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Molecular Structure of 2,5-Dihydrofuran As Determined by Gas-Phase Electron Diffraction

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Abstract: The molecular structure of 2,5-dihydrofuran has been studied by gas-phase electron diffraction. The dimensioned potential function for the ring-puckering motion has been derived from a reanalysis of the far-infrared spectroscopic data taken from the literature. A quartic–quadratic potential function of the form $V(x) = (0.5299 \pm 0.0192) \times 10^6 x^4 + (0.9803 \pm 0.0799) \times 10^4 x^2$ was obtained, where $V(x)$ is in reciprocal centimeters and x is the ring-puckering coordinate. This function was used in the analysis of the electron diffraction data in terms of a dynamic puckering model. The structural parameters determined from a least-squares refinement of the electron diffraction data are as follows: r_g(C═C) = 1.347 (4) Å, r_g(C—C) = 1.502 (3) Å, r_g(C—O) = 1.440 (2) Å, r_g(C–H)$_{av}$ = 1.100 (5) Å, CCC = 109.3 (2)°, ∠HCH = 107.1 (3.5)°, and ∠HC═C = 134.8 (5.6)°. The structure of the molecule is compared with the structures of several related molecules.

Four- and five-membered-ring molecules with large-amplitude low-frequency modes have attracted considerable interest among electron diffractionists and spectroscopists.[1-3] Planar five-membered rings are generally expected to have two out-of-plane skeletal vibrations with low frequency, the ring-bending and ring-twisting modes. In unsaturated five-membered-ring molecules such as cyclopentene and 2,5-dihydrofuran which have endocyclic double bonds, the twisting mode about the double bond is much higher in frequency than that of the ring-bending mode, and therefore the ring puckering in such molecules resembles that of four-membered-ring molecules. For this reason, five-membered rings with an endocyclic double bond have been termed "pseudo-four-membered rings" by Laane and Lord.[4]

A number of spectroscopic studies of pseudo-four-membered-ring molecules by far-infrared, Raman, and microwave spectroscopy have been interpreted by using the quartic–quadratic potential function for the ring-puckering motion in the form

$$V(x) = ax^4 + bx^2 \tag{1}$$

where x is the one-dimensional ring-puckering coordinate. The quartic coefficient, a, in eq 1 is always positive, and the quadratic constant, b, may be positive or negative. If b is positive, the potential function has only one minimum at $x = 0$, and the molecule has a planar equilibrium configuration. If b is negative, then the potential function is of the double-minimum type, and the molecule should be expected to have an envelope equilibrium configuration.

Several pseudo-four-membered-ring molecules have thus far been investigated by electron diffraction.[5-13] While electron diffraction has been successfully used in determining the precise molecular structure at the potential minimum and in characterizing the actual atomic trajectories associated with the large amplitude motions, it has been able to do little to improve upon the accuracy of the potential function governing the ring-puckering motion. It is clearly the case that a more meaningful experimental structure will result from an analysis which incorporates the strongest features of the various available experimental methods. Accordingly, in the study of large motions by electron diffraction, it is beneficial to supplement the diffraction data with as much spectroscopic information as possible. The net result is a more concise description of the average structure and dynamic behavior of the molecule.

The ring-puckering motion of 2,5-dihydrofuran has been studied in detail by far-infrared spectroscopy. The far-infrared spectrum of 2,5-dihydrofuran was originally observed and interpreted by Ueda and Shimanouchi[14] in 1967. They fit the observed frequencies with a single-minimum, one-dimensional potential function in the form of eq 1. Later high-resolution spectra obtained by Carreira and Lord[15] for this molecule have shown a satellite series of transitions between the ring-puckering levels in the first excited state of the ring-twisting vibration in addition to the main series of ring-puckering transitions. Carreira, Mills, and Person[16] have fitted the data of Carreira and Lord with a two-dimensional potential function in ring-puckering and ring-twisting coordinates and have shown that the coupling between these two modes is small but not negligible. Recently, Malloy and Carreira[17] have demonstrated the relationship between the full two-dimensional potential function and the effective one-dimensional potential function which may be used to estimate the coefficients of the cross term connecting the ring-puckering and ring-twisting modes. All of these studies of 2,5-dihydrofuran have confirmed that this molecule has a single minimum potential function with a substantial anharmonicity accompanying the ring-puckering motion.

