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Anomeric Effect in 1,3-Dioxole: A Theoretical Study

D. Suárez, T. L. Sordo, and J. A. Sordo*

Contribution from the Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Principado de Asturias, Spain

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Abstract: A theoretical analysis on planar and puckered-ring conformations of cyclopentadiene, 2,3-dihydrofuran, and 1,3-dioxole is carried out to test the conclusion of Laane and co-workers (*J. Am. Chem. Soc.* **1993**, *115*, 12132) that the unexpected nonplanarity of 1,3-dioxole must be attributed to the anomeric effect. MP4/6-31G**//MP2/6-31G** calculations and NBO analysis show that delocalization involving the oxygen lone pairs and the C−O antibonding orbital, commonly associated with the anomeric effect, plays a decisive role in explaining the above-mentioned experimental fact. A careful analysis of the dipole−dipole interaction energy indicates that, in the present case, the electrostatic theory does not help to rationalize the experimentally observed puckered-ring conformation of 1,3-dioxole.

Introduction

The conformations of many small-ring molecules are determined primarily by ring-angle strain and torsional forces. Thus, for example, the angle strain in cyclopentene tends to keep this molecule planar whereas the CH_2-CH_2 torsional interactions favor a puckered-ring conformation. As a result, cyclopentene shows a puckered-ring conformation with a dihedral angle of 26° and a energy barrier to planarity of 232 cm^{-1}.[1] 2,3-Dihydrofuran has a similar angle strain, but since only one CH_2-CH_2 interaction is present, the barrier reduces to 83 cm^{-1}.[2] Obviously, since no CH_2-CH_2 interactions are present in 1,3-dioxole, a planar conformation should be expected for this molecule. In a recent paper,[3] the analysis of low-frequency vibrational spectra indicated that 1,3-dioxole is a nonplanar molecule with a bending angle of 24° and an energy barrier to planarity of 275 cm^{-1}. Molecular mechanics (MM3) calculations predict a broad minimum at the planar structure of 1,3-dioxole and fail to produce a double minimum in the potential function.[3,4] On the other hand, a previous *ab initio* theoretical study, carried out at the HF/3-21G level, incorrectly predicted 1,3-dioxole to be planar.[4] Very recently, Allen *et al*. have shown[5] that high-level *ab initio* calculations, including correlation effects and extended basis sets, are able to provide a satisfactory prediction of the puckering inversion barrier of cyclopentene. Laane and co-workers suggested[3] that the unexpected nonplanarity of 1,3-dioxole must be attributed to the anomeric effect which can be present in molecules with O−C−O linkages. In this paper, a theoretical analysis on planar and puckered-ring conformations of cyclopentene, 2,3-dihydrofuran, and 1,3-dioxole is carried out to support such a conclusion.

Method

Structures were fully optimized at the Hartree−Fock (HF) and correlated (MP2) levels using the GAUSSIAN 92 package of programs.[6] Pople *et al.*'s 6-31G** [7] and Dunning−Huzinaga's double-ζ polarization ([4s,2p,1d])[8] basis sets were used. The use of different basis sets, generated from quite dissimilar strategies[9] and rendering comparable results, does provide additional support to the validity of the conclusions reached in any *ab initio* study. Pople *et al.*'s 6-31G** is a standard basis set in today's studies on the anomeric effect,[10] and Dunning's contraction from Huzinaga's (9s,5p) basis sets has been used successfully in a recent study on the puckering inversion barrier of cyclopentene.[5] Schlegel's algorithm was used to locate the transition structures.[11] In addition, single-point MP4SDTQ(FC) calculations were carried out on all the MP2(FULL) geometries (MP4SDTQ(FULL) in the case of 1,3-dioxole).

