Partial Hydrogen Bonds: Structural Studies on Thioureidoalkylphosphonates

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X-ray crystal and molecular structures of the following compounds are investigated: diphenyl 1-(3-phenylthioureido)propylphosphonate (**I**), diphenyl 1-(3-phenylthioureido)methylthio-propylphosphonate (**II**), and diphenyl [2-methyl-1-(3-methylthioureido)propyl]phosphonate (**III**). Additionally single point density functional theory calculations at the B3LYP/6-311+G(d) level of theory are performed on dimers whose geometries are taken from the crystal structures. The additional diffuse and polarization components are included on H-atoms which participate in H-bonds. The obtained wave functions are applied later to study theoretical electron densities for these species. Bond critical points are determined for dimers investigated to characterize the nature of interactions, especially bifurcated acceptor hydrogen bonds. The characteristics of bond critical points are investigated in terms of the electron densities and their Laplacians.

Introduction

Hydrogen bonds play a crucial role in many chemical, physical, and biochemical processes, and they are also very important in crystal engineering.[1] These interactions are responsible for the arrangement of molecules in crystals and have influence on the geometry of molecules, especially on their terminal groups which form the so-called H-bridge,[2] usually designated as X−H···Y. For such interactions, there is an X−H proton donating bond and an acceptor of protons (Y-center). However, the single proton donating bond can involve two or more acceptors and one acceptor can involve two or more donating bonds. The most often described interaction of this type is the case with one proton donating bond and two acceptors referred to by Jeffrey[3] as three-centered, since the hydrogen atom is bonded to three atoms: one by a covalent bond and two others by hydrogen bonds. Such a system was found early on in the crystal structure of α-glycine[4] and confirmed later by X-ray and neutron diffraction results.[5] Jeffrey also introduces the term “chelated H-bonds” for the systems with one proton acceptor and two proton donating bonds belonging to the same molecule.[3] A water molecule with two O−H donating bonds and an O-atom of another molecule as an acceptor is an example of such a complex. Another distinction for such type of hydrogen bonds was proposed: the term “bifurcated donor hydrogen bonding” if one donor and two or more acceptors exist and the term “bifurcated acceptor H-bond” if one acceptor and two or more donors exist.[6] Bifurcated H-bonds are not investigated intensively; except for reports on crystal structures where such systems often occur, only a few theoretical studies consider their nature. For example, it was found that bifurcated donor H-bonds (with two acceptors) often exist within the crystal structures and that the sum of the three angles formed by the H-atom and the other three atoms within the X−H···Y_1Y_2 (Y_1Y_2: acceptors) system should be near 360°; in other words, X, H, Y_1, and Y_2 atoms should be close to the plane.[7] One can mention the other examples of studies on bifurcated H-bonds in liquids and solids.[8]

There are different geometrical criteria to detect hydrogen bonds as well as to describe their strength. However it seems that results of crystal structure determinations which provide information on H-bond geometries are not sufficient to get insight into the nature of these interactions.[9] This seems to be meaningful for bifurcated H-bonds where single H···Y distances are usually longer than the corresponding distances for typical H-bonds. Hence bifurcated systems are characterized by rather weak interactions where criteria for the existence of hydrogen bonds are hardly satisfied. This is why other experimental and theoretical techniques should be applied to study bifurcated hydrogen bonds. One of them is the “atoms in molecules” theory (AIM) of Bader.[10] This allows one to localize critical points whose features are very useful to describe the nature of interactions. The characteristics of bond critical points (BCPs), the electron densities at these points and the corresponding Laplacians, are good descriptors of the strength of interactions, especially of hydrogen bonds. It was found that the electron density and its Laplacian correlate with the H-bond energy; there are such correlations not only for homogeneous samples of complexes but also for heteregenous ones.[11] The AIM theory was also applied by Rozas et al. to study bifurcated hydrogen bonds.[12] The authors have found that three-centered hydrogen bonds (according to Jeffrey’s terminology[3]) are energetically weaker than the typical H-bonds. Additionally the electron density is shared by two H···Y contacts showing two H···Y bond paths and the corresponding bond critical points with similar values of electron densities at BCPs and similar values of the corresponding Laplacians.

