Bifurcated Hydrogen Bonds in Crystal Structures of New Phosphorochromone Derivatives

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The crystal and molecular structures of three new phosphorochromones determined by the X-ray diffraction method are presented. For all crystal structures, a similar pattern of centrosymmetric dimer is formed for which bifurcated hydrogen bonds exist with bifurcated acceptor O···(H−N, H−C). For one of the crystal structures, there is additionally the intramolecular resonance-assisted H bond. The analysis of those interactions is performed in terms of their geometries and strengths. Additional calculations on simple model systems are performed to study the nature of bifurcated H bonds. The wave functions are applied for further analysis based on the Bader theory.

1. Introduction

This paper is a part of our X-ray studies on a group of bezopyrane derivatives substituted with phosphorohydrazide at position 3.[1−4]

Compounds involving their molecule benzopyrane moiety could be classified as analogues of chromone and coumarine, natural biologically active compounds. They are known to exhibit diverse pharmacological properties.[5−7] However, phosphoroamides and phosphorohydrazides were found to exhibit anticancer activity[8−10] by alkylating nucleophilic centers of nucleobases and amino acids. Modification of the phosphorohydrazide molecule containing a heterocyclic system makes it possible to design and synthesize novel compounds with interesting properties. Thus, many chromone derivatives with a phosphonic acid substituent have been synthesized.[11,12] They are interesting because of their alkylation properties in vitro in the Preussmann test with 4-(4′-nitrobenzyl)pyridine (NBP)[13] and their expected antitumor activity in vivo by analogy to other chromones.[7] The possible application to cancer chemotherapy makes the knowledge of their molecular structure of great importance.

Hence, in continuation of our previous research, the crystal structures of (*E*)-3-{[(diethoxythiophosphoryl)-hydrazon]-methyl}-4-hydroxy-2*H*-1-benzopyran-2-one (**1**), (*E*)-3-{[(diethoxythiophosphoryl)-hydrazono]-methyl}-4*H*-1-benzopyran-4-one (**2**), and (*E*)-3-{[(diphenoxythiophosphoryl)-hydrazono]-methyl}-4*H*-1-benzopyran-4-one (**3**) have been determined by the X-ray diffraction method. The investigations were undertaken to obtain structural information regarding details of the molecular conformations as well as the weak interactions in the crystal structures.

2. Experimental Section

Synthesis and Spectroscopic Measurements. *Compound* **1**. Equimolar amounts of methyl 4-oxo-4*H*-1-benzopyran-3-carboxylate (0.40 g) and N^1-diethoxythiophosphorohydrazide (0.33 g) were solvated in 5 cm^3 of an anhydrous benzene solution. After refluxing for 2 h and cooling, the product was precipitated and recrystallized from ethanol. The yield of **1** (mp 145−147 °C) was 0.46 g (75%).

IR (KBr) ν_{max} (cm^{-1}): 3214 (NH, OH), 2981 (CH_3), 1688 (C═O), 1624 (C═N), 1034−1021 (POC), 629 (P═S). ^{1}H NMR (DMSO, δ_H): 1.28 (t, 6H, CH_3), 4.07−4.17 (m, 4H, CH_2), 7.34−7.96 (m, 4H, aromat), 8.29 (s, 1H, CH═N), 8.30 (s, broad, 1H, OH), 9.79 (d, J_{P-NH} = 25.0 Hz, 1H, NH). ^{31}P NMR (DMSO, δ_P): 66.04.

Compound **2.** Equimolar amounts of 4-oxo-4*H*-1-benzopyran-3-carboaldehyde (0.82 g) and N^1-diethoxythiophosphorohydrazide (0.87 g) were solvated in 5 cm^3 of an anhydrous methanol solution at room temperature. After 24 h, the product was precipitated from solution. Recrystallization from ethanol finally gave 0.92 g (58%) of **2** (mp 210−212 °C). IR (KBr) ν_{max} (cm^{-1}): 3230 (NH), 2980−2926 (CH_3, CH), 1637 (C═O), 1618 (C═N), 1055−1027 (POC), 654 (P═S). ^{1}H NMR (DMSO, δ_H): 1.25 (t, 6H, CH_3), 4.01−4.12 (m, 4H, CH_2), 7.50−8.12 (m, 4H, aromat), 8.33 (s, 1H, −CH═N), 8.58 (s, 1H, CH aromat), 9.98 (d, J_{P-NH} = 34.5 Hz, 1H, NH). ^{31}P NMR (DMSO, δ_P): 64.68.

Compound **3.** Equimolar amounts of 4-oxo-4*H*-1-benzopyran-3-carboaldehyde (0.87 g) and N^1-diphenoxythiophosphorohydrazide (1.40 g) were solvated in 5 cm^3 of anhydrous methanol solution and refluxed for 1 h. After cooling the reaction solution, the product was precipitated. Recrystallization from ethanol finally gave 1.33 g (61%) of **3** (mp 175−177 °C). IR (KBr) ν_{max} (cm^{-1}): 3206 (NH), 1646 (C═O), 1618 (C═N), 1488−1464, 940−900 (CH═CH aromat), 1067 (POC). ^{1}H NMR (DMSO, δ_H): 7.23−730 (m, 5H, aromat − POC_6H_5), 7,53−8.14 (m, 4H, aromat), 8.21 (s, 1H, −CH═N), 8.76 (s, 1H, CH aromat), 10.60 (d, J_{P-NH} = 39.0 Hz, 1H, NH). ^{31}P NMR (DMSO, δ_P): 67.42.

