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Spectroscopic Determination of the Vibrational Potential Energy Surface and Conformation of 1,3-Benzodioxole in Its $S_1(\pi,\pi^*)$ Excited State. The Effect of the Electronic Excitation on the Anomeric Effect

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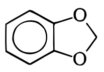
Abstract: The electronic absorption spectra and the laser-induced fluorescence spectra of supersonic-jet-cooled 1,3-benzodioxole molecules have been investigated to map out the vibronic energy levels in the $S_1(\pi,\pi^*)$ electronic excited state. These were used to determine a two-dimensional potential energy surface in terms of the ring-puckering and ring-flapping vibrational coordinates, and the molecule was found to be puckered with a dihedral angle of 22°. The barrier to planarity in the excited state is 264 cm^{-1} (3.16 kJ/mol) as compared to 164 cm^{-1} (1.96 kJ/mol) in the ground state. This increase is attributed to reduced suppression of the anomeric effect by the benzene ring resulting from decreased π bonding character in the $S_1(\pi,\pi^*)$ state. As expected, the motion along the flapping coordinate is governed by a more shallow potential energy well. Ab initio calculations carried out for both the ground and excited states support the experimental conclusions.

Introduction

Recently we reported the far-infrared, Raman, and dispersed fluorescence spectra of 1,3-benzodioxole (**I**) from which we determined the two-dimensional vibrational potential energy surface for the ring-puckering and ring-flapping motions of this molecule in its electronic ground state.[1] The molecule was found to have a barrier to planarity of 164 cm^{-1} (1.96 kJ/mol) and puckering and flapping angles of ±24° and ∓3°, respectively. The lack of planarity was ascribed to the anomeric effect, which is believed to arise from the interaction between a nonbonded oxygen p orbital and the empty σ^*(C−O) orbital on the other oxygen atom.[2−5] The barrier for 1,3-benzodioxole is considerably less than the 275 cm^{-1} (3.29 kJ/mol) barrier determined[6] for 1,3-dioxole (**II**), suggesting a suppression of the anomeric effect by the benzene ring. For 1,3-dioxole the magnitude of the torsional potential energy term for rotation about each C−O bond arising from the anomeric effect was calculated to be 25.0 kJ/mol whereas for 1,3-benzodioxole this is only 8.4 kJ/mol. Ab initio calculations have been carried out for both molecules[7,8] and the predicted barriers were in excellent agreement with our experimental findings.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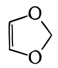
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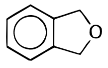
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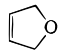
IV

To gain more insight into the diminished anomeric effect in 1,3-benzodioxole, we undertook the investigation of this molecule in its $S_1(\pi,\pi^*)$ electronic excited state. The $S_1(\pi,\pi^*)$ state for 1,3-benzodioxole is very similar to that for phthalan[9] (**III**) and results from an $A_2 \rightarrow A_2$ orbital transition that gives rise to a totally symmetric A_1 state. In the S_0 ground state the benzene ring possesses six π electrons, but after a $\pi \rightarrow \pi^*$ transition the first excited electronic state has five bonding π electrons and one antibonding π^* electron. We therefore wished to determine whether the reduced π bonding character of the benzene ring in the $S_1(\pi,\pi^*)$ state would decrease the suppression of the anomeric effect and result in a higher barrier to planarity.

We have recently investigated both the ground[10,11] and excited electronic states[9] of phthalan, which is similar to 1,3-benzodioxole but lacks the anomeric effect. Phthalan is planar in both states although it possesses a tiny barrier of 35 cm^{-1} (0.4 kJ/mol) in its ground state. The planarity of phthalan, as well as

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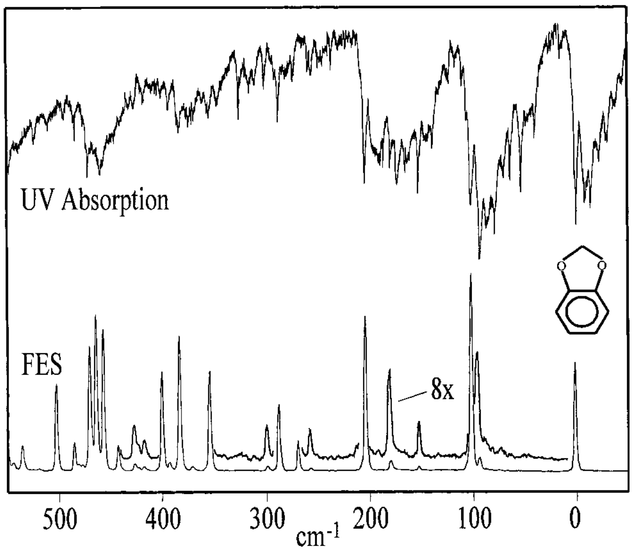

Figure 1. Fluorescence excitation spectrum (FES) and ultraviolet absorption spectrum of 1,3-benzodioxole. The band origin is at 34 789.8 cm^{-1}.

that of the analogous 2,5-dihydrofuran (IV),[12] is expected since there are no torsional forces present to pucker the five-membered ring. The methodology developed for the study of the phthalan excited state[9] was also utilized for the present work. The laser-induced fluorescence spectra of jet-cooled molecules along with the ultraviolet absorption spectra were used to map the ring-puckering and ring-flapping energy levels of 1,3-benzodioxole in its $S_1(\pi,\pi^*)$ state. These levels were then used to determine the two-dimensional potential energy surface which defines the conformational energetics of the molecule and therefore provides a clear indication of the magnitude of the anomeric effect.

