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Exo-axial, Endo-axial and Exo-equatorial Anomeric Effects for Mono and Dihalo[1,4]dioxane in Solvent and Gas Phases

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The stability order of 9 possible diastereomers of 2,6-di-halo[1,4]-dioxane (series 1') and 6 diastereomers of halo[1,4]dioxane (series 2') are calculated and compared them with 2,6-dihalocyclohexane (series 1) and halocyclohexane (series 2). Endo-axial ($n_{O\rightarrow\sigma}{}^{*}{}_{C\text{-}X\text{-}A}$), exo-axial ($n_{X\text{-}A\rightarrow\sigma}{}^{*}{}_{C\text{-}O}$) and exo-equatorial ($n_{X\text{-}E\rightarrow\sigma}{}^{*}{}_{C\text{-}O}$) anomeric effects (AE) on structural parameters as well as relative energies are studied. Generally, exo-equatorial anomeric effects for equatorial halogens has more efficient energetically and structurally effects in series 1' in comparison to series 2'. Whereas, for axial halogens opposite order are found for "net endo" anomeric effects. The solvation analysis illustrates that in polar solvents free solvation energy gaps are larger for series 2' in comparison to their corresponding gap of series 2.

Key Words: Anomeric effect, Exo-axial, Endo-axial, Exo-equatorial, 2,6-Dihalocyclohexane, 2,6-Dihalo[1,4]dioxane.

INTRODUCTION

The replacement of carbon by other elements produces changes in several structural parameters such as stereo-chemical features and consequently affects the conformational characteristics of the molecule. The anomeric effect (AE) plays an important governing role in the stereo-chemical outcome by guiding the relevant electronegative substituents into an axial position[1-5]. This effect is occasionally the excess in the preference for an axial position that electronegative substituents show when they are located at the anomeric position (α-position with respect to the annular heteroatom), instead of the equatorial conformation. The anomalous axial preference of electronegative substituents at the anomeric center of the pyranose ring was first noted by Edward[6] and was clearly defined as the anomeric effect by Lemieux and Chu[7]. Since that time, the anomeric effect has been shown to be a general effect operating in O-C-X and S-C-X fragments[8] and has been classified further in terms

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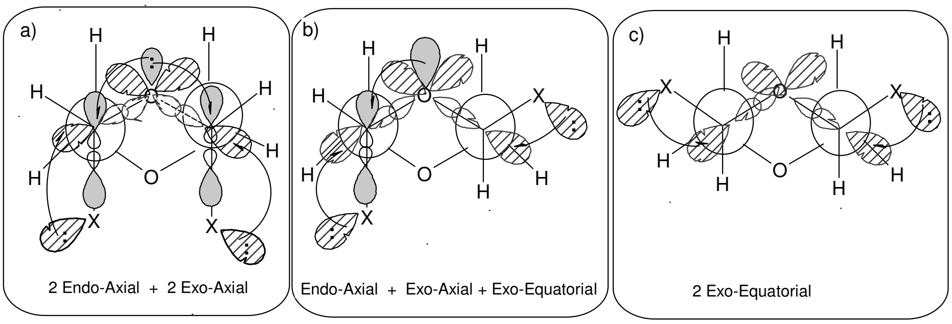
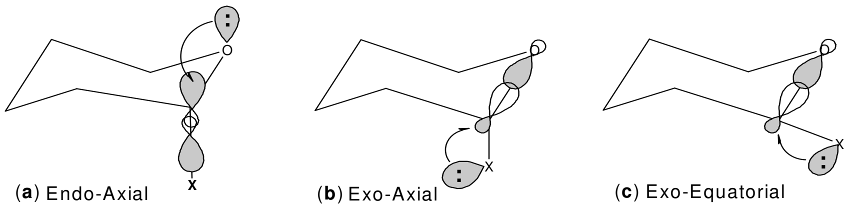
of the endo-AE and the exo-anomeric effect[9]. The endo-anomeric effect refers to the preference of electronegative groups attached to the anomeric carbon for the axial orientation and has been rationalized in terms of stabilizing $n_{O\rightarrow\sigma}*_{C-X}$ orbital interactions (**Schemes Ia-b** and **IIa-b**). The exo-anomeric effect has been rationalized in terms of $n_{X\rightarrow\sigma}*_{C-O}$ stabilizing orbital interactions (**Schemes Ib** and **IIb-c**)[9-11].



