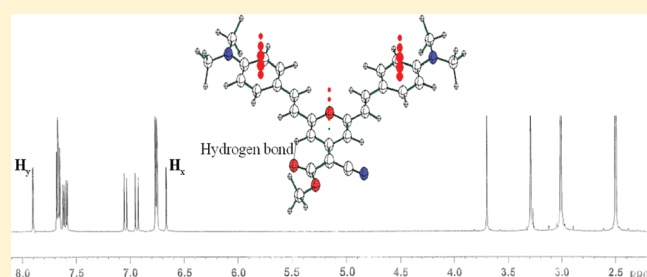


Investigation of ^1H NMR Chemical Shifts of Organic Dye with Hydrogen Bonds and Ring CurrentsSung Soo Park,^{*,†} Yong Sun Won,^{†,‡} Woojin Lee,[‡] and Jae Hong Kim[§][†]Corporate R&D Center, Samsung SDI Co. Ltd., Yongin 446-577, South Korea[‡]Corporate R&D Institute, Samsung Electro-Mechanics Co. Ltd., Suwon 443-743, South Korea[§]School of Display and Chemical Engineering, Yeungnam University, Gyeongsan 712-749, South Korea[‡]Division of Chemical Engineering, Pukyong National University, Pusan 608-739, Korea

Supporting Information

ABSTRACT: The ^1H NMR chemical shifts were theoretically computed for the organic dyes 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-malononitrile (**1**), cyano-(2,6-dimethyl-4*H*-pyran-4-ylidene)-acetic acid methyl ester (**2**), 2-(2,6-bis(4-(dimethylamino)styryl)-4*H*-pyran-4-ylidene)-malononitrile (**3**), and methyl 2-(2,6-bis(4-(dimethylamino)styryl)-4*H*-pyran-4-ylidene)-2-cyanoacetate (**4**) at the GIAO/B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Moreover, the intramolecular rotational barriers of the molecules were calculated to evaluate the internal flexibility with respect to the torsional degrees of freedom, and the nuclear-independent chemical shifts (NICS) were employed to analyze the ring currents. The difference was explained in terms of intramolecular hydrogen bonds and ring currents of the molecules. The ^1H NMR spectra were reproduced by experiments for the comparison with computationally constructed data. Our results suggest a good guideline in interpreting ^1H NMR chemical shifts using computational methods and furthermore a reliable perspective for designing molecular structures.



INTRODUCTION

Nuclear magnetic resonance (NMR) is one of the most powerful tools for the structural elucidation of organic molecules in chemistry and materials science. The joint efforts of experiments and theories offer an even more appealing solution to characterize the molecular structures and conformational properties. Especially, the well-implemented gauge-including-atomic-orbital (GIAO) method provides us fast and accurate interpretation of the NMR chemical shifts of organic molecules.^{1,2} For instance, the approach had been applied for the interpretation of organic molecules with hydrogen–hydrogen ($\text{H}\cdots\text{H}$) repulsion, containing an unsaturated vinyl group bound to both aromatic and antiaromatic rings.^{3–5} Furthermore, the influence of the carbonyl and methoxy groups on the chemical shifts of neighboring protons and hydrogen bonds ($\text{C}-\text{H}\cdots\text{O}$) has been of interest since the advent of NMR. The carbonyl and methoxy oxygens are both nominally capable of functioning as hydrogen-bond acceptors, and hydrogen-bonding interactions are expected to define the specific structure of various complexes.²¹ In particular, the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond contributes to the intramolecular conformation between the donor and acceptor groups in a planar structure.²²

The density functional theory (DFT) method is an economic alternative to electron correlation methods for considering the hydrogen bonding effect and $\text{H}\cdots\text{H}$ repulsion in organic compounds.⁶ Spomer et al. reproduced the hydrogen-bonding

energies of some base pairs by the B3LYP/6-31G(d,p)//HF/6-31G(d,p) level in good agreement with the results by MP2/6-31G*//HF/6-31G(d,p).⁷ Rablen et al. also reported that the hydrogen-bonding effect of small molecules at B3LYP/6-31++G(2d,p)//B3LYP/6-31++G(d,p) matched well with the results of CBS-Q.⁸ The DFT method has thus been used to estimate the intramolecular interactions in this study.

