the pure dimethylformamide as a blank at each selected wave length and no absorption was observed. Results are given in Table VI.

Statistical examination of the last four determinations shows a significant correlation with concentration, the equilibrium shifting toward slightly greater dissociation with greater concentration. Correlation coefficient, 0.865. Probability of correlation, about 60 to 1.

Acknowledgment.—One of us (P. E. W.) wishes to acknowledge a grant-in-aid from the Hynson, Westcott, and Dunning Research Fund.

Conformational Analysis. XXXIII. On the Conformation of the Cycloöctane Ring[1,2]

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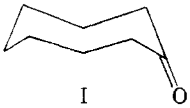
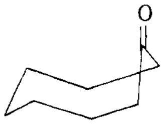
The dipole moments of 5-(*p*-chlorophenyl)-cycloöctane ethylene ketal and appropriate related compounds have been interpreted in terms of a stretched crown conformation for the cycloöctane ring. Reinterpretation of earlier data shows that such a conformation fits all available information. The carbonyl carbon of the ketone prefers to be at a specific location on the crown, while in the ketal a different location is preferred. These results are interpreted in terms of van der Waals and torsional forces.

The basic conformation of the cycloöctane ring appears to be fairly well established as that of a crown.[4–13] The approximate nature of this crown is known in one instance from X-ray diffraction studies.[6] Since cycloöctane and its derivatives in general appear to possess only a single conformation, it seems likely that the same conformation of the ring is to be found in most cases. Such data as are available appear consistent with this idea. There remains the problem in substituted cycloöctanes of the location of the substituents on the different non-equivalent carbons.

Cycloöctanone represents a simple derivative, the geometry of which may be reconsidered in the light of recent work. An earlier interpretation[7] of its conformation appeared to give evidence for a mixture of two conformations (I and II). More recent evidence has shown[5] that the experimental facts are consistent only with I. The structure II is probably of higher energy than previously realized because of the repulsion between the carbonyl carbon and the C-4 and C-6 methylenes. The recently found small values for the 3-alkylketone effect[14] are consistent with this interpretation.


I


II

There appear to be three separate studies in the literature which offer experimental evidence which must be accommodated by any structure for cyclooctanone that is proposed. These are studies on the 5-heterocycloöctanones,[11] on α-bromocyclooctanone,[15] and on 5-*p*-chlorophenylcycloöctanone.[7] If it is assumed that the basic ring structure is the stretched crown (Fig. 1), there remains only the problem of the location of the carbonyl, at C-1, C-2, or C-3. Leonard's dipole moment results[11] show a very small angle between the dipoles of 5-oxacycloöctanone, and are consistent with the carbonyl being at C-1, but not at C-2 or C-3. The dipole moment of 5-(*p*-chlorophenyl)-cyclooctanone[7] is likewise consistent only with the carbonyl being at C-1.

Earlier, the available data on α-bromocycloöctanone was interpreted[15] in terms of an equilibrium involving forms I and II. It was remarked at the time that the data were insufficient to establish that such an equilibrium existed, but it could be shown that the data were consistent with such an equilibrium. Since it is now clear that such an equilibrium does not exist, these data remain to

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[1] Paper XXXII, N. L. Allinger and M. A. DaRooge, *J. Am. Chem. Soc.*, **84**, 4561 (1962).

[2] This research was supported by grants number G 10346 and 19981 from the National Science Foundation.

[3] Predoctoral U. S. Public Health Service Fellow, General Division of Medical Sciences, 1960–1962.

[4] (a) E. Billeter, T. Bürer, and H. H. Günthard, *Helv. Chim. Acta*, **40**, 2046 (1957); (b) T. Bürer and H. H. Günthard, *ibid.*, **40**, 2054 (1957).

[5] (a) N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961); (b) N. L. Allinger and S. Greenberg, *ibid.*, **84**, 2394 (1962).

[6] J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960).

[7] N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **81**, 5733 (1959).

[8] (a) R. Kolinski, H. Piotrowska, and T. Urbanski, *J. Chem. Soc.*, 2319 (1958); (b) H. R. Bellis and E. J. Slowinski, Jr., *Spectrochim. Acta*, 1103 (1959).

[9] (a) G. Chiurdoglu, T. Doehaerd, and B. Tursch, *Chem. Ind.* (London), 1453 (1959); (b) G. Chiurdoglu, T. Doehaerd, and B. Tursch, *Bull. soc. chim. France*, 1322 (1960).

