

allow a more systematic description of the possible geometrical structures for larger rings containing seven or more atoms. The "spherical" coordinate system used for six-membered rings in which the total puckering amplitude is  $Q$  and the "distortion-type" is specified by two angular variables  $\theta$  and  $\phi$  can itself be generalized. Thus for an  $N$  ring, it should be possible to represent all types of puckering by location on the surface of a hypersphere in  $N - 3$  dimensions. Finally, the definition of a unique mean plane passing through the geometrical center should permit a more quantitative approach to the description of substituent orientation relative to such a plane. Studies in these directions are in progress.<sup>21</sup>

**Acknowledgment.** D.C. would like to thank the Deutsche Forschungsgemeinschaft for a generous grant. This research was supported in part by the National Science Foundation under Grant GP-25617. We are indebted to Dr. G. A. Jeffrey for valuable discussions.

### References and Notes

- (1) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947).
- (2) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, N.Y., 1945.
- (3) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959).
- (4) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).
- (5) P. Hazebroek and L. J. Oosterhoff, *Discuss. Faraday Soc.*, **10**, 87 (1951).
- (6) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); **85**, 4059 (1963); **86**, 4854 (1964); **89**, 7048 (1967).
- (7) J. D. Dunitz and J. Waser, *J. Amer. Chem. Soc.*, **94**, 5645 (1972).
- (8) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969).
- (9) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron Lett.*, **15**, 1383 (1967).
- (10) C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, **24**, 13 (1968).
- (11) C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **94**, 8205 (1972).
- (12) J. D. Dunitz, *Tetrahedron*, **28**, 5459 (1972).
- (13) H. M. Pickett and H. L. Strauss, *J. Amer. Chem. Soc.*, **92**, 7281 (1970).
- (14) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **55**, 324 (1971).
- (15) G. M. Brown and H. A. Levy, *Acta Crystallogr., Sect. B*, **29**, 790 (1973).
- (16) International Union of Pure and Applied Chemistry, Reports on Symbolism and Nomenclature, *J. Amer. Chem. Soc.*, **82**, 5517 (1960).
- (17) J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, Oxford, 1965.
- (18) D. Cremer, QCPE, Indiana University, Bloomington, Ind., to be submitted for publication.
- (19) A. Almendinger, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, **23**, 2748 (1969).
- (20) D. Cremer and J. A. Pople, *J. Amer. Chem. Soc.*, following paper in this issue.
- (21) D. Cremer, unpublished work.

## Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXIII. Pseudorotation in Saturated Five-Membered Ring Compounds

D. Cremer and J. A. Pople\*

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received June 10, 1974

**Abstract:** *Ab initio* molecular orbital theory is used to study the potential surfaces associated with ring puckering in cyclopentane, oxolane, 1,3-dioxolane, and cyclopentanone. A geometrical model is used which has fixed bond lengths and fixed angular conformations for methylene groups, but all other degrees of freedom are varied. Extensive geometry exploration is carried out with the minimal STO-3G basis and a more limited study with the split valence 4-31G basis. Estimates are made of changes in the potential surface that would occur if the calculations were carried out using the polarized 6-31G\* basis. It is found that the theory predicts puckering amplitudes in fair agreement with experimental data. For cyclopentane, all methods give nearly free pseudorotation. The oxolane surface also shows that a pseudorotational path is the favored route for conformational interconversion. The final results (6-31G\* estimates) indicate a twist (T) conformation ( $C_2$  symmetry) as the most stable form with a low barrier to pseudorotation into an envelope (E) conformation ( $C_s$  symmetry). Similar results with a somewhat higher barrier are obtained for 1,3-dioxolane. Cyclopentanone is also found to have its energy minimum in the twist (T) form, but in this case conformational interconversion occurs most easily along a path passing close to the planar skeleton form as a transition state, in good agreement with experimental findings. The qualitative factors underlying these results are analyzed in terms of the quantum mechanical calculations.

In 1947, Kilpatrick, Pitzer, and Spitzer<sup>1</sup> introduced the concept of pseudorotation to explain the high gas-phase entropy of cyclopentane. According to their thermodynamic data, they suggested that the cyclopentane ring is puckered rather than planar. This deformation, however, is not static but dynamic, the puckering displacements moving around the ring in a relatively free manner. Since that time, this pseudorotation phenomenon has been extensively documented by various experimental techniques,<sup>2-5</sup> not only for the hydrocarbon cyclopentane but also for various derivatives and compounds with one or more heteroatoms in the ring.<sup>6-19</sup> Unfortunately reliable information on the full pseudorotational potential and the populations of the various conformations is not easily derivable from experimental observation. It is therefore very desirable to develop quan-

tum mechanical treatments of the phenomenon in five-membered ring compounds. This should aid the interpretation of the important structural features influencing the properties of such molecules.

The aim of this paper is to initiate a systematic *ab initio* molecular orbital theory of pseudorotation. This requires a geometrical procedure to allow for finite puckering displacements of five-membered rings, followed by quantum mechanical calculations of the appropriate potential surface. The molecules studied in detail are cyclopentane, oxolane, 1,3-dioxolane, and cyclopentanone.

### I. The Geometry of Pseudorotation

The mathematical description of pseudorotation in a molecule such as cyclopentane is usually based on the out-

of-plane vibrations of a planar five-membered ring. For a planar regular pentagon of five equivalent atoms ( $D_{5h}$  symmetry), it is well known<sup>20</sup> that the degenerate  $e_2''$ -type small displacements move the atoms parallel to the fivefold axis. The displacements of successive atoms ( $i = 1, 2, 3, 4, 5$ ) are given by simple trigonometric functions

$$\begin{aligned} \nu_a(e_2''): z_i^{(a)} &= z_0 \cos [4\pi(i-1)/5] \\ \nu_b(e_2''): z_i^{(b)} &= z_0 \sin [4\pi(i-1)/5] \end{aligned} \quad (1)$$

The individual motions described by  $\nu_a$  and  $\nu_b$  lead to two distinct kinds of ring puckering. The first ( $\nu_a$  in Figure 1) leads to the envelope form (E) which has point-group symmetry  $C_s$ . The second ( $\nu_b$  in Figure 1) is the twist or half-chair conformation (T), belonging to the point-group  $C_2$ . These two forms are interconverted by pseudorotation. If the barrier to such motion is low, the molecule will pass through intermediate conformations with no symmetry (point-group  $C_1$ ), corresponding to linear combinations of  $\nu_a$  and  $\nu_b$ . The general puckering motion can be described mathematically by a set of displacements

$$z_i = (2/5)^{1/2} q \cos(\phi + 4\pi(i-1)/5) \quad (2)$$

$$i = 1, \dots, 5$$

Hence the out-of-plane displacement  $z_i$  of atom  $i$  is related to an overall amplitude  $q$  and a phase angle  $\phi$ .<sup>1</sup> The factor  $(2/5)^{1/2}$  is included for normalization so that

$$\sum_{i=1}^5 z_i^2 = q^2 \quad (3)$$

As  $\phi$  goes from 0 to 360°, the structure goes through all possible E forms ( $\phi = 0, 36, 72, 108, 144, 180, 216, 252, 288, 324^\circ$ ) and all possible T forms ( $\phi = 18, 54, 90, 126, 162, 198, 234, 270, 306, 342^\circ$ ). While the  $(q, \phi)$  motion has some characteristics of rotation, there is no contribution to angular momentum since each atom actually moves perpendicular to the ring. Hence the motion is described as pseudorotation.

Although the above discussion has been in terms of small displacements of a regular pentagon, many of the features can be generalized to finite displacements in five-membered rings with nonequivalent atoms.<sup>21</sup> Given any puckered ring of five atoms, a reference plane  $z = 0$  can be chosen so that displacements perpendicular to this plane satisfy

$$\begin{aligned} \sum_{i=1}^5 z_i &= \sum_{i=1}^5 z_i \cos [2\pi(i-1)/5] = \\ &= \sum_{i=1}^5 z_i \sin [2\pi(i-1)/5] = 0 \end{aligned} \quad (4)$$

The five displacements  $z_i$  must then be given by an expression (eq 2) for some  $(q, \phi)$ . Thus  $q$  and  $\phi$  are amplitude and phase coordinates for pseudorotation in a general sense.