Ring currents corresponding to the aromaticity and antiaromaticity are basic qualitative concepts that are widely used in ^1H NMR chemistry.⁹ Schleyer et al. proposed a new magnetic criterion for the aromaticity and antiaromaticity, the nucleus-independent chemical shifts (NICSs),¹⁰ which are computed as the negative and positive magnetic shielding at some selected points in space, for example, at a ring center. This criterion has been applied in many ab initio and DFT studies, correlated with other energetic, geometric, and magnetic criteria.¹¹ As a rather direct indicator of electron delocalization and ring currents, effective indices are given for the aromaticity of individual rings in polycyclic systems.

The organic molecules used in this study are the 4*H*-pyran derivatives: 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-malononitrile (**1**), cyano-(2,6-dimethyl-4*H*-pyran-4-ylidene)-acetic acid methyl

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ester (2), 2-(2,6-bis(4-(dimethylamino)styryl)-4*H*-pyran-4-ylidene)-malononitrile (3), and methyl 2-(2,6-bis(4-(dimethylamino)styryl)-4*H*-pyran-4-ylidene)-2-cyanoacetate (4). These kinds

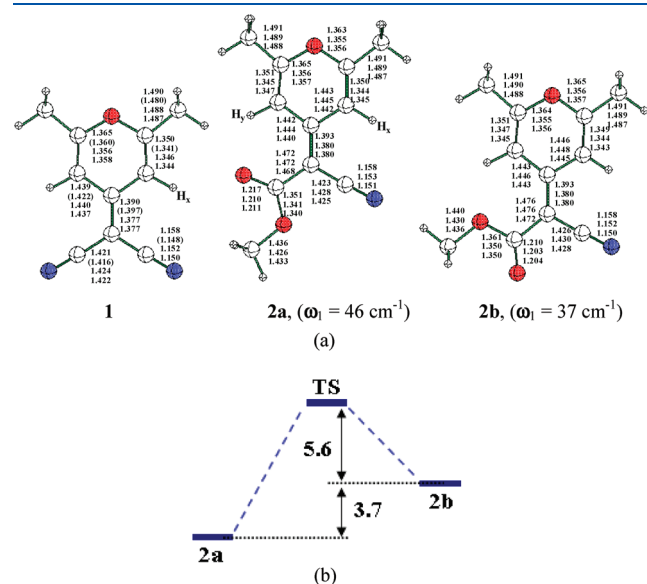


Figure 1. (a) Optimized geometries of compounds 1, 2a, and 2b with their lowest vibrational frequencies (ω_1), and (b) the energetics with the rotational barrier (kcal/mol) of methyl formate-substituted 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-malononitrile derivative calculated on the basis of the 6-311++G(d,p) basis set. The interatomic distances in (a) were calculated using three different methods for comparison. They are in the order of B3LYP, M06-2X, and M05-2X from above, and experimental data are in parentheses. Compound 1 is in C_{2v} symmetry.

