Intramolecular H···H Interactions for the Crystal Structures of [4-((*E*)-But-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate and [4-((*E*)-Pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate; DFT Calculations on Modeled Styrene Derivatives

Sławomir J. Grabowski,*,† Arno Pfitzner,*,‡ Manfred Zabel,‡ Alina T. Dubis,§ and Marcin Palusiak†

Department of Crystallography and Crystal Chemistry, University of Łódź, 90-236 Łódź, ul. Pomorska 149/153, Poland, Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany, and Institute of Chemistry, University of Białystok, Al. J. Piłsudskiego 11/4, 15-443 Białystok, Poland

The crystal and molecular structures of [4-((*E*)-but-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (BDMP) and [4-((*E*)-pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (PDMP) are investigated by low-temperature X-ray diffraction measurements. The geometries of these molecules indicate that intramolecular dihydrogen bonds may exist for these structures. The use of the Bader theory supports this statement. To analyze the nature of such interactions, model calculations on styrene and its derivatives have been performed at B3LYP/6-311++G** level of theory.

Introduction

Hydrogen bonding is one of the most important interactions influencing the arrangement of molecules in crystals and having a dominant role for their physical properties.[1–5] The problem of this interaction is connected with the fact that the definition and the criteria of existence of hydrogen bonding are not unequivocal. Early works claim that an H-bond, often designated as X−H···Y, exists between the proton donating X−H bond and the proton acceptor Y usually containing at least one lone electron pair; the hydrogen atom of the X−H bond should be positively charged and the Y-accepting center should have the excess of electron charge.[6] Early works report that for such X−H···Y interactions X and Y should be electronegative atoms. However, there are so-called unconventional hydrogen bonds with X or Y being carbon atoms; these are C−H···Y or X−H···C interactions or hydrogen bonds with π-electrons as the proton acceptors.[4] Such unconventional H-bonds early on described and found in crystal structures[7] have been commonly admitted after the appearance of the work of Taylor and Kennard where the statistical justification of the existence of hydrogen bonds with C−H donating bonds based on the data taken from Cambridge Structural Database (CSD)[8] was given.[9] The problem is more complicated because other kinds of hydrogen bonds were detected in past decade; among them are dihydrogen bonds[10,11] and blue-shifting hydrogen bonds.[12]

A dihydrogen bond was defined as that one for which the typical X−H proton donating bond exists and the weak base component is a metal hydride or B−H bond.[10,11] It was pointed out that a dihydrogen bond is similar to typical, conventional hydrogen bonding. For example, a correlation between the H-bond energy and the H···H distance was found or a correlation between the H-bond energy and the elongation of the proton donating bond due to the dihydrogen bond formation.[13,14] The nature, the structure, and energetic characteristics of dihydrogen bonds were extensively studied,[15,16] the topological analysis based on the Bader theory[17] was also applied.[14,18–20] The theoretical evidence of the existence of intramolecular dihydrogen bonds has been described[21,22] and it was also detected that for some of such intramolecular systems there is the π-electron delocalization which exists for the so-called resonance assisted hydrogen bonds (RAHBs).[23,24]

The blue-shifting hydrogen bonds were detected for some C−H···Y systems for which there is no typical elongation of the donating bond connected with the normal red shift of the C−H stretch frequency but a blue shift is observed connected with the decrease of the C−H bond length.[12]

The aim of the present study is to analyze the crystal structures of [4-((*E*)-but-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (BDMP) and [4-((*E*)-pent-1-enyl)-2,6-dimethoxy-phenyl]pyridine-3-carboxylate (PDMP) because in such structures intramolecular H···H contacts exist that might be treated as dihydrogen bonds. Additionally, these compounds are important due to their biological activity; such activities were detected during studies on α-asarone derivatives.

α-Asarone is the principle active component of the bark extract of *Guatteria gaumeri*[25] and *Acorus calamus*.[26] These extracts have been used traditionally to prevent elevation of plasma lipids. Earlier works[27,28] suggest that some of the α-asarone derivatives could be effective hypolipidaemic agents. A detailed ^{1}H NMR study of a series of α-asarone isomers was also made.[29] Furthermore, the crystal structures of 1,2,5-trimethoxy-3-(1-propenyl)benzene and 1,3,5-trimethoxy-2-(1-propenyl)benzene have been determined by X-ray diffraction methods.[30] In both cases existence of the intra- and intermolecular C−H···O hydrogen bonds was observed.

† University of Łódź.
‡ Institut für Anorganische Chemie der Universität Regensburg.
§ University of Białystok.

Experimental Section

Melting points were determined on a Mettler DSC30 in aluminum sample containers. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200F spectrometer using CDCl$_3$ solution with TMS as internal standard (chemical shifts in δ ppm). IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer in chloroform solutions. Column chromatography was performed using Merck Kieselgel 60, 70-230 mesh. Thin-layer chromatograms were developed on aluminum TLC sheets precoated with silica gel F$_{254}$. The spots were visualized with 50% sulfuric acid after heating. All the solvents were dried and freshly distilled prior to use.