Melting points are uncorrected. IR spectra were taken on a Pye-Unicam 200 G spectrometer. ^{1}H NMR spectra at 100 MHz were recorded on a Tesla BS 567A, and ^{31}P NMR spectra were recorded on a Bruker HX360 spectrometr with H_3PO_4 as the external standard.

X-ray Measurements. Transparent, colorless crystals of the three investigated compounds suitable for X-ray diffraction were

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TABLE 1: Crystallographic Data and Structure Refinement Details

	1	**2**	**3**
		Crystal Data	
formula	$C_{14}H_{17}N_2O_5PS$	$C_{14}H_{17}N_2O_4PS$	$C_{22}H_{17}N_2O_4PS$
fw	356.33	340.33	436.41
crystal description	colorless plate	colorless plate	colorless prism
crystal size, mm	0.20 × 0.15 × 0.05	0.35 × 0.25 × 0.10	0.20 × 0.10 × 0.10
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.2108(4)	8.0932(12)	7.8515(5)
b, Å	9.0347(5)	8.1171(4)	8.3698(5)
c, Å	12.4332(6)	13.4513(10)	16.0105(6)
α, deg	83.332(4)	85.321(5)	98.083(3)
β, deg	92.868(4)	105.969(8)	92.383(3)
γ, deg	112.446(3)	99.123(7)	91.739(5)
V, Å^3	846.66(7)	838.14(15)	1040.09(10)
Z	2	2	2
d_x, g/cm^3	1.398	1.349	1.393
		Data Collection	
diffractometer		Rigaku AFC5S	
radiation type (λ), Å		Cu Kα (1.54178)	
μ, mm^{-1}	2.831	2.788	2.385
temp, K		293(2)	
data collected (h,k,l)	$-10 \le h \le 9$; $0 \le k \le 11$; $-15 \le l \le 15$	$-9 \le h \le 9$; $-5 \le k \le 10$; $-16 \le l \le 16$	$-9 \le h \le 9$; $-8 \le k \le 10$; $-19 \le l \le 19$
no. of reflns measd	3427	3395	4136
no. of indp reflns	3202	3162	3869
R_{int}	0.014	0.026	0.017
no. of $I > 2\sigma(I)$ reflns	1905	2205	2306
		Solution and Refinement	
solution method		direct methods	
refinement method		full-matrix least squares on F^2	
H-atoms treatment		mixed	
no. of params	247	247	340
$R(F)^a$ for all data	0.0823	0.0625	0.0787
$wR(F^2)^b$ for all data	0.1000^c	0.1193^d	0.1147^e
$R(F)^a$ for $I > 2\sigma(I)$	0.0383	0.0389	0.0370
$wR(F^2)^b$ for $I > 2\sigma(I)$	0.0898^c	0.1121^d	0.0902^e
$(\Delta/\sigma)_{max}$	0.001	0.000	0.001
diff. peak/hole, e/Å^3	0.052/−0.248	0.185/−0.228	0.237/−0.211

[a] $R(F) = \sum(|F_o - F_c|)/\sum|F_o|$. [b] $wR(F^2) = [\sum w(|F_o - F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] $w = \exp(1.5 \sin^2 \theta/\lambda)/[\sigma^2(F_o^2) + (0.0415P)^2]$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$. [e] $w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$ where $P = [(F_o^2) + 2(F_c^2)]/3$.

obtained after recrystallization from ethanol by the slow evarporation of the solvent at room temperature. The procedure of data collection was the same for all three compounds. Single crystals mounted on glass fiber were used for measurements at room temperature on a Rigaku AFC5S diffractometer[14] using a Cu Kα X-ray source and a graphite monochromator. The unit-cell dimensions were determined from a least-squares fit to setting angles of 25 reflections. The monitoring of 3 standard reflections measured after each group of 150 reflections showed no significant decays under X-ray irradiation. Reflection intensities were corrected for Lorentz and polarization effects, and absorption corrections were applied.[15]

The structures were solved by direct methods using SHELXS-86[16] and refined by a full-matrix least-squares method on F^2 using SHELXL97.[17] After the refinement with isotropic displacement parameters, refinement was continued with anisotropic displacement parameters for all non-hydrogen atoms. Relatively high anisotropy parameters and inaccurate bond lengths of ethyl groups in crystal structures of **1** and **2** were the reasons for modeling positional disorder. There is one terminal C atom of ethyl groups disordered over two positions with occupancy factors equal to 0.64 for the major component and 0.36 for the minor component in **1**. For **2** ,one ethyl group is disordered over two sites with occupancies of about 0.5, and the comparatively high thermal parameters of the other ethyl group may mask some kind of disorder. However, for this group, no reasonable model of disorder was postulated. Some constrains using SADI, SIMU, DELU, and ISOR instructions were included to order the geometry of the ethyl groups. In this way, the distances between corresponding atom pairs of different components were treated equally.

Hydrogen atoms of the ethyl groups (**1** and **2**) were introduced in calculated positions with idealized geometry and refined using the rigid body model. They were given isotropic displacement parameters equal to 1.2 (in the case of a secondary C parent atom) or 1.5 (in the case of a tertiary C parent atom) times the equivalent displacement parameters of the C atoms to which they are attached. Positions of the other hydrogen atoms were found on a difference Fourier map and refined with isotropic thermal displacement parameters. In the final step of refinement, all the non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of crystallographically relevant data is given in Table 1.