If, for given values of  $(q, \phi)$ , all other geometrical degrees of freedom are optimized (by energy minimization), we are led to a pseudorotational potential surface  $V(q, \phi)$ , which is the central feature of this investigation. Such a potential may be expanded in a Fourier series in the phase angle  $\phi$ .

$$V(q, \phi) = V_0(q) + \sum_{n=1}^{\infty} [V_n(q) \cos n\phi + V_n'(q) \sin n\phi] \quad (5)$$

For puckering displacements which are not too large, the  $V_n(q)$  and  $V_n'(q)$  may be expanded in a Taylor series.

For all the molecules considered in this paper, both sides of the ring are equivalent and there is a left-right symmetry such that the symmetric planar form of the molecule

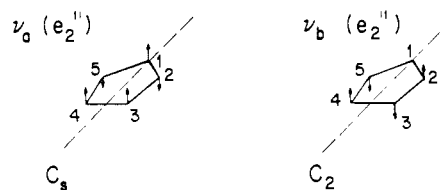


Figure 1. " $e_2''$ " vibrations of a five-membered ring with  $D_{5h}$  symmetry.

belongs to the point-group  $C_{2v}$ . Under these circumstances,  $V$  is an even function of  $q$  and  $V_n'(q) \equiv 0$  (if atom 1 lies on the in-plane symmetry axis). Then

$$V(q, \phi) = V_{00} + V_{02}q^2 + V_{04}q^4 + \dots + V_{22}q^2 \cos 2\phi + V_{24}q^4 \cos 2\phi + \dots + V_{44}q^4 \cos 4\phi + \dots \quad (6)$$

For cyclopentane, the potential must be invariant under the pseudorotation  $\phi \rightarrow \phi + 2\pi/10$ . This means that the first  $\phi$ -dependent term in the series (eq 6) is  $q^{10} \cos 10\phi$ . Such a high-order term is likely to be small giving nearly free pseudorotation as is indeed found. For the other molecules, such as oxolane, an appropriate approximate form for the potential (taking  $V_{00}$  as the energy zero) is

$$V = (V_{02}q^2 + V_{04}q^4) + (V_{22}q^2 + V_{24}q^4) \cos 2\phi \quad (7)$$

The behavior of this potential can be classified into the following four categories.

Case A

$$V_{02} + V_{22} > 0, V_{02} - V_{22} > 0$$

Under these conditions, the origin  $q = 0$  is a minimum of  $V(q, \phi)$  and the equilibrium structure is the symmetrical  $C_{2v}$  form with a planar skeleton.

Case B

$$V_{02} + V_{22} < 0, V_{02} - V_{22} > 0$$

Here the potential minimum is in a direction  $\phi = 0$  or  $180^\circ$ , so that the lowest energy is in the envelope conformation. The origin  $q = 0$  is a saddle point, and the lowest energy path for inversion of the E form is through the symmetrical planar-skeleton form.

Case C

$$V_{02} + V_{22} > 0, V_{02} - V_{22} < 0$$

The minimum now occurs along  $\phi = 90$  or  $270^\circ$  and the lowest energy occurs for the twist conformation. Again the origin is a saddle point and inversion occurs most easily through the planar-skeleton form.

Case D

$$V_{02} + V_{22} < 0, V_{02} - V_{22} < 0$$

Under these conditions, the origin is a maximum of  $V(q, \phi)$ . The equilibrium structure may be either envelope or twist depending on the relative values of the parameters. However, the lowest energy route for inversion will be by pseudorotation.

## II. Quantum Mechanical Procedure

The molecular orbital methods used are fairly standard. Closed shell single determinant wave functions are found by solution of the Roothaan equations.<sup>22</sup> A series of basis sets is used with successive refinements of the theory. The simplest set employed is the minimal Gaussian-fitted Slater-type basis STO-3G<sup>23</sup> which will be used for initial energy optimization of structures with respect to certain geometrical parameters. A variety of calculations indicates that this basis set leads to equilibrium geometries in moderate agreement with experiment.<sup>24-26</sup> The second basis is of the split-

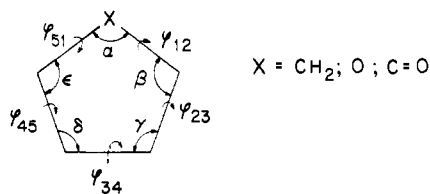


Figure 2. Bond and torsional angles in a five-membered ring.

valence extended type (4-31G)<sup>27</sup> and is used for some further reoptimization starting at the geometries determined with the minimal basis. Previous experience has indicated that the split-valence basis reflects relative energies in a more satisfactory manner. The second step has been carried out in a number of earlier studies of organic compounds in this laboratory.<sup>24-30</sup> Finally, consideration has to be given to the consequences of further extension of the basis by addition of polarization functions. The simplest basis of this type is 6-31G\*<sup>31</sup> which includes a set of d-type functions on nonhydrogenic atoms as well as more precise (6-Gaussian) inner-shell functions. Unfortunately, all the molecules treated in this paper are too large for full study using the 6-31G\* basis, so we are limited to making estimates of the expected changes due to polarization functions using studies of small molecules.

In previous work on C<sub>3</sub> hydrocarbons,<sup>25</sup> complete geometrical optimization of structures at the STO-3G level was undertaken. For these larger molecules, however, the number of variables is too great and some partly constrained model has to be selected. To allow a high degree of conformational flexibility, this is done in the following manner for five-membered rings. For the skeleton substructure consisting only of the five atoms making up the ring, there will be nine degrees of freedom (apart from translation and rotation). The bond lengths within the ring are then constrained to standard values specified previously<sup>32</sup> ( $R(C4,C4) = 1.54 \text{ \AA}$ ,  $R(C4,C3) = 1.52 \text{ \AA}$ ,  $R(C4,O2) = 1.43 \text{ \AA}$ ). This reduces the number of degrees of freedom to four and these are treated as variables. The remaining geometrical parameters refer to atoms external to the ring (hydrogen or oxygen in cyclopentanone). These are also held in fixed geometries. All bond lengths to external atoms are standard<sup>32</sup> ( $R(C4,H) = 1.09 \text{ \AA}$ ,  $R(C3,O1) = 1.22 \text{ \AA}$ ). HCH angles are taken as tetrahedral and remaining angles are chosen so that each ring carbon, its two ring bonds, and its bonds to external atoms have local C<sub>2v</sub> symmetry. For tetravalent carbon, these angles are not all tetrahedral, since the ring valence angle is varied in the geometry optimization.

In order to handle the remaining four degrees of freedom associated with the ring angles, it is desirable to connect them with pseudorotation coordinates ( $q, \phi$ ) defined previously. If the ring bond angles are  $\alpha, \beta, \gamma, \delta,$  and  $\epsilon$  (Figure 2), then two of these may be specified (say  $\alpha$  and  $\beta$ ) to fix the full geometry together with  $q$  and  $\phi$ . Given the parameter set  $\{\phi, q, \alpha, \beta\}$ , the remaining bond and dihedral angles are all determined.

Our procedure for studying pseudorotation is now as follows. First the pseudorotation phase angle  $\phi$  is fixed. (For certain values of  $\phi$  this may imply a symmetry constraint.) Then the STO-3G energy is minimized with respect to the pseudorotation amplitude  $q$  and the other bond angles  $\alpha$  and  $\beta$ . This leads to a pseudorotation potential curve  $V(\phi)$  for the STO-3G surface. The second step is to use the extended 4-31G basis for single runs at the STO-3G geometry already determined. Finally, in some cases, we have proceeded further with a partial geometry reoptimization at the 4-31G level. The necessity of this step is suggested by earlier calculations on cyclobutane<sup>33</sup> which showed that the

degree of puckering is significantly underestimated by the STO-3G method. A complete minimization with the extended 4-31G basis set for molecules with many degrees of freedom would demand too much computation time. Therefore, an approximate approach to the local minima is made by using just one cycle of the Fletcher-Powell descent method.<sup>34</sup> Further structure optimization is waived if the first derivatives of the total energy with respect to each variable indicate a reasonable approximation. These results lead to a pseudorotation potential surface for the 4-31G extended basis set.