Synthesis. 1-Bromoalkane (0.1 mol) in 20 mL of THF was added dropwise to the mixture of 2.4 g (0.1 mol) of magnesium turnings in 15 mL of dry THF. The solution of 3.64 g (0.02 mol) of 3,5-trimethoxy-4-hydroxybenzaldehyde in 50 mL of THF was cooled to -70 °C (dry ice–acetone bath) and magnesium alkylbromide (propyl or butyl, respectively) was added. After 10 min the ice bath was removed. The reaction mixture was stirred 2 h at room temperature. After completion of the reaction (TLC control) the mixture was quenched with 50 mL of methanol and water and product was extracted with ether. The organic extract was washed with water and dried over magnesium sulfate and evaporated. The resulting 4-(hydroxyalkyl)-2,6-dimethoxyphenol was subjected to the next step.

A solution of the crude alcohol (0.02 mol) in 50 mL of dry toluene was treated with 4.8 g (0.03 mol) of CuSO$_4$.[31] The reaction mixture was refluxed for 2 h. An inorganic material was filtered off and washed with toluene. The solvent was removed, yielding the crude alkene, which was purified by silica gel column chromatography. Elution with hexane/ether; 7:3 (v/v), yielded 0.01 mol of 4-((1E)-but-1-enyl)-2,6-dimethoxyphenol or 4-((1E)-pent-1-enyl)-2,6-dimethoxyphenol.

A solution of 0.01 mol of 4-((1E)-alkyl-1-enyl)-2,6-dimethoxyphenol in 15 mL of dry pyridine was treated under inert gas (argon) with 0.056 mol of nicotinoyl chloride hydrochloride. The reaction mixture was heated overnight at 50 °C with catalytic amounts of 4-(dimethylamino)pyridine (DMAP). After cooling, the reaction mixture was poured into a cold solution of ammonium chloride and extracted twice with chloroform. After evaporation of the solvent the residue was purified by silica gel column chromatography (elution with hexane/ether; 1:1; v/v). The nicotinic acid ester was crystallized from ethanol/hexane to give the pure product as a white needle (0.005 mol, 50% yield).

[4-((*E*)-But-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate. Mp: 127 °C (decomposition). IR (CHCl$_3$), ν (cm^{-1}): 1746, 1597, 1508, 1420, 1352, 1327, 1279,1134, 1090, 1023, 964, 853. ^1H NMR (200 MHz, CDCl$_3$), δ: 9.42 (s, 1H, ArH), 8.84 (dd, 1H, ArH), 8.44 (m,1H, ArH), 7.43 (m, 1H, ArH), 6.64 (s, 2H, ArH), 6.43 (m, 1H, CH=), 6.32 (m, 1H, =CH), 3.81 (s, 6H, $-$OCH$_3$), 2.24 (dt, 2H, $-$CH$_2$), 1.10 (t, 3H, CH$_3$). ^{13}C NMR: δ 163.2 (C), 153.6 (CH), 152.0 (C), 151.5 (CH), 137.6 (CH), 136.7 (C), 133.1 (CH), 128.5 (CH), 127.2 (C), 125.0 (C), 123.2 (CH), 102.5 (CH), 55.9 (CH$_3$), 25.8 (CH$_2$), 13.4 (CH$_3$). MS (M + H)$^+$ = 314.

[4-((*E*)-Pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate. Mp: 117 °C (decomposition). IR (CHCl$_3$), ν (cm^{-1}): 1746, 1597, 1508, 1463, 1420, 1329, 1327, 1279, 1134, 1091, 1023, 964, 842. ^1H NMR (200 MHz, CDCl$_3$), δ: 9.42 (s, 1H, ArH), 8.84 (dd, 1H, ArH), 8.48 (dt, 1H, ArH), 7.44 (m, 1H, ArH), 6.64 (s, 2H, ArH), 6.32 (m, 1H, CH=), 6.24 (m, 1H, =CH), 3.81 (s, 6H, $-$OCH$_3$), 2.18 (dt, 2H, $-$CH$_2$), 1.50 (m, 2H, CH$_2$), 0.96 (t, 3H, CH$_3$). ^{13}C NMR: δ 163.2 (C), 153.6

TABLE 1: Crystallographic Data and Structure Refinement

	1	2
formula	C$_{18}$H$_{19}$NO$_4$	C$_{19}$H$_{21}$NO$_4$
M	313.34	327.37
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	9.0694(7)	8.9277(6)
b (Å)	22.470(2)	23.583(1)
c (Å)	8.1591(6)	8.1672(5)
β (deg)	97.872(9)	98.186(8)
V (Å^3)	1647.1(2)	1702.0(2)
Z	4	4
D_x (g cm^{-3})	1.264	1.278
μ (mm^{-1})	0.089	0.090
T (K)	173(1)	173(1)
λ (Å)	0.71073	0.71073
index ranges	$-11 \le h \le 11$	$-10 \le h \le 10$
	$-27 \le k \le 27$	$-26 \le k \le 28$
	$-10 \le l \le 9$	$-9 \le l \le 10$
no. of data collected	12753	12544
no. of unique data	3132	3244
R_{int}	0.0531	0.0632
no. of $I > 2\sigma(I)$ data	2314	2527
no. of parameters	284	294
R_1 (all data)	0.0485	0.0682
wR_2 (all data)	0.0851	0.1633
R_1 [$I > 2\sigma(I)$]	0.0325	0.0555
wR_2 [$I > 2\sigma(I)$]	0.0801	0.1545
$\Delta\rho_{min}$ (e Å^{-3})	-0.129	-0.292
$\Delta\rho_{max}$ (e Å^{-3})	0.181	0.839