Scheme-I: Orbital interactions (Newman skeleton) in 2,6-di-halo-1,4-dioxane (Series 1'): a) X2A6A O; b): X2A6E O, c): X2E6E O



Scheme-II: Orbital interactions in halo-1,4-dioxane (series 2'): (a) X2A O endo-axial anomeric effect, (b) X2A O: exo-axial anomeric effect; (c) X2A O: exo-equatorial anomeric effect

There has been comparatively less work reported on 1,4-dioxane. Electron diffraction shows this molecule to have a chair conformation that is slightly more puckered than cyclohexane[12,13]. For 1,4-dioxane, 10 different conformers were studied. These conformations are included: chair as the most stable conformer, two twist-boats, two boats, two half-chairs, two sofas and a planar structure. The half-chairs have four coplanar atoms, while the sofas have five coplanar atoms. Theoretical studies of 1,4-dioxane evaluated the energies of all significant conformations and illustrate that chair and planar conformers are most stable and less stable conformer, respectively[14].

In this manuscript stability order of nine possible diastereomers of 2,6-dihalo-[1,4]dioxane (compounds with ability of showing anomeric effect) are computed and compared with those of nine possible diastereomers of 2,6-dihalocyclohexane (compounds without ability of showing anomeric effect).

COMPUTATIONAL METHODS

Using Gaussian 98 system of programs[15] with basis set of McGrath, Curtiss included the diffuse functions (6-311++G (3df, 2p)) through density functional theory (UB3LYP) which was selected, with the Becke three-parameter exchange functional[16] and the nonlocal correlation functional of Lee, Yang and Parr[17] for obtaining more accurate values of structures and energies. In order to perform solvation analysis of structures in series 1 and 2, their optimizations are carried out (solvents: chloroform; tetrahydrofuran and acetone), using the polarizable continuum solvation model (PCSM)[18]. Following of our research program dealing with molecular modeling of compounds[19-23], we look at the theoretical study in solvent phase.

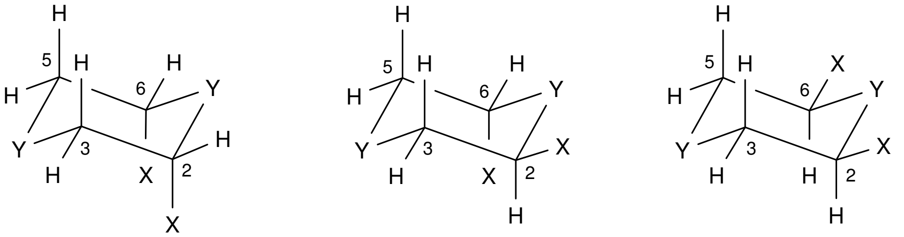
RESULTS AND DISCUSSION

An attempt is made to enlist all the results, before opening the discussion. Hence, the stability order of nine possible diastereomers of 2,6-dihalo[1,4]dioxane (series 1'; compounds with ability of showing anomeric effect): X2A6A O, X2A6E O and X2E6E O are calculated and compared with those of 2,6-dihalocyclohexane (series 1; compounds without ability of showing anomeric effect): X2A6A C, X2A6E C and X2E6E C (X = F, Cl and Br; A = Axial, E = Equatorial) (Fig. 1, Table-1 and **Scheme-I**). The benchmark calculations are done for halo[1,4]dioxane (series 2'; compounds with ability of showing anomeric effect): X2A O and X2E O as well as halocyclohexane (series 2; compounds without ability of showing anomeric effect): X2A C and X2E C and compared them to each other.

Geometrical parameters including bond length for series 1, 1' and 2, 2' are performed using B3LYP/6-311++G (3df, 2p) level and presented in Tables 3 and 4.