Experimental Section

1,3-Benzodioxole was purchased from Aldrich Chemical Co. and purified by vacuum distillation. Fluorescence excitation and dispersed fluorescence spectra were taken using an experimental apparatus described elsewhere.[13,14] The excitation source was a Nd:YAG pumped dye laser with Rhodamin 590 as the laser dye. The sample was cooled through a pulsed supersonic jet, and spectral lines were detected using a photomultiplier detector.

Ultraviolet absoprtion spectra were recorded on a Bomem DA8.02 spectrometer equipped with a quartz/UV beam splitter, Si/UV detector, and deuterium lamp as a source. The sample of 1,3-benzodioxole was contained in a glass cell with quartz windows with pressures ranging from 200 to 500 mTorr. Spectra were acquired at resolutions of 0.5, 0.25, and 0.1 cm^{-1} with acquisitions ranging from 5000 to 7500 scans.

Results and Discussion

Analysis of Spectra. Figure 1 shows an overview of both the fluorescence excitation spectrum (FES) of the jet-cooled molecules and the ultraviolet absorption spectrum recorded at ambient temperature. The electronic band origin is at 34 789.8 cm^{-1}. We have carried out an ab initio calculation at the td-B3LYP/6-31+G(d)//CIS/6-31+G(d) level for the S_1 state and the transition frequency was calculated to be 36 986 cm^{-1}. The jet-cooled molecules for the FES have a vibrational temperature of about 50 K, so only the ground ring-puckering level ($\upsilon_P = 0$) and the first excited level ($\upsilon_P = 1$), which lies 9.6 cm^{-1} above the ground state, will be significantly populated. Hence the FES bands originate from only these two states. Table 1 lists the FES bands up to 580 cm^{-1} along with the corresponding absorption frequencies and assignments. The spectra were recorded numerous times under different jet conditions resulting in colder and warmer spectra thus making it possible to identify hot bands resulting from vibrationally excited states (usually $\upsilon_P = 1$). These are labeled as H in the table and distinguished from the bands originating from the $\upsilon_P = 0$ ground state (G). The assignments for the bands are also given. Single and double primes on the ring-puckering quantum numbers refer to the ring-flapping $\upsilon_F = 1$ and 2 states, respectively. Figure 2 shows the vibronic levels for the $S_1(\pi,\pi^*)$ state determined from these spectra and compares them to the vibrational levels previously reported[1] for the S_0 electronic ground state. With the molecule assumed to have C_{2v} symmetry (planar approximation) and to lie in the *xz* plane, both the ring-puckering and ring-flapping vibrations have B_2 symmetry. The vibrational coordinates for these modes were defined in our investigation of phthalan.[11] The ring-puckering is essentially the movement of the CH_2 group out of the five-membered ring while the flapping is the bending of the five-membered ring relative to the benzene ring in a butterfly-like motion. Thus in Figure 2 all of the ring-puckering levels with υ_P = even for $\upsilon_F = 0$ or 2 have A_1 symmetry whereas the υ_P = odd levels have B_2 symmetry. When

Table 1. Fluorescence Excitation Frequencies (cm^{-1}) for 1,3-Benzodioxole Compared to the Corresponding Absorption Bands

freq[a]	absorption[a]	transition[b]	type[c]
0 s	0.0	0−0	G
1 sh	1.4 m sh	1−1	?
54 vvw	53.4 m		H
86 sh	86.4 mw br	$37_0^1 38_1^0 39_0^1$	H
93 m	92.9 vs	1−2	H
102 ws	101.8 vs	0−2	G
153 mw	152.9 m	1−3	H
180 m	179.9 w	1−0′	H
189 vvw	189.1 w	0−0′	?
204 vw	204.4 ms	0−1′	G
257 w	255.4 w	$37_0^1 39_1^2$	H
271 ms	273.5 w	0−4	G
290 s	288.1 m	1−2′	H?
301 mw	301.3 w	2−3′	H
354 s	354.1 w br	$37_0^1 39_0^1$	G
372 w	373.8 vw	1−5	H
383 vs	383.1 mw	0−0″	G
393 mw	393.0 mw	1−1″	H
400 s	400.1 w	0−3′	G
417 mw	417.3 mw		H
427 m	426.8 mw		H
444 ms	445.5 vw	$37_0^1 39_1^2$	H
457 vs	459.1 m br		G
464 vs			G
471 vs	471.1 m		H
478 vw	476.0 w		H
483 vwsh	483.4 mw		H
487 ms	485.1 w		
504 s		0−2″	G
537 m	538.5 vvw br		
545 m	547.4 ms		
551 ms	553.1 w		
566 s	567.2 vw		H
571 vs	574.1		G

[a] Relative to the 0_0^0 band at 34 789.8 cm^{-1}; s strong; m medium; w weak; v very; br broad. [b] $\upsilon_P(S_0) \rightarrow \upsilon_P(S_1)$; prime indicates $\upsilon_F = 1$; double prime indicates $\upsilon_F = 2$. [c] G, from the S_0 ground state; H, hot band.