The origins of ring-puckering potential functions have been discussed in terms of the relative contributions from torsional motions about ring bonds and deformations of ring angles.[18,19] The single-minimum potential function in 2,5-dihydrofuran, in contrast with the double-minimum potential function for cyclopentene,[20] can be explained by considering these two contributions. In cyclopentene the torsional contribution has a maximum at the planar ring configuration since the three adjacent pairs of methylene hydrogen atoms are all eclipsed whereas in 2,5-dihydrofuran the absence of adjacent eclipsed methylene groups in

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the planar ring may be expected to lead to a minimum in the torsional contribution. On the other hand, the replacement of a carbon atom (CH_2) by an oxygen atom is expected to cause no significant change of the ring angle strain contribution because the appropriate angles in the strain-free compounds $(CH_3)_2CH_2$[21] and $(CH_3)_2O$[22] are essentially the same as those observed in the planar ring. It is not surprising to find therefore that 2,5-dihydrofuran has a single minimum potential function associated with the ring-puckering vibration.

In contrast with the numerous spectroscopic studies of the ring-puckering motion in 2,5-dihydrofuran, there is only one study on the gas-phase molecular structure of this molecule by electron diffraction, and that study by Beach[23] is more than 4 decades old. We therefore undertook the present study of this molecule in order to determine a more precise molecular structure for the molecule and to further characterize the dynamic behavior of the molecule associated with its low-frequency puckering vibration. In the course of the analysis we also found it useful to reanalyze the far-infrared spectroscopic data and to determine a vibrational force field for the molecule.

Experimental

A sample of 2,5-dihydrofuran was obtained from Columbia Organic Chemicals Co. The quoted purity was 97% which was checked by gas-liquid chromatography. The sample was used without further purification. Electron-diffraction data were collected at room temperature (298 K) on the North Dakota State University electron-diffraction instrument using nozzle-to-plate distances of 244 and 95 mm. The accelerating voltage used was 40 keV, and the background pressure was maintained at 1.4×10^{-5} torr during exposure by means of a liquid-nitrogen cold trap situated opposite the stainless-steel inlet. Exposure times for the 0.6 μA beam current were 45 s for the long camera distance and 120 s for the short camera length. The Kodak 4 × 5 in. Electron Image photographic plates were developed at room temperature with Nitrogen burst agitation. Approximate voltage/distance calibrations were obtained from digital voltmeter readings and cathetometer measurements; however, all final calibrations were made on the basis of benzene calibrations[24] (r_a(C—C) = 1.397 (4) Å) that were obtained under operating conditions identical with those used for the sample.

Three photographic plates for each camera distance were traced on the NDSU microcomputer controlled microdensitometer. The optical densities were recorded at 0.150-mm intervals. The data were corrected in the usual manner for emulsion saturation, plate flatness, and sector imperfections after which they were interpolated at integral $q = [(40/\lambda) \sin(\theta/2)]$ for analysis. The data were analyzed by using a least-squares procedure similar to the one employed by Gundersen and Hedberg[25] with elastic scattering factors and phase-shift parameters calculated by Schäfer, Yates, and Bonham.[26]

Far-Infrared Data Analysis

In most cases potential functions for ring puckering have been calculated in terms of a reduced or dimensionless coordinate. These functions may be transformed to a dimensioned form if the reduced mass as a function of the ring-puckering motion is known. The reduced mass function in turn depends critically on a precise dynamic structure for the molecule. Unfortunately most of the dimensioned potential functions thus far determined for 2,5-dihydrofuran have been derived with use of unreliable structural information in the derivation of the reduced mass function, and these potential functions are inadequate for the present purposes. We therefore decided to reanalyze the far-infrared data in order to obtain a more reliable dimensioned ring-puckering potential function for 2,5-dihydrofuran.

Far-infrared vibrational-transition frequencies for the ring-puckering vibration observed by Carreira and Lord[15] were analyzed by using a one-dimensional Hamiltonian of the form

$$H = -(\hbar^2/2)(\mathrm{d}/\mathrm{d}x)g_{44}(x)(\mathrm{d}/\mathrm{d}x) + V(x) \qquad (2)$$

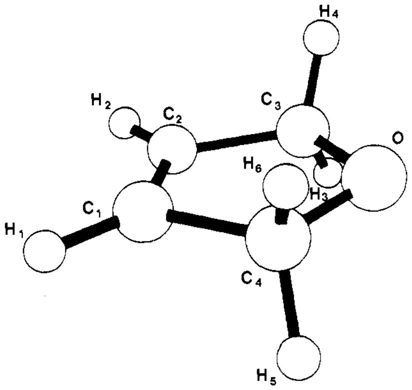

Figure 1. The numbering of atoms used in defining structural parameters for 2,5-dihydrofuran.

where x is the one-dimensional ring-puckering coordinate which is defined as half the perpendicular distance between the tie line of atoms C_3 and C_4 and a line from atom O through the center of the double bond. The reduced mass function $g_{44}(x)$ is the **G** matrix element corresponding to the ring-puckering vibration. The atomic numbering used in defining the structural parameters for 2,5-dihydrofuran is indicated in Figure 1. Although the coupling between the ring-puckering and ring-twisting vibrations has been found to be non-negligible in a previous investigation,[16] the one-dimensional approximation should be satisfactory for the present study. It is expected that this approximation will not adversely affect the puckering potential function parameters.

