

An analysis of bifurcated H-bonds: crystal and molecular structures of *O,O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate and *O,O*-diphenyl 1-(3-phenylthioureido)butanephosphonate[†]

Lilianna Chęcińska, Sławomir J. Grabowski* and Magdalena Małecka

Department of Crystallography and Crystal Chemistry, University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland

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ABSTRACT: In the crystal structures of *O,O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate (**1**) and *O,O*-diphenyl 1-(3-phenylthioureido)butanephosphonate (**2**) analysed here, bifurcated H-bonds within $R_2^1(6)$ motifs are formed. It seems that such interactions play a crucial role in the crystal architecture. This is supported by *ab initio* MP2/6–311 ++ G** calculations on simple, modelled complexes of urea, thiourea and their derivatives with water, where the oxygen atom of water molecule is the bifurcated proton-accepting centre. The calculations show that single H-bonds within bifurcated systems are of medium strength (2.7–3.6 kcal mol⁻¹). The topological parameters obtained from the Bader theory are applied for the analysis of these bifurcated H-bonds. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: bifurcated H-bonds; *ab initio* calculations; Bader theory; bond critical points

INTRODUCTION

Hydrogen bonds belong to the most important interactions which influence the arrangement of molecules in crystals.^{1–4} The hydrogen-bond motifs found in organic crystals were classified to be used in crystal engineering and organic synthesis.^{1,5} Such a classification has led to the term supramolecular synthons, many of which involve different kinds of H-bonds such as O—H...O, N—H...N, N—H...O, C—H...O, etc. A graph-set approach has also been used to describe the topology of motifs involving H-bonds.⁶ This topological treatment yields a description of H-bonded systems. The following main patterns may be pointed out: chains (C), rings (R), intramolecular H-bonds (S) and finite dimers (D). Additionally, the designator of the motif contains a subscript which corresponds to the number of donors and a superscript which corresponds to the number of acceptors. For example, the $R_2^2(8)$ topological motif designates a ring containing eight atoms with two donors and two acceptors. This H-bonded pattern is one of the

most often formed motifs in crystals, for example, for centrosymmetric dimers of carboxylic acids.⁷

Hydrogen bonds with a bifurcated donor and hydrogen bonds with a bifurcated acceptor may exist.⁸ Studies on such systems may be exemplified. The three-centre hydrogen bond in diarylamides was investigated by IR, ¹H NMR and crystallographic methods.⁹ Zimmerman and Murray examined intermolecular three-centre hydrogen bonding in base-pairing models and found that two-centre H-bonds were more favourable than three-centre H-bonds.¹⁰ X-ray analysis and solution studies support the formation of the bifurcated hydrogen bonding motif for these systems. IR data for some of dipeptides indicated that three-centre interaction is less energetically favourable than a two-centre H-bond.^{11,12} The IR and ¹H NMR spectra of solutions containing 2,6-disubstituted phenol derivatives with strong intramolecular H-bonds confirmed the existence of the bifurcated H-bonds in the liquid state.¹³

The aim of this paper is to describe bifurcated N—H...O hydrogen bonds with two N—H donors and one oxygen-accepting centre. Such H-bonds were recently found, for example, for the crystal structures of *O,O*-diphenyl *N*-phenylthioureidoalkane phosphonates^{14,15} and may be partly described in terms of $R_2^1(6)$ topological motifs (Scheme 1).

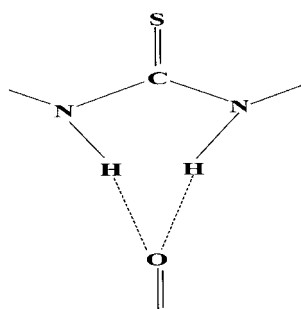
Different topological motifs were described according to their frequency of occurrence and according to their probabilities of formation¹⁶ and it was found that the

*Correspondence to: S. J. Grabowski, Department of Crystallography and Crystal Chemistry, University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland.

E-mail: slagra@uni.lodz.pl

†Dedicated to Professor Zofia Kosturkiewicz on the occasion of her 75th birthday.

