JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 119–127 (1996)

CONFORMATIONAL ANALYSIS OF 2-CYANO DIHYDROXYETHANE IN SOLUTION

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The conformational space of the 2-cyano-1,1-dihydroxyethane molecule was studied at the semi-empirical PM3 level and *ab initio* MP2/6–31G//6–31G level in the gas phase and in a low-polarity medium. This system has been chosen as a model compound for 2-cyanocyclohexanone propylene and ethylene acetals. This has allowed the study of the role of polar groups on the relative conformation of two adjacent OH groups, which is of interest also in relation to the anomeric effect in carbohydrate chemistry. Solvent effects are taken into account using a continuum model with general cavity shapes.**

INTRODUCTION

There has been experimental and theoretical interest in the stereochemical properties of systems containing electron pairs and polar bonds in alicyclic[1] and cyclic compounds[2] for long time.

During the last decade, rotational isomerism of 1,2-dihaloethanes,[3] 1,1,2-trihaloethanes and 1,1,2,2-tetrahaloethanes[4] has received considerable attention. In 1,2-hetero-substituted ethanes, a preference for the *gauche* arrangement is observed for small electronegative substituents, even though highly electronegative substituents generate high dipole moments in the C—X and C—Y bonds which should lead to enhanced dipole repulsion in the *gauche* form. In the series XCH_2CH_2X (X = halogen), there is a gradual increase in the proportion of the *gauche* conformation in the order $I < Br < Cl < F$, so that in the gas phase *gauche*-1,2-difluoroethane predominates.[5] While the preference for the *anti* structures observed when $X = Y = Cl, Br, I$ may be ascribed to a combination of steric and dipolar effects alone, there is no easy interpretation to account for the conformational equilibrium of the difluoride. In contrast to the case for CH_2FCH_2F, experimental and theoretical studies have shown that in the gas phase the staggered *trans* (i.e., *anti*) configurations of CH_2FCHF_2 (C_1 symmetry) is favored over the *gauche* conformer (C_s symmetry).[4] The *gauche* conformation has been shown to exist for 2-fluoroethylacetate,[6] 2-methoxyacetate,[6] 1,2-dicyanoethane,[7] 1,2-dimethoxyethane[8] and the $—OCH_2CH_2O—$ fragment in polyoxyethylene.[9] A considerable amount of theoretical work has been also devoted to the study of hydroxy-substituted ethanes, in particular the 1,2-dihydroxy derivative.[10] These systems are interesting because they allow to model common molecules such as carbohydrates or cyclic compounds such as dioxanes or acetals and to discuss the properties associated with the anomeric and related effects.

An important aspect of the analysis of rotational equilibrium is the effect of solute–solvent interactions since they may change the relative stability of conformations substantially. Several solvent models are available nowadays. Among them, continuum models are interesting since they allow one to include the perturbation in the solute's Hamiltonan. Therefore, quantum chemical computations of a solvated molecule can be carried out at a low cost.

In previous work, we used a self-consistent reaction field (SCRF) model to study solvent effects on conformational equilibria. In particular, the axial–equatorial equilibrium of 1,3-dioxanes[11] and 2-substituted acetals[12] was investigated. PM3 calculations confirmed the experimental findings for 5-cyano-1,3-dioxane, the relative axial–equatorial stability of which is increased through the electrostatic solvent effect.[13] As previously pointed out,[14] in 2-substituted-cyclohexanone ethylene

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CCC 0894–3230/96/020119–09

Received 30 June 1995
Revised 17 October 1995

and propylene acetal derivatives, the behavior of the substituent may depend on the structure of the acetal group, which determines the conformational characteristics of the acetal derivatives. Experimentally, with ^{1}H NMR data, the cyano group has been shown to occupy the equatorial position in ethylene acetal and the axial position in propylene acetal.[15] However PM3 calculations for both 2-cyanocyclohexanone ethylene acetal and 2-cyanocyclohexanone propylene acetal predict that the preference of the substituent is for the equatorial position.[12]

These results showed the difficulties in correctly predicting conformational stabilities of substituted acetals at the semi-empirical level. In addition, explanation of the pseudohalogen character of the CN group in these molecules requires further study. Therefore, in the present work, we considered a model system (2-cyano-1,1-dihydroxyethane) that can be studied at the *ab initio* level. Some semi-empirical PM3 calculations were also carried out for comparison. Solvent effects were taken into account using an SCRF model described below.