The reduced mass function, $g_{44}(x)$, was calculated with the aid of a computer program recently written in our laboratory. In this calculation the molecule was treated as a semirigid model of the type described by Malloy.[27] In this model it is assumed that the molecular coordinates change only as a function of the puckering coordinate. Several additional assumptions regarding the geometry of the model were also employed, and since the results obtained depend to some extent upon these assumptions, they are outlined in detail as follows: (1) The molecule was assumed to have C_s symmetry and to maintain that symmetry throughout its puckering motion. (2) All of the bond lengths were assumed to maintain constant values throughout the puckering motion. (3) All C–H bond lengths were constrained to be equal. (4) The ∠HCH planes were constrained to be the perpendicular bisectors of the ∠CCO planes and vice versa. (5) The ∠HCH valence angles were assumed to remain constant. (6) The olefinic hydrogen atoms were assumed to be coplanar with the carbon atoms C_1, C_2, C_3, and C_4.

In earlier studies it was possible to deduce information about the dynamics of the ring-puckering vibrations from model calculations which simulated the puckering vibrational state dependence of the effective rotational constants.[28-30] More specifically, information regarding the dynamic dependence of the ring skeletal angles on the puckering amplitude was obtained by attempting to reproduce the observed trends in rotational constants as a function of vibrational quantum number. Unfortunately there is no reported microwave spectrum for 2,5-dihydrofuran. We therefore decided to construct a dynamic model for the motion of the ring skeletal atoms on the basis of model calculations on related molecules. Model calculations aimed at simulating the observed variations in rotational constants with vibrational quantum number were carried out for three molecules—cyclopentene,[31] cyclopent-3-enone,[32] and 1-pyrazoline[33]—using the

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Table I. Observed and Calculated Ring-Puckering Vibrational Frequencies for 2,5-Dihydrofuran

transition	obsd[a]	calcd	obsd − calcd
0-1	99.9	101.62	−1.72
1-2	116.2	115.42	0.78
2-3	126.8	125.68	1.12
3-4	135.2	134.11	1.09
4-5	142.1	141.36	0.74
5-6	148.1	147.74	0.36
6-7	153.6	153.54	0.06
7-8	158.5	158.79	−0.29
8-9	163.2	163.62	−0.42
9-10	167.5	168.12	−0.62
10-11	171.3	172.31	−1.01
11-12	175.3	176.27	−0.97
12-13	181.1	179.98	1.12

[a] Observed frequencies taken from ref 15.

method described previously.[28] Experimentally observed variations were found to be well reproduced by a model which quadratically couples ring-bending angles to the puckering amplitude as follows:

$$\theta = \theta^{(0)} + \theta^{(2)}\phi^2 \tag{3}$$

In this equation θ is the ∠C=C—C or ∠N=N—C angle and ϕ is the ring-puckering angle which for 2,5-dihydrofuran is defined as the dihedral angle between the $C_4C_1C_2C_3$ plane and the C_3OC_4 plane. The constants $\theta^{(0)}$ and $\theta^{(2)}$ are coefficients in the quadratic expansion of $\theta(\phi)$ when both θ and ϕ have units of degrees. The best agreement between the experimental and calculated variations in the rotational constants is obtained for $\theta^{(2)}$ values of 0.0010, 0.0008, and 0.0013 for cyclopentene, cyclopent-3-enone, and 1-pyrazoline, respectively. From these results we estimated the parameter $\theta^{(2)}$ for 2,5-dihydrofuran to be 0.0010 ± 0.0002, and this value was employed in subsequent reduced mass calculations.