TABLE-1
RELATIVE ENERGIES (E_r), ENTHALPIES (H_r) AND GIBBS FREE ENERGIES (G_r) FOR 2,6-DIHALO-SUBSTITUTED CYCLOHEXANES (SERIES 1) AND 1,4-DIOXANE (SERIES 1') WHERE X = F, Cl and Br [A (AXIAL) AND E (EQUATORIAL)] AND Y= C AND O *via* B3LYP/6-311++G (3df, 2p). THE LOWEST VALUE OF E, H AND G FOR EACH SUBSTITUENT (X) IS SET AT ZERO

2,6-Dihalo-substituted cyclohexane (series 1)				2,6-Dihalo-substituted 1,4-dioxane (series 1')			
	E_r	H_r	G_r		E_r	H_r	G_r
F2E6E C	1.81	1.81	1.82	F2E6E O	2.84	2.84	2.78
F2A6E C	0.28	0.27	0.31	F2A6E O	0.15	0.15	0.09
F2A6A C	0.00	0.00	0.00	F2A6A O	0.00	0.00	0.00
Cl2A6A C	4.06	4.06	4.32	Cl2A6A O	2.13	2.13	2.15
Cl2A6E C	0.18	0.18	0.32	Cl2E6E O	1.94	1.94	1.88
Cl2E6E C	0.00	0.00	0.00	Cl2A6E O	0.00	0.00	0.00
Br2A6A C	4.89	4.89	5.18	Br2A6A O	2.67	2.67	2.72
Br2A6E C	0.35	0.35	0.53	Br2E6E O	2.15	2.15	2.10
Br2E6E C	0.00	0.00	0.00	Br2A6E O	0.00	0.00	0.00



X2A6A Y **X2E5A Y** **X2E6E Y**

Fig. 1. 2,6-Dihalo-substituted cyclohexane and 2,6-dihalo-1,4-dioxane where X = F, Cl and Br [A (Axial) and E (Equatorial)] and Y= C (series 1) and O (series 1′)

Energies (E), enthalpies (H) and free energies (G) for all series are done at the level B3LYP/6-311++G**. Using these data relative energies (E_r), enthalpies (H_r) and free energies (G_r) for all substituents (X) in gas phase are deliberate and presented in Tables 1 and 2. These Tables facilitate the ground states comparison within series. It is subdivided into many boxes. Each box represents relative E_r, H_r and G_r values corresponding to a specific substituent (X). The lowest entry in each box is set at zero. Others are adjusted accordingly.

TABLE-2

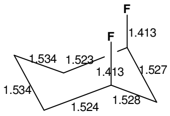
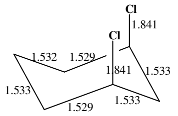
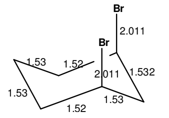
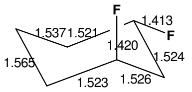
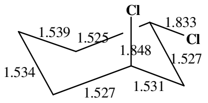
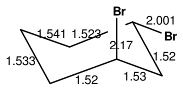
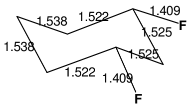
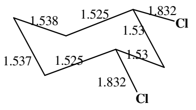
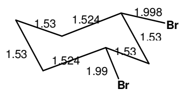
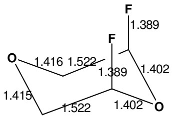
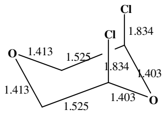
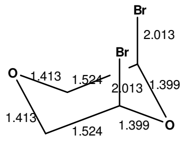
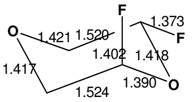
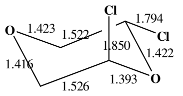
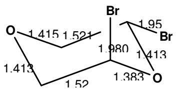
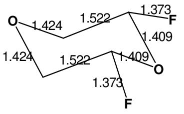
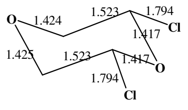
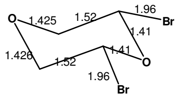
RELATIVE ENERGIES (E_r), ENTHALPIES (H_r) AND GIBBS FREE ENERGIES (G_r) FOR HALO-SUBSTITUTED CYCLOHEXANES (SERIES 2) AND 1,4-DIOXANE (SERIES 2') WHERE X = F, Cl AND Br [A (AXIAL) AND E (EQUATORIAL)] & Y= C AND O *via* B3LYP/6-311++G (3df, 2p). THE LOWEST VALUE OF E, H AND G FOR EACH SUBSTITUENT (X) IS SET AT ZERO