The molecular geometry was calculated by PARST97[18] and PLATON.[19] Selected bond distances, angles, and geometries of hydrogen bonds are summarized in Tables 2 and 3. The drawings were made using PLATON. Further experimental details, coordinates, and displacement parameters are deposited with CCDC.[20]

TABLE 2: Selected Geometric Parameters

Bond Lengths (Å)

	1	2	3
P(1)−S(2)	1.912(2)	1.921(1)	1.909(1)
P(1)−O(11)	1.571(2)	1.567(2)	1.579(2)
P(1)−O(14)/O(21)	1.570(2)	1.573(2)	1.586(2)
P(1)−N(3)	1.650(2)	1.635(2)	1.630(2)
N(3)−N(4)	1.383(3)	1.384(3)	1.390(3)
N(4)−C(5)	1.285(3)	1.263(3)	1.271(3)
C(5)−C(63)	1.446(4)	1.461(3)	1.464(3)
C(62)−O(621)	1.210(3)		
C(64)−O(641)	1.328(3)	1.230(3)	1.231(3)
O(61)−C(62)	1.370(3)	1.348(3)	1.344(3)
O(61)−C(69)	1.375(3)	1.374(3)	1.367(3)
C(62)−C(63)	1.437(4)	1.344(3)	1.442(3)
C(63)−C(64)	1.375(4)	1.465(3)	1.340(4)
C(64)−C(70)	1.437(4)	1.465(3)	1.470(3)
C(69)−C(70)	1.385(4)	1.387(3)	1.391(4)

Bond Angles (deg)

	1	2	3
S(2)−P(1)−O(11)	116.0(1)	116.9(1)	118.2(1)
S(2)−P(1)−O(14)/−O(21)	117.8(1)	116.8(1)	117.9(1)
S(2)−P(1)−N(3)	114.9(1)	111.5(1)	112.7(1)
N(3)−P(1)−O(11)	103.7(1)	106.7(1)	102.7(1)
N(3)−P(1)−O(14)/O(21)	100.8(1)	103.9(1)	105.5(1)
O(11)−P(1)−O(14)/O(21)	101.2(1)	99.6(1)	98.7(1)
P(1)−N(3)−N(4)	118.8(2)	119.8(2)	118.7(2)
N(3)−N(4)−C(5)	117.3(2)	116.5(2)	117.0(2)
N(4)−C(5)−C(63)	120.0(3)	120.9(2)	120.2(3)
C(5)−C(63)−C(62)	117.3(3)	121.3(2)	120.2(3)
C(5)−C(63)−C(64)	122.4(3)	118.9(2)	119.9(2)
C(62)−C(63)−C(64)	120.3(3)	119.8(2)	119.8(2)
O(61)−C(62)−C(63)	121.7(2)	125.1(2)	125.2(3)
O(61)−C(62)−O(621)	116.4(2)		
O(63)−C(62)−O(621)	125.5(3)		
C(69)−O(61)−C(62)	121.7(2)	118.4(2)	118.4(2)
C(63)−C(64)−O(641)	122.6(3)	122.5(2)	122.6(2)
C(70)−C(64)−O(641)	117.0(2)	122.5(3)	122.2(3)
C(63)−C(64)−C(70)	120.4(3)	114.9(2)	115.2(2)
C(62)−C(63)−C(5)−N(4)	−177.2(3)	−7.9(4)	−21.1(4)
C(64)−C(63)−C(5)−N(4)	4.0(2)	173.0(3)	161.4(3)
C(63)−C(5)−N(4)−N(3)	−178.4(2)	177.6(2)	176.2(2)
C(5)−N(4)−N(3)−P(1)	169.0(2)	175.6(2)	165.4(2)
N(4)−N(3)−P(1)−S(2)	49.1(2)	174.6(2)	176.2(2)
N(4)−N(3)−P(1)−O(11)	−78.6(2)	−58.8(2)	−55.5(2)
N(4)−N(3)−P(1)−O(14)/O(21)	176.9(2)	45.9(2)	47.5(2)

TABLE 3: Possible Hydrogen-Bonding Geometry (Å, deg)

	D−H	H···A	D···A	D−H···A
1				
O(641)−H(641)···N(4)	0.80(4)	1.87(4)	2.589(4)	148(4)
N(3)−H(31)···O(621)[a]	0.85(5)	2.05(5)	2.895(4)	174(4)
C(5)−H(51)···O(621)[a]	0.96(4)	2.75(3)	3.477(4)	133(2)
2				
N(3)−H(31)···O(641)[b]	0.75(3)	2.22(3)	2.956(3)	165(3)
C(5)−H(51)···O(641)[b]	0.94(3)	2.49(3)	3.265(3)	140(2)
3				
N(3)−H(31)···O(641)[b]	0.72(3)	2.20(3)	2.911(3)	167(3)
C(5)−H(51)···O(641)[b]	0.94(2)	2.60(2)	3.360(3)	138(2)

[a] $-x + 1, -y + 1, -z + 1$ symmetry codes. [b] $-x + 1, -y + 2, z + 1$ symmetry codes .