When these assumptions and structural parameters obtained from a preliminary analysis of the diffraction data were used, the reduced mass function for 2,5-dihydrofuran was calculated to be

$$g_{44}(x) = (0.10379 \times 10^{-1}) - (0.2490 \times 10^{-1})x^2 + (0.1238 \times 10^{-1})x^4 \tag{4}$$

when g_{44} is expressed in amu and x is in angstroms. The potential energy function was assumed to have the quartic–quadratic form of eq 1. The coefficients a and b of this potential function were then adjusted by least-squares analysis to obtain a better fit between the observed and calculated far-infrared frequencies. A computer program written in our laboratory was used for this refinement. When the reduced mass function in eq 4 was used, the dimensioned puckering potential function for 2,5-dihydrofuran was calculated to be

$$V(x) = [(0.5297 \pm 0.0192) \times 10^6]x^4 + [(0.9803 \pm 0.0799) \times 10^4]x^2 \tag{5}$$

when V is expressed in reciprocal centimeters and x is in angstroms. The uncertainties in the potential function constants represent 3 standard deviations. The observed and calculated transition frequencies are indicated in Table I.

Normal Coordinate Analysis

Although the vibrational frequencies for 2,5-dihydrofuran have been observed by infrared and Raman spectroscopy,[34] no force field has previously been reported for this molecule. A Urey–Bradley force field for 2,5-dihydrofuran was therefore determined by fitting the observed vibrational frequencies reported by Fortunato.[34] A least-squares-analysis program written in our laboratory was used for this refinement. As a starting point for the analysis the Urey–Bradley force constants for alkanes determined by Schachtschneider and Snyder[35] were used. In addition, Shimanouchi's Urey–Bradley force constants[36] for the ether portion of the molecule were used. In the course of the refinement, the

Table II. Vibrational Force Field for 2,5-Dihydrofuran

force constant[a]	value	force constant	value
$K_{C=C}$	7.70	$F_{C\cdots C}$	0.782
K_{C-C}	2.224	$F_{C\cdots O}$	0.782
K_{C-O}	2.224	$F_{H\cdots H}$	0.055
K_{C-H_1}	4.862	$F_{H_1\cdots C}$	0.310
K_{C-H_3}	4.260	$F_{H_3\cdots C}$	0.231
H_{CCC}	0.720	$F_{H\cdots O}$	0.231
H_{CCO}	0.720	Y_{C-H}	0.239
H_{COC}	0.720	$T_{C=C}$	0.87
$H_{HC=C}$	0.160	T_{C-C}	0.015
H_{HC-C}	0.569	T_{C-O}	0.015
H_{HCO}	0.569	κ_{CH_2}	0.03
H_{HCH}	0.468	$H_{HCC,HCO}$	0.07

[a] Stretching and nonbonded Urey–Bradley force constants have units of mdyn/Å, bending and torsional force constants have units of mdyn Å, and intermolecular tension and bend–bend interaction force constants have units of mdyn Å.

Table III. Calculated and Observed Frequencies for 2,5-dihydrofuran[a]

assignment	obsd	calcd	assignment	obsd	calcd
A_1 Species			B_1 Species		
C–H1 str	3096	3096	C–H1 str	3096	3096
C–H3 str	2863	2861	C–H3 str	2863	2864
C=C str	1618	1617	CH_2 def	1482	1478
CH_2 def	1482	1486	CH_2 wag	1347	1358
CH_2 wag	1363	1364	C–H bend	1097	1108
C–H bend	935	936	C–O str	982	993
C–C str	920	955	C–C str	900	861
C–O str	801	803	ring bend	744	722
ring bend	744	739			
A_2 Species			B_2 Species		
C–H3 str	2888	2888	C–H3 str	2888	2889
CH_2 twist	1167	1179	CH_2 twist	1200	1188
C–H bend	1080	1075	CH_2 rock	1036	1030
CH_2 rock	1011	996	C–H bend	662	661
C=C torsion	398	409	ring pucker	100	101

[a] Observed frequency assignments were taken from ref 34 with minor modifications where necessary. The quoted assignments are based on the magnitudes of the potential energy distribution values obtained from the normal coordinated calculation.

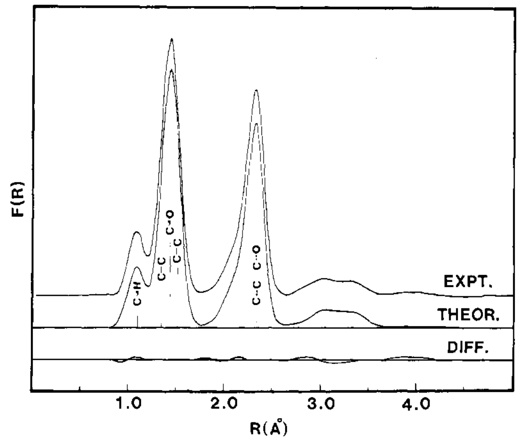

Figure 2. The experimental and theoretical radial distribution curves for 2,5-dihydrofuran. The ordinate units are arbitrary. Only principal peaks are labeled.