Natural bond orbital (NBO)[12] analysis is used to evaluate delocalization effects. In the NBO method, the atomic orbital basis set is orthogonalized and the canonical delocalized HF molecular orbitals are transformed into localized hybrids (NBOs). The filled NBOs describe covalency effects in molecules while unoccupied NBOs are used to describe noncovalency effects. Among the latter, the most important are the antibonds. Small occupancies of these antibonds correspond, in HF theory, to irreducible departures from the idealized Lewis picture and thus to small noncovalent corrections to the picture of localized covalent bonds. The energy associated with the antibonds can be numerically assessed by deleting those orbitals from the basis set and recalculating the total energy (E_{tot}) to determine the associated variational energy lowering. In this way one obtains a decomposition

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[10] See for example: (a) Salzner, U.; P.v.R. Schleyer, P.v.R. *J. Am. Chem. Soc.* **1993**, *115*, 10231. (b) Salzner, U.; Schleyer, P.v.R. *J. Org. Chem.* **1994**, *59*, 2138. (c) Salzner, U. *J. Org. Chem.* **1995**, *60*, 986.

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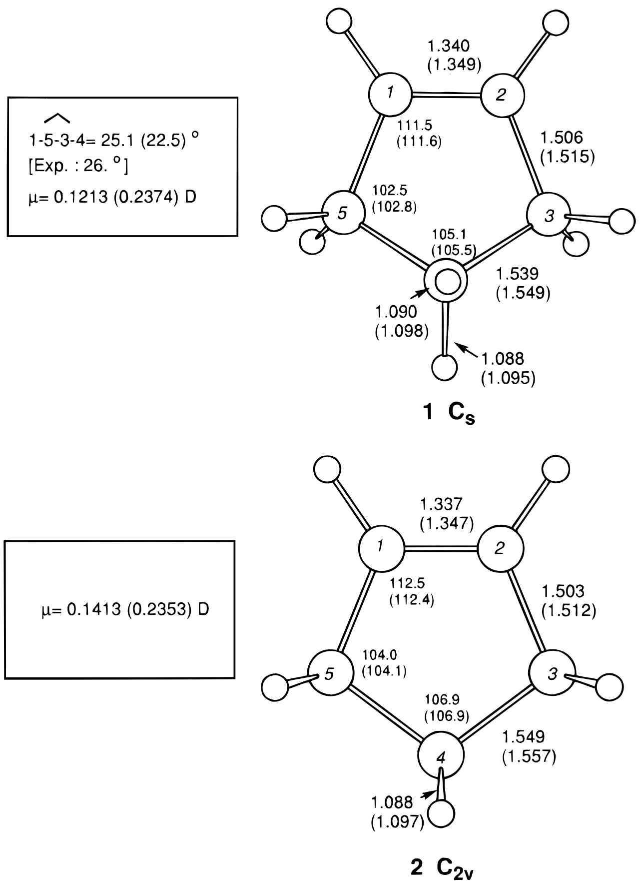

Figure 1. MP2(FULL)/6-31G** (Dunning−Huzinaga double-ζ polarization basis set results in parentheses) fully optimized structures corresponding to puckered (**1**) and planar (**2**) cyclopentene (**1** and **2** have zero and one imaginary frequencies, respectively). Bending angles (degrees) and dipole moments (μ, D) are also indicated.

of the total into components associated with covalent (E_{Lewis}) and noncovalent ($E_{\text{non-Lewis}}$) contributions.

The NBO method has been shown to be a useful tool to analyze the type of interactions involved in the anomeric effect.[10]

Results and Discussion

Figures 1−3 depict the MP2(FULL) geometries of the two significant conformations from a ring-puckering potential function, corresponding to cyclopentene, 2,3-dihydrofuran, and 1,3-dioxole, respectively. Structures **1**, **3**, and **5** correspond to one of the double minima on the potential function (structures corresponding to the second minima **1′**, **3′**, and **5′** are readily obtained from these by symmetry considerations) and structures **2**, **4**, and **6** to the transition structures connecting the double minima. Vibrational frequency calculations, carried out at the HF level, confirmed that **1**, **3**, and **5** have only real frequencies while **2**, **4**, and **6** have one imaginary frequency each. The total energies at the different computational levels for all the structures are collected in Table 1. Table 2 shows the theoretical and experimental values for the energy barriers to planarity.

The numbers in Table 2 show that the agreement between theoretical and experimental energy barriers to planarity is very satisfactory for the two basis sets considered, Pople *et al.*'s 6-31G** being slightly superior in general.[13] Particularly remarkable is the good agreement found between the experimental and computed ring-puckering dihedral angles (see Figures 1 and 3). In all cases, the MP4SDTQ(FC)//MP2(FULL) calculations predict a double-minimum potential energy function with a planar structure (**2**, **4**, **6**) being the transition structure connecting the two minima (**1** and **1′**, **3** and **3′**, **5** and **5′**) in full agreement with experimental evidence.[1−3] This result contrasts with MM3[3] and HF/3-21G *ab initio*[4] calculations which predict 1,3-dioxole to be planar.