METHOD OF CALCULATION

Ab initio calculations were performed as follows. First, geometry optimization was carried out for all the possible staggered rotamers at the HF/6–31G level, then single-point calculations for the minima obtained were performed at the MP2/6–31G** level (referred to below as MP2/6–31G**//6–31G calculations) both in the gas phase and in solution. Semi-empirical calculations were made with full geometry optimization. Geometry optimization was carried out both for the isolated and the solvated systems.

The solvent is represented by an infinite dielectric and polarizable continuum in which a cavity is created. The solute is placed in this cavity and its charge distribution polarizes the continuum which in turn creates an electric field inside the cavity. The electrostatic free energy variation corresponding to the solvation process may be written as[16]

$$\Delta G_{\mathrm{ele}} = -\frac{1}{2} \sum_{l,l'=0}^{l'} \sum_{m=-l'}^{l'} \sum_{m=-l}^{l} f_{ll'}^{mm'} \langle M_{l'}^{m'} \rangle \langle M_l^m \rangle \quad (1)$$

where M_l^m is a component of the multipole moment of order l and the reaction field factors, $f_{ll'}^{mm'}$, depend only on the dielectric properties of the medium and on the cavity shape. In this work we employed a cavity of general shape as proposed previously.[16c] The induction energy was obtained by carrying out an SCRF calculation in which the intrinsic energy of the solute plus the solvation free energy were optimized. It was assumed that the electrostatic and induction energies are responsible for the main variations of the total solvation energy on the rotational equilibrium, so the cavitation and dispersion energies were neglected. Previous work[17] has discussed the role of these terms on *gauche*/*trans* equilibria and justifies our approximation.

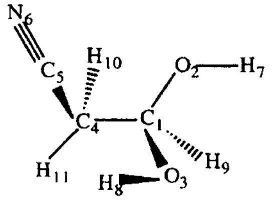
We have used the Gaussian 92 program[18] with extra links for the SCRF options.[16b] Semi-empirical calculations with the PM3 method were carried out in a similar way using the program MOPAC[19] for the calculations in the gas phase and the program Geomos for those in solution.[20]

Transition states on the rotational energy surface were located using the Berny algorithm in *ab initio* calculations whereas the option TS was used within MOPAC. In all cases, second derivatives of the energy were calculated in order to confirm the nature of the critical points.

RESULTS

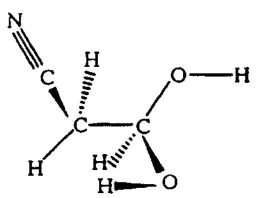
Gas phase

2-Cyano-1,1-dihydroxyethane may undergo internal rotation around the C_1–C_4, C_1–O_2 and C_1–O_3 bonds (see structure 1).



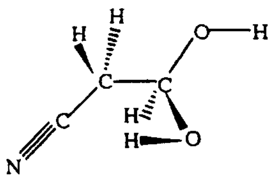
Possible minimum energy conformations about each bond are *trans* (t), *gauche* (g) or *gauche'* (g'). Five non-equivalent minimum energy conformers were located with all the methods used and they are shown in Figure 1 (structures **1**–**5**) together with three eclipsed conformations (structures **6**–**8**). Structures **6** (E), **7** (E') and **8** (E'') correspond to the transition states between **1** and **3**, **1** and **2**, and **2** and **3**, respectively. Structural parameters are listed in Table 1. The relative energies for the minima in vacuum are given in Table 2. Results obtained with PM3 calculations are also included in Table 2 for comparison.

Comparison of the first three structures, **1** ($G'tg'$), **2** (Ttg') and **3** (Gtg'), of the 2-cyano-1,1-dihydroxyethane molecule indicates that the bond lengths in the three conformers are similar. In particular, the CO bond length is close to 1·4 Å in all cases. All of them have intramolecular hydrogen bonds between $O_2 \ldots H_8$ and $O_3 \ldots H_7$ with lengths varying between 2·54 and 2·59 Å. For structures **4** ($Gg't$) and **5** ($G'g'g'$), only one hydrogen bond is present with a slightly shorter bond length. For these structures, the CO distance is shorter for the oxygen donating the proton, as expected. Finally, for the TS structures **6**–**8**, two hydrogen bonds are also predicted and the CO distances are again closer