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Scheme 1

$R_2^1(6)$ motif occurs frequently in organic crystals. Similar H-bonded patterns to that presented in Scheme 1 were found in proteins but one of the N—H donors is replaced by a C—H bond. Hence in the case of the structure of proteins the $R_2^1(6)$ motif contains N—H and C—H donating bonds and an oxygen acceptor belonging to a C=O carbonyl group.^{8,17}

In this study, the crystal structures of *O,O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate (**1**) and *O,O*-diphenyl 1-(3-phenylthioureido)butanephosphonate (**2**) were analysed. Both of them contain the above-mentioned H-bond patterns. Additionally MP2/6-311++G** calculations were performed for simple modelled complexes containing $R_2^1(6)$ motifs with two N—H donors and an oxygen atom as an accepting centre. The relationships between geometric and energetic parameters of the calculated systems are also given for a better understanding of the interactions that occur in the more complicated crystal structures. The Bader theory¹⁸ was also applied to gain a better insight into the nature of bifurcated H-bonds. Such systems are analysed in terms of properties of bond critical points (BCPs).

EXPERIMENTAL

Colourless crystals [$0.5 \times 0.5 \times 0.2$ mm (**1**) and $0.5 \times 0.3 \times 0.25$ mm (**2**)] were used for measurements on a Rigaku AFC5S diffractometer.¹⁹ X-ray intensities were collected using graphite monochromatized Cu $K\alpha$ radiation and ω scan. After each group of 150 reflections three standard intensities were monitored and no evidence of crystal decay was observed. All data were corrected for Lorentz and polarization factors.²⁰ Absorption corrections²¹ were applied: minimum and maximum transmission factors were 0.41495, 0.69225 for **1** and 0.48439, 0.65465 for **2**, respectively. The structures were solved by direct methods (SHELXS-86)²² and refined on F^2 by full-matrix least-squares calculation (SHELXL-93).²³ All non-hydrogen atoms were refined anisotropically. All H atoms of the phenyl, methyl and methylenic groups in **1** and **2** were geometrically placed and refined using the

Table 1. Crystal data and structure refinement details for compounds **1** and **2**

	1	2
Formula	C ₂₄ H ₂₇ N ₂ O ₃ PS	C ₂₃ H ₂₅ N ₂ O ₃ PS
<i>M</i>	454.51	440.48
<i>T</i> (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.943(1)	9.873(1)
<i>b</i> (Å)	10.841(1)	10.626(1)
<i>c</i> (Å)	11.734(1)	11.709(1)
α (°)	92.64(1)	91.39(1)
β (°)	102.38(1)	102.44(1)
γ (°)	103.82(1)	104.57(1)
<i>V</i> (Å ³)	1193.3(2)	1157.0(2)
<i>Z</i>	2	2
<i>D</i> _c (g cm ⁻³)	1.265	1.264
μ (mm ⁻¹)	2.059	2.108
2 θ range	7.76–145.20	7.76–145.32
<i>F</i> (000)	480	464
No. of data collected	4777	4638
No. of data with $I > 2\sigma(I)$	3654	3270
No. of parameters varied	294	285
<i>R</i>	0.0495	0.0403
<i>wR</i>	0.1483	0.1158

riding model with isotropic displacement parameters equal to $1.2U_{eq}$ of the attached C atom (except for methyl-H atoms for which U_{iso} amounts to 0.18 in **1** and 0.15 in **2**). All other hydrogen atoms were located in difference maps and refined isotropically with the N2—H2 distance restrained to 0.87(3) Å in **1**. The geometries of N—H bonds and H-bonds for **1** and **2** after neutron normalization are applied in the further analysis in this study.

The crystal data and some features of the structure refinement are summarized in Table 1. The other crystal data and geometric parameters (bond lengths and angles) have been deposited at the Cambridge Crystallographic Data Centre with reference numbers CCDC 188439 and CCDC 188440 for **1** and **2**, respectively.