3. Computational Details

The calculations have been performed with the use of the Gaussian 98 set of codes.[21] For the dimers taken from crystal structures **1**, **2**, and **3**, single-point HF/6-31+G* and B3LYP/6-31+G* calculations have been made to obtain wave functions that were then used to find critical points using the AIM2000 program.[22] The characteristics of bond critical points (BCPs)—electron densities and their Laplacians—were used to describe H-bond interactions.

Additionally, the calculations for model complexes were performed to gain better insight into the nature of hydrogen bonds. Hence, the full B3LYP/6-311++G** and MP2/6-311++G** optimizations were performed for methyl hydrazine, methylene hydrazine, 3-hydrazono-propen-1-ol, and their complexes with formaldehyde. There are no imaginary frequencies for these species, showing that they do not correspond to transition states. The binding energies for complexes were calculated as differences in energy between the complex on one hand and the energies of monomers on the other hand. Basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi.[23] The Bader theory[24] was also used for these model systems, thus the AIM200 program[22] was used.

4. Results and Discussion

Crystal Structures. 1 is a coumarine derivative; the main difference between its molecules and molecules of the other compounds analyzed here is the presence of an oxo substituent at position 2 of the aromatic ring system. There are also two hydrogen-bonding donor groups (−OH and −NH) for **1**, but there is only one (−NH) donor for molecules of the other crystal structures (**2** and **3**). These two aspects are responsible for the existence of different hydrogen-bonding patterns.

First, there is an intra O(641)−H(641)···N(4) hydrogen bond closing a six-membered π-conjugated ring for **1**. This kind of interaction was described in detail in our previous paper,[4] especially taking into consideration the proton-transfer reaction N−H···O ⇔ O−H···N within such systems as well as the existance of two different molecular tautomers. Interestingly, for coumarine derivatives, there are two possible ways to form such an intramolecular bond. One can imagine two different molecular conformations with an oxygen atom at position 2 or 4 taking part in a hydrogen bond. Ab initio calculation for a related compound[2] undoubtedly indicated that the O(641)···N(4) isomeric form is energetically more favorable than the O(621)···N(4) isomeric form. It is not surprising that such a contact is always observed as an intramolecular interaction in the crystal structure of other phosphorocoumarine derivatives.[1,4]

In contrast, the interaction of the N(3)−H(3) donor group leads to the formation of an intermolecular centrosymmetric dimer designated as $R_2^2(14)$ according to graph set theory notation.[25] This hydrogen-bonding pattern is observed for all three crystal structures. However, because the O(641) atom in **1** is arranged in an intramolecular H bond, there is a O(621) atom that takes part in dimerization in comparison with the O(641) atom observed in the intermolecular hydrogen bond between molecules of the remaining crystal structures. The resulting patterns are shown in Figure 4. Because of π conjugation along O(621)/O(641)−C(63)−C(5)−N(4)−N(3) bonds, molecules undergoing ring closure to form dimers could also be regarded as a system with resonance-stabilized hydrogen bonds.

Taking into consideration the C(5) atom as a nonconventional donor, an oxygen atom (O(621) in **1** and O(641) in **2** and **3**) can be treated as an acceptor of a bifuracated hydrogen bond. It should be mentioned that H(5)···O(641) distances are evidently shorter than the sum of van der Waals radii. Moreover, C(5)···O(621)/O(641) distances are also very close to the sum of van der Waals radii (3.22 Å), but this C−H···O contact in **1** with an angle much further from linearity seems to be the weakest bonding in comparison with that in **2** and **3** (Table 3).

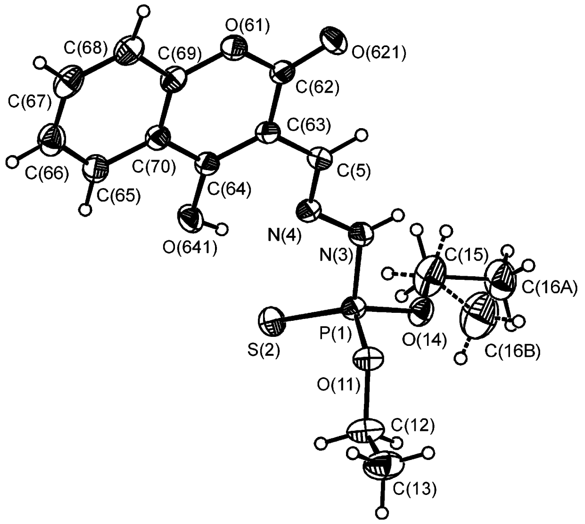

Figure 1. Molecular drawing of **1**. Displacement ellipsoids are drawn at the 30% probability level. Covalent bonds within the minor component of the disordered group are shown as dotted lines.

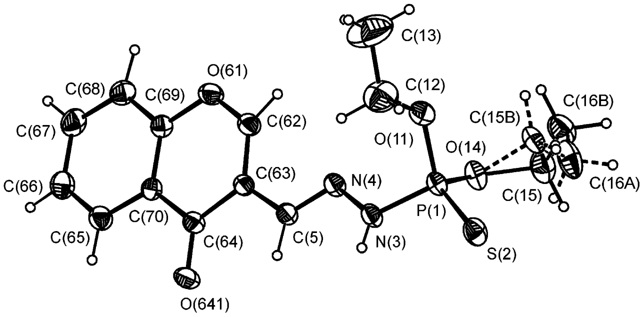

Figure 2. Molecular drawing of **2**. Displacement ellipsoids are drawn at the 30% probability level. Covalent bonds within the minor component of the disordered group are shown as dotted lines.