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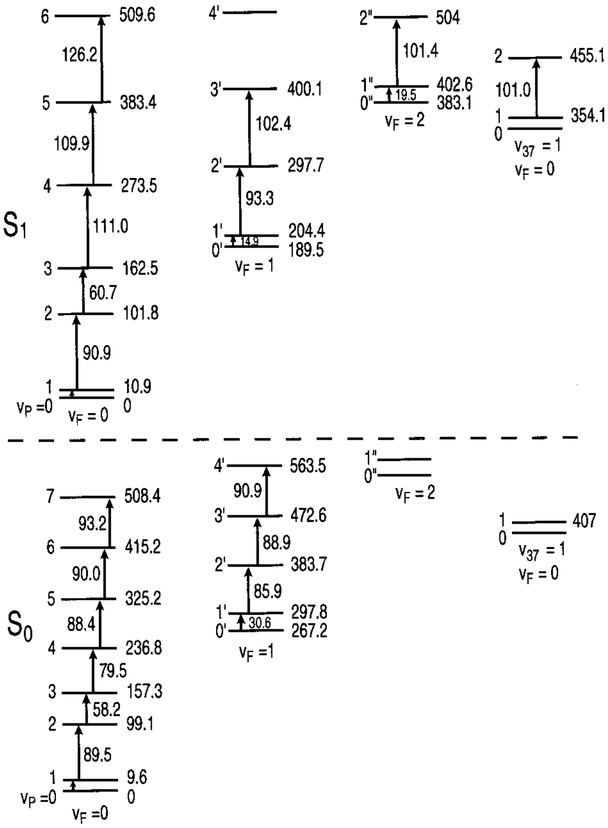

Figure 2. Energy diagram for the ring-puckering (υ_P), ring-flapping (υ_F), and υ_{37} vibrations of 1,3-benzodioxole in its ground (S_0) and excited (S_1) electronic states. Single and double primes on the ring-puckering (υ_F) quantum numbers indicate the $\upsilon_F = 1$ and 2 states, respectively.

$\upsilon_F = 1$ or when $\upsilon_{37} = 1$ (υ_{37} is a B_2 vibration, as shown in Table 2), the symmetries are reversed as the υ_P = odd levels have A_1 symmetry and the υ_P = even levels have B_2 symmetry. In the spectra (either FES or absorption) most of the observed features with significant intensity are expected from transitions which involve no change in vibrational symmetry ($A_1 \rightarrow A_1$ originating from $\upsilon_P = 0$ or $B_2 \rightarrow B_2$ originating from $\upsilon_P = 1$). This is verified in Table 1 where all of the FES bands except the $1 \rightarrow 2$ at 93 cm^{-1} are of this type. This exception can be explained by the fact that the $\upsilon_P = 0$ and 1 levels, as will be seen, are below the barrier of this puckered molecule which actually has C_s symmetry. Thus, the $1 \rightarrow 2$ transition is actually a symmetric $A' \rightarrow A'$ transition.

The dispersed fluorescence spectra from many of the bands in the FES have also been recorded and these are available elsewhere.[1,15] These were helpful in determining the symmetries of the S_1 vibronic levels. For example, the dispersed spectra from the 101.8 ($\upsilon_P = 2$) and 204.4 cm^{-1} ($\upsilon_P = 1'$) S_1 levels, which are both of A_1 symmetry, showed only transitions to A_1 bands such as 99.1, 236.8, and 297.8 cm^{-1} in the S_0 ground state. Dispersed spectra from the B_2 levels such as 162.5 cm^{-1} ($\upsilon_P = 3$) involved transitions to 9.6 and 157.3 cm^{-1} as well as to other B_2 states. For the phthalan dispersed fluorescence spectra[9] similar observations were made.

Figure 2 does not show the energy levels associated with the ring-twisting (υ_{20} with quantum number υ_T) vibration which is at 214 cm^{-1} in the S_0 state and predicted to be about 14 cm^{-1} lower in the S_1 state by the ab initio calculation (see Table 2). The ring-twisting vibration has A_2 symmetry in the $C_{2\upsilon}$ (planar) approximation. Hence the ring-puckering levels for $\upsilon_T = 1$ will have either A_2 (υ_P = even) or B_1 (υ_P = odd) symmetry. Since transitions from the S_0 ground state (A_1) to the A_2 levels are forbidden and since transitions to the B_1 levels give type B bands (with no sharp features), none of these play a role in the interpretation of the spectra. However, transitions to the $\upsilon_T = 2$ state of A_1 symmetry in $S_1(\pi,\pi^*)$, which is expected to be about 400 cm^{-1} above the ground vibronic levels, can be seen. The FES becomes considerably more congested above 400 cm^{-1} and this is due to both the presence of the $\upsilon_T = 2$ twisting state as well as to energy levels associated with the other vibrations listed in Table 2.