Finally we attempt to make some estimates of the changes in the potential surface due to the addition of d functions. Ideally we should proceed with further basis set refinement 4-31G  $\rightarrow$  6-31G  $\rightarrow$  6-31G\*. We have learned in the past that inner-shell refinements (4-31G  $\rightarrow$  6-31G) lead to little change in geometry predictions.<sup>35</sup> However, the addition of d functions (6-31G  $\rightarrow$  6-31G\*) is known<sup>36</sup> to lead to reduction of valence angles at nitrogen and oxygen correcting a general overestimation found with 4-31G or 6-31G. The valence angles at oxygen and carbonyl carbon are most important for the molecules considered here, so we estimate the local d lowering of energy for such atoms from the valence angles found by optimization and from corresponding calculations on water and formaldehyde at these same valence angles.

### III. Results and Discussion

The general procedure outlined in section II has been applied to various conformations of cyclopentane, oxolane, 1,3-dioxolane, and cyclopentanone. The results are given in Tables I-V. Table IA contains the total energies obtained with the minimal STO-3G basis and with the extended 4-31G basis. Table IB gives energies relative to the minima together with estimates for the polarized 6-31G\* basis obtained as indicated below.

**Cyclopentane.** According to the symmetry of cyclopentane, ten mutually indistinguishable E forms as well as ten T forms are passed during a complete pseudorotation path. There should be only a very small  $\phi$  dependence of the pseudorotation potential  $V$

$$V = (V_{02}q^2 + V_{04}q^4) + (V_{10,2}q^2 + V_{10,4}q^4) \cos 10\phi \quad (8)$$

with  $V_{10,2} \ll V_{02}$  and  $V_{10,4} \ll V_{04}$ . A reasonable approximation for  $V$  is given by the first term in (8).

$$V = V_{02}q^2 + V_{04}q^4 \quad (9)$$

All known empirical results<sup>1-5</sup> confirm the  $\phi$  independence of  $V$ . Pseudorotation is, within experimental accuracy, free in cyclopentane. Three different conformations with  $\phi = 0^\circ$  (C<sub>5</sub>),  $\phi = 9^\circ$  (C<sub>1</sub>), and  $\phi = 18^\circ$  (C<sub>2</sub>) have been fully calculated at the STO-3G level as well as the planar form (Tables I and II). The results show the same energy for the puckered forms with a nearly constant amplitude  $q = 0.37 \text{ \AA}$ . This constancy also applies if 4-31G calculations are done with these geometries. Thus all points along the pseudorotation circuit are of equal stability and are equally populated. The pseudorotation path of cyclopentane would be described by a circle with a radius of  $q = 0.37 \text{ \AA}$  around the origin corresponding to the planar  $D_{5h}$  form. In terms of the classification chosen above, cyclopentane represents a case D example ( $V_{02} \pm V_{22} < 0$ ) with  $V_{22} = 0$ . The values of the  $V$  constants required to fit the theoretical energies are given in Table VI.

The planar and twist ( $\phi = 18^\circ$ ) forms were geometrically reoptimized at the 4-31G level. This led to a slight increase in the twist puckering amplitude to  $0.39 \text{ \AA}$  but little change

**Table I.** Total Energies (hartrees) (A) and Relative Energies (kcal mol<sup>-1</sup>) (B)

Molecule	Pseudorotation Angle $\phi$ , deg	Symmetry	STO-3G	4-31G (STO-3G geometries)	4-31G <sup>a</sup> (reoptimized)	6-31G* (estimate)	Exptl results
A							
Cyclopentane	Planar	$D_{5h}$	-192.88563	-194.87123	-194.87123		
	0	$C_s$	-192.89098	-194.87777			
	9	$C_1$	-192.89098				
Oxolane	18	$C_2$	-192.89098	-194.87779	-194.87784		
	Planar	$C_{2v}$	-228.14559	-230.62905	-230.63037		
	0	$C_s$	-228.14925	-230.63188	-230.63248		
	18	$C_1$	-228.14910				
	36	$C_1$	-228.14875				
	54	$C_1$	-228.14843				
1,3-Dioxolane	72	$C_1$	-228.14827				
	90	$C_2$	-228.14822	-230.63322	-230.63459		
	Planar	$C_{2v}$	-263.40805	-266.38545	-266.38853		
	0	$C_s$	-263.41115	-266.38632	-266.38876		
Cyclopentanone	90	$C_2$	-263.40941	-266.38761	-266.39042		
	Planar	$C_{2v}$	-265.54095	-268.46173	-268.46174		
	0 <sup>f</sup>	$C_s$	-265.54138	-268.46161	-268.46162		
	90	$C_2$	-265.54477	-268.46589	-268.46591		
B							
Cyclopentane	Planar	$D_{5h}$	3.36	4.10	4.15	4.2	5.21 <sup>b</sup>
	0	$C_s$	0	0			0
	9	$C_1$	0				0
Oxolane	18	$C_2$	0	0	0	0	0
	Planar	$C_{2v}$	2.30	2.62	2.65	3.0	
	0	$C_s$	0	0.84	1.33	0.3	~0.1 <sup>c</sup>
	18	$C_1$	0.09				
	36	$C_1$	0.31				
	54	$C_1$	0.51				
1,3-Dioxolane	72	$C_1$	0.61				
	90	$C_2$	0.65	0	0	0	0
	Planar	$C_{2v}$	1.94	1.36	1.18	1.9	
	0	$C_s$	0	0.81	1.04	0.8	~0.1 <sup>d</sup>
Cyclopentanone	90	$C_2$	1.09	0	0	0	0
	Planar	$C_{2v}$	2.40	2.61	2.62	2.6	2.15 <sup>e</sup>
	0 <sup>f</sup>	$C_s$	2.13	2.69	2.69	2.7	
	90	$C_2$	0	0	0	0	0

<sup>a</sup> For the  $C_s$  and  $C_2$  conformations the first cycle of the Fletcher-Powell optimization procedure<sup>34</sup> was implemented. <sup>b</sup> Reference 5. <sup>c</sup> Reference 7. <sup>d</sup> References 15 and 8. <sup>e</sup> Reference 14. <sup>f</sup> The 4-31G energies are evaluated at  $q = 0.22 \text{ \AA}$  and do not correspond to the local  $C_s$  minimum at  $q = 0.13 \text{ \AA}$ .

**Table II.** Theoretical and Experimental Structural Parameters for Cyclopentane<sup>a</sup>

Sym	$\phi$ , deg	$q$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\varphi_{12}$	$\varphi_{23}$	$\varphi_{34}$	$\varphi_{45}$	$\varphi_{51}$
STO-3G Geometries												
$D_{5h}$	Planar	0	108					0				
$C_s$	0	0.371	103.36	104.70	106.53			36.27	22.50	0		
$C_1$	9	0.375	103.19	104.28	106.01	106.75	105.26	38.06	27.36	6.04	17.60	34.34
$C_2$	18	0.373	106.79	105.74	103.69			11.91	31.07	38.31		
4-31G Geometries												
$C_2$	18	0.394	106.56	105.54	103.18			12.54	32.73	40.30		
Experimental Geometries <sup>b</sup>												
$C_s$	0	0.435	102.13	103.95	106.13			40.26	25.01	0		
$C_1$	10	0.435	102.31	103.19	105.71	106.37	104.71	41.89	30.57	7.40	18.67	37.43
$C_2$	18	0.435	106.43	105.26	102.68			13.16	34.34	42.29		

<sup>a</sup> All angles in Tables II, III, IV, and V in degrees with the absolute values of torsional angles reported. <sup>b</sup> Reference 4; the puckering was evaluated by using a constrained geometrical model with only three degrees of freedom for the  $C_1$  forms and two for the  $C_2$  and  $C_s$  forms.

in the barrier to inversion *via* the planar form. No major changes are expected with further basis set refinement (4-31G  $\rightarrow$  6-31G  $\rightarrow$  6-31G\*). For the valence angle at saturated carbon in methane, the energy minimum is at the tetrahedral value both with and without d functions, so the variation of the d lowering of energy with bond angle is likely to be small.