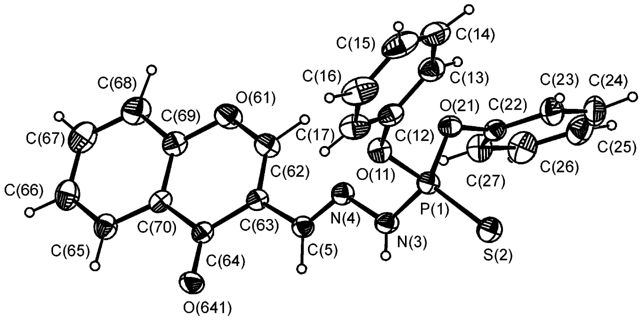

Figure 3. Molecular drawing of **3**. Displacement ellipsoids are drawn at the 30% probability level.

This statement needs additional investigation if one remembers that C(5) is also involved in intramolecular hydrogen-bonding π-conjugated systems, which could influence its donor properties.

It seems that the formation of bifurcated H bonds in dimers induces changes in the geometry of molecules in comparison with that of isolated molecules not involved in intermolecular H bonds. Such changes are probably the greatest for the C(5)−N(4)−N(3)−P(1)−S(2) skeleton and are reflected in C(5)−N(4)−N(3)−P(1) and N(4)−N(3)−P(1)−S(2) torsion angles (Table 2).

The existence of such a complicated H-bond resonance-assisted system turned our attention to the possibilities of further investigations with the use of ab initio and DFT calculations and in particular using the AIM theory of Bader.

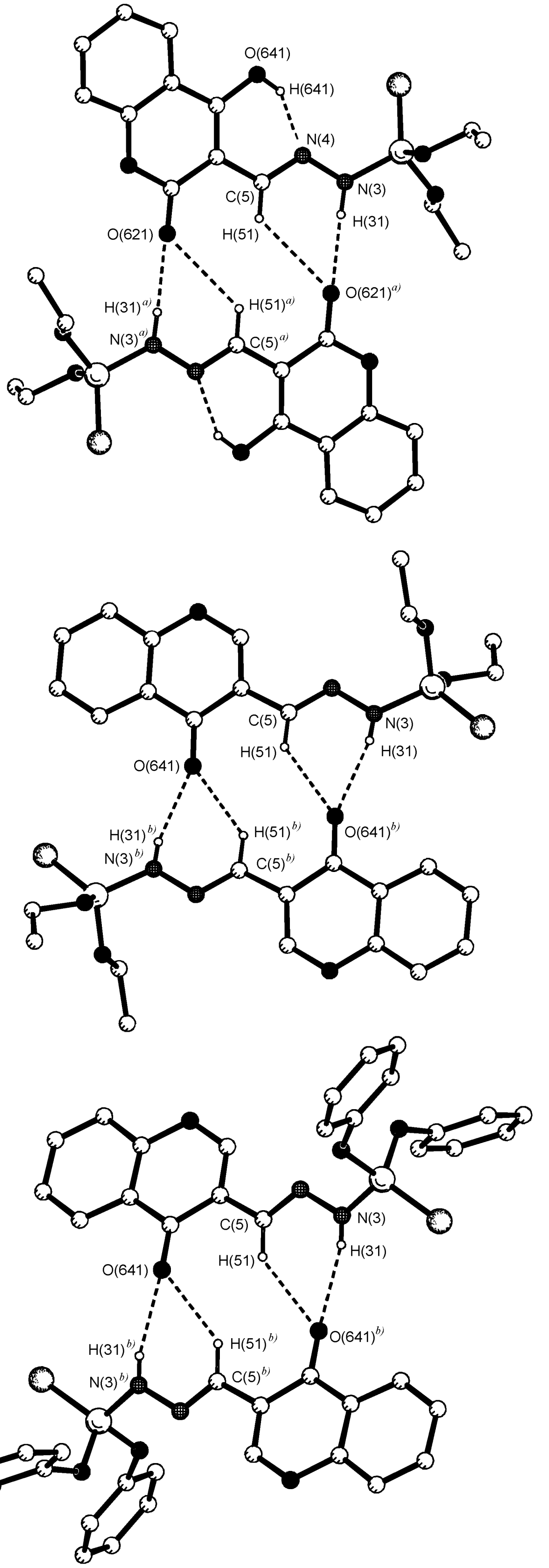

Figure 4. Scheme of hydrogen bonding between molecules. Hydrogen atoms except of those taking part in H bonds and atoms of minor components of disordered groups are omitted for clarity.

Calculations on Dimers of Crystal Structures. The geometries of dimers from crystal structures **1**, **2** ,and **3** investigated here (Figure 4) were taken for the single-point calculations. Only the bond lengths containing hydrogen atoms were corrected. It is well known that the positions of hydrogen atoms for the crystal structures determined by X-ray measurements are not

TABLE 4: Topological Parameters[a]

hydrogen bonding	$\rho_{H\cdots A}$/*	$\nabla^2\rho_{H\cdots A}$/*	$\rho_{H\cdots A}$/**	$\nabla^2\rho_{H\cdots A}$/**
1				
O(641)−H(641)⋯N(4)	0.0346	0.1153	0.0362	0.1066
N(3)−H(31)⋯O(621)[b]	0.0244	0.1054	0.0259	0.1086
C(5)−H(51)⋯O(621)[b]	0.0062	0.0261	0.0067	0.0247
2				
N(3)−H(31)⋯O(641)[c]	0.0149	0.0613	0.0159	0.0579
C(5)−H(51)⋯O(641)[c]	0.0083	0.0334	0.0088	0.0313
3				
N(3)−H(31)⋯O(641)[c]	0.0202	0.0962	0.0214	0.1036
C(5)−H(51)⋯O(641)[c]	0.0088	0.0347	0.0093	0.0301

