$, in $CS_2$ below 1350 cm$^{-1}$ (top).

the chair. A way out of this impasse is to postulate that the free molecule is an energetically better balanced extended twist-boat *c* of $C_2$-symmetry having the low-torsional-barrier bonds adjacent to the carbonyl groups in the four partially eclipsed positions, leaving the two staggered positions for the remaining high-torsional-barrier bonds. This implies of course that no pseudorotation can take place and that crystal packing forces favour an unsymmetrical twist-boat. Conformation *c* explains the zero dipole moment of the gas,[15] and that the main infrared spectral differences occur in the $CH_2$-scissoring region around 1420 cm$^{-1}$ (Fig. 10). Thus, a single scissoring frequency in solution is in accord with one type of $CH_2$ in a molecule with a two-fold axis, while the crystal conformer *b* has two types so that the number of bands may be further increased to four by crystal splitting, commonly observed in such compounds.

In conclusion, it should be stressed that in this series of cyclic diketones the choice of ring conformation, and of carbonyl position on this, seems to be determined by a variety of factors: $\beta$-Carbonyl-$\alpha$-hydrogen stabilization across corners in large rings, elimination of transannular hydrogen repulsion as well as dipole interaction in medium rings, the fitting of low-torsional-barrier bonds to the most eclipsed positions in six- and eight-membered rings, and packing forces in the solid.

## CONFORMATIONS OF CYCLIC BIS-KETALS

The dipole moments (Table 2 and Fig. 11) of the bis-ethylene ketals (II) are seen to hardly vary with ring size, in striking contrast to the strong alterna-

*Table 2.* Physical properties of bis-ethylene ketals (II).

| $n$ | Number of ring atoms | M.p. °C | $\Delta H_m$ (kcal/mol) | $\Delta S_m$ (e.u.) | Dipole moment in benzene (D) | Infrared spectrum in $CS_2$-solution as compared with solid |
|-----|-----|-----|-----|-----|-----|-----|
| 2 | 6  | 80  | 5.16  | 14.6 | 1.26 | practically identical |
| 3 | 8  | 23  | 4.31  | 14.6 | 1.61 | practically identical |
| 4 | 10 | 177 | 7.81  | 17.4 | 1.30 | as sharp bands, identical |
| 5 | 12 | 205 | 8.83  | 18.5 | 1.33 | as sharp bands, identical |
| 6 | 14 | 184 | 7.33  | 16.0 | 1.23 | as sharp bands, identical |
| 7 | 16 | 131 | 10.07 | 24.9 | 1.23 | almost identical, but broader bands |
| 8 | 18 | 105 | 8.02  | 21.2 | 1.22 | very different, broad abs. regions |
| 9 | 20 | 89  | 10.45 | 28.9 | 1.33 | very different, broad abs. regions |

tion observed (Fig. 1) for the diketones (I) from which they are derived. As the dipole moment contribution of one ketal group should be about 1.1 D,* the statistical value for free relative orientation is around 1.5 D ( = 1.1 D × $\sqrt{2}$). Only the 8-membered ring has a value slightly higher; all the others are similar and well below. Even if the ethylene-ketal dipole may be less well-defined
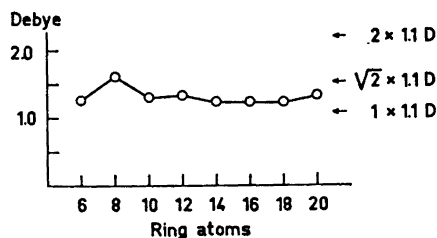


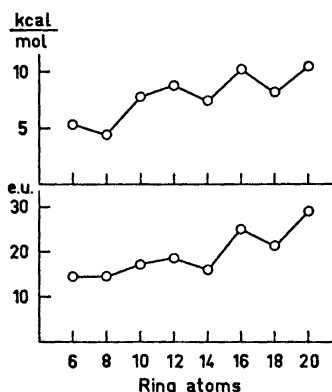*Fig. 11.* Dipole moments in benzene solutions at 25° of cycloalkanedione bis(ethyleneketals)(II).