COMPUTATIONAL DETAILS

All computations were performed using the Gaussian 94²⁴ and Gaussian 98²⁵ sets of programs. Calculations in the framework of the MP2²⁶ theory were carried out on H-bonded complexes of urea and thiourea derivatives with water. The binding energy was calculated as the difference between the total energy of the complex and the sum of the total energies of isolated monomers.²⁷ Basis set superposition error (BSSE) was corrected by the counterpoise method of Boys and Bernardi.²⁸ Geometries of monomers and complexes were fully optimized. All of the computations employed the 6-311++G** basis set. The inclusion of diffuse components in the basis is a clear

requirement to describe hydrogen-bonded systems adequately.

Topological properties of the electronic density were characterized using the atoms-in-molecules (AIM) methodology.¹⁸ By means of the AIMPAC series of programs,^{29,30} the bond critical points were located. Information on the relative strength of the linkage can be obtained in terms of electron density at proton...acceptor (H...Y) bond critical point ($\rho_{\text{H}\cdots\text{Y}}$), and in terms of the Laplacian ($\nabla^2\rho_{\text{H}\cdots\text{Y}}$).

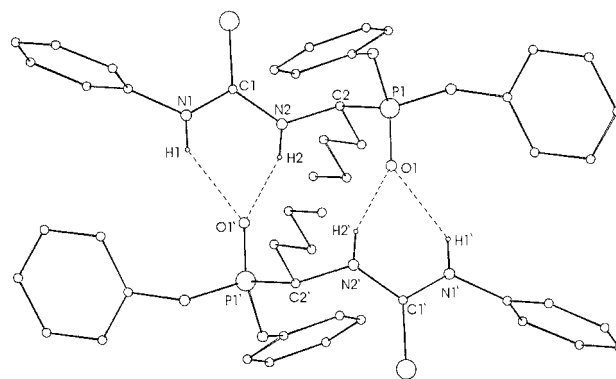
RESULTS AND DISCUSSION

Crystal structures

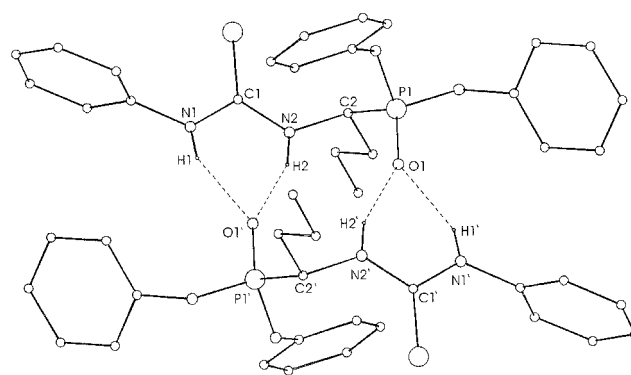
It was found earlier^{14,15} for thioureidophosphonate derivatives that bifurcated H-bonds dominate in the crystal architecture of these compounds. For the above-mentioned structures the following patterns may be pointed out: $R_2^2(14)$, $R_2^2(10)$ and $R_2^1(6)$. A similar situation occurs for the crystal structures of *O*, *O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate (**1**) and *O*, *O*-diphenyl 1-(3-phenylthioureido)butanephosphonate (**2**) (Fig. 1) investigated here. In both structures the oxygen atom designated O1 (Figs 1 and 2) is a bifurcated acceptor for two N—H...O bonds, N1—H1...O1' and N2—H2...O1' (prime means the symmetry relation for structures **1** and **2**). For such an interaction the simple $R_2^1(6)$ motif may be indicated (Scheme 1) consisting of the following atoms: H1—N1—C1—N2—H2...O1' (Fig. 1). For **1** and **2** $R_2^2(14)$ patterns also exist within dimers (Fig. 1), created by two symmetry-related fragments: H1—N1—C1—N2—C2—P1—O1 and H1'—N1'—C1'—N2'—C2'—P1'—O1'. Moreover, N2—H2...O1' bonds exist within $R_2^2(10)$ patterns which consist of two fragments related by symmetry: H2—N2—C2—P1—O1 and H2'—N2'—C2'—P1'—O1' (Fig. 1).