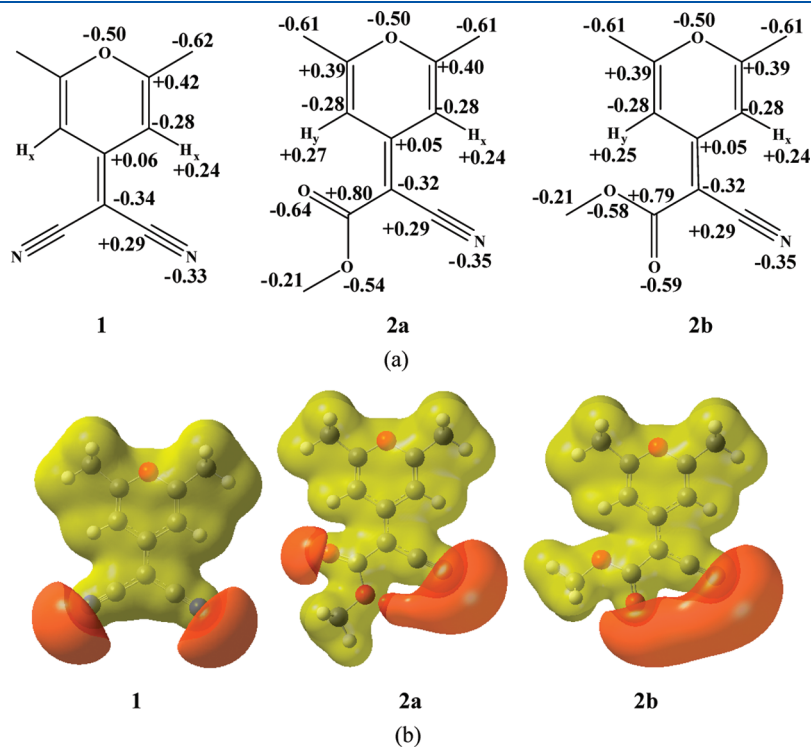


Figure 2. (a) Natural atomic charges and (b) electrostatic potentials by the isodensity contours ($\text{au} = \pm 0.04 \text{ e}/\text{\AA}^3$) of compounds 1 and 2 with trans (2a) and cis (2b) forms.

of compounds such as 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylamino)styryl)-4*H*-pyran (DCM) and 4 have shown high electroluminescence and photoluminescence in organic light-emitting devices¹² and dye-sensitized solar cells.¹³ Because their optical properties are highly sensitive to the intramolecular geometries,¹⁴ the accurate interpretation of NMR spectra of those materials is essential to develop further innovative molecular structures.

In this study, we addressed the question of to what extent the geometries, energies, and ^1H NMR chemical shifts of the molecules are influenced by intramolecular interactions such as $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding, $\text{H}\cdots\text{H}$ repulsion, and ring currents. The GIAO-NMR chemical shifts were computationally constructed for the selected organic dyes (1–4) and compared to experimentally reproduced NMR data to elucidate shielding modes in the species and investigate energy barriers involved in the stable rotational structures. The NICs were also computed to analyze the ring current effect.

COMPUTATIONAL DETAILS

We have investigated all possible complexes derived from the isomers corresponding to the rotations of methyl-acetate, 4*H*-pyran, phenyl, and dimethylamine moieties. Structures were optimized using the DFT method at the B3LYP/6-311++G(d,p) level implemented in the Gaussian 09 package.¹⁵ The computed geometries were then verified by frequency calculations at the same level of theory in the gas phase. In addition, global minima were determined by comparing the energies of the resulting optimized structures from manually adjusted different initial geometries. Additional calculations using M05-2X and M06-2X methods were carried out for comparison. The agreement of B3LYP/6-311++G(d,p) results with those is typically