Halo-substituted cyclohexane (series 2)				Halo-substituted 1,4-dioxane (series 2')			
	E_r	H_r	G_r		E_r	H_r	G_r
F2E C	0.23	0.23	0.24	F2E O	2.14	2.14	2.12
F2A C	0.00	0.00	0.00	F2A O	0.00	0.00	0.00
Cl2A C	0.79	0.79	0.93	Cl2E O	1.90	1.90	1.86
Cl2E C	0.00	0.00	0.00	Cl2A O	0.00	0.00	0.00
Br2A C	0.84	0.84	0.98	Br2E O	2.28	2.28	2.23
Br2E C	0.00	0.00	0.00	Br2A O	0.00	0.00	0.00

In order to execute solvation analysis in selected solvents (chloroform; tetrahydrofuran and acetone); optimizations are carried out with polarizable continuum solvation model (PCSM) method[14,15] for all series. The physical properties of the systems, such as free energies (sum of non-electrostatic and electrostatic interaction) are found. Relative free energies (G_r) for all substituents (X) in three solvents are presented in Tables 5 and 6. These Tables are subdivided into many boxes and adjusted Tables 1 and 2, accordingly.

To facilitate interpretation of obtained results, one needs to introduce three kinds of anomeric effects. For axially substituted halogen in C2 of 1,4-dioxane

TABLE-3
OPTIMIZED GEOMETRIC DATA OF 2,6-DIHALO-SUBSTITUTED CYCLOHEXANE (SERIES 1) AND 2,6-DIHALO-SUBSTITUTED 1,4-DIOXANE (SERIES 1') AT 6-311++G (3df, 2p) LEVEL OF THEORY; BOND LENGTHS ARE IN ANGSTROMS

		2,6-Dihalo-substituted cyclohexane (series 1)	
X2A6A			
X2A6E			
X2E6E			
		2,6-Dihalo-substituted-1,4-dioxane (series 1')	
X2A6A			
X2A6E			
X2E6E			

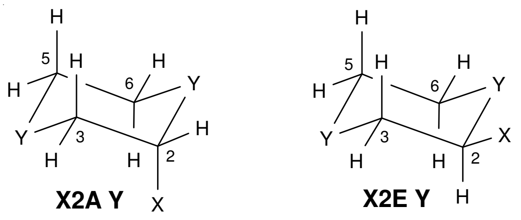


Fig. 2. Halo-substituted cyclohexane and 1,4-dioxane where X = F, Cl and Br [A (Axial) and E (Equatorial)] and Y = C (Series 2) and O (Series 2′)

(**Scheme-II**) two anomeric effects can be assigned: endo-axial ($n_{O\rightarrow\sigma}*_{C\text{-}X\text{-}A}$) and exo-axial ($n_{X\text{-}A\rightarrow\sigma}*_{C\text{-}O}$) anomeric effect. For equatorially substituted halogen in C2 of 1,4-dioxane, only one anomeric effect can be assigned: exo-equatorial ($n_{X\text{-}E\rightarrow\sigma}*_{C\text{-}O}$). Exo (exo-axial; exo-equatorial) and endo (endo-axial) anomeric effects have exactly an opposite consequences on variation of C2-X and C2-O bond length. It means that the existence of exo (exo-axial; exo-equatorial) anomeric effect contrary to endo-axial anomeric effect, causes shorter C2-X bonds and longer C-O bonds.

TABLE-4

OPTIMIZED GEOMETRIC DATA OF HALO-SUBSTITUTED CYCLOHEXANE (SERIES 2) AND HALO-SUBSTITUTED-1,4-DIOXANE (SERIES 2') AT B3LYP/6-311++G (3df, 2p) LEVEL OF THEORY; BOND LENGTHS ARE IN ANGSTROMS

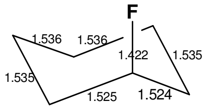
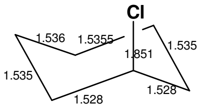
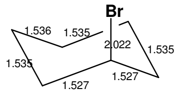
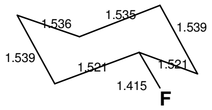
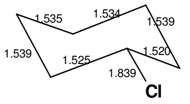
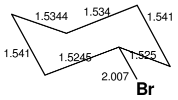
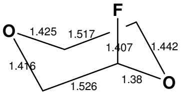
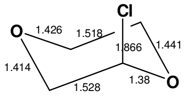
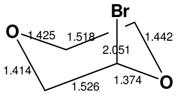
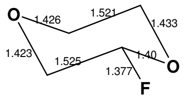
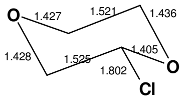
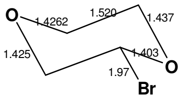
	Halo-substituted cyclohexane (series 2')		
XA			
XE			
	Halo-substituted-1,4-dioxane (series 2')		
XA			
XE			