Table 2. Low-Frequency Vibrational Frequencies (cm^{-1}) of 1,3-Benzodioxole in Its S_0 and $S_1(\pi,\pi^*)$ States

			S_0			S_1
		approximate description	obsd	MM3	ab initio[a]	ab initio[b]
A_1	υ_{12}	benzene ring-bending	799	720	723	604
	υ_{13}	benzene ring-bending	736	606	703	597
	υ_{14}	ring bending	534	498	527	472
A_2	υ_{19}	benzene out-of-plane bend	614	661	601	486
	υ_{20}	ring twisting	214	294	211	197
B_1	υ_{31}	benzene ring-bending		541	545	377
	υ_{32}	ring bending		391	398	268
B_2	υ_{37}	benzene out-of-plane bend	405	521	410	373
	υ_{38}	ring-flapping	267	383	269	203
	υ_{34}	ring-puckering	91		78	120

[a] B3LYP/6-31G(d). [b] CIS/6-31+G(d).

The absorption spectra recorded at ambient temperature arise even from energy levels more than 500 cm^{-1} above the ground state. For example, a level at 520 cm^{-1} is still 8% as populated as the ground state. As shown in our ground state study,[1] there are seven ring-puckering levels in the ground ($\upsilon_F = 0$) flapping state and another four in the $\upsilon_F = 1$ state below 520 cm^{-1}. In addition, below 500 cm^{-1} there are five ring-puckering levels in the first excited ($\upsilon_T = 1$) ring-twisting state and another two in the $\upsilon_T = 2$ state. The first excited state of υ_{37} will have three levels below 520 cm^{-1}. All together 21 energy levels will be at least 8% as populated as the ground state at ambient temperatures. If states up to 800 cm^{-1} are considered, where the populations still exceed 2% of the ground state value, transitions from several dozen additional vibrational states come into play. In addition, there are potentially a hundred or more vibronic levels in the $S_1(\pi,\pi^*)$ state to which transitions can readily go so there could be several thousand observable absorption bands in the spectrum of a molecule such as 1,3-benzodioxole. This prospect is made less daunting by the fact that Franck−Condon factors limit many of the transitions and that typically only the totally symmetric transitions, as discussed above, show significant intensity. 1,3-Benzodioxole has C_s symmetry, but in its planar approximation it becomes $C_{2\upsilon}$. Since many of the puckering levels lie above the barrier in the ground state and also, as will be seen, in the excited state, the $C_{2\upsilon}$ approximation is suitable for consideration of most of the transitions.

The electronic absorption spectra are very rich, but our detailed knowledge of the ground state energy levels and the symmetries of the transitions make the assignments feasible. This is especially true since the FES readily helps to identify the transitions from the $\upsilon_P = 0$ and 1 states to more than a dozen of the vibronic levels in the $S_1(\pi,\pi^*)$ electronic excited state. Figure 3 shows a number of the assigned transitions in the ultraviolet absorption spectrum and Table 3 lists many of the assigned bands. A comprehensive listing of the absorption bands can be found elsewhere.[16] An important feature in the

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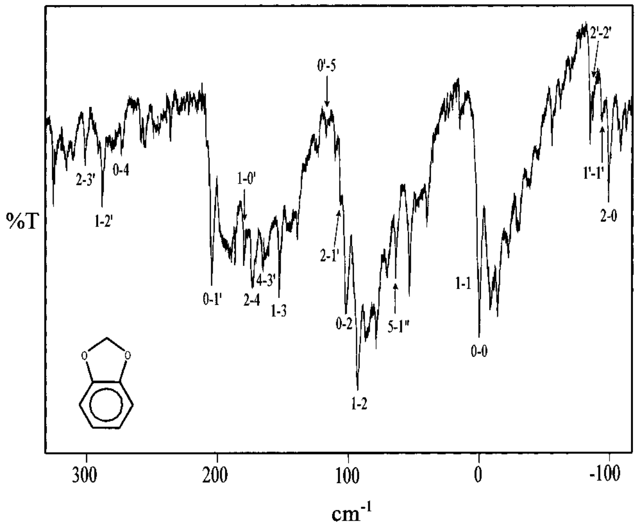

Figure 3. Absorption spectra and assignments for 1,3-benzodioxole near the band origin.

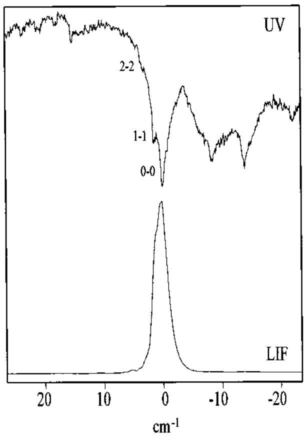

Figure 4. FES and absorption spectra showing the splitting between the 0−0 and 1−1 transitions.

observed spectra is that the 0−0 and 1−1 transitions are only 1.4 cm^{-1} apart, and this is shown in Figure 4. The separation is clear in the absorption spectrum but shows up as a shoulder in the lower resolution FES. While many of the absorption bands in the spectrum have been assigned with confidence with the help of the FES, many others cannot readily be assigned. As discussed above, transitions from numerous excited levels of vibrations other than the ring-puckering and ring-flapping may occur. Each of these possesses combination levels with the puckering, flapping, ring-twisting, etc., which further complicate matters. A portion of the assigned bands no doubt involve the ring-twisting levels where $A_2 \rightarrow A_2$ and $B_1 \rightarrow B_1$ transitions should show significant intensity. A sharp absorption band at $-14.0\ \text{cm}^{-1}$ very likely results from the $v_T = 1\ (S_0) \rightarrow v_T = 1\ (S_1)$ transition, for example. This is also predicted by the ab initio calculation to be at $-14\ \text{cm}^{-1}$, as shown in Table 2.