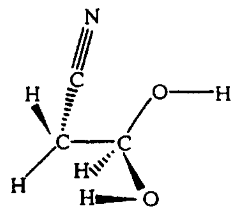
G't g'

1



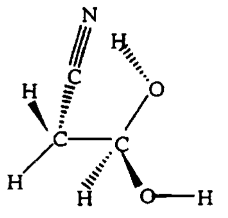
T t g'

2



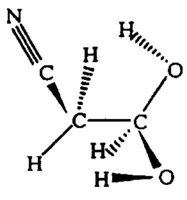
G t g'

3



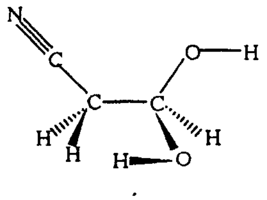
G g't

4



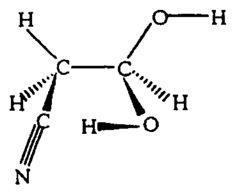
G'g'g'

5



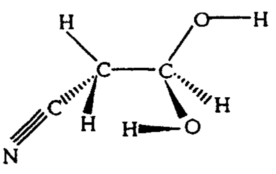
E

6



E'

7



E''

8

Figure 1. Different conformers of 2-cyano-1,1-dihydroxyethane in the gas phase

to 1·41 Å. Another common feature is noticed among the transition states **6**–**8**: they all have a C_1—C_4 bond longer than in the staggered structures owing to the repulsion between eclipsed groups. The same type of intramolecular hydrogen bonds have been observed in ethylene glycol[3e] for which the length varies between 2·25 and 2·75 Å at the MP2/6–31G** level.

The stability order predicted by the *ab initio* calculations for the conformers is different from that predicted by PM3. This is probably due to the fact that PM3 underestimates the interactions of the lone pairs with hydrogens at long distances (>2 Å). Thus, structures **1**, **2** and **3**, which have two hydrogen bonds, are the most stable in the *ab initio* calculations but not in the semi-empirical calculations that predict structure **4** to be the most stable. The relative energies of the first three minima (**1**–**3**) are small [1·26 kcal mol^{-1} (1 kcal = 4·184 kJ) when electron correlation is taken into account]. Note that in rotamer **1** the cyano group is *gauche* to both oxygens. The electrostatic interaction between the positive charge on the C atom (+0·50) of the CN group and the negative oxygens (−0·65) is

Table 1. Optimized parameters for $CH(OH)_2CH_2CN$ at the 6–31G level

	1 (*g'tg'*)	**2** (*tTg'*)	**3** (*gTg'*)	**4** (*gG't*)	**5** (*'GTIMq2g*)	**6** (*E*)	**7** (*E'*)	**8** (*"*)
Interatomic distances (Å)								
C_1O_2	1·411	1·412	1·410	1·419	1·418	1·406	1·414	1·415
C_1O_3	1·409	1·408	1·413	1·400	1·399	1·414	1·412	1·406
C_1C_4	1·523	1·523	1·522	1·522	1·530	1·542	1·538	1·543
C_4C_5	1·462	1·460	1·460	1·462	1·460	1·460	1·461	1·460
C_5N_6	1·146	1·146	1·146	1·147	1·146	1·145	1·146	1·146
O_2H_7	0·952	0·952	0·952	0·951	0·950	0·952	0·952	0·952
O_3H_8	0·955	0·953	0·954	0·952	0·954	0·954	0·953	0·953
C_1H_9	1·078	1·077	1·076	1·083	1·080	1·076	1·076	1·076
C_4H_{10}	1·081	1·084	1·083	1·082	1·085	1·083	1·081	1·082
C_4H_{11}	1·082	1·082	1·082	1·081	1·082	1·083	1·082	1·081
O_2H_8	2·582	2·590	2·542	2·334	2·257	2·532	2·539	2·639
O_3H_7	2·561	2·590	2·578	3·124	3·133	2·602	2·592	2·564
Bond angles (°)								
$O_3C_1{}^{*}{}_{2}$	111·6	111·5	111·3	107·3	106·6	111·2	110·9	111·4
$O_4C_1{}^{*}{}_{2}$	106·6	104·7	106·7	111·9	112·0	108·6	106·1	105·3
$O_5C_4{}^{*}{}_{1}$	112·1	113·0	112·9	111·8	112·6	115·5	113·0	114·1
$O_7C_2{}^{*}{}_{1}$	113·7	113·6	113·9	115·4	116·3	113·9	113·6	113·3
$O_8C_3{}^{*}{}_{1}$	113·9	114·1	113·5	112·7	112·4	113·3	113·5	115·0
$O_9C_1{}^{*}{}_{2}$	111·3	111·5	111·7	109·7	111·03	111·1	111·2	110·6
$O_{10}C_4{}^{*}{}_{2}$	108·9	108·8	108·5	109·2	110·13	109·3	108·4	110·0
$O_{11}C_4{}^{*}{}_{1}$	109·0	108·6	108·6	107·8	108·11	108·5	109·5	107·6
Torsional angles (°)								
$C_4C_1O_2O_3$	123·7	122·8	120·8	116·0	121·2	123·2	122·7	125·5
$C_5C_4O_1O_2$	−66·0	179·2	66·2	64·9	−56·7	1·6	121·8	−124·1
$H_7O_2C_1C_4$	180·0	−176·2	180·0	−80·8	−60·0	−173·3	−174·9	−176·7
$H_8O_3C_1O_4$	−61·0	−57·5	−64·1	−154·7	−100·1	−67·6	−64·2	−53·8
$H_9C_1O_2O_3$	−116·6	−116·5	−116·8	−120·3	−116·6	−115·2	−115·5	−115·0
$H_{10}O_4C_1O_2$	55·2	−58·6	−54·8	−173·3	65·5	123·8	0·8	113·6
$H_{11}O_4C_1O_2$	173·4	57·5	−172·4	−56·0	182·8	−120·7	−117·3	−3·2