TABLE-5

RELATIVE SOLVATION GIBBS FREE ENERGIES (ΔG_r) CALCULATED AT B3LYP/6-311++G (3df, 2p) FOR STRUCTURES IN SERIES 1 AND 1' IN THREE SOLVENTS (CHLOROFORM, TETRAHYDROFURAN AND ACETONE) USING THE "POLARIZABLE CONTINUUM SOLVATION MODEL" (PCSM). THE LOWEST VALUE OF E, H AND G FOR EACH SUBSTITUENT (X) IS SET AT ZERO

Chloroform	ΔG_r	Tetrahydrofuran	ΔG_r	Acetone	ΔG_r
F2A6A C	1.46	F2A6A C	1.43	F2A6A C	1.30
F2E6E C	0.28	F2E6E C	0.24	F2E6E C	0.24
F2A6E C	0.00	F2A6E C	0.00	F2A6E C	0.00
Cl2A6A C	3.67	Cl2A6A C	3.63	Cl2A6A C	3.60
Cl2A6E C	0.35	Cl2A6E C	0.37	Cl2A6E C	0.42
Cl2E6E C	0.00	Cl2E6E C	0.00	Cl2E6E C	0.00
Br2A6A C	4.51	Br2A6A C	4.45	Br2A6A C	4.38
Br2A6E C	0.61	Br2A6E C	0.63	Br2A6E C	0.65
Br2E6E C	0.00	Br2E6E C	0.00	Br2E6E C	0.00
F2E6E O	4.04	F2E6E O	4.17	F2E6E O	4.48
F2A6E O	1.04	F2A6E O	1.17	F2A6E O	1.41
F2A6A O	0.00	F2A6A O	0.00	F2A6A O	0.00
Cl2E6E O	1.98	Cl2E6E O	1.97	Cl2E6E O	1.98
Cl2A6A O	1.05	Cl2A6A O	0.94	Cl2A6A O	0.92
Cl2A6E O	0.00	Cl2A6E O	0.00	Cl2A6E O	0.00
Br2E6E O	3.33	Br2E6E O	3.60	Br2E6E O	4.01
Br2A6A O	2.14	Br2A6A O	2.18	Br2A6A O	2.05
Br2A6E O	0.00	Br2A6E O	0.00	Br2A6E O	0.00

TABLE-6
RELATIVE SOLVATION GIBBS FREE ENERGIES (ΔG_r) CALCULATED AT B3LYP/6-311++G (3df, 2p) FOR STRUCTURES IN SERIES 2 AND 2' IN THREE SOLVENTS (CHLOROFORM, TETRAHYDROFURAN AND ACETONE) USING THE "POLARIZABLE CONTINUUM SOLVATION MODEL" (PCSM). THE LOWEST VALUE OF E, H AND G FOR EACH SUBSTITUENT (X) IS SET AT ZERO

Chloroform	ΔG_r	Tetrahydrofuran	ΔG_r	Acetone	ΔG_r
F2E C	0.08	F2A C	0.00	F2A C	0.01
F2A C	0.00	F2E C	0.00	F2E C	0.00
Cl2A C	0.92	Cl2A C	0.94	Cl2A C	0.95
Cl2E C	0.00	Cl2E C	0.00	Cl2E C	0.00
Br2A C	0.97	Br2A C	0.97	Br2A C	0.96
Br2E C	0.00	Br2E C	0.00	Br2E C	0.00
F2E O	2.25	F2E O	2.22	F2E O	2.28
F2A O	0.00	F2A O	0.00	F2A O	0.00
Cl2E O	2.31	Cl2E O	2.34	Cl2E O	2.50
Cl2A O	0.00	Cl2A O	0.00	Cl2A O	0.00
Br2E O	3.03	Br2E O	3.12	Br2E O	3.32
Br2A O	0.00	Br2A O	0.00	Br2A O	0.00