Table 3. Ring-Puckering and Ring-Flapping Bands (cm^{-1}) in the Electronic Absorption Spectrum of 1,3-Benzodioxole

Δv_P	Δv_F	sym	transition[a]	obsd[b]	inferred[c]	intensity[d]
0	0	A_1	0−0	0.0	0.0	vs
			1−1	1.4	1.3	m, sh
			2−2	3.0	2.7	w, sh
			3−3	6.0	5.2	w, sh
			4−4	35.8	36.7	vw
0	0	A_1	0′−0′	−77.5	−77.7	w
			1′−1′	−93.4	−93.4	mw
			2′−2′	−86.7	−86.0	mw
0	1	B_2	0−0′	189.1	189.5	w
1	0	B_2	1−2	92.9	92.2	s
			2−3	63.7	63.4	m
			3−4	116.9	116.2	w
1	0	B_2	0′−1′	−62.3	−62.8	w
1	−1	A_1	0′−1	−256.0	−256.3	w
			1′−2	−198.6	−196.0	m, br
			3′−4	−198.6	−199.1	m, br
			2′-3	−223.6	−221.2	mw, br
1	1	A_1	0−1′	204.4	204.4	s
			1−2′	288.1	288.1	m
			2−3′	301.0	301.0	m
2	0	A_1	0−2	101.8	101.8	s
			1−3	152.9	152.9	m
			2−4	173.0	174.4	m, br
2	−1	B_2	1′−3	−136.7	−135.3	w
3	0	B_2	0−3	~163	162.5	w, br
			1−4	264.2	263.9	vw
3	0	B_2	0′−3′	400.1	400.1	w, br
4	0	A_1	0−4	273.5	273.5	mw
			1−5	373.8	373.8	w
5	−1	A_1	0′−5	116.8	116.2	w
6	0	A_1	0−6	509.6	509.6	w, br
−1	0	B_2	1−0	−8.4	−8.4	ms
			3−2	−55.4	−55.4	mw
−1	0	B_2	2′−1′	−179.1	−179.3	w
			3′−2′	−174.2	−174.9	w
−1	−1	A_1	1′−0	−298.4	−297.8	mw
−1	1	A_1	1′−0	179.8	179.9	mw
			2−1′	106.3	105.3	w
			3−2′	138.9	140.4	w
			4−3′	163.0	163.3	w, br
−1	1	A_1	1′−0	−298.4	−297.8	w
−2	0	A_1	2−0	−99.4	−99.1	s
			3−1	−147.2	−146.4	ms
			4−2	−135.1	−135.0	w, br
			5−3	−161.7	−162.7	vw
−2	0	A_1	2′−0′	−193.2	−194.2	vw
			4′−2′	−265.5	−265.8	mw
−3	1	A_1	3−0′	32.4	32.2	vw
−4	0	A_1	4−0	−273.3	−236.8	vw
			5−1	−315.1	−341.3	w
−6	0	A_1	6−0	−415.2	−415.2	vw
0	2	A_1	0−0″	383.1	383.1	mw
			1−1″	393.0	393.0	mw
−4	2	A_1	4−0″	~146	146.3	w, br
			5−1″	78.8	77.4	m

Calculation of Potential Energy Surface. The determination of the ring-puckering and ring-flapping vibronic levels for the $S_1(\pi,\pi^*)$ state (Figure 2) makes it possible to calculate the vibrational potential energy surface for these two motions in the excited state. This was done in a manner similar to that used for the ground-state investigations[1] using computer programs developed in our previous work.[16−19] First, an approximate structure was required to carry out the kinetic energy calculation. This was obtained from the ab initio calculation for the S_1 state and the result is shown in Figure 5 along with the ground-state structure.[8] The one-dimensional kinetic energy function for the ring-puckering vibration was calculated to be

$$g_{44} = 0.0068924 - 0.053521x_1^2 + 0.18837x_1^4 - 0.61333x_1^6 \quad (1)$$

where x_1 is the ring-puckering coordinate in Å. An attempt to

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Table 4. Observed and Calculated Ring-Puckering and Ring-Flapping Energy Separations (cm^{-1}) for the $S_1(\pi,\pi^*)$ of 1,3-Benzodioxole

levels	obsd	calcd I[a]	Δ	calcd II[b]	Δ
0−1	10.9	9.9	1.0	11.7	−0.8
1−2	90.9	97.6	6.7	92.1	−1.2
2−3	60.7	71.5	10.8	61.1	−0.4
3−4	111.0	99.7	11.3	111.2	−0.2
4−5	109.9	111.1	−1.2	108.4	1.5
0−0′	189.5			184.0	5.5
0′−1′	14.9	22.3	−7.4	13.6	1.3
1′− 2′	93.3	95.3	−2.0	93.1	0.2
2′− 3′	102.4	93.2	9.2	107.8	−5.4
0−0″	383.1			384.4	−1.3