[10] T. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960).

[11] N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).

[12] (a) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951); (b) N. L. Allinger, *ibid.*, **81**, 5727 (1959).

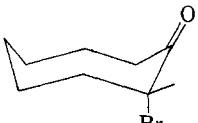
[13] For a summary of earlier work, see V. Prelog, *J. Chem. Soc.*, 420 (1950).

[14] (a) N. L. Allinger and L. A. Freiberg, *ibid.*, **84**, 2201 (1962); (b) B. Rickborn, *ibid.*, **84**, 2414 (1962).

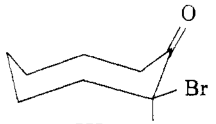
[15] J. Allinger and N. L. Allinger, *J. Org. Chem.*, **25**, 262 (1960); *J. Am. Chem. Soc.*, **81**, 5736 (1959).

be reinterpreted on the basis of what is now believed to be the correct conformational picture, and should confirm or deny this picture.

The conformational situation in 2-bromocyclohexanone is well understood.[16] Dipole moment data[15] show that in 2-bromocycloöctanone the mean average angle between the dipoles is somewhat larger and is less solvent dependent than in 2-bromocyclohexanone. The extended crown form of 2-bromocycloöctanone would, if the carbonyl is at C-1, be expected to be a conformational mixture of IIIa and IIIe. From Catalin models, the dihedral angles between the dipoles are approximately 174° in IIIa, and 55° in IIIe. This means that the angles between the dipoles are about 168 and 72°, respectively. To calculate the moment of each conformation, the group moments are necessary. Because of mutual induction, the group moments of the individual dipoles will be smaller in the equatorial conformer than in the axial. For the latter, mutual induction was neglected, the C–Br moment used was that of cyclohexyl bromide (2.24 D.),[17] and the carbonyl moment was that of cycloöctanone (2.93 D.).[18] For the equatorial conformer, since the dihedral angle is 55° here (compared to 16° in the cyclohexanone case), the inductive effect was taken (somewhat arbitrarily) to be only half that found for the six-membered ring, and group moments of 2.08 D. for the C–Br dipole and 2.88 D. for the carbonyl were used. These numbers gave calculated moments of 1.3 and 4.0 D. for the axial and equatorial conformers, respectively. The observed moments (3.30 D. in heptane, 3.36 D. in benzene, and 3.42 D. in dioxane) indicate that an equilibrium exists, IIIe being the main component (to the extent of about 70%), and it predominates to the greater extent in the more polar solvents. The repulsion between the dipoles is less serious here for both conformers than for the corresponding conformers in the six-membered ring. Consequently, it is expected that the conformational equilibrium will be less solvent dependent than in the six-membered ring, as is found. In the eight-membered ring, the axial bromine appears to be in a considerably more crowded position than that found in the six-membered ring, which should shift the equilibrium more toward the equatorial conformer in the present case. In agreement with this prediction, in benzene solution the amount of equatorial conformer is 67% for the eight-membered ring, as opposed to 24% in the six-membered case.



IIIa



IIIe

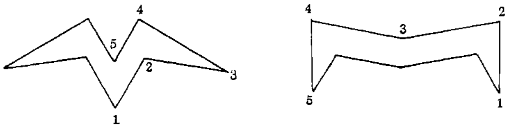


Fig. 1.—Geometry of the assumed structure of the cyclooctane crown (C_{2v}).

The carbonyl band in the infrared spectrum of 2-bromocycloöctanone is broad and not well resolved. The spectral shift appears to be some 10 cm.$^{-1}$, which is similar to what is found with bromocamphor[19] (14 cm.$^{-1}$), and is consistent with a majority of IIIe in the mixture. Similarly, the ultraviolet spectra show log ϵ values near 2 and a $\Delta\lambda$ of about +20 mμ, which values vary little with solvent, and again this is comparable with values found for the 3-bromocamphors (log ϵ 1.95 and $\Delta\lambda$ of +22 mμ for the α and +24 mμ for β)[20] and suggests that the conformation of the compound is very largely IIIe. Thus, all of the available data appear to indicate that the carbonyl group of cycloöctanone is located at C-1. This preference for the C-1 position of the carbonyl must be due to torsional barriers, nonbonded interactions, or both. A model does not indicate any very serious nonbonded interaction if the ketone is at C-3 except between the hydrogens at C-1 and C-5, which probably are much closer together than the sum of their van der Waals radii. If the ketone is at C-1, this interaction is eliminated. A van der Waals calculation using the method of Hill[21] assuming the H—H distance is 1.8 Å. (by analogy with the larger rings[6]) gives for this interaction an energy of 0.78 kcal., so this may be a significant factor in determining the position of the carbonyl.