(CH), 152.1 (C), 151.5 (CH), 137.6 (CH), 136.7 (C), 131.5 (CH), 129.6 (CH), 127.3 (C), 125.4 (C), 123.2 (CH), 102.5 (CH), 56.01 (CH$_3$), 34.93 (CH$_2$), 22.3 (CH$_2$), 13.6 (CH$_3$). **MS** (M + H)$^+$ = 328.

X-ray Measurements. Transparent, colorless crystals of each compound, mounted on glass fiber, were used for diffraction measurement. The data were collected on a STOE IPDS imaging plate single-crystal diffractometer[32] with a low-temperature device, using Mo Kα source and a graphite monochromator. Data reduction was performed with the STOE IPDS-software package.[32] The Lorentz and polarization corrections were applied. Cell parameters were determined by indexing of 8000 reflections with $I/\sigma(I) > 6.0$.

The structures were solved by direct methods using SIR-97[33] and refined by full-matrix least-squares methods on F^2 using SHELXL97.[34] All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were located geometrically using AFIX in SHELXL97.[34] At the final stage of both structure refinements all H-atoms, except for H61(C60) and H62(C60) of the PDMP molecule, were fully refined with isotropic thermal displacements. The positions of H61(C60) and H62(C60) atoms were left according to AFIX location. Molecular geometries were calculated by PARST.[35] Graphical presentation of molecules was performed using PLATON.[36]

The crystal data and details of the X-ray analysis are given in Table 1. It has to be stated that the quality of the PDMP crystals was significantly lower than that of the BDMP crystals. This becomes immediately obvious from the data in Table 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; No. CCDC 212706 and No. CCDC 212707.

Computational Details

The calculations have been performed using the Gaussian98 set of codes.[37] The B3LYP method is applied; this method is a hybrid density functional theory approach that combines Becke's

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three-parameter nonlocal exchange potential[38] with the nonlocal correlation functional of Lee, Yang, and Parr.[39] The 6-311++G** basis set was applied because the inclusion of the diffuse components in the basis set is desired to describe properly the hydrogen bonding interaction.[5] In other words, the B3LYP/6-311++G** level of theory was applied for all calculations performed here. The wave functions obtained were used with the AIM2000 program[40] (based on the Bader theory[17]) to calculate the topological properties of the systems under investigation. Hence the critical points (CPs) may be localized, and their properties such as electron densities at CPs and their Laplacians may be analyzed.

In this study the single point B3LYP/6-311++G** calculations have been performed on [4-((E)-but-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (BDMP) and [4-((E)-pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (PDMP) molecules for geometries taken from the X-ray measurement; only the neutron diffraction corrections for C−H bond were done before calculations.[41,42] Further, the obtained B3LYP/6-311++G** wave functions of BDMP and PDMP were applied for the topological analysis. There are the C=C−H···H−C(benzene ring) H···H contacts within BDMP and PDMP, and hence the calculations were also performed for the modeled systems where similar contacts exist. The calculations have been performed for styrene and its fluorine derivatives, and the Bader theory was also used to analyze the intramolecular interactions.

Results and Discussion

FTIR and NMR Spectra. The FTIR spectra of [4-((E)-but-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate and [4-((E)-pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate revealed a strong absorption of the carbonyl group at 1746 cm^{-1}. This position and intensity is typical for esters. An additional intense band at 1279 cm^{-1} due to the C−O stretching vibration in esters is also observed in both spectra. The ether C−O stretching bands appear at 1134, 1092, and 1091 cm^{-1}. The presence of unsaturation in the molecules is recognized by the presence of a sharp band at 1597 cm^{-1}. It is worthy of note that the C=C bond in the butenyl and pentenyl chain is conjugated with an aromatic ring. As a consequence the C=C bond has less double-bond character and the absorption band $\nu_{C=C}$ is shifted to lower wavenumbers in comparison with simple alkenes. Additionally, the band at 964 cm^{-1} is due to the C−H out-of plane bending vibration of hydrogen atoms attached to unsaturated carbon and is consistent with a trans substitution pattern. The ^{1}H NMR spectrum also exhibits a trans arrangement of the olefinic protons. The chemical shift values of the hydrogen atoms attached to the unsaturated carbon atoms are 6.43 (6.24) and 6.32 ppm and the coupling constant is $J_{12} = 15.8$ Hz.