Table 2. Relative energies, ΔE (kcal mol^{-1}, and dipole moments, μ (D), of different conformers in vacuum

	PM3		6–31G		6–31G**//6–31G	MP2/6–31G**//6–31G
Structure	ΔE	μ	ΔE	μ	ΔE	ΔE
1 (*g'Tg'*)	1·39	3·13	0·00	3·85	0·00	0·00
2 (*tTg'*)	1·03	2·90	0·43	4·24	0·79	1·24
3 (*gTg'*)	0·98	2·67	0·77	4·21	0·97	1·26
4 (*gG't*)	0·00	1·34	1·70	2·54	1·73	2·76
5 (*g'G'g'*)	2·01	3·53	4·55	4·78	4·32	4·86
6 (*E*)	3·75	3·04	6·33	3·96	6·36	6·40
7 (*E'*)	1·53	2·82	4·20	4·31	4·59	5·00
8 (*E"*)	2·80	3·06	4·15	3·88	4·53	4·42

probably an important stabilizing factor. The energy difference between conformers **1** and **5**, which have the CN group *gauche* to both oxygens and differ only in the position of H_7, may be considered as a measure of the strength of the hydrogen bond. This reaches 4·86 kcal mol^{-1} using the MP2/6–31G** values. No experimentally determined rotational barriers for the 2-cyano-1,1-dihydroxyethane molecule were found in the literature. The transition state **6** (*E*) connecting the *anti* structure **3** and the *gauche* structure **1** is energetically less favorable than the transition state **7** (*E'*), which also connects a *gauche* to an *anti* structure (**1** to **2**). One can explain this result by the stabilizing attractive interaction between H_9 and N which is present in **7** (*E'*) but is absent in **6** (*E*).

Dipole moments are given in Table 2. Note that conformer **4** has the smallest dipole moment owing to opposite orientations of the O—H bonds. Although this structure has the minimum energy with PM3, it is not the global minimum in the *ab initio* calculations. This indicates that in 2-cyano-1,1-dihydroxyethane, stabilization through hydrogen bonding is dominant with respect to the electrostatic repulsions between OH and CN groups.

Solution

All the conformers and the transition states were analyzed in a low-polarity medium of dielectric permittivity $\varepsilon = 4{\cdot}81$, which corresponds to chloroform, the solvent used in the experimental study of 2-cyano-substituted ethylene and -propylene acetals. Considering the *ab initio* results, the most stable conformer (Table 3) does not change from vacuum to solution. The optimized geometries in solution are similar to those in vacuum, except for conformer **4**, where the dihedral angle 8–2–1–4 has changed from −80° to −165°. This causes a large change in dipole moment. Solvation free energies are given in Table 4. They show the same trend as the dipole moments, i.e. conformers with high dipole moments are stabilized to a larger extent.