The aim of this study is to investigate bifurcated acceptor hydrogen bonds (chelate systems according to the terminology applied by Jeffrey[3]) existing in dimers of thioureidoalkylphosphonates. The following crystal structures of such compounds are presented here: diphenyl 1-(3-phenylthioureido)propylphosphonate (**I**), diphenyl 1-(3-phenylthioureido)methylthiopropylphosphonate (**II**), and diphenyl [2-methyl-1-(3-methylthioureido)propyl]phosphonate (**III**). The other derivatives of thioureidoalkylphosphonates were investigated earlier;[13] hence the relationships between the geometrical and topological

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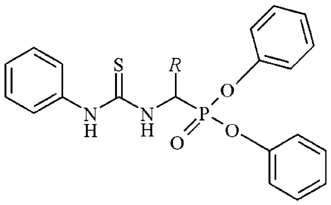
TABLE 1: The Systems Analyzed in This Work[a]

compound	abbreviation	formula	substituent R[b]	ref
diphenyl 1-(3-phenylthioureido)ethylphosphonate	P_Me	$C_{21}H_{27}N_2O_3PS$	CH_3-	13b
diphenyl 1-(3-phenylthioureido)butylphosphonate	P_nPr	$C_{23}H_{25}N_2O_3PS$	$CH_3CH_2CH_2-$	13d
diphenyl 1-(3-phenylthioureido)pentylphosphonate	P_nBu	$C_{24}H_{27}N_2O_3PS$	$CH_3CH_2CH_2CH_2-$	13d
diphenyl [2-methyl-1-(3-phenylthioureido)propyl]phosphonate	P_iPr	$C_{24}H_{25}N_2O_3PS$	CH_3CH_2-	13a
diphenyl 1-(3-phenylthioureido)propylphosphonate	P_Et	$C_{22}H_{23}N_2O_3PS$	$(CH_3)_2CH-$	**I**
diphenyl 1-(3-phenylthioureido)methylthiopropylphosphonate	P_MeTEt	$C_{23}H_{25}N_2O_3PS_2$	$CH_3SCH_2CH_2-$	**II**
diphenyl [2-methyl-1-(3-methylthioureido)propyl]phosphonate	M_iPr	$C_{18}H_{23}N_2O_3PS$	$(CH_3)_2CH-$	**III**

[a] Abbreviations given here are applied in the following tables. [b] The location of the R-substituent is given in Chart 1.

CHART 1: Thioureidoalkylphosphonates Considered in This Study (Me instead of Ph for Structure III)



parameters derived from the Bader theory for the larger group of these species are analyzed (Chart 1). Table 1 collects the names of species considered in this study.

Bifurcated H-bonds are not well-known; however it seems that similarly to typical hydrogen bonds they influence the arrangement of molecules in crystals. Recent studies have provided some information on their nature.[13d] For example, it was found in the crystal structures of thioureidoalkylphosphonates that for bifurcated acceptor hydrogen bonds the energies of two H···O interactions are additive.[13d] This means that for such systems the H-bond energy is the sum of two H···O interactions. A similar approach was also applied recently to study interactions between DNA base pairs; the sum of all of the electron densities of BCPs for intermolecular contacts was treated as a measure of the binding energy.[14]

Experimental Methods

Compounds **I**−**III** were prepared according to the method described earlier.[15] The X-ray measurements were made on a Rigaku AFC-5S diffractometer[16] applying graphite-monochromated Cu Kα radiation. The data were collected at room temperature using the *ω* scan technique. The data were corrected for Lorentz and polarization effects.[17] The analytical correction was also applied.[18] All structures were solved by direct methods using the SHELXS86 program[19] and refined on F^2 by full-matrix least-squares calculations (SHELXL97).[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bonded H atoms were included in the calculated positions and refined using a riding model with isotropic displacement parameters equal to $1.2U_{eq}$ of the attached C atom or equal to $1.5U_{eq}$ of the carbon atom in the case of the methyl group. The amide H atoms (H1 and H2) were located from difference maps and refined isotropically with distance restraints. Basic information concerning experimental details is given in Table 2. Selected geometrical parameters of the structures investigated are deposited as Supporting Information.