Crystal and Molecular Structures. Table 2 shows the possible intramolecular and intermolecular hydrogen bonds. Table 2 shows only those contacts for which the proton··· acceptor distances are shorter than the corresponding sum of van der Waals radii. We see that there are only a few such intermolecular and intramolecular contacts for the structure of BDMP, whereas for the structure of PDMP there are only intramolecular contacts that may be treated as hydrogen bonds.

For both crystal structures intramolecular C−H···O contacts are detected, such a situation was also observed previously for the crystal structure of ethyl 3,4,5-trimethoxybenzoate (ETMB).[43] However, to study those intramolecular interactions only the geometrical parameters were aanalyzed.[43] For benzene derivatives the possibility of the existence of intramolecular

TABLE 2: Possible Hydrogen Bonds (Bonds and Distances in Ångstroms and Angles in Degrees) for Structures of 1 and 2

donor-H	donor···acceptor	H···acceptor	donor-H···acceptor
	For **1**		
C1−H1	C1···O21(0)^a	H1···O21(0)	C1−H1···O21(0)
0.96(0.02)	2.875(0.001)	2.58(0.01)	97.8(0.9)
1.08		2.57	95.2^b
C3−H3	C3···O20(0)	H3···O20(0)	C3−H3···O20(0)
0.98(0.02)	2.722(0.001)	2.42(0.01)	97.4(0.9)
1.08		2.41	95.0^b
C23−H23	C23···N1(1)	H23···N1(1)	C23−H23···N1(1)
0.97(0.01)	3.703(0.002)	2.77(0.01)	161.4(1.1)
1.08		2.67	160.7^b
C40−H40	C40···N1(1)	H40···N1(1)	C40−H40···N1(1)
0.96(0.02)	3.600(0.002)	2.69(0.02)	159.9(1.5)
1.08		2.57	159.0^b
C25−H25	C25···O26(2)	H25···O26(2)	C25−H25···O26(2)
0.98(0.02)	3.535(0.002)	2.65(0.02)	150.3(1.2)
1.08		2.56	149.2^b
	For **2**		
C1−H1	C1···O21(0)	H1···O21(0)	C1−H1···O21(0)
0.97(0.03)	2.871(0.002)	2.56(0.02)	99.0(1.6)
1.08		2.54	96.5^b
C3−H3	C3···O20(0)	H3···O20(0)	C3−H3···O20(0)
0.95(0.02)	2.721(0.002)	2.47(0.02)	95.1(1.5)
1.08		2.46	92.0^b

^{a} Equivalent positions denoted in parentheses: (0) x, y, z; (1) $x − 1$, $+y$, $+z − 1$; (2) x, $−y + 1/2 + 1$, $+z − 1/2$. ^{b} C−H distances were normalized by moving the position of the H-atom along the C−H vector.
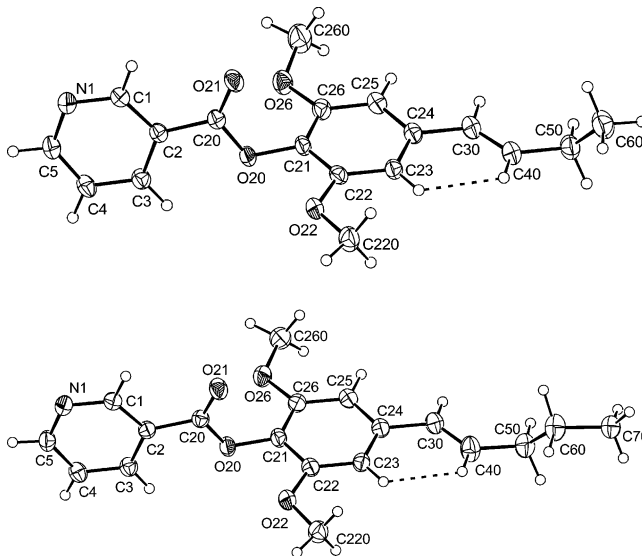

Figure 1. Molecular structures of BDMP and PDMP with atom labeling scheme. The displacement ellipsoids are drawn at 50% probability level.

H-bonds between substituents and C−H donors being in ortho positions, according to them, is the additional problem that needs explanation. It will be considered in detail in the next section describing the results of ab initio calculations. Such a situation was observed for ETMB and also for BDMP and PDMP crystal structures (C1−H1···O21 and C3−H3···O20 contacts; see Figure 1).

Figure 1 shows for both structures the intramolecular H···H contacts (dotted lines); the H···H distances amount to 2.20 and 2.17 Å for BDMP and PDMP respectively. This kind of interaction is also described in the next section in detail.