[a] $V(\text{cm}^{-1}) = (1.83 \times 10^6)x_1^4 - (3.15 \times 10^4)x_1^2$ for $\upsilon_F = 0$; $V = (2.33 \times 10^6)x_1^4 - (2.99 \times 10^4)x_1^2$ for $\upsilon_F = 1$. [b] $V(\text{cm}^{-1}) = (2.641 \times 10^6)x_1^4 - (5.284 \times 10^4)x_1^2 + (2.625 \times 10^3)x_2^4 - (6.073 \times 10^2)x_2^2 + (1.618 \times 10^6)x_1^2x_2^2$.

fit the data one-dimensionally resulted in the potential energy function

$$V(\text{cm}^{-1}) = (1.83 \times 10^6)x_1^4 - (3.15 \times 10^4)x_1^2 \qquad (2)$$

which has a barrier to planarity of 127 cm^{-1}, but gives poor agreement with the experimentally observed frequencies, as shown in Table 4 as calcd I. This clearly indicates that the ring-puckering cannot be considered independently but couples strongly with the ring-flapping motion. This was also the case in the electronic ground state.[1]

A two-dimensional computation involving both the puckering and flapping was therefore undertaken for the electronic excited state. The kinetic energy functions for the puckering (g_{44}), flapping (g_{55}), and the interaction (g_{45}) were all calculated in terms of the puckering (x_1) and flapping (x_2) coordinates:

$$\begin{aligned} g_{44} = {} & 0.011116 - 0.10636x_1^2 + 0.53172x_1^4 - 2.58851x_1^6 - {} \\ & 0.00071578x_2^2 + 0.00043068x_2^4 - 0.00089162x_2^6 + {} \\ & 0.010416x_1^2x_2^2 + 0.021844x_1x_2^3 + 0.095087x_1^3x_2 \qquad (3) \end{aligned}$$

$$\begin{aligned} g_{55} = {} & 0.12461 - 0.14250x_1^2 + 1.01118x_1^4 - 5.64517x_1^6 - {} \\ & 0.12648x_2^2 + 0.048531x_2^4 - 0.022371x_2^6 + {} \\ & 0.14199x_1^2x_2^2 + 0.18758x_1x_2^3 + 0.81658x_1^3x_2 \qquad (4) \end{aligned}$$

$$\begin{aligned} g_{45} = {} & -0.022863 + 0.15608x_1^2 - 0.66490x_1^4 + 3.68901x_1^6 + {} \\ & 0.013019x_2^2 - 0.0032337x_2^4 + 0.0032952x_2^6 - {} \\ & 0.068117x_1^2x_2^2 - 0.11931x_1x_2^3 - 0.58547x_1^3x_2 \qquad (5) \end{aligned}$$

Since the structures for the S_0 and S_1 states are fairly similar (as shown in Figure 5), so are the kinetic energy functions. Figures 6−8 in ref 1 show the appearance of these ground-state functions. It should be noted that in ref 1, the equations for g_{45} and g_{55} for the S_0 state were reversed [eq 4 is for g_{55}]. In addition, there were other errors in signs and exponents. Hence, these are correctly reproduced for the S_0 ground state below

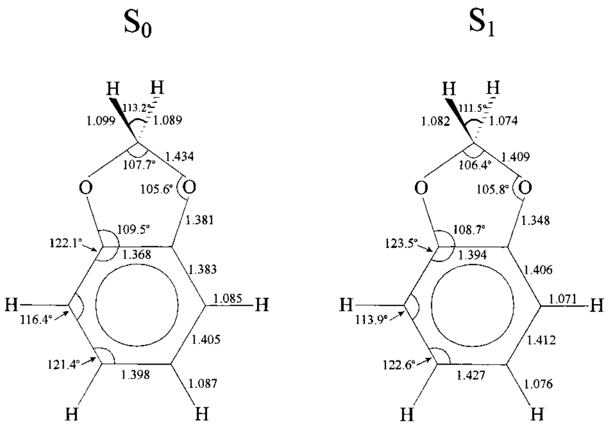

Figure 5. Calculated structures for 1,3-benzodioxole in its S_0 and $S_1(\pi,\pi^*)$ states. The calculated dihedral angles are 24.2° and 21.3°, respectively, and the flapping angles are −2.6° and −1.9°. The five-membered ring is puckered "up" and flapped "down".