Within series 2', two possible statuses (**Scheme-II**) can be considered: halo-1,4-dioxanes with equatorial halogen (XE O) have only exo-equatorial anomeric effect (**Scheme-IIc**) and so these species have shorter C2-X and longer C2-O bonds. However, halo-1,4-dioxane with axial halogen (XA O) confirms both endo-axial and exo-axial anomeric effect (**Schemes IIa** and **b**). Consequently, these two anomeric effects deactivate each other. Calculated structural parameters show shorter C2-O and longer C2-X bonds (Table-4). Therefore, endo-axial anomeric effect relative to exo-axial anomeric effect is more efficient factor in variation of C2-X and C2-O bond length. Consequently, any axial halogen in halo-1,4-dioxane has 'net endo' anomeric effect. In respect of the stability order in series 2' (XA O > XE O) the efficiency order of anomeric effect is: endo-'net endo' anomeric effect > exo-equatorial anomeric effect. Although exo anomeric effect (average change in C2-X bond length: - 0.37 Å) relative to net endo anomeric effect (average change in C2-X in bond length: + 0.015 Å) have more efficient net effect in bond length variation (Tables 3 and 4). However, it should be considered that net endo anomeric effect have two conflicting components (endo-axial and exo-axial anomeric effect), that reduce its structural and energetical effects.

The stability orders of relative Gibbs free energies (G_r) for series 1': X2A6E O > X2E6E O > X2A6A O may well explain about three possible interactions between anomeric effects (**Scheme-I** and Fig. 1): (a) When both halogens in 2 and 6 positions have an axial position (X2A6A O), we can assign two exo-axial, two endo-axial (total two 'net endo' anomeric effect) around one oxygen. Only one lone pair of oxygen has a proportional orientation and then will contribute in anomeric effect with two axially halogens. It means two 'net endo' anomeric effect counterbalance each other due to cross delocalization of one lone pair. Longer C2-O and shorter C2-X bond lengths in X2A6A O relative to X2A O approve this claim. As a result, X2A6A O diastereomers have the lowest stability in series 1'. (b) X2E6E O with two halogens in equatorial positions have two exo-equatorial anomeric effect around oxygen. It means two exo anomeric effect reinforce each other, slightly. The shorter C2-X and longer C2-O bond lengths in X2E6E O relative to X2E O, approve this claim. As a result, X2E6E O diastereomers have midpoint stability in series 1'. (c) X2A6E O with two halogens in axial and equatorial location has exo-axial; endo-axial (total one 'net endo' anomeric effect) and exo-equatorial anomeric effect around oxygen, respectively. Such orientation, due to a huge delocalization, causes both exo and 'net endo' anomeric effect to be strengthened. Longer C2-O *vicinal* to endo halogen and shorter C2-O vicinal to exo halogen, approve this statement. As a result, X2A6EO diastereomers have highest stability in series 1'.

For equatorial halogens, each exo-equatorial anomeric effect in series 1' is more strength than series 2', Tables 3 and 4 ($C2\text{-}X_{Series1'} < C2\text{-}X_{Series2'}$ and $C2\text{-}O_{Series1'} > C2\text{-}O_{Series2'}$).

In addition, this calculation shows each 'net endo' anomeric effect, arises from axial halogens, in series 1' relative to series 2' to be weakened ($C2\text{-}X_{Series1'} < C2\text{-}X_{Series2'}$ and $C2\text{-}O_{Series1'} > C2\text{-}O_{Series2'}$). In contrary to series 2', highly preference for axially halogens cannot be expected in series 1'. The comparison stability orders of relative Gibbs free energies (G_r) for series 1' with those of series 2', aprove the above assertion (Tables 1 and 2):

Series 1': X2A6E O > X2E6E O > X2A6A O & Series 1:
X2E6E C > X2A6E C > X2A6A C
Series 2': X2A O > X2E O & Series 2: X2E C > X2A C

The assumption is made that the F2A6A O (opposite to Cl2A6A O and Br2A6A O) in series 1' is an exception, but a better look reveals that its stability is similar to F2A6A C in series 1.

It is found that in polar solvents, free solvation energies (also their energy gaps) are larger for series 1' in comparison to their corresponding gap in series 1 (Figs. 3 and 4). It is due to a higher polarity of series 1' in contrast to series 1. Similar order exists for series 2' relative to series 2 (Figs. 3-5).