DFT and AIM Calculations for BDMP and PDMP Molecules. Figures 2 and 3 present the molecular graphs of
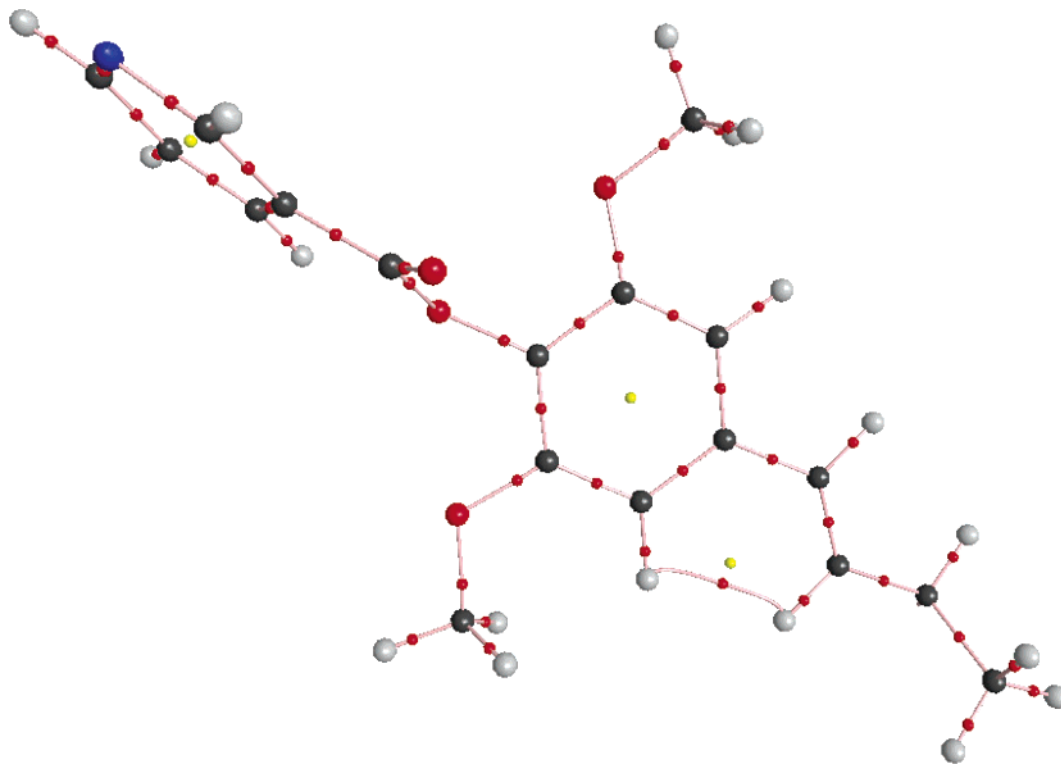
Figure 2. Molecular graph of BDMP. The positions of atoms, BCPs, and RCPs are given.
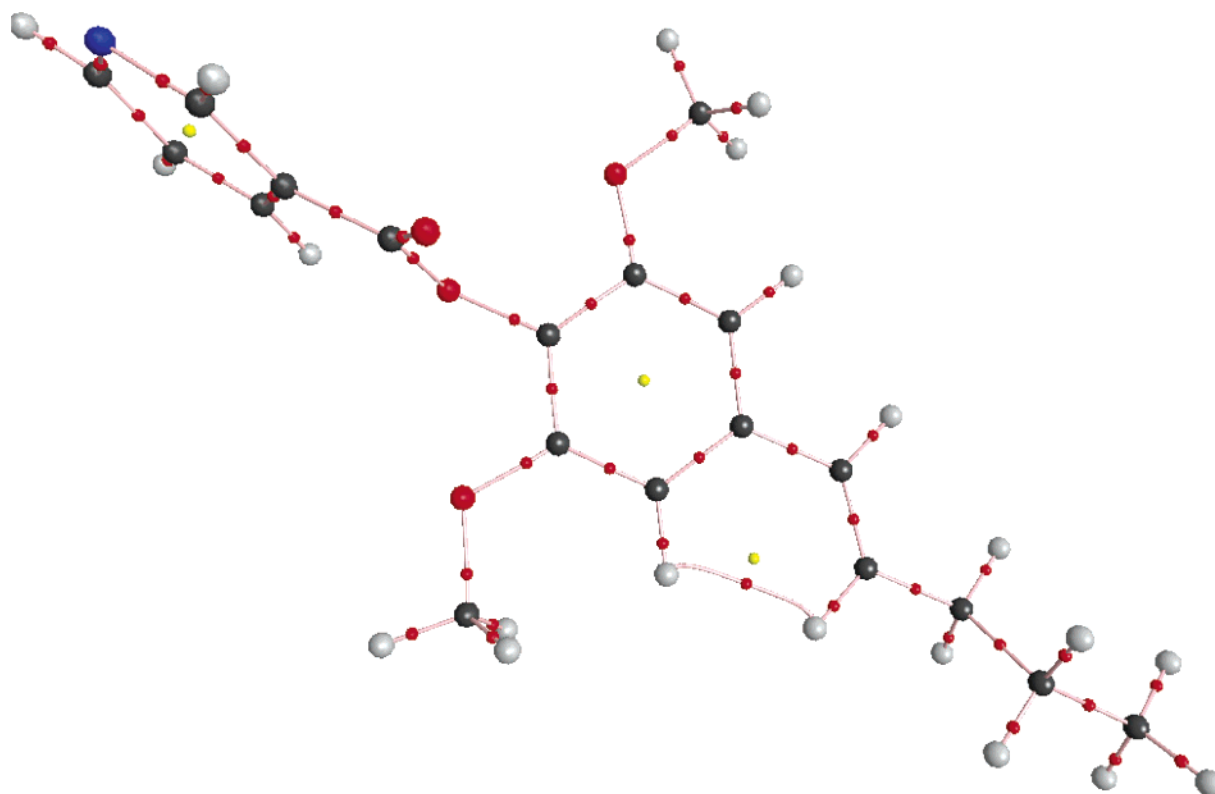

Figure 3. Molecular graph of PDMP. The positions of atoms, BCPs, and RCPs are given.