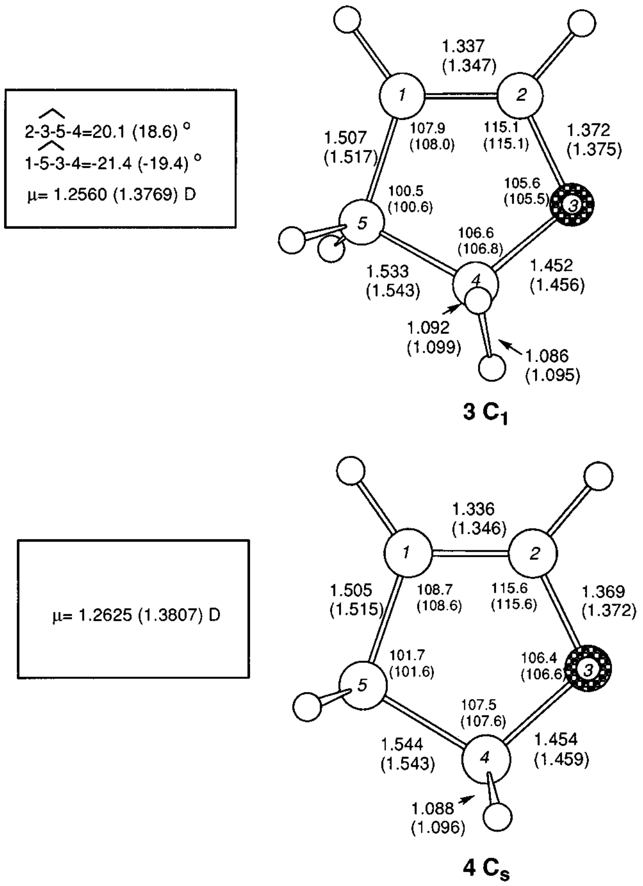

Figure 2. MP2(FULL)/6-31G** (Dunning−Huzinaga double-ζ polarization basis set results in parentheses) fully optimized structures corresponding to puckered (**3**) and planar (**4**) 2,3-dihydrofuran (**3** and **4** have zero and one imaginary frequencies, respectively). Bending angles (degrees) and dipole moments (μ, D) are also indicated.

Table 1. Total Energies (au) of the Structures Considered in This Work As Computed at Different Computational Levels[a]

structure		HF	MP2	MP4[b]
cyclopentene	**1**	−193.990 234	−194.708 157	−194.759 319
		(−194.002 000)	(−194.701 298)	(194.701 904)
	2	−193.989 709	−194.706 751	−194.758 253
		(−194.001 484)	(−194.700 425)	(−194.701 301)
2,3-dihydro-furan	**3**	−229.799 128	−230.545 341	−230.589 934
		(−229.829 728)	(−230.573 701)	(−230.566 528)
	4	−229.799 111	−230.544 723	−230.589 538
		(−229.829 702)	(−230.573 287)	(−230.566 254)
1,3-dioxole	**5**	−265.603 943	−266.379 031	−266.416 986
		(−265.652 625)	(−266.411 991)	(−266.426 888)
	6	−265.603 719	−266.377 768	−266.415 973
		(−265.652 307)	(−266.440 613)	(−266.425 737)

[a] 6-31G** and Dunning−Huzinaga full double-ζ polarization (in parentheses) basis sets were used. [b] MP4(FC)SDTQ//MP2(FULL).

As mentioned above, in order to justify the ring-puckering conformation exhibited by 1,3-dioxole, one must invoke the anomeric effect.[14] From a theoretical viewpoint the NBO[12] analysis of HF wave functions using orthogonalized atomic orbital bases has been shown to be a useful tool[10] for such a

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(13) In the case of 1,3-dioxole, where MP4SDTQ(FULL)/6-31G**//MP2(FULL)/6-31G** calculations were feasible, the energy barrier to planarity computed at that level was found to be 275 cm^{-1}, in full agreement with MP4SDTQ(FC)/6-31G**//MP2/6-31G** calculations (see Table 2).