*Fig. 12.* Enthalpies (top) and entropies (bottom) of melting for cycloalkanedione bis(ethyleneketals)(II).

* Adopted from the measured molecular dipole moment of the ethylene ketals of cyclohexanone, 1.06 D, and of acetone, 1.13 D.

in direction than the ketone dipole, the systematic low value for all members, except the 8-ring, strongly suggests that in all of these the ketal groups are in corner-like positions of diamond-lattice conformations and, unlike the carbonyl group, avoid side positions. It may thus be concluded that the *gem*-dialkoxy group behaves like the *gem*-dimethyl group, and that the adjacent ring CC-bonds may not differ markedly as regards torsional barrier from the other ring CC-bonds. Essentially then, these compounds behave conformationally like saturated hydrocarbons.

The infrared spectra (Table 2) are identical or nearly so in solid and solution for rings up to and including the 16-membered, suggesting that these are all conformationally homogeneous in solution. However, the melting entropies (Table 2 and Fig. 12) would rather indicate that the 16-membered ring follows the higher rings, which are seen without any doubt to be conformer mixtures from the complexity of their infrared solution spectra. We consider it more hazardous to rely on the interpretation of the melting entropy than the criterion of infrared spectroscopy, and conclude that the  16-membered ring has a single conformer, the square one shown in Fig. 13 with the ketal
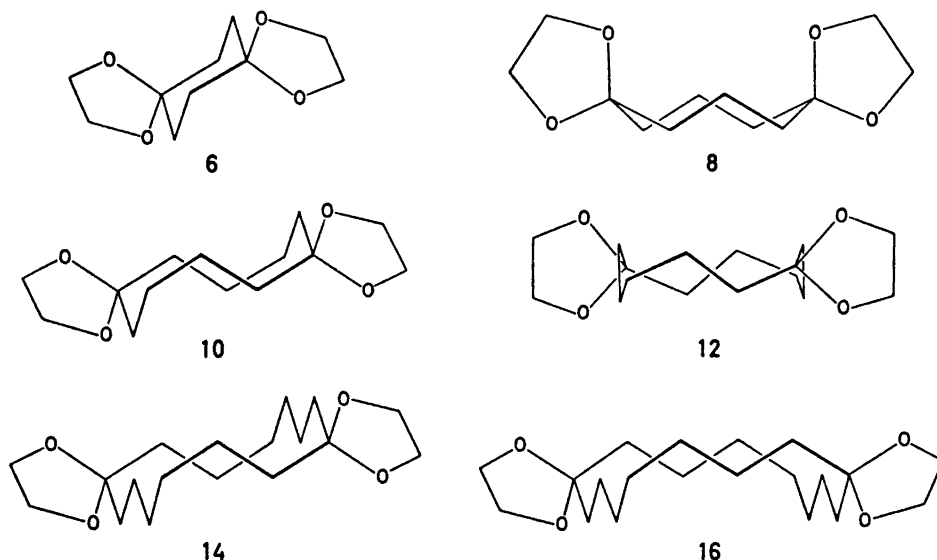


**Fig. 13.** The most probable conformations of cycloalkanedione bis(ethyleneketals) (II). Numbers indicate ring size.

groups in corner positions. The melting entropy of the 18-membered ring, on the other hand, is lower than expected in view of the complex infrared spectrum. Compared with cyclooctadecane itself [16] ($\Delta S_m = 30.1$ e.u.) the diametric ketal groups lower the melting entropy considerably ($\Delta S_m = 21.2$ e.u.), even more than do diametric gem-dimethyl groups [16] ($\Delta S_m = 26.3$ e.u.), but both are definitely conformer mixtures. It seems likely that the variations in

melting entropy of the bis-ketals are due at least partially to differences in packing, since the melting enthalpy varies in the same sense (Fig. 12).