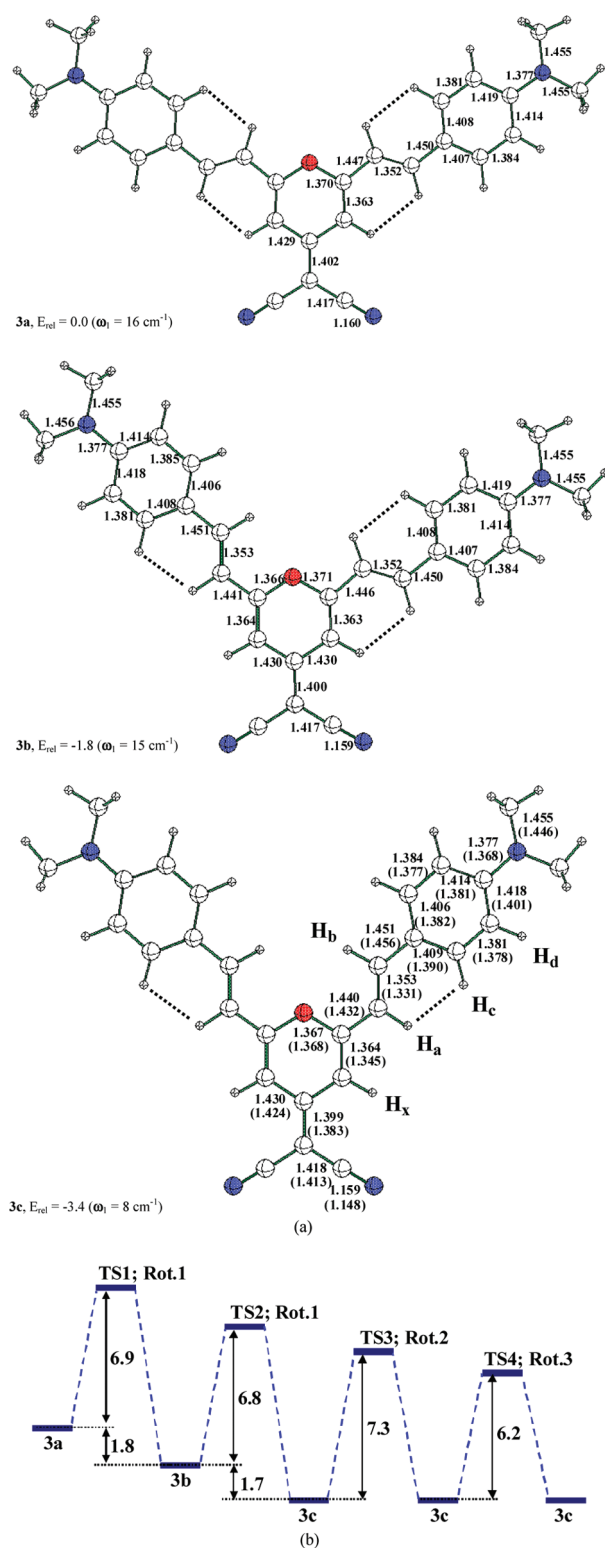


Figure 3. (a) Optimized geometries of the three possible isomers of 2-(2,6-bis(4-(dimethylamino)styryl)-4H-pyran-4-ylidene)-malonitrile, **3a**, **3b**, and **3c**, with their lowest vibrational frequencies (ω_1), and (b) the rotational barriers (kcal/mol) between the compounds. Relative energies (kcal/mol) in (a) and the rotational barriers in (b) were calculated at the B3LYP/6-311++G(d,p) level of theory. Structure **3c** is the most stable. Compounds **3a** and **3c** are in C_2 symmetry. Experimental data for the geometry are given in (a) and in parentheses. The dotted lines mean the number of H...H repulsions.

on the order of 1%. Figures 1–4 summarize the molecular structures, relative energies (E_{rel}), and lowest vibrational frequencies (ω) of the compounds (1–4) relative to their rotamers. The computation of NMR chemical shifts was carried out by the GIAO method in which the nuclear shielding tensor is calculated. To convert ^1H NMR chemical shifts of the molecules to ppm, the isotropic values of hydrogens in the molecules were subtracted from those of the hydrogens in tetramethylsilane (TMS): δ (ppm) = H for TMS – H for molecules. The GIAO chemical shifts referenced to hydrogens in TMS were 31.98 ppm at the same level of theory. As for the ring current effect, the NICS values¹⁰ were evaluated at the centers of all rings of the investigated species.

RESULTS AND DISCUSSION

Geometrical Features. The geometrical parameters and frequency analyses of the investigated molecules (1–4) are summarized in Figures 1, 3, and 4. It has been shown that the DFT calculation produces better geometries than do other theoretical levels.⁶ According to the comparison between the X-ray crystallographic data and computation of species **1**, the computed geometry showed a small bond elongation of about 0.5% on average.¹⁷ Because the direct structural data were not available for the compounds (2–4), the optimized parameters were compared to X-ray crystallographic data for similar kinds of molecules.¹⁸ The comparison showed that the species (3c and 4c) undergo similar bond elongation by 0.9% on average. The discrepancy is due to the difference between experimental X-ray crystallographic data with intermolecular interactions involved and calculated results for free molecules in the gas phase. The computational results, however, explained the geometries of the investigated molecules (1–4) with acceptable quality.

Compound **2**, a methyl acetate-substituted derivative instead of cyano group in **1**, exists as either trans (**2a**) or cis (**2b**) isomer. The isomers own the intramolecular hydrogen bonding between the hydrogen (H_y) of 4H-pyran and the carbonyl and methoxy oxygens of the methyl-acetate moiety, respectively. To check that the isomers are in the rotamers, their geometries and energies were calculated as shown in Figure 1. In **2a** and **2b**, the distances of $H_y \cdots O$ are 2.140 and 2.127 Å, respectively, which indicates that hydrogen bonds are formed to stabilize **2a** and **2b**. The trans rotamer **2a** is electrostatically more stable than the cis rotamer **2b**, by 3.7 kcal/mol in energetics. The internal rotational barriers from trans to cis and from cis to trans were obtained as 9.3 and 5.6 kcal/mol, respectively. The dihedral angle of the transition state is 93.1°. The rotating axis at the dihedral angle has a single bond characteristic that leads to acceptable bond lengths, 1.472 Å for **2a** and 1.476 Å for **2b**, respectively. Detailed geometries for the isomers are included in the Supporting Information. As shown in Figure 2, the computation has shown that the free electron pairs of oxygen atom are delocalized around the hydrogen, just as electrons are shared on average by bonded atoms in nominal covalent bonding. It is correlated to the ^1H NMR chemical shifts performed on these 4H-pyran derivatives,¹⁹ as discussed later in more detail.