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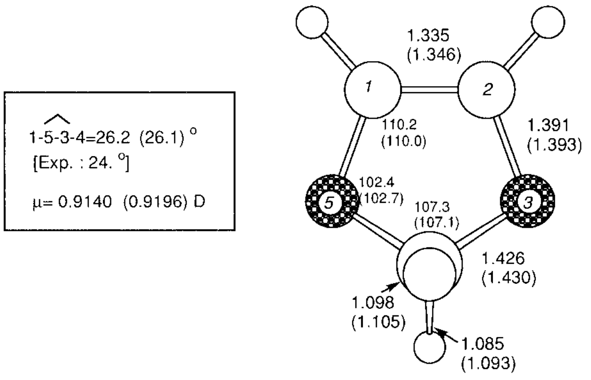
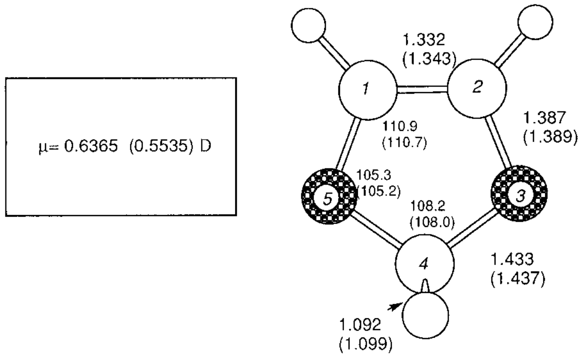


5 C_s



6 C_{2v}

Figure 3. MP2(FULL)/6-31G** (Dunning−Huzinaga double-ζ polarization basis set results in parentheses) fully optimized structures corresponding to puckered (**5**) and planar (**6**) 1,3-dioxole (**5** and **6** have zero and one imaginary frequencies, respectively). Bending angles (degrees) and dipole moments (*μ*, D) are also indicated.

Table 2. Barrier to Planarity (Energy Differences in cm^{-1} between Planar and Puckered-Ring Conformations) of Cyclopentene, 2,3-Dihydrofuran, and 1,3-Dioxole As Computed at Different Computational Levels[a]

structure	HF	MP2	MP4[b]	exptl
cyclopentene	115	309	234	232
	(113)	(192)	(132)	
2,3-dihydrofuran	4	136	87	83
	(6)	(91)	(60)	
1,3-dioxole	49	277	222	275
	(70)	(302)	(253)	

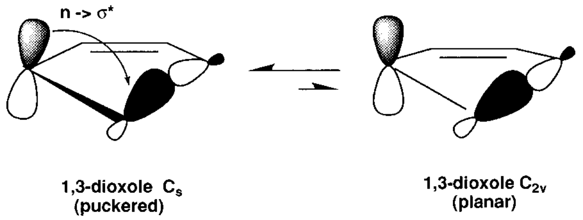
[a] A positive number indicates that the nonplanar conformation is more stable. 6-31** and Dunning−Huzinaga full double-ζ polarization (in parentheses) basis sets were used. [b] MP4(FC)SDTQ//MP2(FULL).

Table 3. NBO Energies (kcal/mol) Corresponding to the Main Interactions in 1,3-Dioxole:[a] $lp_O \rightarrow \sigma^*_{C-H}$ (ϵ_{OCH}); $lp_O \rightarrow \sigma^*_{C_1-C_2}$, $lp_O \rightarrow \pi^*_{C_1-C_2}$ (ϵ_{OCC}); $lp_O \rightarrow \sigma^*_{C-O}$ (ϵ_{OCO})

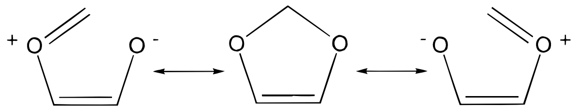
	C_s (**5**)	C_{2V} (**6**)	$C_{2V} - C_s$
ϵ_{OCH}	26.0	26.3	0.3
ϵ_{OCC}	48.6	49.4	0.8
ϵ_{OCO}	11.0	9.7	−1.3
$n_\sigma \rightarrow \sigma^*_{C_4-O}$	8.5	9.4	0.9
$n_p \rightarrow \sigma^*_{C_4-O}$	2.1	0.0	−2.1

[a] lp_O stands for both lone pair orbitals of the two oxygen atoms O_3 and O_5: n_σ and n_p. C−X (X = H, O) indicates contributions from the C−X bonds. C_4−O refers to C_4−O_3 and C_4−O_5 bonds.