BDMP and PDMP, respectively. These graphs were obtained from the B3LYP/6-311++G** wave functions after the use of the AIM2000 program. The calculations have been performed for geometries taken from crystal structures. The C−H bond lengths have been corrected because it is well-known that X-ray diffraction methods do not reflect properly the X−H bond lengths. The positions of atoms are determined from the electron density maxima and hence the errors are mainly connected with positions of hydrogen atoms. The neutron diffraction measurements deliver the proper atomic positions for all atoms considered. In the case of results of X-ray measurements it is common to correct the hydrogen atom positions; C−H bonds are fixed to be 1.083 Å—an average value for C−H bond length obtained from spectroscopy and neutron diffraction measure-

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ments.[4] Hence C−H distances were normalized in the present work by moving the position of the H atom along the C−H vector to the fixed value of 1.083 Å.

We see that the application of the Bader theory indicates the bond path between the hydrogen atoms and there are the bond critical points (BCPs) for such interactions (Figures 2 and 3). This may suggest that intramolecular dihydrogen bonds exist for BDMP and PDMP molecules. We also see that there are no bond paths for C−H···O intramolecular contacts similar to those described earlier for ETMB[43] as intramolecular hydrogen bonds. Hence the use of the Bader theory may be treated as a decisive tool for the characterization of the type of interaction because the geometrical criteria are not decisive if H-bonds exist.

The above-mentioned H···H contacts were analyzed in terms of electron density. For BDMP the electron density at the H···H bond critical point is equal to 0.0105 au whereas for PDMP it is 0.0112 au. The corresponding Laplacians of these densities are equal to 0.0396 and 0.0419 au, respectively. It is well-known that the electron density at the H-bond BCP may be treated as the measure of the hydrogen bond strength.[44−46] The topological criteria of hydrogen bonding have been given by Koch and Popelier.[47,48] According to them the BCP and the bond path should exist for an X−H···Y hydrogen bond; the electron density and its Laplacian for an H···Y contact should be within the ranges 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian. We see that both H···H interactions for BDMP and PDMP fulfill these criteria. We may conclude that those intramolecular dihydrogen bonds are of medium/weaker strength; for example, for the linear (trans) water dimer the electron density at H···O BCP is equal to 0.023 au for the B3LYP/6-311++G** level of theory[49] for which the H-bond energy is about 5 kcal/mol. It may suggest that the intramolecular dihydrogen bond energy is in the range 2−3 kcal/mol. It is worth mentioning that the topological parameters are insensitive to the level of calculation; for example, for the same linear (trans) dimer of water the electron density at H···O BCP is equal 0.024 au if the MP2/6-311++G** level is applied.[49] For intramolecular H-bonds the properties of ring critical points (RCPs) may be also treated as measures of H-bond strength.[50,51] The electron densities for RCPs of BDMP and PDMP amount to 0.0102 and 0.0107 au, respectively, and the corresponding values of Laplacians are equal to 0.0508 and 0.0542 au. For comparison, for the RCP created due to the formation of intramolecular H-bond for malonaldehyde the electron density at RCP is equal 0.0205 au and its Laplacian to 0.1277 au, for the MP2/6-311++G** level of calculation. The roughly estimated intramolecular H-bond energy for malonaldehyde suggests the value of about 12 kcal/mol. The correlations between the properties of RCPs and H-bond energy are not linear but the above-mentioned results indicate that H···H interactions for BDMP and PDMP are not meaningless.

For the investigated crystal structures there are the following Mulliken charges for hydrogen atoms: +0.138 and −0.050 au for BDMP for H(C=) and H−C(benzene) hydrogen atoms and the corresponding charges for PDMP amount to 0.144 and −0.046 au, respectively.

DFT and AIM Calculations for Styrene Derivatives. Chart 1 presents the styrene molecule, which may be treated as a fragment of BDMP and PDMP molecules containing the corresponding H···H interaction (hydrogen atoms designated as X and Y).