The crystallographic data (excluding structure factors) for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. The CCDCs are as follows: **I**-213529, **II**-213530, and **III**-213531.

TABLE 2: Crystallographic Data, Data Collection and Refinement for I−III

	I	**II**	**III**
empirical formula	$C_{22}H_{23}N_2O_3PS$	$C_{23}H_{25}N_2O_3PS_2$	$C_{18}H_{23}N_2O_3PS$
crystal color	colorless	colorless	colorless
crystal size [mm]	0.5 × 0.25 × 0.1	0.4 × 0.25 × 0.15	0.5 × 0.3 × 0.2
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.953(1)	9.8729(7)	9.944(1)
b [Å]	10.207(1)	10.7325(4)	10.322(1)
c [Å]	12.266(1)	11.8858(5)	11.703(1)
α [deg]	98.05(1)	95.895(4)	115.03(1)
β [deg]	101.28(1)	104.168(4)	104.31(1)
γ [deg]	113.71(1)	99.416(4)	102.67(1)
V [Å^3]	1085.2(2)	1191.18(11)	980.2(2)
Z	2	2	2
formula weight	426.45	472.54	378.41
density [g/cm^3]	1.305	1.317	1.282
absorption coeff [mm^{-1}]	2.230	2.882	2.396
F(000)	448	496	400
diffractometer	AFC5S Rigaku	AFC5S Rigaku	AFC5S Rigaku
radiation [Å]	Cu Kα (1.54178)	Cu Kα (1.54178)	Cu Kα (1.54178)
temperature [K]	293(2)	293(2)	293(2)
2θ range [deg]	3.79−72.61	3.88−67.50	4.52−72.61
scan type	ω	ω	ω
index ranges, *hkl*	$-12 \leq h \leq 11$ $0 \leq k \leq 12$ $-15 \leq l \leq 15$	$-11 \leq h \leq 11$ $-9 \leq k \leq 12$ $-14 \leq l \leq 14$	$-12 \leq h \leq 12$ $-12 \leq k \leq 12$ $-14 \leq l \leq 13$
reflns collected	4372	4403	3963
reflns independent	4114	4161	3737
reflns observed [$I \geq 2\sigma(I)$]	2674	3123	2960
no. of parameters	275	293	246
absorption correction	analytical	analytical	analytical
T_{min}; T_{max}	0.4018; 0.8078	0.3919; 0.6718	0.3774; 0.6907
extinction coeff	0.0086(6)	0.0043(6)	0.063(4)
goodness of fit	1.019	1.141	1.105
R [$I \geq 2\sigma(I)$]	0.0368	0.0431	0.0483
wR [$I \geq 2\sigma(I)$]	0.0957	0.1316	0.1475
R	0.0599	0.0568	0.0585
wR (all data)	0.0985	0.1347	0.1565
largest diff peak [e Å^{-3}]	0.173	0.551	0.302
largest diff hole [e Å^{-3}]	−0.253	−0.391	−0.391

[a] Weighting scheme: (**I**) $w = [1.0 \exp(2.0(\sin \theta/\lambda)^2)]/[\sigma^2(F_o^2) + (0.0506P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$; (**II**) $w = 1/[\sigma^2(F_o^2) + (0.0754P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$; (**III**) $w = 1/[\sigma^2(F_o^2) + (0.1031P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Computational Details

The single point calculations have been performed with the use of the Gaussian 98 set of codes;[21] the standard 6-311+G(d) Pople-type basis set[22] and the hybrid Hartree−Fock density functional method (B3LYP)[23] were applied. The calculations were carried out on H-bonded dimers of the investigated molecules (**I**−**III**). Additionally, four analogous systems of previously published structures of *N*-phenyltioureidoalkylphosphonates[13] were considered. The additional diffuse and polarization components were included for H-atoms participating in H-bonds; thus 6-311++G(d,p) basis sets were taken into account for them. The geometries of all H-bonded dimers were taken from the results of crystal structure determinations, those