Scheme 1



Scheme 2



purpose. It is noteworthy from the data collected in Table 2 that the role played by correlation in the calculation of the energy barriers to planarity and the dihedral angles is important. From the energy viewpoint the geometrical changes when going from the HF to the MP2 structures seem not to be crucial. Indeed, the MP2(FULL)/6-31G**//HF/6-31G** energy barriers to planarity are 255, 32, and 173 cm^{-1} for cyclopentene, 2,3-dihydrofuran, and 1,3-dioxole, respectively (compare with the MP2(FULL)/6-31G** values in Table 2). This result supports the validity of conclusions arising from the application of the NBO analysis at the HF level to the anomeric effect.[10] Following the deletion procedure,[15] one obtains for the n → σ* interactions involving the oxygen lone pairs and the C−X (X = H, C, O) vacant antibonding orbitals of the structures **5** and **6** of 1,3-dioxole (see Scheme 1, X = O) the values collected in Table 3.

It is very interesting to note that the hyperconjugative interactions involving the lone pairs of the two oxygen atoms and the C1−C2 (ϵ_{OCC}) and C−H (ϵ_{OCH}) antibonding orbitals, respectively, are both larger in the case of the planar (C_{2v}) structure. On the contrary, the hyperconjugation contributions (in valence bond terms the hyperconjugation contribution is associated with the double bond/no bond resonance structures depicted in Scheme 2) $n_{\sigma O3} \rightarrow \sigma^*_{C4-O5}$, $n_{pO3} \rightarrow \sigma^*_{C4-O5}$, $n_{\sigma O5} \rightarrow \sigma^*_{C4-O3}$, and $n_{pO5} \rightarrow \sigma^*_{C4-O3}$ (the most important contributions to ϵ_{OCO} in Table 3),[16] which are the ones commonly associated with the anomeric effect,[14] clearly favor the nonplanar (C_s) structure. Therefore, although the preference for the C_s structure over the C_{2v} one is the result of a wide variety of interactions, the data in Table 3 indicate that, according to expectations,[3] those commonly associated with the anomeric effect are most important and favor the puckered-ring conformation exhibited by 1,3-dioxole.[17] Moreover, consideration of the so-called Lewis energy (E_{Lewis}) which includes all energy contributions apart from delocalization effects (in particular, steric and electrostatic effects which cannot be separated with the NBO method) provides extra support to the importance of the anomeric effect in the stabilization of the nonplanar structure of 1,3-dioxole. Indeed, the estimated Lewis energies for the C_s and C_{2v} structures are −265.235 782 and −265.238 303 au, respectively. Consequently, the steric and electrostatic effects do favor the C_{2v} planar structure by 1.5 kcal/mol. The interactions involved in the anomeric effect constitute an important component[17] of the forces overcoming the steric and

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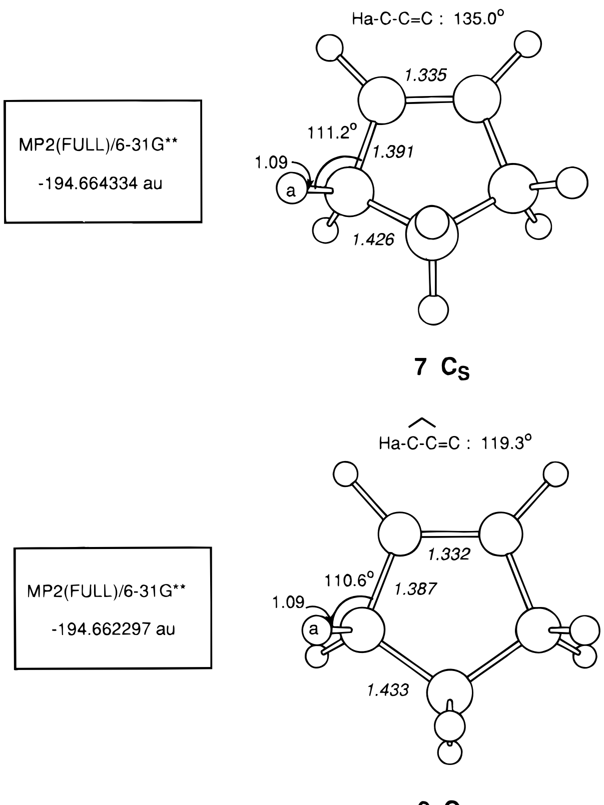
(15) See ref 12. The NBO deletion procedure allows one to compute the energy (E_{ocx}) after zeroing the off-diagonal Fock matrix elements connecting the oxygen lone pairs n with the C−X (X = H, C, O) σ* antibonds. The difference $E_{tot}-E_{ocx}$ ($=\epsilon_{ocx}$) is the energy corresponding to the n → σ* interactions.