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Table IV. Calculated Mean Amplitude and Shrinkage Corrections for 2,5-Dihydrofuran[a]

distance[b]	$l_{ij} \times 10^4$	$(r_g - r_\alpha) \times 10^4$
C=C	422	36
C–C	527	23
C–O	528	15
C_1-H_1	766	191
C_3-H_3	794	140
$C_1 \cdot\cdot C_3$	543	13
$C_3 \cdot\cdot C_4$	563	13
$C_1 \cdot\cdot O$	551	14
$C_1 \cdot\cdot H_2$	1133	112
$C_1 \cdot\cdot H_6$	1066	74
$O \cdot\cdot H_{gem}$	1059	65

[a] Atomic numbering employed is illustrated in Figure 1. l_{ij} parameters are the parallel mean amplitudes of vibration in angstroms, and $r_g - r_\alpha$ values are the perpendicular amplitude parameters in angstroms. All of the values in this table were calculated by removing the contribution of the large-amplitude ring-puckering motion. [b] Only calculated values for prominent distances in the radial distribution curve are shown.

Table V. Structural Parameters for 2,5-Dihydrofuran Obtained from Least-Squares Analysis[a]

	static model		dynamic model	
parameters	model I	model II	model III	model IV
independent[b]				
C=C	1.342 (3)	1.345 (4)	1.350 (3)	1.347 (4)
C–C	1.500 (2)	1.501 (3)	1.505 (2)	1.502 (3)
C–O	1.438 (2)	1.440 (2)	1.441 (2)	1.440 (2)
$C-H_{av}$	1.101 (6)	1.100 (5)	1.100 (6)	1.100 (5)
∠CCC	110.2 (1)	110.0 (2)	109.3 (2)	109.3 (2)
∠HCH	117.0 (3.3)	117.3 (3.5)	109.5 (3.5)	107.1 (3.5)
∠HC=C	135.4 (4.9)	137.0 (4.7)	136.1 (5.0)	134.8 (5.6)
ϕ_0[d]	0.0[e]	11.8 (4.6)		
$A \times 10^3$ [f]			0.2342[e]	0.58 (45)
B[f]			0.2037[e]	0.32 (26)
dependent[c]				
∠CCO	104.1 (3)	103.9 (3)	106.4 (5)	106.5 (4)
∠COC	111.4 (4)	110.8 (6)	108.5 (6)	108.3 (5)
∠HC–C	108.8 (9)	108.7 (1.0)	110.2 (9)	110.8 (9)
R,[g] %	5.0	4.8	5.3	4.9

[a] Distances are reported as r_g values in angstroms and angles are reported as r_α values in degrees. A and B are in cm⁻¹. Quoted errors are 3σ values obtained from least-squares analysis. [b] Independent parameters are those used to construct the model for the molecule. [c] Dependent parameters were calculated from the final results, and the reported errors were calculated by transforming the errors obtained for the independent parameters. [d] ϕ_0 is the dihedral angle between the $C_4C_1C_2C_3$ plane and the C_3OC_4 plane. [e] Assumed value. [f] The puckering potential function is given by $V(\phi) = A\phi^4 + B\phi^2$. [g] R factors defined as $R = \Sigma[W_i(I_{obsd} - I_{calcd})^2]/[\Sigma W_i I_{obsd}^2])^{1/2}$

HCC,HCO bending interaction force constant was included in order to obtain better agreement between the observed and calculated frequencies of the methylene rocking and twisting modes. A few minor modifications in the assignments are based on the magnitudes of the potential energy distribution obtained from the normal coordinate calculation. The refined force field is shown in Table II, and the observed and calculated vibrational frequencies are shown in Table III. The mean amplitudes, l_{ij}'s, and shrinkage corrections, $r_g - r_\alpha$, for some of the more prominent internuclear distances in the radial distribution curve (Figure 2) are listed in Table IV.

Electron-Diffraction Analysis

Rigid Model. The first model which was explored in the analysis of the electron-diffraction data was a rigid model. Although this model is not expected to be realistic, all of the previous electron-diffraction studies on pseudo-four-membered rings have been performed by using this model, so we included this analysis for the purpose of comparison. In order to make the analysis tractable, assumptions 3, 4, and 6 employed in the earlier section of this study were retained.