The theoretical bond and dihedral angles as they are depicted in Table II closely correspond to the experimental data.<sup>4</sup> On the other hand, it is evident that the degree of puckering is predicted to be too small by the STO-3G meth-

od. The evaluated  $q$  value of  $0.37 \text{ \AA}$  deviates significantly from both the spectroscopic result of  $0.47 \text{ \AA}$ <sup>3,5</sup> and the electron-diffraction result of  $0.43 \text{ \AA}$ .<sup>4</sup> The reoptimization of the  $C_2$  structure at the 4-31G level shows some improvement of the puckering amplitude (Table II). A complete optimization of all parameters would probably increase  $q$  further, but the evaluated first derivative of the energy with respect to  $q$  is too small for significant improvement. It may be that polarization functions would also influence the degree of puckering but it is not yet possible to test this.

Because of maximum bond eclipsing, planar cyclopent-

**Table III.** Theoretical and Experimental Structural Parameters for Oxolane

Sym	$\phi$ , deg	$q$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\varphi_{12}$	$\varphi_{23}$	$\varphi_{34}$	$\varphi_{45}$	$\varphi_{51}$
STO-3G Geometries												
$C_{2v}$	Planar	0	110.07	109.84	105.13			0				
$C_s$	0	0.340	105.04	106.96	103.70			36.43	21.83	0		
$C_1$	18	0.337	105.35	106.31	103.03	103.96	108.07	37.82	29.34	10.14	11.95	31.05
$C_1$	36	0.327	106.78	106.10	102.47	103.93	108.74	34.72	32.98	18.71	0.93	22.20
$C_1$	54	0.321	107.83	106.63	101.94	103.41	109.15	28.87	33.82	25.29	9.62	11.85
$C_1$	72	0.315	108.82	107.38	101.92	102.76	108.90	20.40	31.36	29.23	18.87	0.68
$C_2$	90	0.314	109.06	108.30	102.18			10.34	26.30	30.57		
4-31G Geometries												
$C_{2v}$	Planar	0	113.11	107.49	105.95			0				
$C_s$	0	0.370	106.40	104.57	104.09			39.86	23.32	0		
$C_2$	90	0.365	111.60	105.56	101.90			11.77	30.07	35.95		
Experimental Geometries												
$C_s^a$	0	0.364 <sup>b</sup>	106.2	105.0	104.0 <sup>b</sup>			39.2 <sup>b</sup>	23.0 <sup>b</sup>	0 <sup>b</sup>		
$C_s^c$	0	0.38	106.4	105.0	104.1			38.8	22.8	0		
$C_2^c$	90	0.38	110.5	106.5	101.8			11.6	29.6	35.0		

<sup>a</sup> Reference 10. <sup>b</sup> Calculated from the experimentally detected bond angles (this work). <sup>c</sup> Reference 9 (the puckering was achieved with a constrained geometrical model).

**Table IV.** Theoretical Structural Parameters for 1,3-Dioxolane

Sym	$\phi$ , deg	$q$	$\alpha$	$\beta$	$\gamma$	$\varphi_{12}$	$\varphi_{23}$	$\varphi_{34}$
STO-3G Geometries								
$C_{2v}$	Planar	0	111.22	107.73	106.66	0		
$C_s$	0	0.319	107.56	104.44	105.56	34.85	20.52	0
$C_2$	90	0.265	110.78	106.28	104.46	9.29	22.58	28.32
4-31G Geometries								
$C_{2v}$	Planar	0	106.58	111.45	105.26	0		
$C_s$	0	0.265	104.29	109.05	104.54	28.70	17.72	0
$C_2$	90	0.266	106.55	109.60	103.19	9.60	23.17	27.80

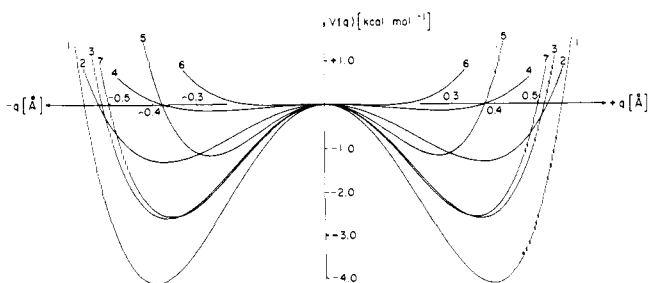
**Table V.** Theoretical and Experimental Structural Parameters for Cyclopentanone

Sym	$\phi$ , deg	$q$	$\alpha$	$\beta$	$\gamma$	$\varphi_{12}$	$\varphi_{23}$	$\varphi_{34}$
STO-3G Geometries								
$C_{2v}$	Planar	0	110.36	106.74	108.08	0		
$C_s$	0	0.222	108.67	105.49	107.57	22.55	13.56	0
$C_2$	90	0.344	109.43	104.76	104.45	10.94	28.51	35.55
4-31G Geometries								
$C_{2v}$	Planar	0	110.47	106.66	108.11	0		
$C_2$	90	0.354	109.51	104.54	104.27	11.23	29.26	36.55
Experimental Geometry <sup>a</sup>								
$C_2$	90	0.375 <sup>b</sup>	110.5 <sup>b</sup>	104.5	103.0	11.8 <sup>b</sup>	30.5 <sup>b</sup>	37.6 <sup>b</sup>

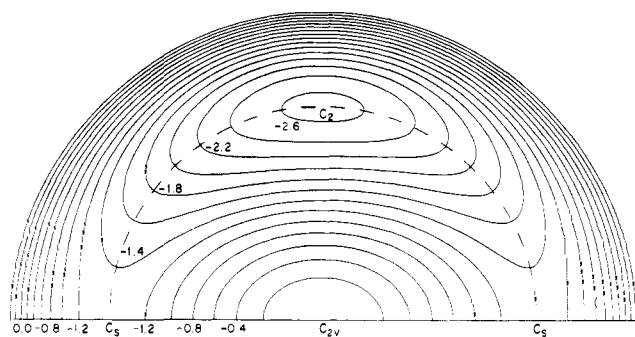
<sup>a</sup> Reference 12. <sup>b</sup> Calculated from experimental bond angles (this work).

**Table VI.** Pseudorotational Potential Coefficients for Cyclopentane, Oxolane, 1,3-Dioxolane, and Cyclopentanone

	$V_{02}$	$V_{04}$	$V_{22}$	$V_{24}$	$V_{02} + V_{22}$	$V_{02} - V_{22}$	Case	$V_{22}$	Minimum
STO-3G (Optimized Structures)									
Cyclopentane	-48.2	173.0			<0	<0	D		(Free pseudorotation)
Oxolane	-36.7	171.6	-3.1	0.9	<0	<0	D	<0	$C_2$
1,3-Dioxolane	-31.2	180.3	-6.9	6.3	<0	<0	D	<0	$C_4$
Cyclopentanone	-25.7	141.1	14.8	-29.6	<0	<0	D	>0	$C_2$
4-31G (STO-3G Structures)									
Cyclopentane	-59.0	211.7			<0	<0	D		(Free pseudorotation)
Oxolane	-42.0	202.0	11.2	-68.7	<0	<0	D	>0	$C_2$
1,3-Dioxolane	-24.7	164.4	14.0	-111.9	<0	<0	D	>0	$C_2$
Cyclopentanone	-23.5	139.9	20.5	-45.5	<0	<0	D	>0	$C_2$
4-31G (Optimized Structures)									
Cyclopentane	-53.5	172.2			<0	<0	D		(Free pseudorotation)
Oxolane	-29.5	109.8	10.3	-39.6	<0	<0	D	>0	$C_2$
1,3-Dioxolane	-18.8	132.8	14.6	-102.5	<0	<0	D	>0	$C_2$
Cyclopentanone	-22.3	129.7	19.4	-36.7	<0	<0	D	>0	$C_2$



**Figure 3.** Barriers to inversion for the  $C_s$  and  $C_2$  conformers of cyclopentane (line 1), oxolane (2, 3), 1,3-dioxolane (4, 5), and cyclopentanone (6, 7) (4-31G optimized structures).