(16) It must be recalled that the energies of individual orbital interactions are not strictly additive because the charge redistributions resulting from the deletions are different.

(17) The NBO analysis shows that there are other interactions favoring the C_s nonplanar structure (e.g., those involving Rydberg NBOs), but they are individually smaller (in absolute value) than $\Delta\epsilon_{oco}$ in Table 3.



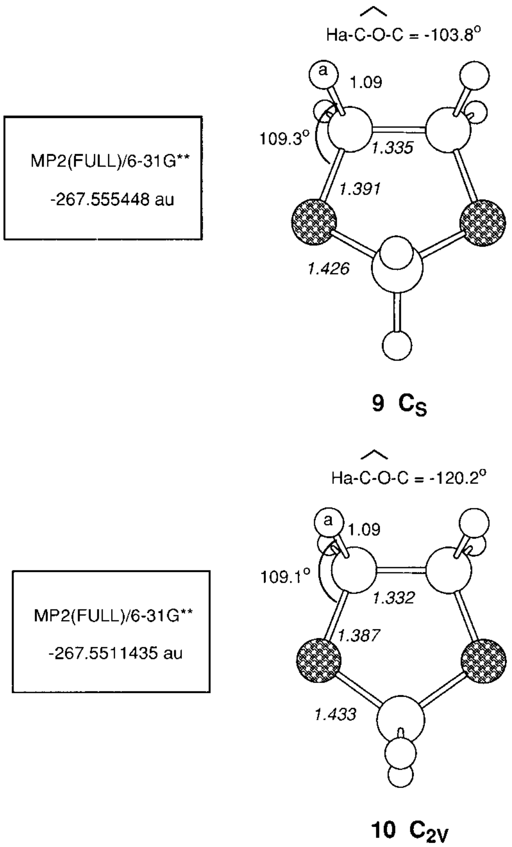
7 C_s

8 C_{2v}

Figure 4. Model structure for *1,3-dioxole with no four-electron repulsions between p-type lone pair orbitals on oxygen atoms* (see the text for more details).

electrostatic effects in order to stabilize the experimentally observed nonplanar conformation.

The above considerations do not permit one to exclude entirely other alternatives to explain the greater stability of the puckered conformation of 1,3-dioxole. Thus, the role played by other interactions such as four-electron repulsions between p-type lone pair orbitals on oxygen atoms or interactions between π-type electrons of the double bond and lone pair orbitals in the relative stability of puckered conformers has been qualitatively analyzed by performing calculations on single models. In order to avoid contributions from four-electron repulsions between p-type lone pair orbitals on oxygen atoms, we considered the systems presented in Figure 4. The oxygens of 1,3-dioxole were substituted by $-CH_2$ groups with no lone pair orbitals, using plausible geometrical parameters.[18] The data in Figure 4 show that the four-electron repulsions between p-type lone pair orbitals on oxygen atoms tend to destabilize the puckered conformers of 1,3-dioxole. Indeed, the stabilization in favor of the C_s conformer of the model structure presented in Figure 4 (with no four-electron repulsions present) is greater (1.3 kcal/mol) than for the case of 1,3-dioxole (0.8 kcal/mol; see Table 1) which includes four-electron repulsions. This result does reinforce our conclusion on the important role played by the anomeric effect to stabilize the puckered-ring conformation of 1,3-dioxole. Exactly the same kind of argument applies for the case of the model structure presented in Figure 5 where the interactions between π-type electrons of the double bond and lone pair orbitals on oxygen atoms are avoided. The stabilization in favor of the C_s conformer of such a model structure is also greater (2.7 kcal/mol) than for the case of 1,3-dioxole (0.8 kcal/mol; see Table 1). Therefore, the two types of interactions considered above, present in 1,3-dioxole, clearly favor the planar conformer, thus emphasizing the need for invoking the delocalization involving the oxygen lone pairs and the C$-$O antibonding orbital (see above), commonly associated with the anomeric effect, as one important factor in order to stabilize the experimentally observed puckered-ring conformation of 1,3-dioxole.