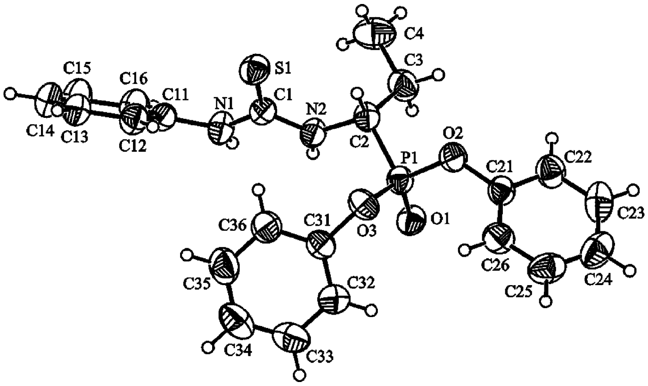


Figure 1. The molecular structure of **I** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level, and H atoms are shown as small spheres of arbitrary radii.

considered in this study and those analyzed previously.[13] The small modifications were performed for these geometries. The neutron diffraction normalization of N−H bonds to the length of 1.009 Å[6] was applied. The justification for such an approach is as follows: the X−H bond lengths known from X-ray results do not correspond exactly to the distances between nuclei of atoms but correspond to the maxima of the electron density.[24] For strongly electronegative X-atoms such as O or N, the X-ray X−H bonds are shorter than real bonds since the maxima of the electron densities of H-atoms are moved toward the heavier atoms. Additionally the positions of the H-atom maxima are less precisely determined than the maxima for heavier atoms. Hence the neutron diffraction normalization is often applied for X-ray results. One may say that in such a case the effect of the proton donating bond elongation due to the H-bond formation is not taken into account. However it is known that N−H donating bonds are usually only slightly elongated in comparison with O−H donating bonds within H-bridges.[25] The other studies also justify the approach applied here since, for example, Rozas et al.[12] found that the N−H distance of the donating bond increases only by around 0.01 Å in bifurcated hydrogen bonds.

Each dimer considered in this study contains two molecules related through the inverse symmetry operation. Hence for each dimer two bifurcated acceptor hydrogen bonds, related by symmetry, exist. Bader's theory[10] was applied here to gain a better insight into the nature of the H-bonds investigated. The AIM2000 program[26] was used to localize attractors, BCPs, and ring critical points (RCPs). The electron densities at BCPs, RCPs, and their Laplacians were calculated. The bond paths corresponding to all interactions, covalent bonds as well as atom−atom contacts (in this study H-bonds), were also found.

Results and Discussion

Crystal and Molecular Structures. Table 2 presents crystallographic data, data collection, and refinement for **I**−**III**; their molecular structures as observed in crystals are presented in Figures 1−3, respectively. Figure 4 shows the dimer of **I** where moieties are connected through bifurcated H-bonds; two such connections exist for this dimer and for the other thioureidoalkylphosphonates since the crystal structures are centrosymmetric and the bifurcated acceptor H-bond is related through the inversion center. The $R_1HNCSNHR_2$ group with two N−H bonds acts as a donating system and the O═P− bond is an acceptor with the oxygen atom being the acceptor center. The following motifs exist for the dimers of the crystal structures investigated: $R_2^2(14)$, $R_2^2(10)$, and $R_2^1(6)$ according to the Bernstein and Etter topological designations.[27]