The geometry of the bifurcated $R_2^1(6)$ motifs is in accordance with those of related structures reported earlier.^{14,15} It is interesting that the H1...H2 intramolecular contacts within the bifurcated system are 2.17 and 2.03 Å for **1** and **2**, respectively; the values are slightly shorter than the sum of van der Waals radii. This may be justified since both hydrogen atoms are connected with the same oxygen atom-accepting centre.

Table 2 presents the geometry of N1—H1...O1' and N2—H2...O1' hydrogen bonds existing in the crystal structures. Both N—H...O interactions within the $R_2^1(6)$ bifurcated motifs of **1** and **2** are not mutually related by symmetry but they are practically equivalent. The donor-acceptor distance (N...O) for all H-bridges is about 2.9 Å, while the N—H...O angle ranges from 144 to 153°, far from linearity as justified for bifurcated systems.



(a)



(b)

Figure 1. View of the dimers of (a) *O*,*O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate (**1**) and (b) *O*,*O*-diphenyl 1-(3-phenylthioureido)butanephosphonate (**2**)

Ab initio results

One of the aims of the present study was to investigate in detail the bifurcated (N—H)₂...O bonds existing within the crystal structures reported here. Since such interactions play a crucial role in the architecture of crystals investigated in this study, it would be interesting to know more about the nature of such H-bonds. Hence MP2/6-311++G** calculations were performed on simple modelled complexes of urea and thiourea with water. Additionally, the complexes of fluoro and chloro derivatives of urea and thiourea with water were taken into account. For all systems investigated two N—H donors exist and the oxygen atom of water is an acceptor. For some cases there is a bifurcated motif (Scheme 2).

R^1 and R^2 in Scheme 2 designate H, F and Cl atoms and R3 an oxygen or sulphur atom. For systems for which $R^1 = R^2 = \text{H}$ (or Cl) the calculations show the approximate twofold axis symmetry (the axis contains R^3 , C and O atoms); for example, the differences between corresponding bonds are <0.01 Å and for the complex of urea with water they are <0.001 Å. For systems for which R^1 or/and R^2 is fluorine there are two-centre hydrogen bonds and bifurcated motifs are not observed. For two

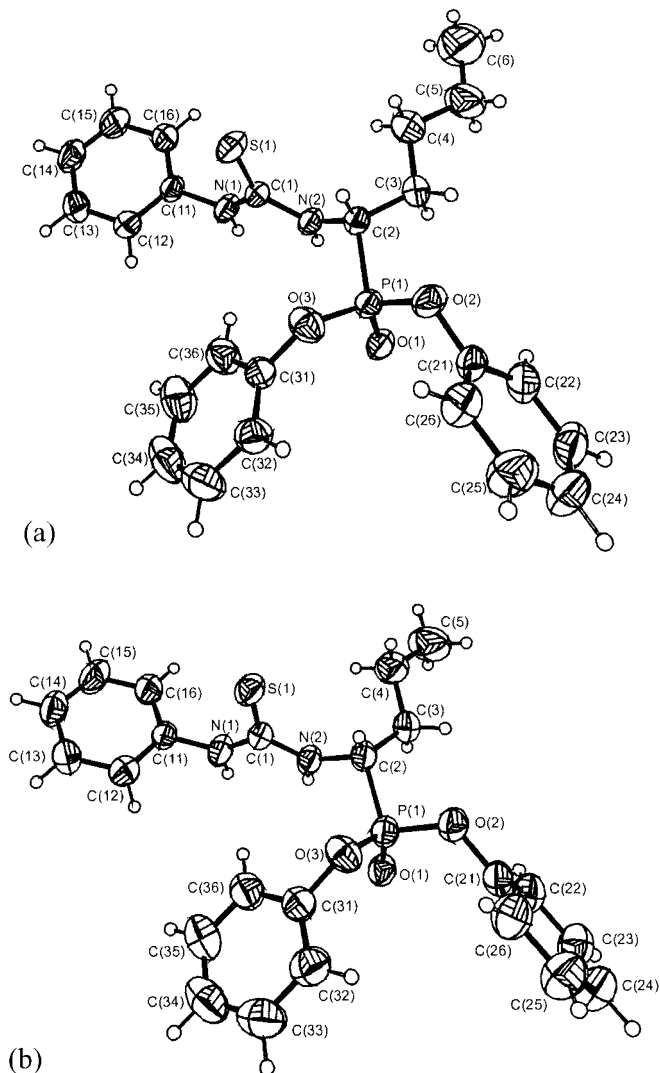
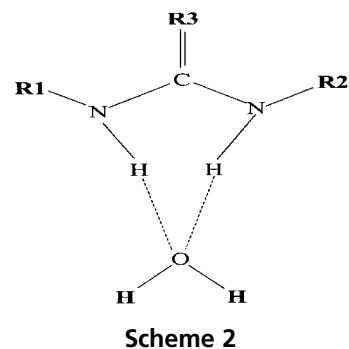