9 C_s

10 C_{2v}

Figure 5. Model structure for *1,3-dioxole with no interactions between π-type electrons of the double bond and lone pair orbitals on oxygen atoms* (see the text for more details).

It is also noteworthy that the present calculations reflect the existence of the so-called Perlin effect;[19] that is, the $^{13}\text{C}-^{1}\text{H}$ coupling constant for an axial C$-$H bond adjacent to oxygen is smaller by a significant amount (8$-$10 Hz) than ^{1}J for a C$-$H equatorial bond ($^{1}J_{\text{C}-\text{H}_{\text{eq}}} > {}^{1}J_{\text{C}-\text{H}_{\text{ax}}}$).[20] In fact, the NBO analysis shows that the $n_O \rightarrow \sigma^*_{\text{C}-\text{H}_{\text{ax}}}$ interaction (15.3 kcal/mol) in 1,3-dioxole (**5**) dominates over the $n_O \rightarrow \sigma^*_{\text{C}-\text{H}_{\text{eq}}}$ one (8.2 kcal/mol), thus producing the lengthening of the $\text{C}-\text{H}_{\text{ax}}$ bond (see Figure 3), which should lead to a smaller $^{13}\text{C}-^{1}\text{H}$ coupling.

Another important conclusion arises from the analysis of the dipole moments (see Figures 1$-$3) as computed using the MP2 density.[6] The electrostatic theory[14] invokes the preference for the conformation with the smallest resultant dipole moment. Thus, in the gas phase, it is generally found that the conformer with the larger dipole moment has the larger electrostatic energy, and an increased overall energy.[21] This is the case for both cyclopentene and 2,3-dihydrofuran. As shown in Figures 1 and 2 the dipole moments of the most stable conformers **1** and **3** (puckered-ring structures) are slightly smaller (almost equal in

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(18) Of course, since we want to simulate *1,3-dioxole with no four-electron repulsions between p-type lone pair orbitals on oxygen atoms* in Figure 4 and *1,3-dioxole with no interactions between π-type electrons of the double bond and lone pair orbitals on oxygen atoms* in Figure 5 to compare with 1,3-dioxole in Figure 3, no geometry optimizations were carried out.

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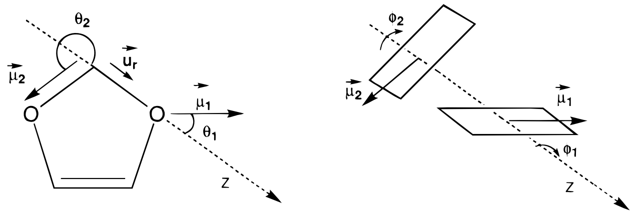
(20) Juaristi, E.; Cuevas, G. *Tetrahedron Lett.* **1992**, *33*, 1847.

(21) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616.

Scheme 3



the case of [4s,2p,1d] calculations for cyclopentene) than those of the planar conformations **2** and **4**, respectively. However, in the case of 1,3-dioxole the dipole moment of the puckered conformation **5** is notably larger than the one for the less stable planar conformer **6** (see Figure 3). Similar findings have been reported in a recent study on the origin of the anomeric effect.[10c] In this regard, it has been pointed out in the recent literature[22] that the dipole−dipole interaction energy, $E_{\mathrm{d-d}}$[23]