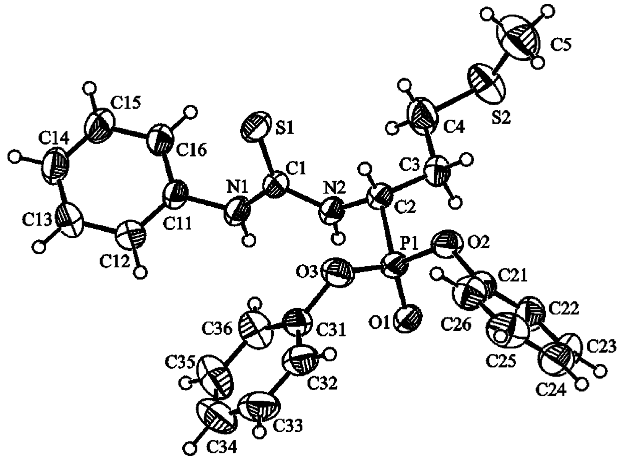


Figure 2. The molecular structure of **II** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level, and H atoms are shown as small spheres of arbitrary radii.

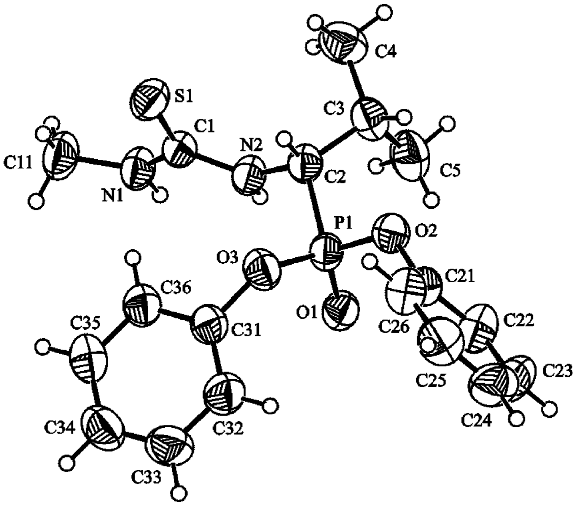


Figure 3. The molecular structure of **III** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level, and H atoms are shown as small spheres of arbitrary radii.

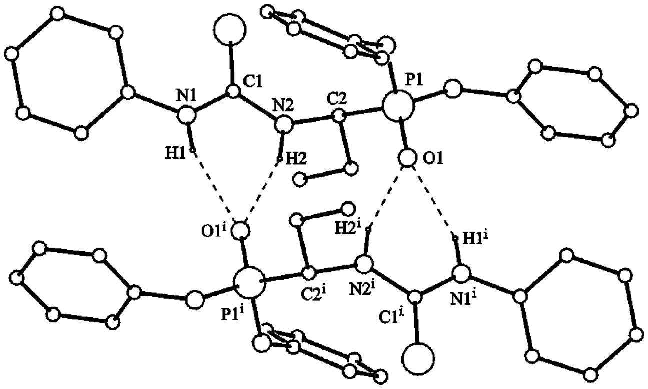


Figure 4. A view of the dimeric molecules of **I** [symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*]. All H atoms, except H1 and H2 and their symmetry equivalents, have been omitted for clarity.

Table 3 presents the geometries of H-bridges existing within dimers. Two H···O contacts are presented since the hydrogen bonding is the acceptor bifurcated one, and the corresponding N−H···O angles and N···O contacts are also given. For all N−H donating bonds, the neutron diffraction normalization is applied (the N−H bond length amounts to 1.009 Å). One can see that H···O contacts within the bifurcated H-bonds existing are not

TABLE 3: Hydrogen Bonding Geometries of N−H···O after Normalization Distance N−H = 1.009 Å (Distances in Å, Angles in deg)

	H1···O1	N1−H1···O1	N1···O1	H2···O1	N2−H2···O1	N2···O1	symmetry code
I	1.99	157	2.945	1.91	158	2.871	$1 - x, 1 - y, 1 - z$
II	1.93	156	2.881	2.06	147	2.958	$-x, -y, -z$
III	2.03	155	2.975	1.97	158	2.930	$-x, -y, -z$