The isomers shown in Figure 3 have the geometries containing a vinyl group bound to both 4H-pyran and phenyl ring. Thus, it requires understanding the steric interactions governing these systems. The geometry of **3c** with two H...H steric repulsions keeps it as global minimum as shown in Figure 3 (same for **4c** in Figure 4), while the π -conjugation between the phenyl and vinyl

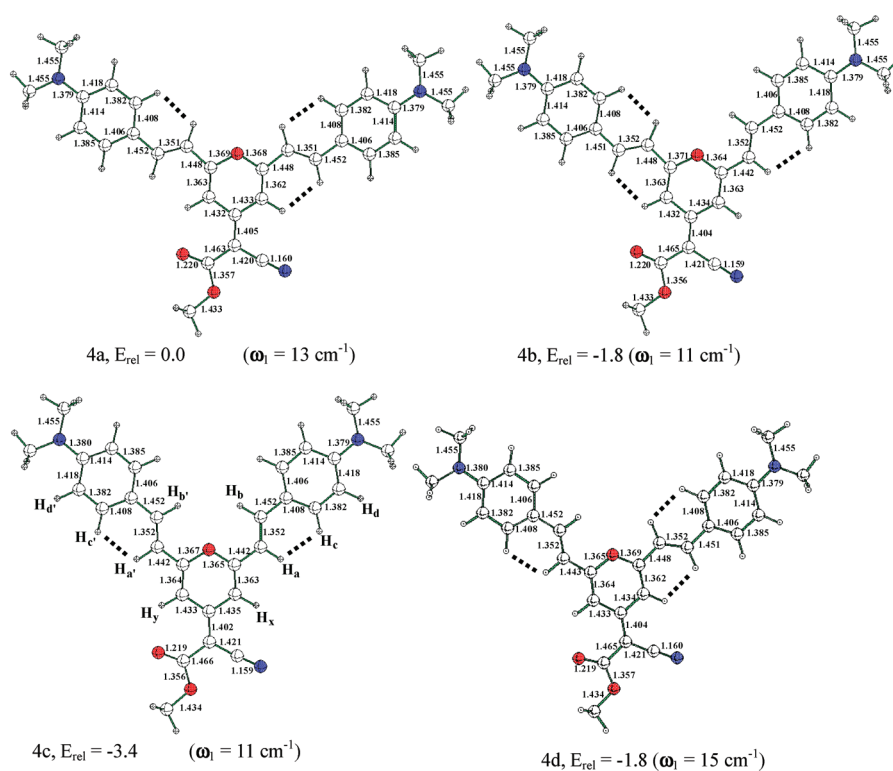


Figure 4. Four possible isomers of methoxy-substituted 2-(2,6-bis(4-(dimethylamino)styryl)-4H-pyran-4-ylidene)-malononitrile at the B3LYP/6-311++G(d,p) level of theory. The dotted lines mean the number of H···H repulsions. Structure **4c** is the most stable among them.

groups stabilizes the coplanar conformer. Because three or four H···H repulsions are involved in the isomers **3a** and **3b**, **3c** is expected to be more stable only with two H···H repulsions. Accordingly, **3c** with less hydrogen repulsion is more stable energetically by 3.5 and 1.7 kcal/mol than are **3a** and **3b**, respectively. Because of the intramolecular rotations of **3**, Scheme 1 illustrates three possible rotational modes, Rot.1, Rot.2, and Rot.3. The forward and backward rotations of Rot.1 had different potential energies, 8.5 and 6.8 kcal/mol, respectively, while those of Rot.2 and Rot.3 were of the same potential energies, 7.3 and 6.2 kcal/mol, respectively. It suggests that Rot.2 and Rot.3 are facile and reversible, but Rot.1 is irreversible in a relative way. The detailed structural parameters for the conformers are also in the Supporting Information. Figures 3 and 4 also show the comparison of the optimized geometrical parameters for the species to available X-ray structural data,¹⁸ and the agreement is fairly good. It confirms that the coplanar geometry is formed throughout the 4H-pyran, vinyl, and phenyl group. The slight overestimation of the calculated bond lengths is due to the gas-phase calculations as previously mentioned. The geometry of **4c** was determined to be most stable among the structures considering the barriers combined with the rotations of **2a** and **3c**, as shown in Figure 4.