$$\begin{aligned} g_{44} = {} & 0.010051 - 0.16875x_1^2 + 1.7290x_1^4 - 14.9557x_1^6 - {} \\ & 0.018393x_2^2 - 0.282863x_2^4 - 1.0264x_2^6 + {} \\ & 0.170831x_1^2x_2^2 + 0.019758x_1x_2^3 + 0.009369x_1^3x_2 \qquad (6) \end{aligned}$$

$$\begin{aligned} g_{55} = {} & 0.130578 - 0.0040853x_1^2 - 6.81894x_1^4 - 83.09016x_1^6 - {} \\ & 0.1496885x_2^2 + 0.1276195x_2^4 - 0.3156069x_2^6 + {} \\ & 0.21724x_1^2x_2^2 + 0.2062571x_1x_2^3 + 0.0208667x_1^3x_2 \qquad (7) \end{aligned}$$

$$\begin{aligned} g_{45} = {} & -0.020376 + 0.23319x_1^2 - 1.65439x_1^4 + 14.4207x_1^6 - {} \\ & 0.014229x_2^2 + 0.39786x_2^4 - 1.44954x_2^6 - {} \\ & 0.36573x_1^2x_2^2 - 0.118277x_1x_2^3 - 0.131152x_1^3x_2 \qquad (8) \end{aligned}$$

The two-dimensional calculation for the $S_1(\pi,\pi^*)$ excited state of 1,3-benzodioxole was very successful and resulted in the surface

$$\begin{aligned} V(\text{cm}^{-1}) = {} & \\ & (2.641 \times 10^6)x_1^4 - (5.284 \times 10^4)x_1^2 + (2.625 \times 10^3)x_2^4 - {} \\ & (6.073 \times 10^2)x_2^2 + (1.618 \times 10^6)x_1^2x_2^2 \qquad (9) \end{aligned}$$

which has a barrier to planarity of 264 cm^{-1}. This is shown in Figure 6. The energy minima correspond to $x_1 = \pm 0.10$ Å and puckering dihedral angles of 24°. The energy minima are at $x_2 = 0.0$, reflecting a 0° flapping angle in the S_1 state. The observed and calculated (calcd II) frequencies are compared in Table 4. The agreement is excellent, especially considering how much the energy levels are perturbed from "normal" puckering patterns and how much the puckering levels differ in the $\upsilon_F = 0$ and 1 states. For example, the 0′ and 3 levels at 189.5 and 162.5 interact strongly and their calculated values are very sensitive to the potential energy constants. Hence, the 5.5 cm^{-1} deviation for the 0−0′ transition is not surprising. It is also not of great concern as it could be better fit with the use of higher order potential energy terms which would not affect the potential energy surface or barrier to planarity to any great extent.

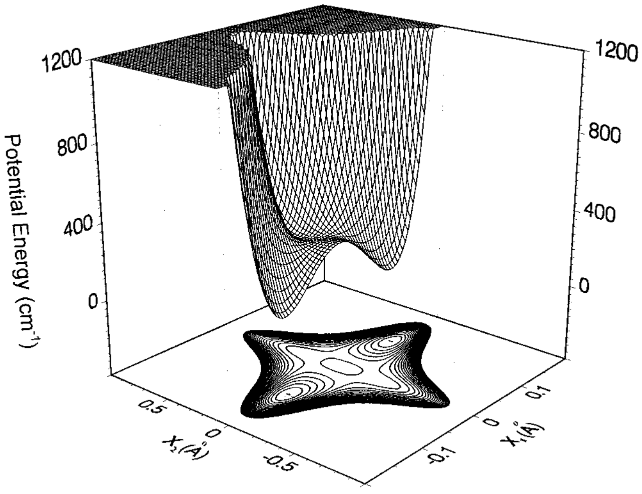

Figure 6. Two-dimensional potential energy surface (cm^{-1}) of 1,3-benzodioxole in its $S_1(\pi,\pi^*)$ state: x_1 = ring-puckering; x_2 = ring-flapping.

For the S_0 ground state the corresponding potential energy surface was found to be

$$V(cm^{-1}) = (1.929 \times 10^6)x_1^{\,4} - (3.557 \times 10^4)x_1^{\,2} + (6.033 \times 10^3)x_2^{\,2} + (2.806 \times 10)^5 x_1^{\,2}x_2^{\,2} \quad (10)$$

with a barrier to planarity of 164 cm^{-1} and dihedral angles of puckering of ±21°. [The asymmetric potential energy surface in ref 1, eq 7 gives ±24°.] In addition to the increased barrier to planarity the most notable other change in the S_1 surface is the flattening of the surface along the flapping (x_2) coordinate. This is reflected in the decrease in the flapping frequency from 267.2 to 189.5 cm^{-1} as shown in Figure 2. The ab initio calculations are in good agreement as a shift from 269 to 203 cm^{-1} is predicted (Table 2). For phthalan[9] the shift was from 216 to 187 cm^{-1}. For both molecules the decreased π character of the benzene ring more readily allows the carbon or oxygen atoms of the five-membered ring to bend out of the plane. The more substantial shift for 1,3-benzodioxole (66 cm^{-1} vs 29 cm^{-1}) also reflects the fact that there is significant interaction between the benzene π orbitals with the oxygen nonbonded p orbitals.

The large drop in flapping frequency for 1,3-benzodioxole from the S_0 to S_1 state also has a pronounced effect on the puckering levels for the $v_F = 0$ ground state. In S_0 the $v_P = 4$ and 1′ levels at 236.8 and 297.8 cm^{-1} are both of A_1 symmetry and have clearly pushed each other apart resulting in a large (30.6 cm^{-1}) splitting between the 0′ and 1′ levels. For the S_1 excited state the splitting between the 0′ and 1′ levels is only 14.9 cm^{-1} as the $v_P = 3$ state of B_2 symmetry pushes 0′ up while $v_P = 4$ slightly pushes 1′ down. This is confirmed by examination of the mixing in the calculated wave functions for these levels.