The single preferred conformer for the 6-, 10-, and 14-membered rings is also no doubt of diamond-lattice type (Fig. 13), well established [6],[11] for saturated hydrocarbon ring skeletons. The 12-membered ring is assumed to adopt the same ring-conformation as found [11] for cyclododecane itself, approximately square, but not of diamond-lattice type (Fig. 13). The 8-membered ring is the only ambiguous case, since with the requirement that the dipoles shall not be antiparallel and that steric hindrance must be avoided, then, using calculated methyl substituent interaction energies [2] as a guide, there remain a limited number of possibilities within the crown family, of which we favour the chair-chair (stretched crown) with substituents as indicated in Fig. 13. Once again, the 8-membered ring occupies a very special position amongst carbocyclic rings.

## EXPERIMENTAL

*Preparation of cycloalkanediones (I)*. These are all described compounds, although the method of preparation was different in two cases (see below).

*Cyclohexane-1,4-dione* was a commercial product (Fluka).

*Cyclooctane-1,5-dione* was prepared from cycloocta-1,5-diene by hydroboration in tetrahydrofuran to give 9-borabicyclo[3,3,1]nonane,[17] subsequent oxidation with alkaline hydrogen peroxide to *cis*-cyclooctane-1,5-diol,[17] and final oxidation to the diketone with chromic acid oxidizing reagent,[18] the last step in 85 % yield.

*Cyclodecane-1,6-dione* was prepared by ozonation of $\Delta^{9,10}$-octalin,[19] obtained by partial reduction of naphthalene with lithium in an alkylamine mixture.[20] The best yields were obtained when the ozonation was carried out rapidly (2 – 3 h instead of 18 – 24 h [19]).

*Cyclododecane-1,7-dione* was prepared from cyclododeca-1,5,9-triene as already reported.[4]

*Cyclotetradecane-1,8-dione* was prepared from suberic acid by ketene cyclization.[21]

*Cyclohexadecane-1,9-dione* was prepared from azelaic acid, also by ketene cyclization.[22]

*Cyclooctadecane-1,10-dione* was prepared from sebacic acid diester by Dieckmann cyclization.[23]

*Cycloeicosane-1,11-dione* was prepared from undecanedioic acid dinitrile by Ziegler cyclization.[24]

*Preparation of bis-ethylene ketals (II)*. All bis-ketals, except that of cyclodecane-1,6-dione (see below), were prepared by azeotropic distillation of water from a mixture of the diketone and ethylene glycol in benzene containing a little *p*-toluene sulfonic acid, in the same way as described for other ketones by Hartley.[25] The higher-melting compounds were recrystallized from methanol. The bis-ketal of cyclooctane-1,5-dione was lower-melting and more soluble and had to be crystallized from a mixture of petrol and methanol at − 20°. This compound should not be kept long in contact with water or humid air, as partial hydrolysis takes place easily. The yields were in all cases about 90 % after recrystallization.

*Cyclodecane-1,6-dione bis(ethylene ketal)*. A solution of 4,4,9,9-tetramethoxy-*cis,cis*-cyclodeca-1,6-diene [26] (2 g), ethylene glycol (5 g) and *p*-toluenesulfonic acid (0.2 g) in benzene (200 ml) was stirred overnight. The solution was washed first with sodium hydrogen carbonate solution (10 %), then twice with water, dried and evaporated to yield *cis,cis*-cyclodeca-1,6-diene-4,9-dione bis(ethylene ketal) [5] (1.9 g), m.p. 186°. This was dissolved in dioxan and hydrogenated over palladium on charcoal at room temperature and 90 atm. Several attempts at lower pressure failed to give complete saturation. Recrystallization from methanol afforded cyclodecane-1,6-dione bis(ethylene ketal) (95 % yield), m.p. 174 – 176°.

*Physical measurements*. Dipole moments, calorimetric values and infrared spectra were obtained as specified in a preceding paper (*cf.* note on p. 1805).

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