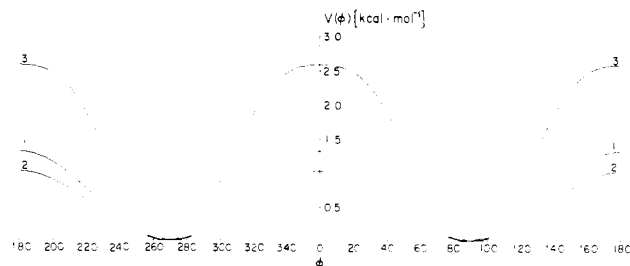
**Figure 4.** Potential surface of oxolane.

tane should be less stable than all puckered conformations with  $q \leq 0.52 \text{ \AA}$  (STO-3G) or  $q \leq 0.56 \text{ \AA}$  (4-31G). The STO-3G and 4-31G energies (Table I) indicate a loss of stability of 3.4 and 4.1 kcal/mol, respectively, going from  $q = 0.37$  or  $0.39 \text{ \AA}$  to planar cyclopentane. The 4-31G value turns out to be in better agreement with the direct spectroscopic result of Carreira, et al.,<sup>5</sup> (5.21 kcal/mol) than the theoretical value of an earlier *ab initio* calculation (8.27 kcal/mol).<sup>37</sup> Besides this symmetry-retaining path, the ring is able to undergo inversion in a sense by going around the high planar barrier and following the pseudorotation circuit. The latter mode of conformational interconversion is distinguished by a smooth change of all dihedral and bond angles, exhibiting a very low barrier. During the symmetrical mode, however, where most of the deformation occurs at bond  $C_3-C_4$  ( $C_2$ ) or at the  $C_2-C_1-C_5$  entity ( $C_s$ ) a rapid change of some torsional and some bond angles causes a high barrier as shown in Figure 3.

**Oxolane.** If one of the methylene groups in cyclopentane is replaced by oxygen, the symmetry of the molecule is reduced and the pseudorotation potential function (eq 6) will contain terms in  $\cos 2\phi$ ,  $\cos 4\phi$ , ... If only the  $\cos 2\phi$  term is retained, the potential in (7) is appropriate.

The results of the quantum mechanical calculations on oxolane are summarized in Tables I and III. The geometrical model was optimized fully with the STO-3G basis for the planar structure ( $q$  constrained to be zero) and for a series of six values of  $\phi$  with puckering (variable  $q$ ). This results in a pseudorotation potential surface with its minimum at  $\phi = 0$  corresponding to the E form. The T form ( $\phi = 90^\circ$ ) is a maximum along the pseudorotational path with an energy  $0.65 \text{ kcal mol}^{-1}$  higher. The planar form is higher in energy (at  $2.3 \text{ kcal mol}^{-1}$  relative to  $C_s$ ) than any point along this path. Fitting the results to (6) indicates that the  $\cos 4\phi$  terms are relatively small.

When 4-31G calculations are carried out at the STO-3G geometries, the ordering of the puckered conformation energies is reversed and the twisted  $C_2$  form becomes more stable than the envelope  $C_s$  form by  $0.84 \text{ kcal mol}^{-1}$ . After



**Figure 5.** Pseudorotation potential  $V(\phi)$  for oxolane (line 1), 1,3-dioxolane (2), and cyclopentanone (3) (4-31G optimized structures).

**Table VII.** Effect of Polarization Basis Functions on Energies of Water and Formaldehyde

Molecule	Angle HXH, deg	—Total energies, hartrees—		Lowering, kcal mol <sup>-1</sup> Δ
		6-31G	6-31G*	
Water	105	-75.98412	-76.01041	16.5
	109.47	-75.98508	-76.00987	15.6
	115	-75.98474	-76.00772	14.4
Formaldehyde	110	-113.80658	-113.86239	35.0
	115	-113.80809	-113.86389	35.0
	120	-113.80789	-113.86370	35.0

a geometry refinement with the 4-31G basis, this ordering is retained, but the energy difference is increased to  $1.33 \text{ kcal mol}^{-1}$ . The planar form then is  $2.65 \text{ kcal mol}^{-1}$  above the minimum, so the pseudorotation path remains the lowest path for interconversion.

The computed geometries show substantial puckering amplitudes  $q$  (Table III). For the STO-3G basis, there is some  $\phi$  dependence of the optimized  $q$ , but for the 4-31G basis the values for the E( $C_s$ ) and T( $C_2$ ) forms are very close at about  $0.37 \text{ \AA}$ . One other feature of interest is that for both basis sets, the computed angle at oxygen ( $\alpha$ ) is significantly larger in the T form than in the E form.

If the 4-31G results are fitted to the potential in (7), values for the  $V$  constants shown in Table VI are obtained. Figure 4 shows a part of this potential in ( $q, \phi$ ) space and again indicates the low-energy pseudorotation interconversion path (4-31G optimized structures). The potential surface is, of course, symmetrical with respect to  $\phi = 0^\circ, 180^\circ$  and  $\phi = 90^\circ, 270^\circ$ . Therefore, only the range between  $\phi = 0$  and  $180^\circ$  is shown in Figure 4. The contour lines are drawn at intervals of  $0.2 \text{ kcal mol}^{-1}$  starting at the  $C_{2v}$  oxolane as the chosen zero level. The dashed line connecting the  $C_2$  minimum ( $\phi = 90^\circ, q = 0.365 \text{ \AA}$ ) and the most stable  $C_s$  conformations ( $\phi = 0^\circ, q = 0.370 \text{ \AA}$  and  $\phi = 180^\circ, q = 0.370 \text{ \AA}$ ) symbolizes the pseudorotation path. In Figure 5 (line 1) the energy change along this path, *i.e.*,  $V = V(\phi)$ , is displayed. In addition, two cuts through the potential surface have been made in order to show the inversion barriers of the  $C_s$  and  $C_2$  conformation (lines 2 and 3 of the  $V(q)$  diagram in Figure 3).

The pseudorotation potential surface for oxolane is likely to be significantly modified by the addition of d functions to the basis set. This is because the optimized valence angle at oxygen ( $\alpha$ ) varies with the phase angle  $\phi$  and the d lowering of the energy is known to vary quite sharply with this angle. In order to make estimates of the relative energies with the 6-31G\* basis, we have carried out calculations on water (with  $R_{OH} = 0.96 \text{ \AA}$ ) at three angles using 6-31G (no d functions) and 6-31G\*. The results (Table VII) show the dependence of the energy lowering,  $\Delta$ , caused by oxygen d functions on the valence angle at oxygen. For the oxygen angles in oxolane (4-31G results, Table III), interpolated values of  $\Delta$  are easily obtained and then lead to the estimat-

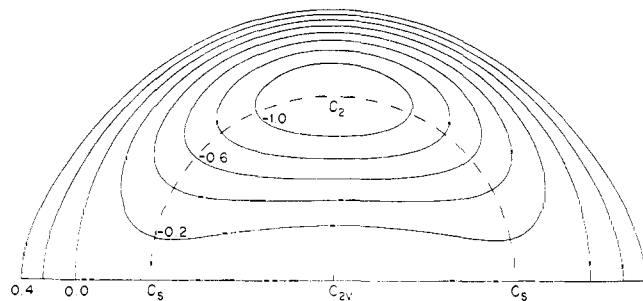


Figure 6. Potential surface of 1,3-dioxolane.

ed relative energies shown in Table IB. These 6-31G\* estimates of relative energy indicate little change in the planar barrier, but a reduction of the pseudorotation barrier to about 0.3 kcal mol<sup>-1</sup>.

There is a limited amount of experimental information on the structure of oxolane. The results reported in the literature are all consistent with the occurrence of almost free pseudorotation. A microwave investigation<sup>7</sup> led to the assignment of certain lines to the pseudorotation motion which implied a low barrier of only 0.1 kcal mol<sup>-1</sup>. In this study some evidence was noted favoring the twisted  $C_2$  form although the proposed potential also contained significant  $4\phi$  terms leading to four equivalent minima in asymmetric ( $C_1$ ) forms roughly half-way between E- and T-type conformations. Other studies using far-infrared spectroscopy<sup>6,8</sup> and electron diffraction<sup>9,10</sup> are apparently consistent with this except that electron diffraction is unable to distinguish between  $C_2$  and  $C_s$ . No direct measurement of the barrier to planarity has been published.

The theoretical results show partial agreement with these experimental findings. Although the STO-3G and 4-31G methods lead to rather larger barriers to pseudorotation, the estimates for the 6-31G\* basis are more consistent with the low barriers found. However, we find little evidence for dominant  $\cos 4\phi$  terms in  $V(\phi)$ . With the larger bases, the theory favors a T-type minimum. It may be worth noting that many crystal data on substituted oxolanes show a preponderance of structures close to the T form.<sup>38</sup> Substituent effects and intermolecular forces may influence such structures but they are broadly consistent with our predictions.