In this analysis the following seven structural parameters were used to define the model: (1) the C=C bond length, (2) the C—C bond length, (3) the C—O bond length, (4) an average C—H bond length, (5) the ∠CCC valence angle, (6) the ∠HCH valence angle, and (7) the ∠HC=C valence angle. It was discovered in the early stages of analysis that most of the prominent peaks had vibrational amplitudes that were strongly correlated with structural parameters. It is advantageous in such situations to constrain the amplitudes to calculated values in an effort to obtain the maximum amount of information concerning the molecular geometry. All of the amplitude parameters were therefore constrained to their calculated values during the least-squares refinements. The asymmetry parameters, k, for bonded distances were estimated by using a diatomic approximation[37] with Morse anharmonicity parameters, a, of 2.0 Å^{-1} for the C=C and C—C bonds, 2.5 Å^{-1} for the C—H bonds, and 2.3 Å^{-1} for the C—O bond.[38] The asymmetry parameters for nonbonded distances were all assumed to be zero in the analysis.

In the first refinement of the structure of 2,5-dihydrofuran it was assumed that the molecule had C_{2v} symmetry with a planar ring configuration consistent with the equilibrium geometry found from the far-infrared analysis. In spite of the several assumptions including the rigid model approximation, this model gave excellent agreement with the experimental data. The results of this analysis are given in Table V under the heading of model I.

Next a non-planar rigid model was also tried in which the planarity constraint was relaxed and the angle ϕ_0 was introduced as an additional parameter in the least-squares refinement. This is entirely appropriate in spite of the fact that the far-infrared experimental data indicate conclusively that the equilibrium structure is planar. It is important to remember that the electron-diffraction experiment observes the vibrationally averaged structure for the molecule and this may be quite different from the equilibrium structure even when corrections for shrinkage effects are made. This is particularly true in a molecule such as 2,5-dihydrofuran where the large amplitude puckering motion is also anharmonic. The results of this analysis are given in Table V under the heading of model II. In spite of the rather large puckering angle, 11.8 (4.6)°, all of the other structural parameters were in good agreement with those obtained for model I. It should also be noted, however, that the improvement in the fit is not statistically significant enough to justify the inclusion of an additional parameter.

Dynamic Model. A dynamic model involving a ring-puckering potential function was also investigated. For computational convenience, the potential function governing the ring-puckering motion was assumed to have the form:

$$V(\phi) = A\phi^4 + B\phi^2 \qquad (6)$$

The molecule was treated as a semirigid framework where the structure was assumed to depend only upon the ring-puckering motion. In addition to assumptions 1–6 employed in the earlier section, the following additional assumption was also introduced: (7) The ∠CCC valence angle was assumed to change its value as a function of the ring-puckering angle as follows:

$$\angle CCC = \angle CCC^{(0)} + 0.0010\phi^2 \qquad (7)$$

In this model the two potential function parameters, A and B, were used instead of the ring-puckering angle, ϕ_0, which was used in the rigid-model analysis. All of the amplitude parameters were constrained to their calculated values as in the rigid-model analysis except that they were all recalculated for a planar model with the puckering frequency set to zero. This procedure effects a separation of harmonic framework contributions from the large-amplitude contributions to the vibrational amplitudes.[38] Two of the amplitudes showed strong dependences on the angle ϕ and were

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Table VI. Comparison of the Structure of 2,5-Dihydrofuran with the Structures of Related Molecules[a]

molecule	C=C	C–C	C–O	∠C=C–C	∠C–C–O	∠C–O–C	ref
2,5-dihydrofuran	1.347 (4)	1.502 (3)	1.440 (2)	109.3 (2)	106.5 (4)	108.3 (5)	*b*
ethane		1.534 (4)					40
ethylene	1.337 (2)						41
propene	1.342 (2)	1.506 (3)		124.3 (4)			42
cis-2-butene	1.348 (9)	1.509 (6)		125.4 (1.2)			43
dimethyl ether			1.418 (3)			111.5 (1.5)	44
ethyl methyl ether			1.418 (2)		109.4 (3)	111.9 (5)	45

[a] Bond lengths are r_g values in angstroms and angles are in degrees. [b] Present study.

therefore included in the analysis as the following functions of the puckering angle:

$$l_{C3C4} = l_{C3C4}{}^{(0)} - (0.0009\phi)^2 \qquad (8)$$

$$l_{H10} = l_{H10}{}^{(0)} + (0.0011\phi)^2 \qquad (9)$$

A total of six pseudoconformers were included in the analysis between $\phi = 0°$ and $\phi = 48°$. The composite molecular intensity curve for the mixture of pseudoconformers is given by:

$$sM(s) = \sum W_i(\phi_i)\cdot sM(s,\phi_i) \qquad (10)$$

where $sM(s,\phi_i)$ is the molecular intensity for the *i*th pseudoconformer, and $W_i(\phi_i)$ is the weight assigned to this conformer. A comparison between the calculated exact quantum mechanical distribution function and the classical approximation revealed that the classical distribution function was adequate for the present analysis at room temperature. The weights assigned to each conformer were therefore taken to be:

$$W_i(\phi_i) = \exp(-V(\phi_i)/RT)/\sum \exp(-V(\phi_i)/RT) \qquad (11)$$

The formulation of the Jacobian elements of the molecular intensity curve with respect to the potential function parameters has been described elsewhere.[39]