NICS. As mentioned in the Introduction, the aromatic criteria are often defined via the magnetic property based on NICSs. The ring center of the molecules has the negative NICS values (in ppm) for the aromaticity, while the antiaromaticity has positive NICS values, and the nonaromaticity is described by the values close to zero. We calculated NICS values at the ring centers of 4H-pyran and phenyl, respectively, to provide measuring criteria for the ring current effect. As shown in Table 1, the computed

NICS values at the phenyl rings are negative (−6.6 ppm), suggesting the existence of delocalization and the aromaticity; the value at the ring center of benzene is −8.0 ppm for reference. On the other hand, the ring center of 4H-pyran is likely to have the nonaromaticity by the values in the range of +0.4 to −0.9 ppm. The different aromatic characteristics between them are also related to the ring currents; the phenyl moiety has higher ring current than does the 4H-pyran. The influence of the ring current on the ¹H NMR chemical shifts is discussed in the next section.

¹H NMR Chemical Shifts with Respect to the Intramolecular Interaction and Ring Current. The issues of how many shielding signals in the ¹H NMR spectrum of a complex molecule have rarely been addressed. Hydrogens have different NMR chemical shifts unless they are chemically equivalent, obviously with the possibility of overlaps. However, it is often not obvious even which hydrogens are chemically equivalent in various compounds.¹⁹ For example, the chemical shifts of the hydrogens are far downfield when hydrogens interact with strong electronegative atoms, as compared to the hydrogens bound to carbon.

As shown in Figure 1 and Table 2, the chemical shift of hydrogens attached to the 4H-pyran of **1** appears at 6.67 ppm, while the chemical shifts of hydrogens (H_x and H_y) attached to the substituted methyl acetate in **2a** appear 6.92 and 8.74 ppm, respectively. It is quite noted that the peaks for the hydrogen, H_{yy}, interacting with the carbonyl (**2a**) and methoxy (**2b**) groups of **2** appear in the downfield region of 8.74 to 7.88 ppm. Based on the planar structure of **2**, the downfield is due to the hydrogen-bonding effect between the oxygen of methyl-acetate and H_y of 4H-pyran moiety.

Scheme 1. Rotational Barriers Considered in Compound 3

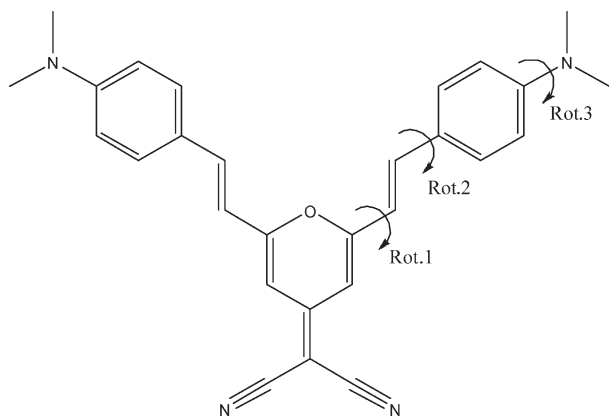


Table 1. NICS Values of the Species Computed at the GIAO-B3LYP/6-311++G(d,p) Level As Compared to benzene

species	4 <i>H</i> -pyran ring	phenyl ring
1	-0.7	
2a	-0.9	
2b	-0.8	
3c	+0.4	-6.6
4c	+0.3	-6.6
benzene		-8.0