The remaining geometrical parameters are in fairly good agreement with the theoretical data (Table III) despite the fact that no optimization of the standard bond lengths used in our five-membered ring model was implemented. A substantial improvement of the structural parameters is obviously obtained by using the split-valence 4-31G basis set. Theoretical and electron diffraction puckering amplitudes<sup>9,10</sup> parallel each other quite closely. Only the early infrared study of Lafferty, et al.,<sup>6</sup> predicts a larger  $q$  value of 0.44 Å.

**1,3-Dioxolane.** The symmetry of 1,3-dioxolane is the same as oxolane. The pseudorotation potential in (6) will again contain terms in  $\cos 2\phi$ ,  $\cos 4\phi$ , ... The quantum mechanical results are given in Tables I and IV. Only the planar ( $C_{2v}$ ), E-type ( $C_s$ ), and T-type ( $C_2$ ) forms were examined. The results parallel those for oxolane. For the STO-3G basis, the E form was found to be most stable. However, the next step with the 4-31G basis led to a reversal and the prediction of an energy minimum in the T conformation. After refinement of the geometry with the split-valence basis, the E form was found to have an energy of 1.04 kcal mol<sup>-1</sup> higher than the T form. The planar form is only 1.18 kcal mol<sup>-1</sup> above the minimum and not far above the E-type structure.

The theoretical geometries show significant puckering

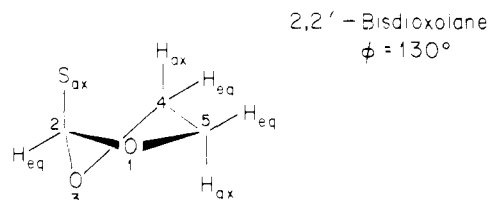


Figure 7. Conformation of 2,2'-bisdioxolane (S stands for the second dioxolane ring).

amplitudes  $q$  (Table IV) although they are somewhat smaller than those for oxolane. Again, the 4-31G basis gives an amplitude almost independent of the phase angle  $\phi$ . It may be noted that the split valence basis gives substantially larger C-O-C angles than STO-3G.

The potential surface using the 4-31G results is shown in Figure 6. This indicates that inversion of the T form can occur almost as easily through the planar ( $C_{2v}$ ) form as by pseudorotation. Figures 3 and 5 show the corresponding sections  $V(q)$  and  $V(\phi)$ . This surface is close to case C of section I, ring inversion and pseudorotation being competitive.

Table IB again gives estimates of the relative energies after the addition of polarization functions. Using the results of Table VII and noting that the angles  $\beta$  and  $\epsilon$  are slightly less in the  $C_s$  and  $C_{2v}$  forms than in the  $C_2$  form, we predict that d functions will preferentially stabilize the E-type and planar forms. This leads to a slight reduction in both the pseudorotation and planar barriers.

For this molecule, there is less agreement with experimental results. Two far-infrared studies indicated small barriers to pseudorotation,<sup>8,15</sup> a conclusion that has recently received support from a microwave investigation.<sup>39</sup> The latter leads to a potential  $V(\phi)$  with four equivalent minima corresponding to structures intermediate between  $C_2$  and  $C_s$ . Our theoretical study has made no investigation of such intermediate ( $C_1$ ) structures but does suggest that the  $\cos 2\phi$  term in the potential is larger than that proposed by Baron and Harris.<sup>39</sup> The only experimental information about the puckering amplitude  $q$  is an approximate estimate of 0.41 Å by Durig and Wertz<sup>15</sup> from their infrared data. This is somewhat larger than the experimental value for oxolane<sup>9</sup> while the theory suggests a significantly smaller degree of puckering.

One further piece of relevant experimental information is an early crystal structure of 2,2'-bisdioxolane<sup>40</sup> (Figure 7). This has two equivalent five-membered rings. The structure of each ring (using the atom C(5) as apex of the planar ( $C_{2v}$ ) form) corresponds to  $\phi = 130^\circ$ . If we fix this value and then determine  $q$  and the other angles using the 4-31G (optimized) potential in (7) and other corresponding expansions for the angles  $\alpha$  and  $\beta$ , we obtain the geometrical parameters shown in Table VIII. The degree of puckering (0.27 Å) is in reasonable agreement with the experimental data. However, it should of course be emphasized that this structure may well be modified by intermolecular interactions.

**Cyclopentanone.** As in the case of the cyclic ethers oxolane and 1,3-dioxolane, planar cyclopentanone belongs to the point-group  $C_{2v}$ . Therefore, the form in (7) of the potential function  $V(q, \phi)$  is appropriate. The calculated energies of the planar ( $C_{2v}$ ), E( $C_s$ ), and T( $C_2$ ) form are displayed in Table I. The corresponding geometrical parameters can be found in Table V. Both the minimal and the split-valence bases predict twisted cyclopentanone to be the most stable ring conformation. The barrier through planarity amounts to 2.4 (STO-3G) and 2.6 kcal mol<sup>-1</sup> (4-31G). The relative stability of the E form turns out to be very

**Table VIII.** Comparison of the Experimental Geometry of One Dioxolane Ring of 2,2'-Bisdioxolane with the 4-31G Geometry of 1,3-Dioxolane at the Corresponding  $\phi$  Value

	$\phi$ , deg	$q$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$
X-Ray <sup>a</sup>	130	0.27	105	111	104	102	109
4-31G (reoptimized)	130	0.27	105.6	108.2	107.5	100.1	110.4

<sup>a</sup> Reference 41.

close to that of the planar conformation. The STO-3G approach predicts a flat minimum for  $\phi = 0^\circ$  at  $q = 0.22 \text{ \AA}$  thus establishing a case D situation for the potential surface, the barrier to pseudorotation being only 0.3 kcal mol<sup>-1</sup> lower than the barrier to inversion. On the other hand, the 4-31G result for  $q = 0.22 \text{ \AA}$  suggests that the lowest  $C_s$  conformation may be the planar ring characterizing case C. However, the section of the potential curve is very flat (and may have a slight minimum at  $q \sim 0.13 \text{ \AA}$ ). A refinement of the structural parameters at the split-valence level does not produce any significant change of either geometries or relative stabilities. The general features of the 4-31G potential surface of cyclopentanone can therefore be summarized in the following way.

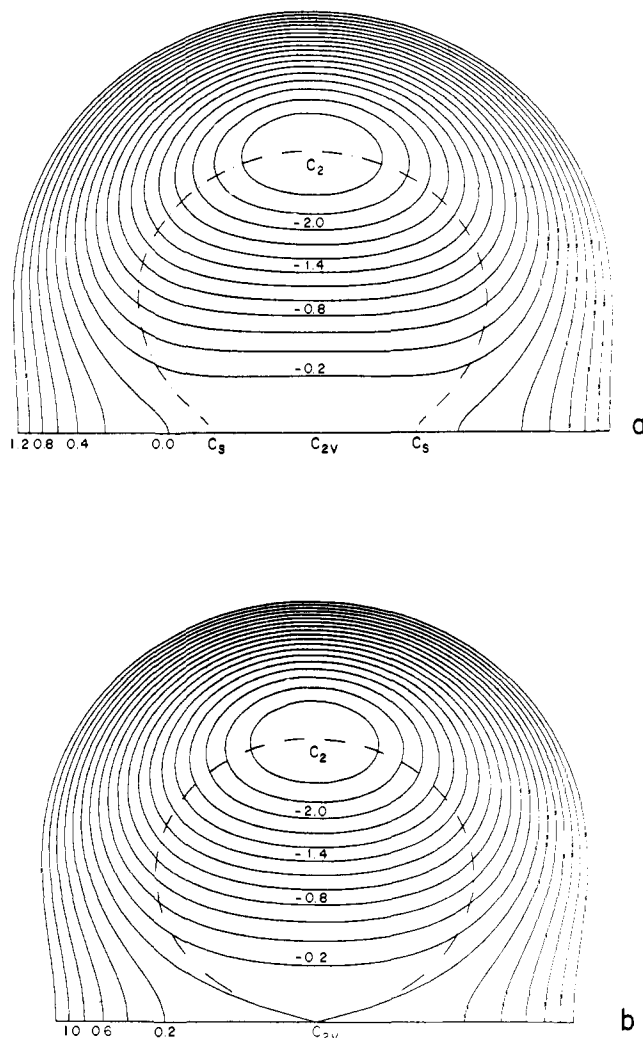
(i) For  $\phi = 0$  and  $270^\circ$  there exist discrete minima at  $q = 0.35 \text{ \AA}$  which represent the cyclopentanone ground-state conformation.