To get a more detailed insight into this kind of interaction, the B3LYP/6-311++G** calculations have been performed on the modeled systems; styrene and its fluoro derivatives. Four

CHART 1: Styrene and Its Derivatives (X,Y = H,H, F,H, H,F, and F,F)
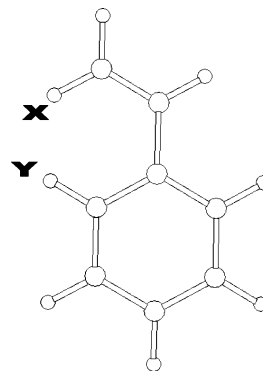
molecular structures have been optimized; styrene, a fluoro derivative for which X = F, a derivative with Y = F, and a fourth molecular structure with X and Y = F. The starting geometries for the styrene derivatives were obtained with the use of the MOLEKEL program.[52] All structures were optimized as planar systems, for the first three the stable structures were obtained without imaginary frequencies but for the fourth one with X, Y = F there is one imaginary frequency, suggesting that the system corresponds to the transition state. It is worth mentioning that the stable configuration was achieved for styrene—the modeled system corresponding to BDMP and PDMP molecules. It strongly supports the idea of the existence of intramolecular dihydrogen bonds for BDMP and PDMP.

Figure 4 shows the molecular graph and the contour density electron map of the styrene molecule. The bond critical point of H···H for the intramolecular dihydrogen bond was found, a situation similar to that observed for BDMP and PDMP. There is also the ring critical point (RCP) close to the BCP of H···H and existing due to the creation of an intramolecular hydrogen bond (Figure 4). A similar situation is observed for the other modeled systems with fluoro substituents. BCPs were found for the X···Y interaction, even if both X and Y are fluoro substituents. And for all cases there are the ring critical points close to the BCPs of X···Y contacts. For two cases of H···F contacts the situation is not surprising; there are intramolecular C−H···F hydrogen bonds, namely, −C=C−H···F and C(benzene)−H···F−C=C− systems. But there is also the bond path and BCP for the F···F interaction; this kind of interaction was described earlier in terms of the Bader theory.[53] The steric interactions in ortho-substituted biphenyl were investigated by Cioslowski and Mixon,[53] the authors explained that BCPs are not necessarily associated with bonding interactions such as covalent bonds or hydrogen bonds. When the distance between two atoms is smaller than their contact interatomic separation (CIS) a bond path with BCP appears for a nonbonding repulsive interaction. We may expect such F···F interaction for the styrene derivative analyzed here because for that structure the transition state is observed. Table 3 presents the topological parameters of X···Y interactions for BDMP, PDMP and the modeled styrene derivative molecules. For all cases the topological criteria of the existence of hydrogen bonding given by Koch and Popelier[47] are fulfilled.

Figure 5 shows the dependence between the energy of the system and the torsion angle. The curves were constructed for all four cases of styrene and its derivatives. The torsion angle is the one concerning the following fragment of the molecule (see Chart 1); (Y)C−C−C=C(X). We have obtained the planar conformation for the torsion angle equal to zero. For that angle being equal to 90° we have the XHC=CH− substituent
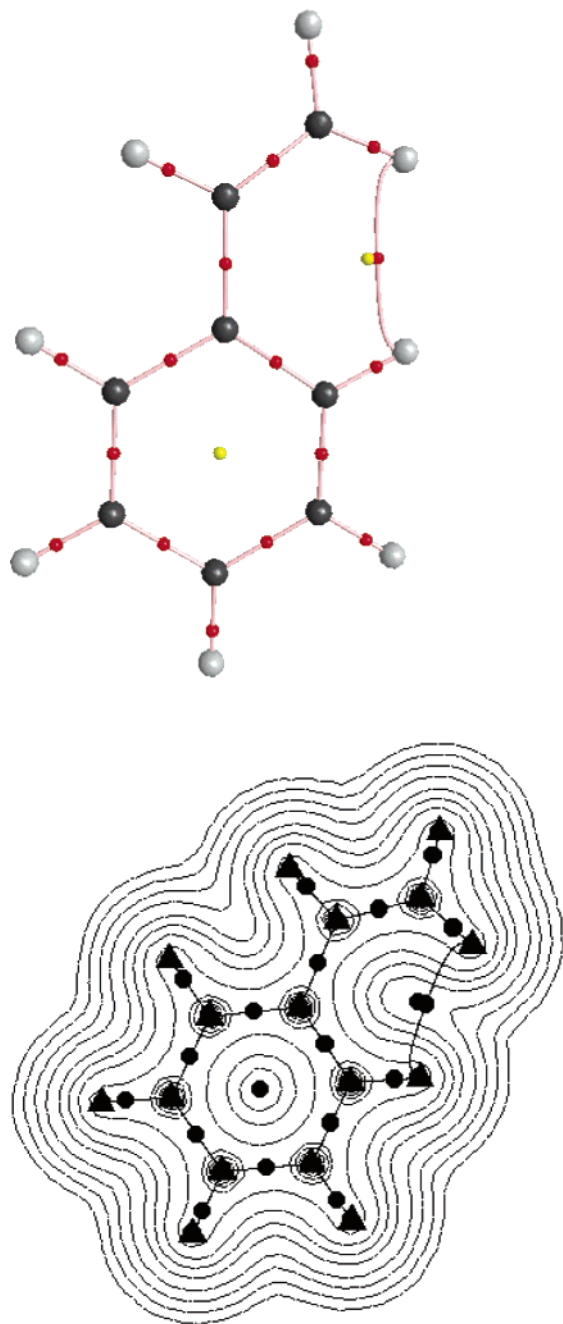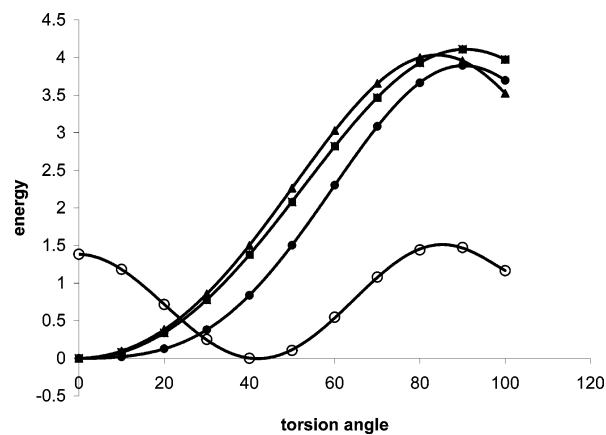
Figure 5. Dependence between the energy of the system and the torsional angle. Circles correspond to styrene, squares to the derivative with C=C−F···H−C(benzene) H-bond, triangles to the molecule with C=C−H···F−C(benzene) H-bond, and open circles to the difluoro derivative. Energies are given in kcal/mol and angles in degrees; for all systems the energies are normalized that the lowest energy corresponds to zero.