The compounds shown in Figure 3 include two different rings. In case of aromatic ring, the π -electrons on the aromatic ring circulate more readily under the external magnetic field than their σ -electrons because the nuclei hold the electrons less strongly. Depending on the ring species in the molecule, the magnetic field of these π -electrons at the hydrogen of interest is aligned with the external magnetic field, resulting in the downfield shifts. This “ring current effect” is distinct especially in benzene derivatives with large downfield shifts for hydrogens attached to the aromatic phenyl ring. The chemical shifts for the hydrogens (H_c and H_d) connected to the phenyl ring of 3c appear at 7.77 and 6.65 ppm, respectively. However, the electron-donating dimethylamine group bound to the phenyl ring leads to the upfield chemical shifts of H_d relative to H_c . A similar but smaller effect induces the hydrogens on the vinyl moiety to appear downfield as well. The chemical shifts for the hydrogens (H_a and H_b) on the vinyl moiety are at 6.64 and 7.70 ppm, respectively. The hydrogen close to the phenyl ring is more downfield-shifted than the one close to 4*H*-pyran, similarly as shown in the chemical shifts of styrene.²⁰

In Figure 4, the geometries on the left and right sides of the molecule that resulted from the replacement of cyano group by methyl acetate are independent of each other. Although the types of hydrogens on both sides appear similar, they may have different chemical shifts if they are not chemically equivalent. The case of 4 is more delicate. Twelve absorptions are expected in the ¹H NMR spectrum of 4: singlet for all 12 hydrogens on dimethylamine, singlet for the three hydrogens on methyl acetate, singlet for H_x , singlet for H_y , doublet for H_a , doublet for $H_{a'}$, doublet for H_b , doublet for $H_{b'}$, doublet for H_c , doublet for $H_{c'}$, doublet H_d , and doublet for $H_{d'}$. Compound 4 also

Table 2. Experimental^a versus Calculated ¹H NMR Chemical Shifts of the Most Stable Derivatives

proton	1		2a		3c		4c	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
H_x	6.68	6.67	6.59	6.92	6.69	6.52	6.66	6.77
H_y			7.80	8.74			7.90	8.69
H_a					7.04	6.64	6.94	6.77
$H_{a'}$							7.04	6.78
H_b					7.65	7.70	7.61	7.67
$H_{b'}$							7.59	7.62
H_c					7.68	7.77	7.66	7.69
$H_{c'}$							7.68	7.73
H_d					6.77	6.65	6.75	6.62
$H_{d'}$							6.76	6.67
O-CH ₃			3.67	3.74			3.69	3.71
N-CH ₃					3.02	3.11	3.01	3.11
CH ₃	2.44	2.24	2.34	2.24				

^a Experimental measurements are in DMSO.

includes the effects of hydrogen bonding, $H \cdots H$ repulsion, and ring currents. The chemical shifts of hydrogens near high electronegative atoms such as oxygen and nitrogen depend on the geometry of the molecule due to the intramolecular interactions by hydrogen bonding. Because the hydrogen bonding serves to increase electron density around highly electronegative atom, a deshielded downfield shift is obtained. The hydrogen (H_y) of 4*H*-pyran interacting with the carbonyl groups of methyl acetate appears even farther downfield (near 8.69 ppm) as a result of the hydrogen-bonding effect, but the hydrogen (H_x) of the other side appears at 6.77 ppm similar to 2a. The peaks for phenyl (H_c , $H_{c'}$, H_d , $H_{d'}$) and vinyl (H_a , $H_{a'}$, H_b , $H_{b'}$) groups usually appear in the region of 6.6–7.8 ppm, while the peaks for dimethylamines and methoxy group emerge near 3.1 and 3.6 ppm, respectively. These chemical shifts are resulted from the combination of hydrogen bonding in 2a and ring current of 3c.

CONCLUSIONS

On the basis of the geometries of some 4*H*-pyran derivatives optimized by the DFT method, the geometric features such as the structural deformation during rotation, hydrogen bonding, and hydrogen repulsion were investigated. Although the Rot.1 to the internal rotation originates from the steric repulsion of hydrogens, Rot.2 and Rot.3 are most likely to be the predominant internal degrees of freedom responsible for the nature of single bond relaxation. In addition, the *cis* and *trans* isomers of the methyl acetate-substituted derivative (2) experience intramolecular hydrogen bonding during internal rotation, where the transition state between them for the Rot.1 has inaccessible kinetics in a relative way. Meanwhile, we have also shown relative aromaticities for the rings of 4*H*-pyran and phenyl group by using NICS values. It turned out that there is no influence of the methyl acetate substituent on the nonaromatic 4*H*-pyran ring. Finally, the inspection of the ¹H NMR chemical shifts of the investigated species was carried out with respect to the effects of hydrogen bonding and ring current. Consequently, our computational analysis on the chemical shifts of molecules combined with those effects was clearly demonstrated to be essential to the interpretation of experimental data.