The second factor which needs consideration is the change in torsional energy between the carbonyl being at C-1 and at C-3, and simultaneously the methylene being at C-3 and C-1. The methylene at C-1 had a dihedral angle of about 0° (eclipsed) with the methylenes on either side, while at C-3 this angle is near 60° (staggered). Thus the latter is favored by about 6 kcal./mole.[12,13] The carbonyl at C-1 is probably more favorable than at C-3, but in any case the difference is small,[22] probably less than 2 kcal./mole. Hence the prediction is clear cut, the ketone should be, and is, at C-1.

Next, one may consider what will happen when cycloöctanone is converted to the ethylene ketal.

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(16) (a) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958); (b) J. Allinger and N. L. Allinger, *J. Am. Chem. Soc.*, **80**, 5476 (1958); (c) N. L. Allinger, J. Allinger, and N. A. LeBel, *ibid.*, **82**, 2926 (1960); and (d) E. J. Corey, *ibid.*, **75**, 2301 (1953).

(17) P. Bender, D. L. Flowers, and H. L. Goering, *ibid.*, **77**, 3463 (1955).

(18) H. H. Günthard and T. Gäumann, *Helv. Chim. Acta*. **34**, 39 (1951).

(19) F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

(20) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

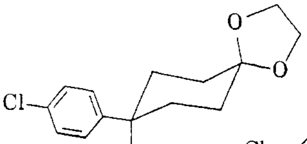
(21) (a) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948); (b) N. L. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

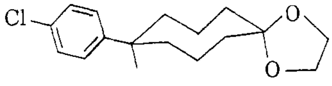
(22) See footnote 12 in ref. 1.

Here all of the advantages of having the oxygenated carbon at C-1 have been lost, and an additional disadvantage has been incurred, namely, the large oxygen at C-1 is now interacting with the hydrogen at C-5. While the energy of the H—H interaction was calculated to be only 0.78 kcal./mole, that of the O—H interaction[21] would be 10.5 kcal./mole if no additional distortion occurred. Consequently, while the ketone prefers to be at C-1, the ketal should prefer to be at C-3.

An experimental test of the prediction regarding the ketal conformation was possible by dipole moment measurements on the 5-(*p*-chlorophenyl) derivative (VII). The synthesis of the ketone was described earlier,[7] and the ketal was obtained from the ketone with ethylene glycol in the usual way.

Since the geometry of the cyclohexanone ring is well known, the following dipole moments were measured as models: cyclohexanone ethylene ketal (IV), 4-(*p*-chlorophenyl)-cyclohexanone ethylene ketal (V), and cycloöctanone ethylene ketal (VIII). The moment of *p*-chlorotoluene was also determined.


V


VII

The dipole moment of IV was initially assumed to lie in the plane of the five-membered ring, that is, along the line connecting C-1 and C-4. The numerical value of the moment was found to be 1.03 D. From the values of the moments of *p*-chlorotoluene (1.95 D.) and cyclohexanone ethylene ketal and the angle between the dipoles 1/2 (109° 28′), the moment of V was calculated to be 2.68 D. The high energy of the axial phenyl[23] makes the neglect of the axial phenyl possible. As long as regular tetrahedral angles are assumed though, the resultant moment is the same whether the phenyl is axial or equatorial.

Now there are at least three points to be considered with regard to errors in this model. First, some deviation in the tetrahedral angle at C-4 is likely and will introduce some error.[24] The very similar geometry in the eight-membered ring should introduce a very similar error however, so in a comparison the errors should very nearly cancel.

A further error is introduced by the lack of planarity which is likely in the five-membered ring. This will mean the lone pairs on the oxygens may contribute a component perpendicular to this plane. Also, the neglect of atomic polarization in determining the moment of IV probably will introduce some error.[25] The direction of the latter two errors is such that the experimental value of the moment of V should be smaller than calculated, and it is only 2.54 instead of 2.68 D. The difference is quite small, however, so it could be ignored. It is felt that a similar difference is to be expected between the calculated and experimental values in the case of VII however, and so a small correction for these effects was made. The experimental moment of VII was 2.73 D. Hence, this value was corrected to a calculated value of 2.87 D., and the angle between the moments was calculated from the latter and the moments of VIII and *p*-chlorotoluene. The angle so calculated was 23°. According to Catalin models, the angle between the dipoles if the ketal is at C-3 is about 30°, while at C-1 it is near 90°. Of the two, the

TABLE I

DIPOLE MOMENT DATA, BENZENE SOLUTION 25°C.