$\Delta G_{solvation}$ values are obtained for series 1, 1' and 2, 2' using B3LYP/6-311++G (3df, 2p) and plotted *vs.* dielectric constant of three solvent. These plots are shown in Figs. 3-5. Linear correlations are found between $\Delta G_{solvation}$ and polarity of solvents, for all series. These figures indicate that each component in series 1' have more $\Delta G_{solvation}$ in comparison to series 1. Similar regulate exists for series 2' relative to series 2. In addition, polarity of solvents increases the $\Delta G_{solvation}$ for series 1 more than series 1'.

Conclusion

Generally, exo-equatorial anomeric effect for equatorial halogens has more efficient energetically and structurally effects in series 1' in comparison to series 2'.

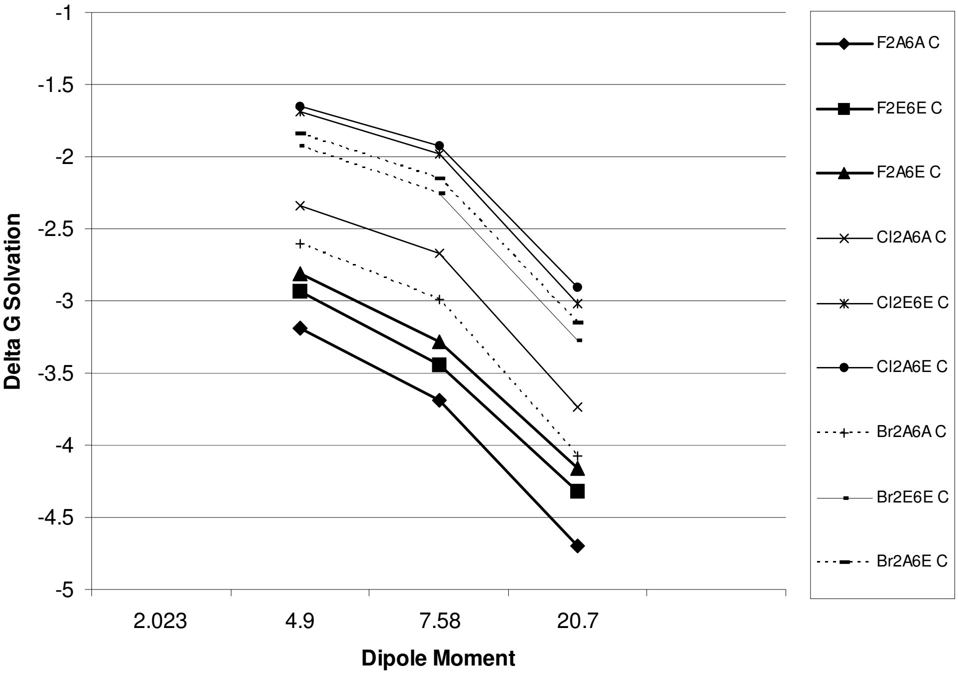


Fig. 3. Calculated $\Delta G_{Solvation}$ *vs.* dielectric constant (4.9, chloroform; 7.58, tetrahydrofuran and 20.7, acetone) for series 1