[a] Electron densities at BCPs and their Laplacians (in au) obtained from HF/6-31+G(d) (designated by a single asterisk) and B3LYP/6-31+G(d) (designated by a double asterisk) wave functions for H⋯A (A = O, N) contacts within D−H⋯A H bonds presented in Table 3. [b] $-x + 1$, $-y + 1$, $-z + 1$ symmetry codes. [c] $-x + 1$, $-y + 2$, $z + 1$ symmetry codes.

precise because they correspond to the electron density maxima of atoms. There are no differences between nuclei and maxima positions for heavier atoms, but there are differences for hydrogen atoms. The effect is that the length of the bond with the hydrogen atom determined from X-ray diffraction measurements is usually shorter than the distance between nuclei. Hence, the correction according to neutron diffraction results is often applied.[26,27] However, such an attitude does not take into account the additional elongation of the proton-donating bond due to H-bond formation, especially for O−H bonds.[28] However, for the structures analyzed here, the effect of the proton-donating bond elongation may be important only for intramolecular O−H⋯N H bonds that exist in **1** because for the other H bonds N−H and C−H bonds are proton donators. It is known that for such bonds only a slight elongation is possible.[29,30] The neutron diffraction corrections for all OH, NH, and CH bonds have been performed here for the structures of dimers. For the dimers, the bond critical points were found for H-bond interactions; the topological results (Table 4) approximately correspond to the geometrical results (Table 3). The geometrical parameters show (Table 3) that N−H⋯O interactions should be stronger than C−H⋯O interactions if we assume that the proton⋯acceptor distance is an approximation of hydrogen bonding strength. Additionally, the N−H⋯O bond for crystal structure **1** should be the strongest of all of the interactions of this type, and C−H⋯O for **1** should be the weakest. The geometrical parameters for the O−H⋯N intramolecular H bond show that this is the strongest interaction for all H bonds existing within the crystal structures investigated here. The electron densities and Laplacians collected in Table 4 correspond to the geometrical results. It is known that the electron density correlates with H-bond energy;[31,32] such correlation is often fulfilled not only for homogeneous samples of complexes but also for heterogeneous ones.[33]

For all hydrogen bonds presented here, the topological criteria of the existence of hydrogen bonding given by Koch and Popelier[34,35] are fulfilled. According to them, the BCP and the bond path should exist for the (D−)H⋯A hydrogen bond. The electron density and its Laplacian for BCP of an H⋯A contact should be 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian.

Calculations for Model Systems. We see that the asymmetry of bifurcated H bonding is greatest for **1** (Table 3) because the difference between (C)H⋯O and (N)H⋯O contacts is greatest for that structure. A brief insight into the existing H-bond patterns suggests that it may be the result of the existence of the additional intramolecular resonance-assisted H bond (RAHB) for **1**. To clarify this situation, the calculations for model complexes have been performed here. The full optimization calculations on methyl hydrazine, methylene hydrazine, 3-hydrazono-propen-1-ol, and their complexes with formaldehyde have been performed. Two levels of calculation have been applied: B3LYP/6-311++G** and MP2/6-311++G**. The results of the MP2 method are mainly analyzed here.

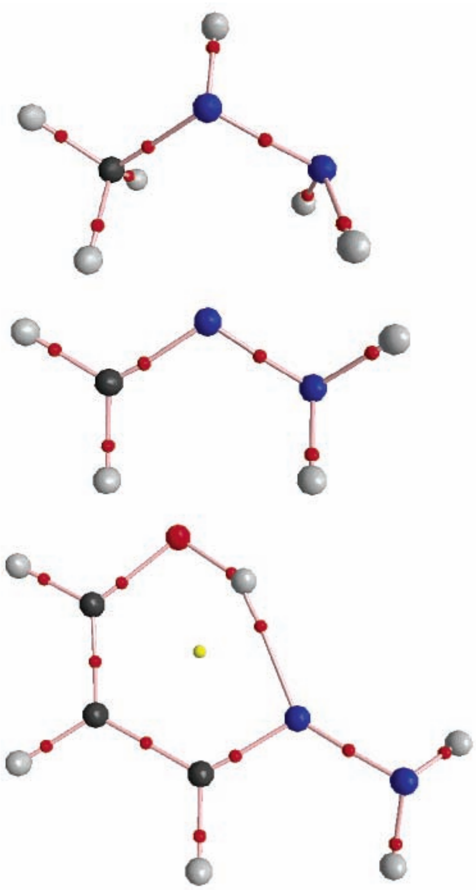

Figure 5. Molecular graphs of methyl hydrazine, methylene hydrazine, and 3-hydrazono-propen-1-ol. Large circles correspond to attractors attributed to atomic positions: gray, hydrogen; blue, nitrogen; black, carbon; red, oxygen. Small circles are attributed to critical points: red, bond critical point (BCP); yellow, ring critical point (RCP).