Figure 7 compares the potential energy change along the puckering coordinate (x_1) for the S_0 and S_1 states. The barrier to planarity has increased significantly from 164 to 264 cm^{-1}, but otherwise the potential energy curves are very similar. The 264 cm^{-1} barrier for the excited state is very similar to the 275 cm^{-1} value found for 1,3-dioxole (**II**) where no benzene ring is present to supress the anomeric effect. This suggests that in the S_1 state of 1,3-benzodioxole the distortion of the π system considerably reduces the interaction with the oxygen nonbonded orbitals thereby allowing them to participate more strongly in the anomeric effect.

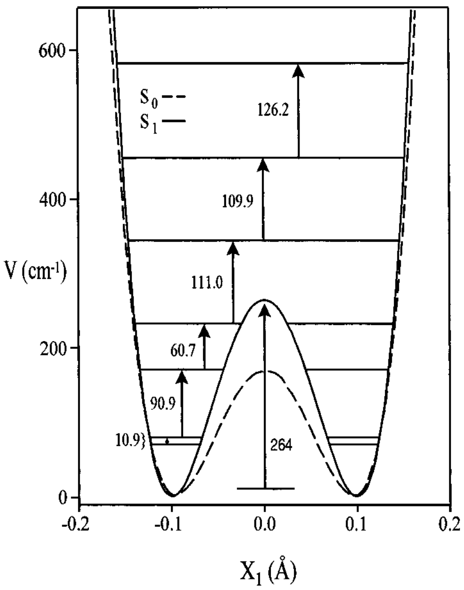

Figure 7. Comparison of the S_0 and $S_1(\pi,\pi^*)$ vibrational potential energy surfaces along the ring-puckering coordinate (x_1). The flapping coordinate $x_2 = 0$.

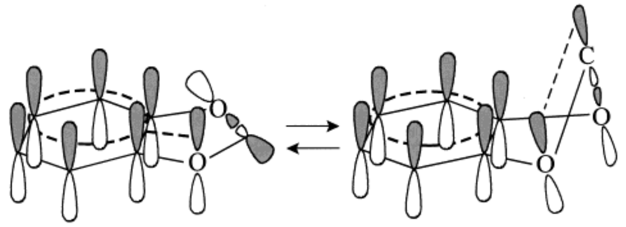

Figure 8. Depiction of the interaction between the benzene π system and the oxygen atoms. Only one oxygen nonbonded p orbital is shown along with a σ^*(C−O) orbital with which the anomeric effect is achieved.

Ab initio calculations for the electronic ground state[8] of 1,3-benzodioxole predict a barrier of 171 cm^{-1} as compared to the experimental value of 164 cm^{-1}. For the $S_1(\pi,\pi^*)$ excited state, our ab initio calculation at the td-B3LPY/6-31+G(d)//CIS/6-31+G(d) level predicts a 516 cm^{-1} barrier, considerably higher than the experimental result. Calculations with CIS/6-31+G(d)//CIS/6-31+G(d) and CIS/6-311+G(2d,p)//CIS/6-31+G* basis sets predict values of 437 and 369 cm^{-1}, respectively. Each of the calculations indicates that in the S_1 state the anomeric effect is increased as the interaction between the benzene π system and the oxygen atoms is decreased.

Conclusions

This study on 1,3-benzodioxole, just as our previous investigation of phthalan,[9] demonstrates how the combination of electronic absorption spectroscopy and fluorescence excitation spectroscopy of jet-cooled molecules can be used to very accurately determine the conformationally significant vibronic levels in an electronic excited state. The data thus obtained enabled us to determine the two-dimensional potential energy surface for this molecule in its $S_1(\pi,\pi^*)$ excited state in terms of the ring-puckering and ring-flapping vibrational coordinates. The rigidity of 1,3-benzodioxole along the flapping coordinate is considerably reduced in the excited state, but the barrier to planarity along the puckering coordinate is increased to 264 cm^{-1} (3.16 kJ/mol) from 164 cm^{-1} (1.96 kJ/mol) in the ground state. In the ground state there is sufficient interaction between the benzene π system and the oxygen atom nonbonded p orbitals to suppress the anomeric effect that is responsible for the nonplanarity of the five-membered ring. This is depicted in Figure 8. If the benzene−oxygen interaction tries to maintain the oxygen p orbitals aligned with its π system, the five-membered ring cannot readily bend to increase the anomeric interaction that has been ascribed to oxygen p orbital overlap with the σ^*(C−O) orbital involving the other oxygen atom.[2−6] In the S_0 ground state the benzene−oxygen interaction is significant, as demonstrated by the relatively low barrier to planarity of 164 cm^{-1}. Following a $\pi \rightarrow \pi^*$ transition, however, the degree of π bonding on the benzene ring has been reduced and the interaction with the oxygen atoms is decreased. This then allows the oxygen p orbitals to participate to a greater degree in the anomeric effect and thus to bend the five-membered ring to a more puckered configuration.

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