Cyclohexanone Ethylene Ketal (IV). M_R 38.50 cc.

N_2	d_{12}	ϵ_{12}
0.00000000	0.873332	2.2728
0.00345069	0.874164	2.2776
0.00430222	0.874255	2.2785
0.00709277	0.875117	2.2819
0.00885484	0.875403	2.2845
$\alpha = 1.299$	$\epsilon_1 = 2.2729$	$d_1 = 0.87331$
$\beta = 0.242$	$P_{2\infty} = 60.21$	$\mu = 1.03 \pm 0.05\ D.$

4-(*p*-Chlorophenyl)-cyclohexanone Ethylene Ketal (V). M_R 67.69 cc.

N_2	d_{12}	ϵ_{12}
0.00000000	0.873052	2.2719
0.00050183	0.873450	2.2762
0.00151145	0.874223	2.2855
0.00217803	0.874717	2.2919
0.00315391	. . .	2.3010
$\alpha = 9.261$	$\epsilon_1 = 2.2717$	$d_1 = 0.87306$
$\beta = 0.765$	$P_{2\infty} = 199.1$	$\mu = 2.54 \pm 0.03$ D.

5-(*p*-Chlorophenyl)-cycloöctanone Ethylene Ketal (VII). M_R 77.22.

N_2	d_{12}	ϵ_{12}
0.00000000	0.873559	2.2763
0.00045491	0.873895	2.2808
0.00111247	0.874378	2.2879
0.00211203	0.875269	2.2990
0.00364816	0.876496	2.3153
$\alpha = 10.766$	$\epsilon_1 = 2.2761$	$d_1 = 0.87353$
$\beta = 0.813$	$P_{2\infty} = 229.0$	$\mu = 2.73 \pm 0.02$ D.

Cycloöctanone Ethylene Ketal (VIII). M_R 47.99.

N_2	d_{12}	ϵ_{12}
0.00000000	0.873213	2.2718
0.00181765	0.873801	2.2741
0.00603969	0.875079	2.2793
0.00876745	0.875814	2.2828
0.00583294	0.874953	2.2790
$\alpha = 1.242$	$\epsilon_1 = 2.2718$	$d_1 = 0.87324$
$\beta = 0.297$	$P_{2\infty} = 67.24$	$\mu = 0.97 \pm 0.04$ D.

p-Chlorotoluene. M_R 35.94 cc.

N_2	d_{12}	ϵ_{12}
0.00000000	0.873646	2.2735
0.00348029	0.874503	2.2920
0.00266930	0.874257	2.2879
0.00388391	0.874599	2.2939
0.00597755	0.875106	2.3054
$\alpha = 5.326$	$\epsilon_1 = 2.2735$	$d_1 = 0.87363$
$\beta = 0.246$	$P_{2\infty} = 113.9$	$\mu = 1.95 \pm 0.02$ D.

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[23] (a) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960); (b) N. L. Allinger, J. Allinger, M. A. DaRooge, and S. Greenberg, *J. Org. Chem.*, **27**, 4603 (1962).

[24] E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).

former is definitely in reasonable agreement with the experimental value while the latter is not.[26]

The infrared spectrum of VII does not show any bands in solution which are not shown by the mull. Hence, a single fixed conformation, rather than an equilibrium, is indicated.

Chiurdoglu and co-workers[9] have shown that the methylene deformation band in the 1450 cm.$^{-1}$ region can be of use as an indication of the minimum number of different kinds of methylenes which are to be found in a molecule. This region of the spectrum was examined for all the compounds discussed, and in each case the number of bands in this region was less than or equal to the number predicted from the different kinds of methylenes thought to be present. This criterion therefore is consistent with what has already been concluded, but yields no new information.

The conclusions drawn are that, as suggested earlier,[4–13] cycloöctane ring in general appears to exist in a single conformation, that of a stretched crown. Ring substituents may be expected to take up various positions depending on their nature. A carbonyl group prefers to be at C-1, while its ketal prefers C-3.