(ii) Within the limitations of our five-membered ring model the  $C_{2v}$  form can be considered as a saddlepoint located in the center of a very shallow potential valley that ranges over all  $C_s$  forms with  $q \leq 0.18 \text{ \AA}$  (Figure 3, line 6). With respect to the  $C_2$  direction the bottom of the potential valley forms a ridge that has to be crossed during an intramolecular process involving the T forms (Figures 3 and 5).

There is no evidence that the addition of polarization functions would change these features of the pseudorotation surface. The results of Table VII show that the energy lowering  $\Delta$  for formaldehyde is almost independent of the HCH angle. If this can be carried over to the CCC angle at the carbonyl group, it would be predicted that all structures would be lowered equally and the relative energies would be unchanged.

All experimental studies of cyclopentanone<sup>11-14</sup> have established the dominance of the T form. From the microwave spectrum<sup>12</sup> the degree of puckering as well as the other structural parameters of the T form were obtained. They are in reasonably good agreement with the theoretical values given in Table V. A recent far-infrared investigation of several deuterated cyclopentanones<sup>14</sup> supplied a reliable description of the potential surface. Both the theoretically and experimentally derived potential surfaces are shown in Figure 8. The far-infrared results<sup>14</sup> prove planar cyclopentanone to be a true saddle point. The empirically obtained expansion terms of  $V$  differ slightly from our values. The barrier to inversion through the planar-skeleton form is predicted to be 2.6 kcal mol<sup>-1</sup> in moderate agreement with the experimental value of 2.1 kcal mol<sup>-1</sup>. The barrier that occurs if the stable T conformer converts to an E-type conformer holding the puckering amplitude constant is 3.7 kcal mol<sup>-1</sup> (4-31G with structure optimization). The corresponding pseudorotation barrier quoted in the experimental study is also 3.7 kcal mol<sup>-1</sup>.

According to the experimental studies, the puckering amplitude is close to our theoretical value (4-31G). For the sake of compatibility of empirical and theoretical puckering parameters the twist angle  $\tau$ , defined as the angle between plane  $C_5C_1C_2$  and bond  $C_3-C_4$ , may be chosen rather than



**Figure 8.** Potential surface of cyclopentanone: (a) evaluated from the 4-31G results after structure optimization; (b) evaluated from experimental results of ref 14.

the puckering amplitude  $q$ . In the microwave study<sup>12</sup>  $\tau$  was found to be  $23.6^\circ$  and in the infrared study<sup>14</sup> it was  $18.8^\circ$ . The theoretical values are 21.5 (STO-3G) and  $22.2^\circ$  (4-31G), respectively.

#### IV. Factors Determining Ring Puckering

The nature and extent of puckering in the studied molecules can be usefully discussed in terms of balanced contributions of two different strain effects. The first is bond angle strain. For five-membered rings, the bond angles are usually constrained to be smaller than their "natural" or open-chain values even if the skeleton is planar. If the ring becomes puckered, the angles generally become still smaller and the corresponding strain is increased further. The second effect is torsional strain which is greatest in the planar form when bonds are in eclipsed conformations. This contribution to the total strain energy is lowered by puckering of the ring. The final extent and conformation of puckering is then determined by the balance of these effects.

Appreciation of these qualitative features is of value in assessing the significance of the quantum mechanical results obtained with the various basis sets. For cyclopentane, the minimal STO-3G basis is known to give a reasonably good description of the torsional potential about a C-C bond. On the other hand, it overestimates binding force constants.<sup>41</sup> Thus, in this theoretical model, the bond angle strain is overestimated and consequently the theoretical



value obtained for the amplitude  $q$  is too small. The 4-31G basis, on the other hand, gives better bending force constants and the agreement with the experimental geometry is improved. These conclusions are consistent with similar results obtained recently on cyclobutane.<sup>33</sup> The theoretical inversion barrier through a planar skeleton is somewhat low, presumably because the calculated  $q$  amplitude is small, but is otherwise consistent with empirical estimates based on valence and torsion angle strain.<sup>1,42</sup>

For oxolane, the general degree of puckering will be determined by similar features. However, the bond angle strain at oxygen will play a key role in determining whether the E or T conformations are lower in energy. Generally, E-type displacements (with oxygen at the apex) lead to large reductions in the oxygen valence angle while T-type displacements give only small changes. This is evident for the optimized angles  $\alpha$  in Table III. Similar qualitative conclusions follow by considering bond angle changes due to infinitesimal out-of-plane displacements of a regular pentagon. An extension of appropriate analysis given by Dunitz<sup>43</sup> (see Appendix) shows that the apex angle is *reduced* by  $1.80q^2$  for an E-type displacement, while it is *increased* slightly by  $0.10q^2$  for a T-type displacement. We can now understand the theoretical results for oxolane in the following manner. The minimal STO-3G basis leads to oxygen valence angles that are too small<sup>41</sup> (e.g.,  $100^\circ$  for  $\text{H}_2\text{O}$  compared with the experimental value of  $104.5^\circ$ ). Consequently, in its application to the puckering of oxolane, this model will predict an E-type displacement to make this angle smaller. On the other hand, the 4-31G basis generally gives oxygen valence angles to be too large ( $111^\circ$  for  $\text{H}_2\text{O}$ )<sup>27</sup> and accordingly the model leads to a preferential T-type displacement. It is only when d-type polarization functions are added, as with the 6-31G\* basis, that oxygen valence angles are described correctly and the theoretical estimates for oxolane then give an intermediate description with only a small barrier to pseudorotation. In fact, the final conclusion appears to be that the bond angle strain at oxygen is quite comparable to that at saturated carbon. Also the torsional barrier about a C-O bond in methyl ether is also close to that about a C-C bond. A balanced contribution from these effects leads to nearly free pseudorotation. However, it appears that this is not described satisfactorily by molecular orbital theory until a polarized basis with d functions is used. The inversion barrier through the planar skeleton is smaller than in cyclopentane, corresponding to smaller puckering amplitude.

For 1,3-dioxolane, similar arguments prevail although the final estimate of the pseudorotational barrier remains higher than the experimental value. The data indicate that the valence angle at oxygen ( $\beta$  in Table IV) again changes with the puckering amplitude (at the 4-31G level). For this molecule, the results may also be influenced by coupling between the two C-O rotational potentials in the O-C-O group, an effect which is known to be important in methanediol. 4-31G theoretical studies on methanediol indicate equivalent potential minima in the (+sc, +sc) and (-sc, -sc) conformations of the H-O-C-O-H chain.<sup>44</sup> This corresponds to a preference for the T-type oxolane, where the C-O-C-O-C chain would be in the conformation closest to (+sc, +sc) or (-sc, -sc).

Finally, the T-type structure found both theoretically and experimentally for cyclopentanone is also understandable on this basis. For this molecule, the valence angle for the carbonyl carbon ( $\alpha$  in Table V) is already strained in the planar form, its unstrained value presumably being around the  $117^\circ$  value found for acetone.<sup>45</sup> There is therefore a marked preference for a T-type displacement which will avoid increasing this strain. An E-type displacement appar-

ently increases the angular strain at this atom so much that inversion through the planar form is found to be more favorable than pseudorotation.

**Acknowledgments.** D. C. thanks the Deutsche Forschungsgemeinschaft for supporting his work. Partial support was furnished by the National Science Foundation under Grant GP-25617.