TABLE 4: Geometrical Parameters of C−X···Y−C Contacts (in Ångstroms and Degrees) for Styrene and Its Derivatives (See Chart 1); Results of B3LYP/6-311++G Calculations**

C−X···Y−C	X···Y	C−X	C−Y	C−X···Y	C−Y···X
C−H···H−C	2.208	1.084	1.084	111.0	115.3
C−H···F−C	2.260	1.080	1.358	115.1	107.2
C−F···H−C	2.282	1.355	1.081	101.3	120.6
C−F···F−C	2.569	1.342	1.349	100.1	110.3

symmetric in the range from 0 to 180° with the maximum at 90°; for two other cases the curves are not symmetric. The main conclusion is that for three cases for which the stable planar conformations were found they are of the lowest energies; for the transition planar state with X, Y = F we have got the most stable conformation for the torsion angle equal to 40°. It strongly supports the idea that for three cases considered here there are the intramolecular hydrogen bonds, intramolecular dihydrogen bond C−H···H−C, and intramolecular C−H···F H-bonds; for one case there is the steric, nonbonding F···F interaction existing for the planar transition state.

Table 4 shows the geometrical C−X···Y−C parameters (see Chart 1) for styrene and its derivatives calculated at the B3LYP/6-311++G** level of theory. These results show that the geometrical criteria again cannot be decisive to define the character of X···Y interactions because H···H and H···F distances are only slightly less than the corresponding sums of van der Waals radii −2.4 and 2.55 Å, respectively. Additionally, C−H···H and C−H···F angles are far from linearity.

Figure 4. Molecular graph and the contour density map of styrene.

TABLE 3: Topological Parameters of Intramolecular Interactions of Styrene Derivatives and of BDMP and PDMP Molecules[a]

X···Y	$\rho_{X···Y}$	$\nabla^2\rho_{X···Y}$	ρ_{RCP}	$\nabla^2\rho_{RCP}$
H···H (BDMP)	0.0105	0.0396	0.0102	0.0508
H···H (PDMP)	0.0112	0.0419	0.0107	0.0542
H···H (styrene)	0.0089	0.0363	0.0089	0.0403
F···H (styr.der.)	0.0130	0.0505	0.0091	0.0518
H···F (styr.der)	0.0141	0.0568	0.0099	0.0572
F···F (styr. der.)	0.0149	0.0639	0.0074	0.0434

[a] X···Y contacts are taken into account and rings created due to such interactions: −Y−C(benzene)−C(benzene)−C(aliphatic)=C−X rings. All values are given in au; results of B3LYP/6-311++G** calculations.

perpedicular to the plane of the benzene ring. The range of the torsion angle of 0−90° is considered here (Figure 5). For two cases, C₆H₅−CH=CH₂ and C₆H₅−CH=CFH, the curves are

Summary

The crystal structures of [4-((*E*)-but-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (BDMP) and [4-((*E*)-pent-1-enyl)-2,6-dimethoxyphenyl]pyridine-3-carboxylate (PDMP) investigated here show that H···H intramolecular contacts exist that may be treated as intramolecular C−H···H−C dihydrogen bonds. The application of the Bader theory to the geometries of BDMP and PDMP molecules taken from the crystal structure measurements shows that the topological criteria of the existence of hydrogen bonding are fulfilled. The additional calculations performed at the B3LYP/6-311++G** level of theory for styrene and its derivatives support the idea of the existence of C−H···H−C intramolecular hydrogen bonds.

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Supporting Information Available: CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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