Experimental

Cyclohexanone Ethylene Ketal (IV).—The preparation was carried out in the usual way.[27] The product was distilled through a spinning band column and the fraction distilling at 60–61° (10 mm.) was collected, wt. 5.1 g., n^{20}_{D} 1.4580 (reported[27] b.p. 65° (10 mm.), n^{21}_{D} 1.4580).

Cycloöctanone Ethylene Ketal (VIII).—Five grams of cycloöctanone, 25 ml. of ethylene glycol, and 0.5 of *p*-toluenesulfonic acid monohydrate were refluxed in dry benzene for 80 hr. using a water separator. The reaction mixture was worked up as described for IV. The fraction distilling at 76–77° at 5 mm., 3.8 g., n^{22}_{D} 1.4755 was collected.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.52; H, 10.67. Found: C, 70.67; H, 10.65.

4-(*p*-Chlorophenyl)-cyclohexanone Ethylene Ketal (V).—The ketal was prepared from *p*-chlorophenylcyclohexanone[23b] exactly as described for IV. The crude material was crystallized from pentane to give a 75% yield of product of m.p. 85–86.5°.

Anal. Calcd. for $C_{14}H_{17}ClO_2$: C, 66.49; H, 6.67. Found: C, 66.73; H, 6.89.

5-(*p*-Chlorophenyl)-cycloöctanone Ethylene Ketal (VII).—The ketal was prepared from 5-(*p*-chlorophenyl)-cycloöctanone[7] exactly as described for the preparation of IV. The crude material (1.2 g.) was crystallized from pentane to give 1.0 g. (66%) of transparent crystals, m.p. 80–81°.

Anal. Calcd. for $C_{16}H_{21}ClO_2$: C, 68.41; H, 7.54. Found: C, 68.51; H, 7.66.

Dipole Moments.—The dipole moments of the various ketones were run at 25° in benzene solution and the data are given in Table I. The dipole moment apparatus has been described previously.[28] The moments were calculated by essentially the method of Halverstadt and Kumler,[29] utilizing an IBM 650 computer programmed as described earlier.[30] The molar refractivities were calculated from tables[31]; atomic polarization was neglected.

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[25] J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 256.

[26] The possibility that the ketal is located at C-2 cannot be eliminated on the basis of the experimental facts, but it seems unlikely. Likewise, a skewed crown can be made to fit the facts.

[27] M. Sulzbacher, E. Bergmann, and E. R. Pariser, *J. Am. Chem. Soc.*, **70**, 2827 (1948).

[28] N. L. Allinger, H. Blatter, M. A. DaRooge, and L. A. Freiberg, *J. Org. Chem.*, **26**, 2550 (1961).

[29] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[30] N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

[31] A. I. Vogel, W. T. Cresswell, G. J. Jeffrey, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

Cycloaddition of Diazo Compounds to Ethyleneboronic and Acetyleneboronio Esters[1]

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Cycloadditions of ethyl diazoacetate and diphenyldiazomethane to dibutyl acetyleneboronate yield pyrazoleboronic acids. Dibutyl ethyleneboronate undergoes similar cycloadditions, but the initial adduct immediately undergoes boron migration from carbon to nitrogen followed by disproportionation to butyl borate and material which yields a 5-substituted 2-pyrazoline on alcoholysis. The rate of addition of ethyl diazoacetate to dibutyl ethyleneboronate is 0.3 times that to ethyl acrylate and is but slightly affected by solvents or changing from the *n*- to the *t*-butyl ester. The evidence supports a concerted mechanism for the cycloaddition. The reactivity of dibutyl ethyleneboronate correlates well with simple molecular orbital calculations if $\alpha_B \cong \alpha_C - 0.7\beta_{C-C}$.

On the basis of simple molecular orbital calculations, the prediction has been made that suitable nucleophilic reagents should attack the β-carbon atom of α,β-unsaturated boronic esters.[2] Difficulty in testing this prediction arises because the boron atom competes rapidly and efficiently for bases—for example, Grignard reagents react at boron.[3] Nucleophilic attack at the β-carbon atom has now been verified with the cycloaddition of diazo compounds to dibutyl ethyleneboronate and

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[1] Supported by National Science Foundation Grants G9916 and G19906; presented at the 141st National American Chemical Society Meeting, Washington, D. C., March, 1962.

[2] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

[3] D. S. Matteson, *J. Org. Chem.*, **27**, 275 (1962).