## Appendix

**Angle Change in a Slightly Puckered Regular Pentagon.** Dunitz<sup>43</sup> has given formulas for the general bond angle change for small puckering displacements of a regular pentagon with edges of unit length. If  $z_j$  are the displacements perpendicular to the ring plane, given by

$$z_j = (2/5)^{1/2} q \cos [\phi + (4\pi/5)(j - 1)] \quad (\text{A1})$$

then the angle at corner 1 will become  $(3\pi/5) - \delta_1$  where

$$\delta_1 = \text{cosec} (2\pi/5) \{ (z_2 - z_1)(z_5 - z_1) +$$

$$1/2 \cos (2\pi/5) [(z_2 - z_1)^2 + (z_5 - z_1)^2] \} \quad (\text{A2})$$

to second order in the  $z_j$ . Substitution of (A1) and (A2) then leads to

$$\delta_1 = 0.8507q^2 + 0.9511q^2 \cos 2\phi \quad (\text{A3})$$

This result indicates that the largest angle decrease occurs for an E-type displacement ( $\phi = 0$ ) ( $\delta = 1.8018q^2$ ) while for the T-type displacement ( $\phi = \pi/2$ ) there is a small increase ( $\delta = -0.1004q^2$ ).

## References and Notes

- (1) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947); K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).
- (2) F. H. Kruse and D. W. Scott, *J. Mol. Spectrosc.*, **20**, 276 (1966).
- (3) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 2118 (1968).
- (4) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).
- (5) L. A. Carreira, G. J. Jiang, W. B. Person, and J. N. Willis, Jr., *J. Chem. Phys.*, **56**, 1440 (1972).
- (6) W. J. Lafferty, D. W. Robinson, R. V. St. Louis, J. W. Russell, and H. L. Strauss, *J. Chem. Phys.*, **42**, 2915 (1965).
- (7) G. G. Engerholm, A. C. Luntz, W. D. Gwinn, and D. O. Harris, *J. Chem. Phys.*, **50**, 2446 (1969).
- (8) J. A. Greenhouse and H. L. Strauss, *J. Chem. Phys.*, **50**, 124 (1969).
- (9) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969).
- (10) A. Almennigen, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, **23**, 2748 (1969).
- (11) J. R. Durig, G. L. Coulter, and D. W. Wertz, *J. Mol. Spectrosc.*, **27**, 285 (1968).
- (12) H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **51**, 1815 (1969).
- (13) L. A. Carreira and R. C. Lord, *J. Chem. Phys.*, **51**, 3225 (1969).
- (14) T. Ikeda and R. C. Lord, *J. Chem. Phys.*, **56**, 4450 (1972).
- (15) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 675 (1968).
- (16) J. Laane, *J. Chem. Phys.*, **50**, 1946 (1969).
- (17) D. W. Wertz, *J. Chem. Phys.*, **51**, 2133 (1969).
- (18) J. R. Durig and J. N. Willis, Jr., *J. Chem. Phys.*, **52**, 6108 (1970).
- (19) W. H. Green, A. B. Harvey, and J. A. Greenhouse, *J. Chem. Phys.*, **54**, 850 (1971).
- (20) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, New York, N. Y., Chapter 3.
- (21) D. Cremer and J. A. Pople, *J. Amer. Chem. Soc.*, preceding paper in this issue.
- (22) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
- (23) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (24) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).
- (25) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).
- (26) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 6377 (1971).
- (27) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (28) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).
- (29) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **95**, 693 (1973).
- (30) W. A. Lathan, L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **95**, 699 (1973).
- (31) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
- (32) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

- (33) R. Ditchfield, unpublished results.  
 (34) R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 6163 (1963); J. S. Binkley, unpublished work.  
 (35) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).  
 (36) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, **27**, 209 (1974).  
 (37) J. R. Hoyland, *Mol. Phys.*, **50**, 2775 (1969).  
 (38) C. Altona and M. Sundarlingam, *J. Amer. Chem. Soc.*, **94**, 8205 (1972).  
 (39) P. A. Baron and D. O. Harris, *J. Mol. Spectrosc.*, **49**, 70 (1974).  
 (40) S. Furberg and O. Hassel, *Acta Chem. Scand.*, **4**, 1584 (1950).  
 (41) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).  
 (42) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).  
 (43) J. D. Dunitz, *Tetrahedron*, **28**, 5459 (1972).  
 (44) G. A. Jeffrey, J. A. Pople, and L. Radom, *Carbohydr. Res.*, **25**, 117 (1972).  
 (45) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965).

## The Interrelationship of Bond Dissociation Energies and Contributing Bond Energies

R. T. Sanderson

*Contribution from the Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Received May 9, 1974*

**Abstract:** The difference between the energy of dissociation of a chemical bond, which breaks a molecule into two fragments, and the contributing bond energy, which is the contribution that that same bond makes to the total atomization energy of the molecule, is the energy of reorganization of any polyatomic fragments formed by the dissociation. A recently developed quantitative theory of polar covalence allows the first simple and accurate calculation of contributing bond energy. This theory is reviewed in brief detail herein, in order to clarify its use in this present study of 76 dissociations of bonds in common molecules. Depending on the kind of data available, it is possible to determine quantitatively the reorganizational energy from the bond dissociation energy and the contributing bond energy or the bond dissociation energy from the contributing bond energy and the reorganizational energy. Reorganizational energies of radicals incapable of rearrangement to form stable molecules present very interesting problems of interpretation for future investigation.

The attractive interactions that hold the atoms of a molecule together are conventionally regarded as somewhat arbitrarily divisible into separate attractions, one between each pair of adjacent atoms. These attractions are known as chemical bonds. The energy required to cause homolytic fission of a chemical bond, or conversely, that is released when such a bond is formed, may be called the bond energy. It has long been recognized that for all but diatomic molecules, the bond energy required to break the molecule into two fragments, at least one of them containing more than one atom, is not the same as the energy assigned to that bond as its contribution to the total atomization energy of the molecule. This paper deals with that difference.

For example, the total atomization energy of gaseous water is 221.6 kcal mol<sup>-1</sup>. There being no basis for assuming other than exact equivalence between the two O-H bonds in the molecule, the bond energy is obtained as 110.8 kcal mol<sup>-1</sup> simply by dividing the total atomization energy by the number of bonds. On the other hand, the reaction, H<sub>2</sub>O → H + OH, requires 119.2 kcal mol<sup>-1</sup>, thus causing the remaining O-H bond to be only 221.6 - 119.2 = 102.4 kcal mol<sup>-1</sup>. The value of 110.8 is commonly called the "average bond energy", to indicate how it was obtained. The separate values, 119.2 and 102.4, are called "bond dissociation energies". The purpose of this paper is to attempt to shed new light on the relationship between average bond energies and bond dissociation energies, in a quantitative manner wherever possible.

The term "average bond energy" is unsatisfactory because the energy is roughly applicable to molecules containing more than one kind of bond, wherein averaging would be inappropriate. I suggest substitution of the term, "contributing bond energy", meaning, that part of the total atomization energy which may be considered to be contributed by that particular bond. In other words, the total atomization energy is the sum of all the individual contributing bond energies of the molecule. (The total atomization

energy is also, of course, the sum of all the successive bond dissociation energies.)

It is generally and logically assumed that any difference between a contributing bond energy, CBE, and a bond dissociation energy, BDE, for the same bond must arise from reorganization within the fragments formed by the dissociation process. However, this has been mainly a qualitative concept, and a study of recent literature discloses that the distinction is not well understood nor always clearly recognized. Recently developed techniques can provide a clearer and more quantitative insight, as described herein.

For diatomic molecules, there is, of course, no distinction between CBE and BDE. For more complex molecules, the only kind of bond energy susceptible to "direct" experimental measurement is the BDE. In addition, for molecules in which all the chemical bonds are exactly alike, a CBE can easily be determined by dividing the total experimental atomization energy by the number of bonds per molecule, but, for molecules containing unlike bonds, it was necessary until a few years ago to assume, only approximately and not always correctly, that the total atomization energy of the molecule could be represented by summing "standard" bond energies empirically determined, usually as "average bond energies", or by combining such data with energy differences.

That such a scheme works at all is somewhat fortuitous, as will be explained later. However, it is hardly dependable, because of various factors not always recognized, that cause seemingly identical bonds to differ in different environments. Some of the difficulties are illustrated by the following examples. (1) The average bond energy in CCl<sub>4</sub> is lower than would otherwise be expected because of significant bond weakening believed to result from the crowding of the chlorine atoms around the carbon atom; it would therefore be inappropriate to use for something like CH<sub>3</sub>Cl. (2) The C=O bond in carbon dioxide is significantly stronger than the C=O bond in a carbonyl derivative of a