Bader theory was also used to find bond critical points characterizing intermolecular interactions for complexes. Figure 5 shows the molecular graphs for monomers and Figure 6 presents the molecular graphs of complexes. There are attractors corresponding to atomic positions and BCPs for typical covalent bonds and for hydrogen bonds. The graphs also present ring critical points (RCPs), which exist for complexes. For each dimer, there are three intermolecular H bonds between the donating molecule and formaldehyde: C−H⋯O and N−H⋯O interactions, usually called a bifurcated hydrogen bond with a bifurcated acceptor, and a C−H⋯N hydrogen bond with formaldehyde as the proton donor. Hence, the binding energy for each complex is mainly composed of these three interactions. The binding energies of methyl hydrazine, methylene hydrazine, and 3-hydrazono-propen-1-ol with formaldehyde, corrected for BSSE, are equal to 2.9, 3.2, and 3.5, respectively, suggesting that the π-electron delocalization influences the donating properties of molecules. For methyl hydrazine, there is the $C(sp^3)-H$ donating bond, and it is known that the acidity of donators decreases as follows: $C(sp)-H > C(sp^2)-H > C(sp^3)-H$.[36] However, we see that the additional intramolecular

TABLE 5: Geometrical Parameters (Å, deg) for Hydrogen Bonds of Complexes with Formaldehyde − Results of MP2/6-311++G Calculations**

	methyl hydrazine			methylene hydrazine			3-hydrazono-propen-1-ol		
D−H···A	D−H	H···A	D−H···A	D−H	H···A	D−H···A	D−H	H···A	D−H···A
C−H···O	1.101	2.908	122.2	1.094	2.799	133.0	1.096	2.728	135.1
N−H···O	1.022	2.515	116.9	1.021	2.568	129.1	1.022	2.363	130.4
C−H···N[a]	1.103	2.630	113.7	1.103	2.632	115.1	1.103	2.643	113.9

[a] Formaldehyde as a proton-donating system.

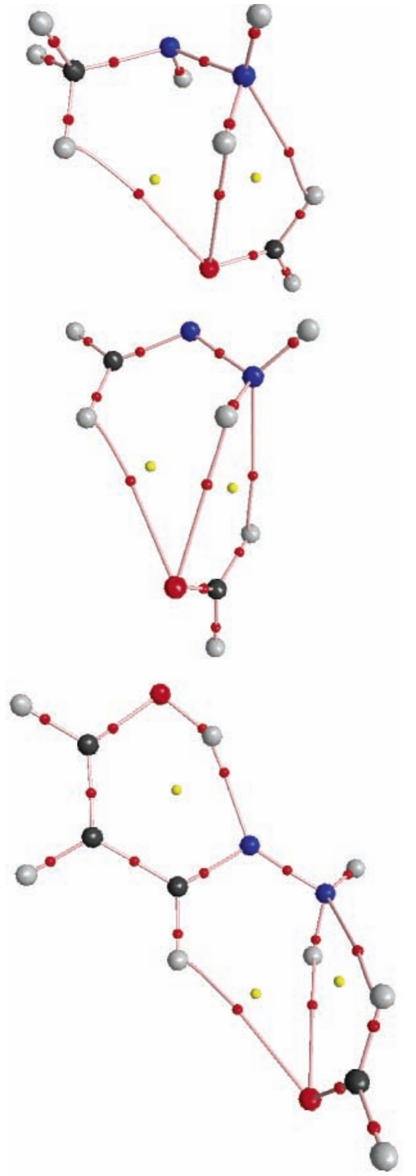

Figure 6. Molecular graphs of complexes of methyl hydrazine, methylene hydrazine, and 3-hydrazono-propen-1-ol with formaldehyde. Large circles correspond to attractors attributed to atomic positions: gray, hydrogen; blue, nitrogen; black, carbon; red, oxygen. Small circles are attributed to critical points: red, bond critical point (BCP); yellow, ring critical point (RCP).

TABLE 6: CN and NN Bond Lengths (in Å) for Model Systems Analyzed Here − MP2/6-311++G Calculations**

system	CN	NN
methyl hydrazine	1.458	1.424
methyl hydrazine + formaldehyde	1.460	1.427
methylene hydrazine	1.285	1.380
methylene hydrazine + formaldehyde	1.286	1.383
3-hydrazono-propen-1-ol	1.301	1.388
3-hydrazono-propen-1-ol + formaldehyde	1.303	1.389

TABLE 7: Topological Parameters − Electron Densities at BCPs and Their Laplacians (in au) for H···A Intermolecular Contacts Existing in Model Complexes Analyzed Here

hydrogen bond	methyl hydrazine[a]	methylene hydrazine[a]	3-hydrazono-propen-1-ol[a]
C−H···O	0.0043	0.0052	0.0060
	0.0161	0.0169	0.0190
N−H···O	0.0094	0.0111	0.0120
	0.0325	0.0356	0.0391
C−H···N	0.0090	0.0090	0.0087
	0.0281	0.0279	0.0278

[a] The proton-donating molecule for C−H···O and N−H···O H bonds. For C−H···N contacts, the formaldehyde molecule is a donating system.

RAHB for 3-hydrazono-propen-1-ol slightly influences the donating properties of C−H and N−H bonds. Table 5 shows the geometrical parameters of hydrogen bonds existing within the analyzed complexes; the (C)H···O and (N)H···O contacts for the bifurcated H bond are shortest for the complex of 3-hydrazono-propen-1-ol with formaldehyde. The geometrical parameters also show that the H···N interactions where formaldehyde is the donating system are of similar strength.