Modeling of 2-cyanocylohexanone ethylene and propylene acetals

In order to interpret the relative stability of the axial–equatorial conformers for 2-substituted cylohexanone ethylene and propylene acetals we carried out a series of additional calculations. Our aim was to analyze with *ab initio* calculations the interactions related to the polar groups that can modify the relative energy of acetal conformations. We shall use for this a series of partially frozen conformations of the 2-cyano-1,1-dihydroxyethane. However, this is too simple a model and cannot account for all the interactions present in the acetals so that extrapolating the results derived from this study has to be done with caution.

The position of the oxygen atoms of the model molecule are fixed to the optimized value of the corresponding angles in the compounds shown in Figure 3.

Table 3. Relative energies, ΔE (kcal mol^{-1}, and dipole moments, μ (D), of different conformers in chloroform ($\varepsilon = 4{\cdot}81$)

	PM3		6–31G		6–31G**//6–31G	MP2/6–31G**//6–31G
Structure	ΔE	μ	ΔE	μ	ΔE	ΔE
1 (*gTg'*)	0·74	4·13	0·00	4·43	0·00	0·00
2 (*tTg'*)	1·03	3·81	0·09	5·02	0·21	0·69
3 (*g'*T*g'*)	0·80	3·46	0·16	4·80	0·19	0·49
4 (*gG't*)	1·66	1·79	1·31[a]	6·15[a]	1·44[a]	1·97[a]
5 (*g'G'g'*)	0·00	4·48	3·47	5·58	3·24	3·80
6 (*E*)	2·80	4·07	5·04	4·62	5·11	5·24
7 (*E'*)	0·85	3·81	4·20	4·89	4·35	4·66
8 (*E''*)	3·57	4·33	4·32	4·88	2·80	2·91

[a] This conformer is not identical with that shown in Figure I (details are given in the text).

Table 4. Solvation energies (kcal/mol^{-1}) of different conformers in chloroform ($\varepsilon = 4{\cdot}81$)

Structure	PM3	6–31G	6–31G**//6–31G	MP2/6–31G**//6–31G
1 (*gTg'*)	7·73	6·73	6·29	4·68
2 (*tTg'*)	7·08	7·08	6·09	5·24
3 (*g'Tg'*)	7·26	7·35	5·51	5·44
4 (*gG't*)	5·42	7·12[a]	5·80[a]	5·46[a]
5 (*g'G'g*)	9·09	7·82	6·59	5·73
6 (*E*)	8·03	8·02	6·76	5·84
7 (*E'*)	7·76	6·74	5·75	5·02
8 (*E''*)	6·31	6·56	7·24	6·19

[a] This conformer is not identical with that shown in Figure 1 (details are given in the text).

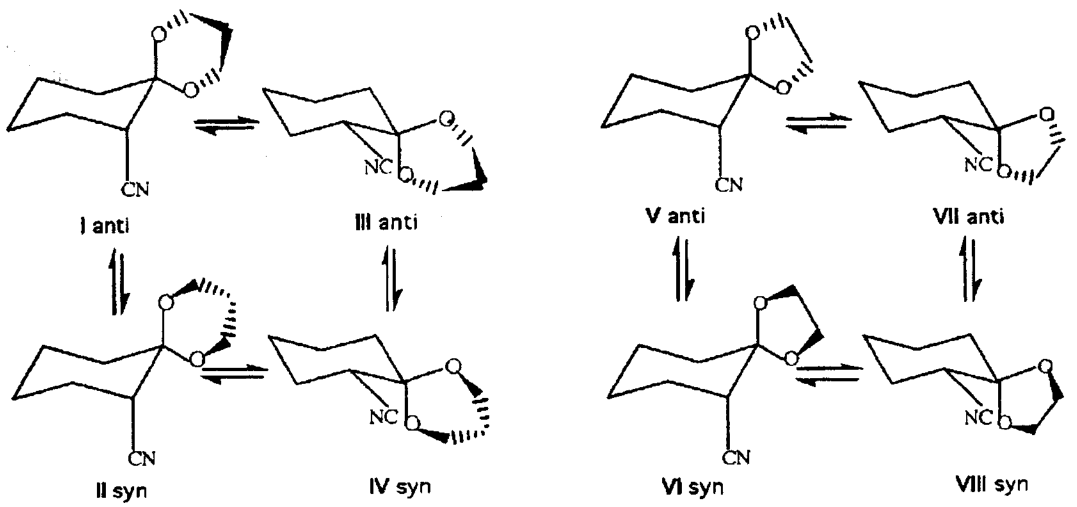


Figure 2. Conformations of 2-cyano-1,1-dihydroxyethane resembling 2-cyanocyclohexanone ethylene acetal and 2-cyanocyclohexanone propylene acetal