$$E_{\mathrm{d-d}} = [(\vec{\mu}_1\cdot\vec{\mu}_2) - 3(\vec{\mu}_1\cdot\vec{u}_r)(\vec{\mu}_2\cdot\vec{u}_r)]/r^3 = (|\vec{\mu}_1||\vec{\mu}_2|/r^3)[\sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) - 2\cos\theta_1 \cos\theta_2] \quad (1)$$

depends not only on the resultant dipole moment, which is a function of $|\vec{\mu}_1|$, $|\vec{\mu}_2|$, and $\phi_1 - \phi_2$, but, as eq 1 shows, also on the angles θ_1 and θ_2 ($\vec{u}_r$ is a unit vector from one dipole to the other; see Scheme 3 for notation). This observation is quite pertinent because it can be demonstrated that a given conformer with the larger molecular dipole moment might well be the most stable one when appropriate values of the θ angles make $E_{\mathrm{d-d}}$ lower.[22] Therefore, the above-mentioned relation between a larger dipole moment and reduced stability must be reexamined case by case, in light of eq 1. Table 4 collects our results for the two conformers **5** and **6** of 1,3-dioxole.[24] It is important to stress that the original electrostatic interpretation of the anomeric effect[25] was related to the dipole−dipole interaction between the dipole moments from C−O bonds ($\vec{\mu}_2$ in Scheme 3) and the oxygen lone pairs ($\vec{\mu}_1$ in Scheme 3). In the present case (1,3-dioxole), the result of the above-mentioned individual moments ($|\vec{\mu}_1 + \vec{\mu}_2|$) is found to be minimal for the planar conformation and the dipole−dipole interaction energy, $E_{\mathrm{d-d}}$, is also lower for this conformation. Consequently, the anomeric effect detected in 1,3-dioxole cannot be rationalized in terms of the electrostatic theory, and the molecular orbital interactions analyzed above must be invoked. Therefore, in agreement with very recent findings,[10c] a more detailed analysis is required to claim general validity for the conclusion reported in a recent study[26] that primarily responsible for the anomeric effect are not the n → σ* molecular orbital interactions but the electrostatic interactions.

Table 4. Dipole−Dipole Energy (D^2, Å^{-3}) for the Two Conformers of 1,3-Dioxole[a]

	$\lvert\vec{\mu}_1 + \vec{\mu}_2\rvert$	θ_1	θ_2	$\phi_1 - \phi_2$	$[(\vec{\mu}_1\cdot\vec{\mu}_2) - 3(\vec{\mu}_1\cdot\vec{u}_r)(\vec{\mu}_2\cdot\vec{u}_r)]/r^3$
C_s (**5**)	0.5408	51.22	252.71	26.24	−0.1018
C_{2V} (**6**)	0.3354	52.51	251.82	0.00	−0.1272

[a] Unit vectors are used for the dipole moments to carry out the calculations (see Scheme 3 for notation).

Summarizing it has been shown that high-level *ab initio* calculations provide results in good agreement with experimental data on the energy barriers to planarity and puckered-ring dihedral angles for five-membered small-ring molecules. The predicted anomeric effect for 1,3-dioxole[3] has been analyzed and associated with n → σ* molecular orbital interactions; that is, although what is known in the literature as an anomeric effect is presumably a rather complex phenomenon, in the present case (1,3-dioxole) a theoretical analysis suggests that delocalization involving the oxygen lone pairs and the C−O antibonding orbital plays a decisive role in explaining the experimentally observed puckered-ring conformation of 1,3-dioxole. Such a result cannot be rationalized in terms of the electrostatic theory. Indeed, the total dipole moment becomes maximal for the most stable puckered-ring conformers, and the dipole−dipole interaction energy between the individual dipole moments from C−O bonds and the oxygen lone pairs is lower for the less stable conformers.

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[23] See for example: Gray, C. G.; Gublins, K. E. *Theory of Molecular Fluids. Volume 1: Fundamentals*; Clarendon Press: Oxford, 1984.

[24] Although unit vectors have been used in Table 4 to compute $E_{\mathrm{d-d}}$ by means of eq 1, the conclusion that $E_{\mathrm{d-d}}(\mathbf{6}) < E_{\mathrm{d-d}}(\mathbf{5})$ does not depend, in the present case, on the values of $|\vec{\mu}_1|$ and $|\vec{\mu}_2|$.

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