TABLE 4: Topological Parameters of the H-Bonded Dimers Considered: Electron Density at the Bond Critical Points of H···O Contacts, Laplacians of These Densities, Local One-Electron Kinetic Energy Densities (G_C's), and Local Potential Energy Densities (V_C's) (All Values in au)

compound[a]	$\rho_{H1\cdots O1}$	$\nabla^2\rho_{H1\cdots O1}$	$G_{C(H1\cdots O1)}$	$V_{C(H1\cdots O1)}$	$\rho_{H2\cdots O1}$	$\nabla^2\rho_{H2\cdots O1}$	$G_{C(H2\cdots O1)}$	$V_{C(H2\cdots O1)}$
P_Me	0.025	0.101	0.0224	−0.0196	0.025	0.099	0.0221	−0.0194
P_Et (**I**)	0.022	0.087	0.0190	−0.0163	0.026	0.104	0.0235	−0.0210
P_nPr	0.024	0.094	0.0209	−0.0183	0.022	0.089	0.0194	−0.0165
P_nBu	0.020	0.080	0.0175	−0.0149	0.022	0.088	0.0192	−0.0163
P_MeTEt (**II**)	0.025	0.101	0.0225	−0.0198	0.019	0.075	0.0162	−0.0135
P_iPr	0.022	0.083	0.0182	−0.0157	0.023	0.094	0.0207	−0.0179
M_iPr (**III**)	0.021	0.080	0.0175	−0.0150	0.023	0.092	0.0202	−0.0173
water dimer[b]	0.024	0.092	0.0206	−0.0183				

[a] The same designations as in Chart 1. [b] Calculated at the B3LYP/6-311++G(d,p) level.

equivalent since the differences between the H···O distances amount to 0.08, 0.13, and 0.06 Å for **I**, **II**, and **III**, respectively. It seems that the greatest difference between H···O distances for **II** is connected with the type of R-substituent, CH_3SCH_2-CH_2, while for the remaining structures **I** and **III** the R-substituents are CH_3CH_2- and $(CH_3)_2CH-$, respectively. It is probable that for the former case the greater repulsion of R and phenyl substituents results in the greater asymmetry of bifurcated H-bonds. The N−H···O angles range from 147° to 158°, far from linearity; this is rather common for bifurcated H-bonds. The H···O contacts are within the 1.91−2.06 Å range, which may show that N−H···O hydrogen bonds are medium or weak. Such contacts for dimers of carboxylic acids are about 1.6−1.8 Å or even less;[28] for the trans-linear water dimer there is an O−H···O hydrogen bond with a H···O contact of 1.936 Å (B3LYP/6-311++G(d,p) level of calculations). The shorter H···O contacts for **I** probably reflect the stronger bifurcated hydrogen bonding for this structure in comparison with those of **II** and **III**. A more detailed analysis of the strength of bifurcated H-bonds existing in the crystal structures of thioureidoalkylphosphonates is given in the next section.

The P═O bond lengths for **I**−**III** are about 1.47 Å, only slightly longer than for the other related phosphorus compounds. A mean P═O bond length of about 1.46 Å was found, and the minimum values are about 1.45 Å for crystals of organic phosphorus compounds.[29] This means that the P═O bond is not sensitive to the intermolecular interactions in crystals. For example, in the case of C−O−H···O═C systems existing in the crystal structures of organic compounds the C═O bond length is within the range 1.214−1.317 Å.[30]

The N−C bond lengths for the crystal structures investigated are equalized since the differences between N−C bonds within the proton donating $R_1HNCSNHR_2$ group are equal to 0.002, 0.006, and 0.019 Å for **I**, **II**, and **III**, respectively; the estimated standard deviations (esd's) for N−C bonds are equal to 0.002−0.003 Å. This is in line with the other observations for thioureidoalkylphosphonates[13] where such equalization was also detected and where it was found that both N-atoms existing within the proton donating groups of bifurcated H-bonds are close to the hybridization sp^2. Such equalization of NC bond lengths is an effect of the π-electron delocalization. The greatest N−C bond equalization for **I** corresponds to the shortest H···O contacts of bifurcated H-bonds, which may suggest that for the greater π-electron delocalization the strength of hydrogen bonding increases.