The equatorial position in the ring corresponds to the *gauche* position of the substituent with respect to both oxygens. The axial position corresponds to the one in which the substituent is *gauche* to one oxygen only. The spiro compounds may exist in four different conformations, as shown in Figure 2. On the one hand, the substituent may be in the axial or equatorial position in the cyclohexane ring. On the other hand, it may be in the *syn* (towards the ring) or in the *anti* (away from the ring) positions with respect to the dioxane or dioxalane

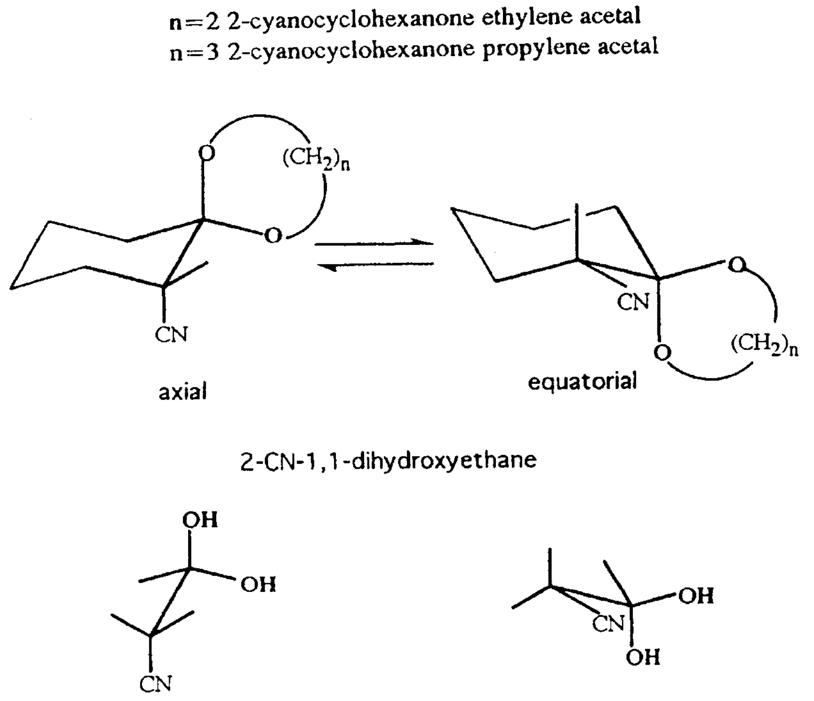


Figure 3. Conformations of 2-cyanocyclohexanone ethylene acetal and 2-cyanocyclohexanone propylene acetal

rings. Thus, compound **I** is modeled by 2-cyano-1,1-dihydroxyethane in which the dihedral angles 7–2–1–4 and 8–3–1–4 have been fixed according to the PM3-optimized geometry of 2-cyanocyclohexanone propylene acetal in the axial-*anti* conformation, whereas for compound **II** the angles are fixed to those obtained for the acetal in the axial-*syn* conformation, etc. The values of these dihedral angles are given in Table 5.

For these compounds, all the other parameters were optimized with the 6–31G basis set in the gas phase and in solution. Single-point calculations were carried out with MP2/6–31G** (Tables 6–8). The results obtained can be interpreted by comparison with our previous semi-empirical work on the spiro compounds[12] and with the experimental results.[15]

Table 5. Dihedral angles (in degrees) used for 2-cyano-1,1-dihydroxyethane (see structure in text) to model propylene acetals (structures **I**–**IV**) and ethylene acetals (structures **V**–**VIII**) (see Figure 3)

CN in axial position	**I**	**II**	**V**	**VI**
H7—O2—C1—C4	171	67	135	100
H8—O3—C1—C4	−172	−65	−137	−100
CN in equatorial position	**III**	**IV**	**VII**	**VIII**
H7—O2—C1—C4	171	82	127	118
H8—O3—C1—C4	−170	−80	−127	−113