EXPERIMENTAL SECTION

Synthesis of 2-(2,6-Dimethyl-4H-pyran-4-ylidene)-malonitrile (1). In a three-neck flask, 2,6-dimethylpyran-4-one (1.2 g, 10 mmol) and malonitrile (1 g, 15 mmol) were dissolved in acetic anhydride while stirring the mixture at 120 °C. The reaction mixture was heated on a steam bath for 2 h and poured into a slurry of crushed ice and water (250 mL). The precipitate was washed with water and extracted with CHCl₃. Viscous liquid product was obtained by column chromatography (CHCl₃) (yield = 70%). ¹H NMR (DMSO, ppm): δ 6.68 (s, 2H, ArH), δ 2.35 (s, 6H, 2(CH₃)).

Synthesis of Cyano-(2,6-dimethyl-4H-pyran-4-ylidene)-acetic Acid Methyl Ester (2). A solution of 1 equiv (5 g, 40 mmol) of 2,6-dimethylpyran-4-one and 1 equiv of methyl cyanoacetate (5.6 g, 57 mmol) in acetic anhydride was refluxed for 2–5 h. The mixture was then poured into a mixture of water. The crude product was extracted with ethyl ether (5 × 30 mL). The extracts were washed with water and dried over MgSO₄. Removal of the solvent left residue, which was subjected to column chromatography, EtOAc–petroleum ether (1:1, v/v) as a dark orange solid (yield = 28%). ¹H NMR (DMSO, ppm): δ 7.80 (s, 1H, ArH), δ 6.59 (s, 1H, ArH), δ 3.67 (s, 3H, CH₃), δ 2.34 (s, 6H, 2(CH₃)).

Synthesis of 2-(2,6-Bis(4-(dimethylamino)styryl)-4H-pyran-4-ylidene) Malonitrile (3). A solution of 1 (1 g, 6.0 mmol), 4-dimethylamino benzaldehyde (1.9 g, 12.8 mmol), and piperidine (0.45 mL) in acetonitrile (30 mL) was refluxed for 8 h. The reaction solution was cooled to room temperature, and the solid product was isolated and washed well with acetonitrile and dried. The crude product was recrystallized from methanol several times (yield = 23%). ¹H NMR (DMSO, ppm): δ 7.68–7.65 (d, 2H, J = 16.2 Hz), δ 7.66–7.65 (d, 4H, ArH), δ 7.07–7.04 (d, 2H, J = 16.2 Hz), δ 6.78–6.77 (d, 4H, ArH), δ 6.69 (s, 2H), δ 3.02 (s, 12H, 4(CH₃)).

Synthesis of Methyl 2-(2,6-Bis(4-(dimethylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate (4). A solution of 2 (1 g, 5 mmol), 4-dimethylamino benzaldehyde (1.6 g, 11 mmol), and piperidine (0.45 mL) in acetonitrile (30 mL) was refluxed for 8 h. The reaction solution was cooled to room temperature, and the solid product was isolated and washed well with acetonitrile and dried. The crude product was recrystallized from methanol several times (yield = 47%). ¹H NMR (DMSO, ppm): δ 7.90 (s, 1H), δ 7.69–7.67 (d, 1H, ArH), δ 7.67–7.65 (d, 1H, ArH), δ 7.62–7.59 (d, 1H, J = 18 Hz), δ 7.61–7.58 (d, 1H, J = 18 Hz), δ 7.06–7.03 (d, 1H, J = 18 Hz), δ 6.95–6.93 (d, 1H, J = 18 Hz), δ 6.77–6.75 (d, 1H, ArH), δ 6.76–6.74 (d, 1H, ArH), δ 6.66 (s, 1H), δ 3.69 (s, 1H, CH₃), δ 3.01 (s, 12H, 4(CH₃)).

ASSOCIATED CONTENT

S Supporting Information. ¹H NMR chemical shift data and optimized geometries of the species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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