AIM Results on Bifurcated H-Bonded Systems. The AIM theory is often applied to study hydrogen bonds. The characteristics of bond critical points, especially H···Y BCPs (where Y designates the proton acceptor), are very useful to estimate the strength of hydrogen bonds. The B3LYP/6-311+G(d) (B3LYP/6-311++G(d,p) for H-atoms participating in H-bonds) wave functions corresponding to the geometries of dimers taken from the crystal structures were applied to analyze the theoretical electron densities and further to obtain bond critical points and to characterize them. Table 4 presents the topological parameters of the dimers investigated here and also of the dimers taken from the other crystal structures of thioureidoalkylphosphonates investigated earlier.[13] The electron densities at H···O BCPs and their Laplacians are given. The energetic properties of BCPs are also included: local one-electron kinetic energy densities (G_C's) and local potential energy densities (V_C's). According to the topological criteria of Koch and Popelier,[31] the H···O contacts may be classified as hydrogen bonds. In the case of hydrogen bonding, the bond path with the BCP should exist. For such BCP the electron density should be within the range of 0.002−0.04 au and its Laplacian within the range of 0.02−0.15 au. Table 4 shows that those criteria are fulfilled for the bifurcated H-bonds analyzed here. One can observe that the topological results are in agreement with the geometrical ones shown in Table 3; the sum of electron densities at H···O BCPs is greater for **I** than for **II** and **III**. Additionally the approximate symmetry of H···O interactions within bifurcated hydrogen bonds is visible since the differences in electron densities at corresponding BCPs amount to 0.006 and 0.004 au for **II** and **I**, respectively, while for the remaining systems collected in Table 4 such differences are not greater than 0.002 au.

The characteristics of BCPs are often applied as measures of the hydrogen bond strength since they correlate with the H-bond energy and with the other descriptors of the strength of this interaction. For example, H···Y distances are often treated as approximate measures of H-bond strength, especially for homogeneous samples of systems where H-bonds exist.[9] Figure 5 shows the relationship between H···O distance and the electron density at the corresponding BCP. Open circles represent N−H···O bonds of the systems of thioureidoalkylphosphonates for which the topological parameters are collected in Table 4.

It was pointed out earlier that if two H···Y connections exist in a bifurcated acceptor H-bond, then their strength is approximately equivalent with the strength of the single X−H···Y H-bond.[13d] Hence individual H···Y interactions within

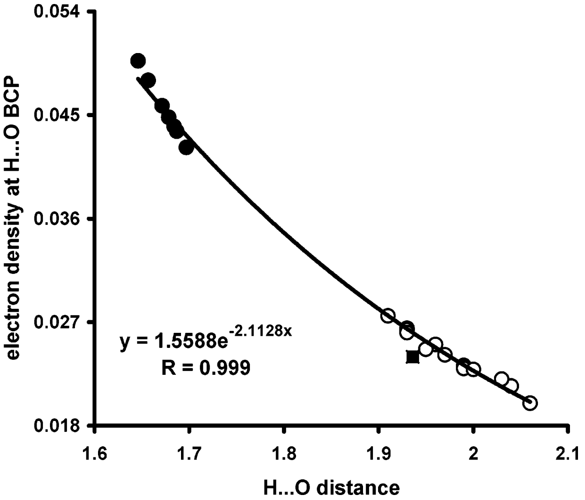


Figure 5. The correlation between the H···O distance (in Å) and the electron density (in au) at the corresponding bond critical point. Open circles correspond to the individual H···O contacts; full circles correspond to the contacts of acceptor bifurcated H-bonds, each replacing two H···O interactions according to the equation of Espinosa et al. (ref 32); the square corresponds to the water dimer.

bifurcated H-bonds are usually weak. Figure 5 shows that the electron densities of H···O BCPs are usually lower than the electron density for the H···O BCP of the trans-linear dimer of water; the full square represents the water dimer calculated at the B3LYP/6-311++G(d,p) level of theory to be consistent with the calculations on thioureidoalkylphosphonates. One can say that the individual H···O interactions within bifurcated acceptor H-bonds are partial hydrogen bonds since they partially contribute to the total H-bond energy.