Table 6. Relative energies, ΔE (kcal mol^{-1}), and dipole moments, μ(D), of structures that correspond to the spiro compounds in vacuum

	6–13G		6–31G**//6–31G	MP2/6–31G**//6–31G
Structure	ΔE	μ	ΔE	ΔE
I	0·00	5·37	0·39	0·56
II	2·75	4·87	1·69	1·50
III	1·40	5·99	1·43	1·07
IV	0·74	1·80	0·00	0·00
V	3·40	5·49	0·90	1·11
VI	0·08	5·34	0·67	0·78
VII	3·66	3·86	0·44	0·37
VIII	0·00	3·23	0·00	0·00

Table 7. Relative energies, ΔE (kcal mol^{-1}), and dipole moments, μ(D), of structures that correspond to the spiro compounds in chloroform ($\varepsilon = 4{\cdot}81$)

	6–13G		6–31G**//6–31G	MP2/6–31G**//6–31G
Structure	ΔE	μ	ΔE	ΔE
I	0·00	6·28	0·00	0·21
II	2·06	5·80	0·71	0·68
III	0·21	7·30	0·02	0·00
IV	2·41	1·76	1·06	0·91
V	0·00	6·39	0·44	0·48
VI	0·31	6·20	0·00	0·00
VII	0·31	4·39	0·43	0·24
VIII	0·41	3·54	0·30	0·11

Table 8. Solvation energies of structures that correspond to the spiro compounds in chloroform ($\varepsilon = 4{\cdot}81$)

Structure	6–31G	6–31G**//6–31G	MP2/6–31G**//6–31G
I	8·41	7·01	6·03
II	9·10	7·60	6·50
III	9·60	8·02	6·75
IV	6·74	5·55	4·78
V	8·51	7·16	6·26
VI	8·74	7·37	6·38
VII	7·89	6·71	5·72
VIII	7·53	6·40	5·48

Obviously, the model used for 2-cyanocyclohexanone propylene acetal cannot reproduce the steric interactions between the cyano substituent and the axial hydrogens in the dioxane moiety. The *syn* conformers for the 2-cyano-substituted propylene acetal would be sterically very unfavored and a realistic approach would be based on the comparison of the *anti* conformers of the model molecule, namely compounds **I** and **III**. Accordingly, in the gas phase the axial conformer is the most stable. In solution, the most polar conformer **III** is stabilized to a larger extent at all levels of computation. The relative axial–equatorial stability in solution depends on the level of computation but it appears to be small.

In 2-cyanocyclohexanone ethylene acetal, the dioxalane ring is flat so that the hydrogens of this moiety do not sterically interfere with the substituent and all four conformers of the model molecule, **V**, **VI**, **VII** and **VIII**, can be taken into account. The computations indicate an almost equal distribution of the axial and equatorial conformers. It is interesting that although in the free molecule the conformer corresponding to the CN in the equatorial position in the spiro compounds (**1**) is the most stable, fixing the position of the oxygens as in the acetal rings, i.e. eliminating the possibility of H-bonds, may change the relative stabilitity of the conformers. This tendency was observed for the models **I** and **III**, in parallel with the experimental results.

CONCLUSIONS

Important differences between the PM3 and *ab initio* results were found for the relative energies of stable conformations and transition states of 2-cyano-1,1-dihydroxyethane. This may be due to the presence of hydrogen bonds with large bond lengths in the conformations studied.

Partially frozen conformers were studied in order to analyze intrinsic interactions between the polar groups in ethylene and propylene acetals. Solvent effects were considered using a general cavity shape continuum model. From these results, it appears that conformers close to the axial and equatorial molecular arrangements in propylene and ethylene acetal have very close energies when solute–solvent interactions are considered. Experimentally, there is a slight preference for the equatorial conformation in the ethylene acetal and a large preference for the axial conformation in the propylene acetal. Other interactions present in the acetals should be considered to account for these findings.

ACKNOWLEDGEMENTS

This work is part of the project TBAG-1 supported by the Turkish National Science Research Institute (TUBITAK) and by the French National Research Centre (CNRS). We also gratefully acknowledge the Boğaziçi University Research Funds (Project 89EB0559).

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