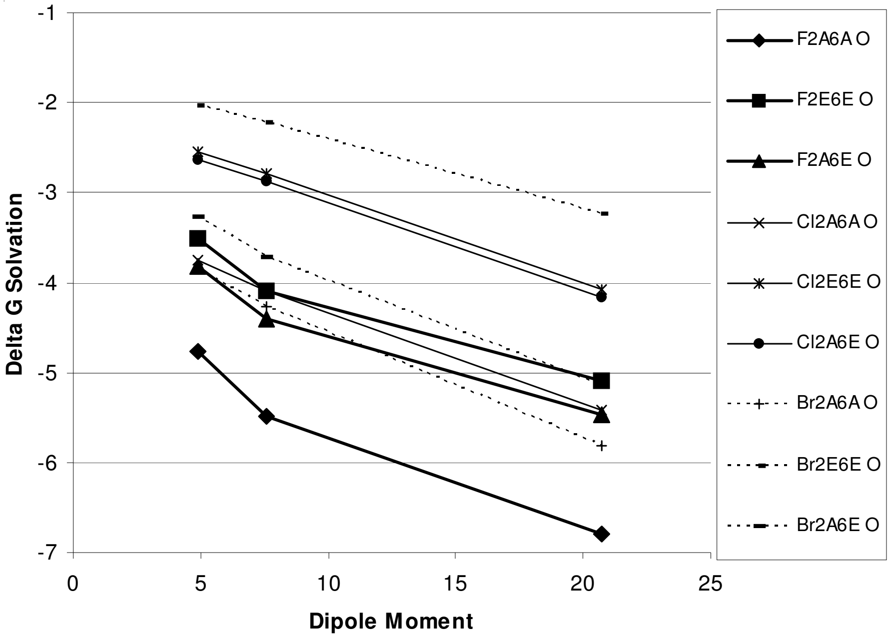


Fig. 4. Calculated $\Delta G_{Solvation}$ *vs.* dielectric constant (4.9, chloroform; 7.58, tetrahydrofuran and 20.7, acetone) for series 1'

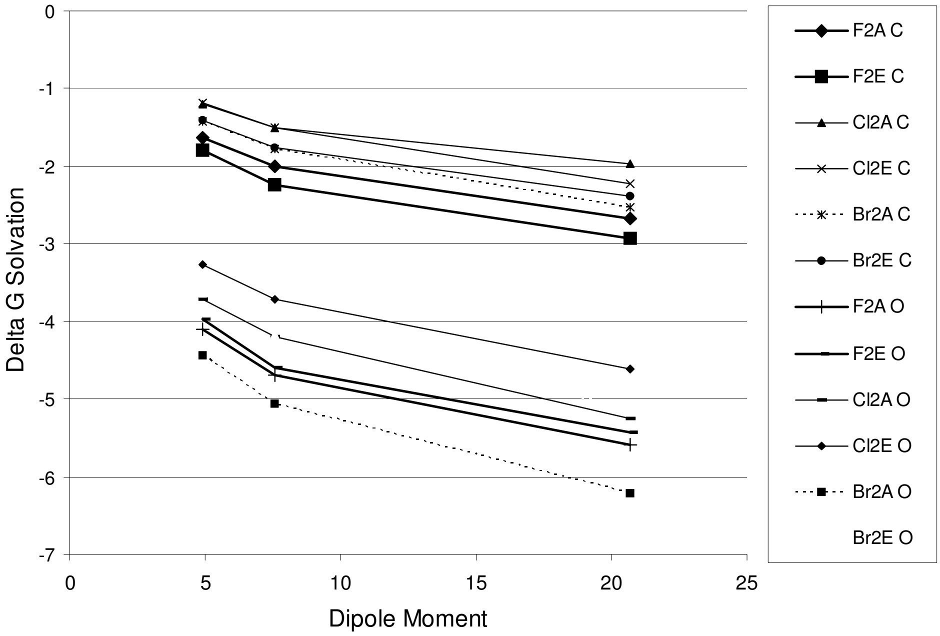


Fig. 5. Calculated $\Delta G_{Solvation}$ *vs.* dielectric constant (4.9, chloroform; 7.58, tetrahydrofuran and 20.7, acetone) for series 2 and 2'

Whereas, for axial halogens opposite order are found for 'net endo' anomeric effect. Hence, the high preference of axial halogens is expected only for series 2'. The comparison stability orders of relative Gibbs free energies (G_r) for series 1' with those of series 2', confirm the above assert:

Series 1': X2A6E O > X2E6E O > X2A6A O & Series 1: X2E6E C > X2A6E C > X2A6A C

Series 2': X2A O > X2E O & Series 2: X2E C > X2A C

Stability orders of G_r for series 1' are explained in respect to three possible interactions between anomeric effect: (a) X2A6A O has two 'net endo' anomeric effect which counterbalance each other due to cross delocalization. As a result, X2A6A O diastereomers have the lowest stability in series 1'. (b) X2E6E O has two exo-equatorial anomeric effect, which slightly reinforce each other. Consequently, X2E6E O diastereomers have middle stability in series 1'. (c) X2A6E O has 'net endo' and exo-equatorial anomeric effect. Such orientation, due to huge delocalization, causes both exo and 'net endo' anomeric effect to be strengthened. Therefore, X2A6EO diastereomers have the highest stability in series 1'.

The solvation analysis illustrates that in polar solvents free solvation energy gaps are larger for series 2' in comparison to their corresponding gap of series 2.

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