It was pointed out very recently that the electron density at a BCP may be treated as an additive characteristic of the complex. The sum of electron densities for all intermolecular contacts of DNA base pairs was treated as a measure of the binding energy or as the strength of connection between the species of the dimer.[14] Hence for H···O contacts within bifurcated acceptor H-bonds the sum of electron densities at their BCPs may be also treated as the measure of the hydrogen bonding strength. One may also apply the relationship found by Espinosa et al.[32] between the H···O distance and the electron density at the corresponding BCP. This dependence was found for organic crystals and from the experimental X-ray charge densities. Equation 1 shows this relationship with the coefficient allowing one to obtain the electron density in atomic units while r(O···H) distances are given in Å.

$$\rho(\mathrm{H\cdots O\ BCP}) = 9.63\ \exp[-3.2\ r(\mathrm{H\cdots O})\} \qquad (1)$$

If one puts the sum of the electron densities at the BCPs of two H···O contacts (Table 4) into eq 1, then it is possible to estimate the H···O distance for the single contact which replaces two H···O interactions. Such calculated contacts are also presented in Figure 5 (full circles). For all points, partial H···O interactions within bifurcated H-bonds and those calculated from eq 1, the exponential relationship was found for which the correlation coefficient amounts to 0.999. The application of eq 1 for bifurcated H-bonds seems to be justified since Koch and Popelier found a good correlation between the interaction energy calculated at the MP2/6-31G** level and the sum of the electron densities of all intermolecular BCPs for the systems investigated.[31] As mentioned before, such an approach was also applied for DNA base pairs.[14]

There are also the other properties of the BCP: the electronic energy density H_C of the charge distribution[33] which may be expressed as the sum $H_C = G_C + V_C$. G_C is a local one-electron kinetic energy density, and V_C is the local potential energy density. The relation between the Laplacian and the components of the local energy density H_C is given by the equation

$$(1/4)\ \nabla^2\rho(r_{\mathrm{BCP}}) = 2G_C + V_C \qquad (2)$$

It was pointed out that in bonds with any degree of covalent character, $|V_C| > G_C$ and hence $H_C < 0$.[34] Rozas et al. have introduced a new classification of hydrogen bonds.[35] Weak hydrogen bonds show positive values for both $\nabla^2\rho(r_{\mathrm{BCP}})$ and H_C, for medium H-bonds $\nabla^2\rho(r_{\mathrm{BCP}}) > 0$ and $H_C < 0$, and for strong hydrogen bonds the Laplacian value as well as the electron density at the BCP are negative. Table 4 shows the G_C and V_C values for H···O contacts of the bifurcated H-bonds considered here. One can see that all partial H···O interactions according to the above classification belong to weak H-bonds.

It was also found that the local potential energy (V_C) well correlates with H-bond energy since there is the approximate relationship $E_{\mathrm{HB}} \sim 1/2V_C$.[36] Hence it is possible to estimate H-bond energies for the single H···O contacts considered here (Table 4). The range of such estimated H-bond energies is 4.2−6.6 as expressed in kcal/mol, while this energy for the water dimer (Table 4) amounts to 5.7 kcal/mol. This is in agreement with the other experimental and theoretical results which usually show values of 5−6 kcal/mol for the H-bond energy of the water dimer.

Conclusions

It was found that for bifurcated acceptor H-bonds existing for the crystal structures of thioureidoalkylphosphonates there are two partial N−H···O interactions. Each of them is partially responsible for the slight elongation of the P═O bond with the oxygen atom acceptor. The electron density at the H···O BCP correlates with the H···O distance. If we assume that both H···O contacts reflect the strength of the connection for the bifurcated H-bond, then we may consider that the sum of the electron densities of the bifurcated H-bond is the measure of the H-bond energy. The analysis of the energetic properties of the individual H···O BCPs shows that the corresponding interactions may be classified as weak hydrogen bonds.

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Supporting Information Available: Selected geometric parameters for **I**−**III**. This material is available free of charge via the Internet at http://pubs.acs.org.

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