Two analyses based on the ring-puckering model were tried. In the first ring-puckering model, the potential function parameters, *A* and *B*, in eq 6 were constrained to the values of 0.2342 × 10^{-3} cm^{-1} and 0.2037 cm^{-1}, respectively, which were obtained from eq 5 by transforming the puckering coordinate, *x*, into the puckering angle, ϕ. The structural parameters obtained from this analysis are listed in Table V under the heading of model III.

In a second refinement, an attempt was made to vary the potential function parameters, *A* and *B*, in the least-squares analysis; however, the strong correlation between the two potential function parameters prevented their simultaneous refinement so instead they were varied in alternative least-squares cycles. The final values for all of the parameters obtained from the least-squares analysis of the puckering model are shown in Table V under the heading of model IV. Systematic errors produced by slight modification in assumption 7 above had negligible effect compared to the observed random errors on all of the parameters. The final radial distribution curves for this model are shown in Figure 2, and the corresponding molecular intensity curves are shown in Figure 3.

Discussion

The two analyses, based on rigid and dynamic models, fit the experimental data almost equally well. We, nevertheless, prefer the results obtained from the dynamic ring-puckering model without hesitation, since this model represents a more realistic estimate of the atomic motions associated with the ring-puckering vibration. While there is good agreement between the results obtained from model I and model II, and also between the results obtained from model III and model IV, there are distinct differences in some of the valence angles when one compares the rigid model (I and II) with the dynamic model (III and IV). The ∠CCC, ∠HCH, and ∠COC valence angles obtained from the rigid-model analysis are all larger than the corresponding results obtained from the dynamic ring-puckering model, while the ∠CCO valence angle appears to be smaller in the rigid model than in the dynamic model.

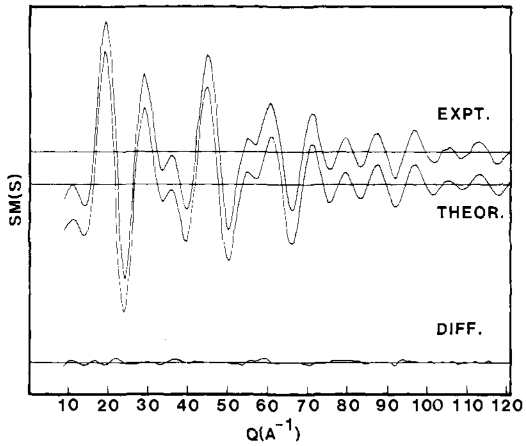

Figure 3. The leveled experimental and theoretical molecular intensity curves for 2,5-dihydrofuran.

Two factors should be considered as contributing to the discrepancies between the rigid and dynamic models. First, it is obvious that the small amplitudes and shrinkage correction parameters for a molecule with a large amplitude puckering motion such as 2,5-dihydrofuran. In fact, the perpendicular amplitudes for the geminal distances, $H_3\cdots C_2$ and $H_3\cdots O$, were too large, and these large corrections caused most of the increase in the ∠HCH valence angle. Second, all of the nonbonded distances between the ring skeletal atoms decrease during the ring-puckering motion. Among others, the C···O nonbonded distance decreases substantially, which causes an apparent decrease in the ∠CCO valence angle and an increase in the ∠CCC and ∠COC valence angles in the rigid model. A detailed inspection of Table V also reveals that the ring skeletal bond lengths determined for the rigid model are slightly shorter than those determined for the puckering model, although these parameters agree with each other within the experimental uncertainties. All of these considerations serve to demonstrate that the rigid-model analysis of the molecule may lead to erroneous structural parameters even if the experimental data are adequately fit by the model. It is for this reason that we prefer the results obtained from the analysis of the dynamic model.

It is interesting to compare the present results with those obtained by Beach[23] using the visual method in 1941. Beach assumed a C═C bond length of 1.34 Å in his analysis and then used the two main features in the radial distribution curve to determine the C—O and C—C distances and the ∠COC angle. He obtained a C—C bond length of 1.54 (3) Å, a C—O bond length of 1.43 (3) Å, and a ∠COC valence angle of 110 (3)°. This structure is surprisingly consistent with the present analysis when one considers the limitations imposed by the visual method.