Table 6 presents the CN and NN bond lengths of donating molecules within corresponding complexes and for molecules not involved in intermolecular interactions. Practically, there are no differences between bond lengths for monomers and for complexes. Hence, there is no influence of complexation on the properties of −C=N−NH− conjugated systems. We also see that the equalization of CN and NN bonds is greater for 3-hydrazono-propen-1-ol than for methylene hydrazine. Such equalization due to π-electron delocalization for 3-hydrazono-propen-1-ol is assisted by an additional intramolecular O−H···N hydrogen bond.

The topological parameters of Table 7 confirm the above statements. There are electron densities and their Laplacians for intermolecular H···A contacts of complexes. The $\rho_{H\cdots A}$ values of bifurcated H bonds are greatest for the complex with 3-hydrazono-propen-1-ol. Again, the values of electron densities at H···N intermolecular contacts are similar. These results are partly in agreement with the topological parameters for dimers taken from crystal structures (Table 4). The strongest [N(3)]-H(31)···O(621)/O(641) interaction is for **1** where the additional intramolecular RAHB exists; there is no such agreement for the [C(5)]H(51)···O(621)/O(641) interaction because of the steric effects in the crystal structure. The molecular structure of (*E*)-3-{[(diethoxythiophosphoryl)-hydrazon]-methyl}-4-hydroxy-2*H*-1-benzopyran-2-one slightly disturbs the parallel arrangement of molecules connected by bifurcated H bonds within the dimer. Hence, for **1**, the (C)H···O contact is longer than the corresponding contacts for **2** and **3**.

Tables 8 and 9 show the geometrical and topological parameters of intramolecular O−H···N RAHB existing for 3-hydrazono-propen-1-ol and its complex with formaldehyde.

TABLE 8: Geometrical Parameters (Å, deg) for Intramolecular Resonance-Assisted H Bonds (RAHBs) Existing for Model Systems Analyzed Here[a]

parameter	3-hydrazono-propen-1-ol	3-hydrazono-propen-1-ol + formaldehyde
	O−H···N	
O−H	0.987	0.988
H···N	1.776	1.767
O−H···N	146.2	146.5
	other geometrical parameters	
C═N	1.301	1.303
C−C	1.448	1.447
C═C	1.361	1.361
C−O	1.338	1.339

[a] The other parameters of the ring created because of the intramolecular H-bond formation are also included along with results of MP2/6-311++G** calculations.

TABLE 9: Topological Parameters − Electron Densities at BCPs and Their Laplacians (in au) for Intramolecular Resonance-Assisted H Bonds (RAHBs) Existing for Model Systems Analyzed Here

parameter	3-hydrazono-propen-1-ol	3-hydrazono-propen-1-ol + formaldehyde
ρ_{OH}	0.3317	0.3303
$\nabla^2\rho_{OH}$	−2.3325	−2.3169
$\rho_{H\cdots O}$	0.0441	0.0453
$\nabla^2\rho_{H\cdots O}$	0.1126	0.1133

There are practically no differences between these H bonds for the monomer and for the dimer, which means that an additional bifurcated H bond for the complex does not influence the strong intramolecular H bond.

It was mentioned earlier that B3LYP/6-311++G** calculations were performed for model structures. However, for the optimized model complexes, there are single N−H···O intermolecular interactions that do not reflect the situation existing within crystal structures for which there are bifurcated H bonds. This may suggest that the DFT method is not a proper tool for the analysis of hydrogen bonding because the MP2 method for the same model systems gives results that are in agreement with experiment. Additionally, for the real systems, the presence of a donor and acceptor in both species forming dimers may force the observed arrangement, and the model systems do not take such a situation into account but consider only part of the interactions. However, the main findings of this study are confirmed here by B3LYP calculations; the electron densities at BCPs of (N)H···O intermolecular contacts for 3-hydrazono-propen-1-ol, methylene hydrazine, and methyl hydrazine with formaldehyde amount to 0.0141, 0.0138, and 0.0107 au, respectively, showing that the binding energy for the complex with an additional intramolecular RAHB is the greatest.

5. Conclusions

Bifurcated H bonds for the crystal structures investigated here were found. For the crystal structure of (*E*)-3-{[(diethoxythiophosphoryl)-hydrazon]-methyl}-4-hydroxy-2*H*-1-benzopyran-2-one (**1**), there is the intramolecular RAHB. To gain more detailed insight into the nature of such interactions, additional B3LYP/6-311++G** and MP2/6-311++G** calculations have been performed, showing that the acidic properties of CH and NH bonds for bifurcated systems are stronger if the additional intramolecular RAHB exists. Comparing calculations for model systems with the results for crystal structures shows that for **1** the bifurcated H bond should be the strongest. However, because of steric effects, this is true only for N−H···O intermolecular contact; the C−H···O interaction is the weakest in this case. The results on model systems also show that bifurcated H bonds are rather weak and that the binding energies are equal to 2.9−3.5 kcal/mol. It is worth mentioning that these values for complexes with formaldehyde correspond to three intermolecular interactions: bifurcated hydrogen bonds with bifurcated acceptor O (two interactions) and a C−H···N H bond with formaldehyde as the donating system. The latter do not exist for the crystal structures. We may also conclude that the H-bond interactions for the crystal structures analyzed here are weak, although the electron densities for BCPs of (N)H···O are greater than in the case of model systems.

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