It is instructive to compare the present results with structures of related molecules in order to examine the effects of ring closure on bond lengths and valence angles. Table VI compares the structure of 2,5-dihydrofuran with structures of related noncyclic

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molecules. The $C=C$ (1.347 (4) Å) and C—C (1.502 (3) Å) bond lengths in 2,5-dihydrofuran agree with those in propene ($C=C$ = 1.342 (2) Å and C—C = 1.506 (3) Å)[42] and *cis*-2-butene ($C=C$ = 1.348 (9) Å and C—C = 1.509 (6) Å)[43] within their respective uncertainties. The $C=C$ bond length also agrees with that in cyclopentene (1.342 (10) Å).[7] In contrast with these bond lengths, the C—O bond length (1.440 (2) Å) in 2,5-dihydrofuran is considerably longer than those in dimethyl ether (1.418 (3) Å)[44] and ethyl methyl ether (1.418 (2) Å),[45] and it is even longer than that found in tetrahydrofuran (1.428 (5) Å).[46] Similar lengthening has been observed in the C—Si bond length in silacyclopent-3-ene (1.901 (3) Å)[13] relative to dimethylsilane (r_s = 1.867 (2) Å)[47] and silacyclopentane (1.892 (2) Å).[48] The observed variation of the C—O bond length is rather difficult to explain, but it may be due to bond stretching introduced by trying to accommodate two sp^2 carbon valence angles in a small five-membered ring. This at least would explain the apparent shortening of the C—O bond length in tetrahydrofuran relative to 2,5-dihydrofuran. The unstrained sp^3 valence angles of 109.5° are more easily accommodated without bond stretching than the 120° sp^2 valence angles. This ring strain is further compounded by the larger bending force constant in the unsaturated molecule.

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Supplementary Material Available: Tables of experimental intensity data and correlation and error matrices (4 pages). Ordering information is given on any current masthead page.

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Structure of Butatrienone ($CH_2=C=C=C=O$)

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Abstract: The structure of butatrienone ($CH_2=C=C=C=O$) has been determined with the aid of ab initio molecular orbital calculations. An orthogonal-bent structure is predicted. Taken together with previous results for propadienone and new results for pentatetraenone and hexapentaenone, the theoretical result for butatrienone suggests that bending of the heavy-atom chain is a general feature of larger cumulenones $CH_2=(C)_n=O$. The preferred bending direction alternates as a function of *n* between in-plane and orthogonal.

The structures of cumulenones ($CH_2=(C)_n=O$, n = 0, 1, 2, 3, ...; Figure 1) have aroused considerable theoretical[1-3] and experimental[4-6] interest. Formaldehyde (n = 0) and ketene (n = 1), of course, have well-established and straightforward structures; however, the structure of propadienone (n = 2) is quite unusual. While naively one might expect cumulenones to have a linear chain of heavy (i.e., non-hydrogen) atoms, resulting in molecules with C_{2v} symmetry, experiment[5] and theory[3] now agree that this is *not* the case for propadienone. If fact, this molecule is planar bent with C_s symmetry and a CCC bond angle in the vicinity of 145°.[3]

The structures of higher members of the series are therefore of interest. For instance, the question arises as to whether all or only some of the higher members have nonlinear chains. In this connection, it is well-known that cumulene molecules exhibit alternating properties, according to whether n is odd or even. A striking related example is the discovery in interstellar space of HC_nN molecules with n = 1, 3, 5, 7, 9 but not with n even.[7]

Only one experimental structural result has so far been reported for higher cumulenones.[6] Although the data were limited, they appeared to be consistent with the molecule of butatrienone (n = 3) having C_{2v} symmetry and not exhibiting the peculiarities of propadienone. Minimal basis set PRDDO calculations[8] also revealed no evidence for deviations from C_{2v} symmetry. In this paper, we describe the results of a detailed study of butatrienone at significantly higher levels of theory. These indicate an *orthogonal-bent equilibrium structure for butatrienone.*

Method and Results

All calculations were carried out by using a modified version[9a] of the GAUSSIAN 80 system of programs.[9b] In the case of propadienone, we have found previously[3] that the Hartree–Fock model predicts an incorrect structure, namely one with C_{2v} symmetry.[1,2] It is necessary to include correlation energy to obtain the correct result,[3] a situation that is rather unusual. Clearly care must be taken in the calculation on butatrienone to take into account such effects.

In our previous work on propadienone[3] we used the following scheme. Optimized Hartree–Fock (HF) geometries we obtained by using the split-valence 4-31G basis set[10] for a series of structures in which the CCC bond angle was fixed at different values. These structures were then empirically corrected to compensate for systematic deficiencies. Single-point calculations were performed

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