Figure 2. Structures of (a) **1** and (b) **2** with atom labelling scheme. Displacement ellipsoids are drawn at the 40% probability level

complexes, $(\text{NH}_2)\text{CO}(\text{NHCl}) + \text{H}_2\text{O}$ and $(\text{NH}_2)\text{CS}(\text{NHCl}) + \text{H}_2\text{O}$, there are $R_2^1(6)$ non-symmetric motifs. We see that there are three types of interactions for this set of complexes: approximately symmetrical bifurcated, non-symmetrical bifurcated and two-centre H-bonds. Selected geometric and energetic parameters of the complexes optimized at the MP2/6-311++G** level are shown in Table 3. The H-bond energies or binding



Scheme 2

energies corrected for the basis set superposition error are given in the last column. Since bifurcated H-bonds are symmetrical, the energies given in Table 3 are those of single N—H...O interactions. In other words, the H-bond energies of the symmetrical systems mentioned above are the differences between the energies of complexes and of isolated molecules divided by two. For the remaining systems for which two-centre H-bonds or non-symmetrical bifurcated motifs exist the binding energies are given in Table 3; it means that there are the differences between the energies of complexes and the energies of monomers. All systems, both symmetrical and non-symmetrical, were fully optimized during the calculations. The absence of imaginary frequencies (negative eigenvalues of the Hessian matrices) confirmed that for the optimized systems true minima were found.

The results presented above show that the nature of the R¹ and R² substituents within $(\text{NHR}^1)\text{CO}(\text{NHR}^2)$ and $(\text{NHR}^1)\text{CS}(\text{NHR}^2)$ molecules strongly affect the type of intermolecular pattern. For the **1** and **2** structures investigated here there are bifurcated motifs with practically equivalent N—H...O H-bonds in spite of different substituents attached to CS groups. It is reasonable to assume that packing and symmetry conditions in the crystals are responsible for the existence of such patterns.

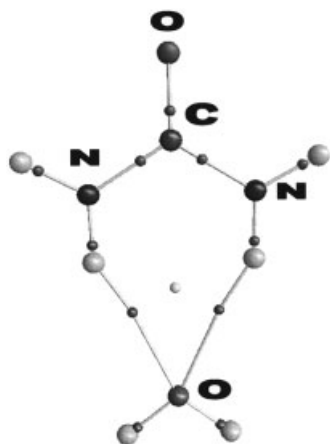
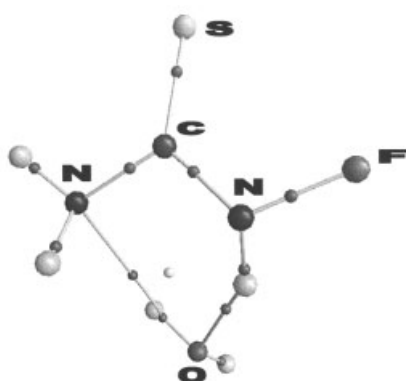
Figure 3 presents the molecular graph of the $\text{O}=\text{C}(\text{NH}_2)_2 \cdots \text{OH}_2$ complex for which the symmetrical bifurcated motif is observed. The bond critical points (BCPs) and the ring critical point (RCP) are shown. There are two critical points corresponding to H...O interactions between water molecules and urea. Figure 4 shows the molecular graph of the $\text{S}=\text{C}(\text{NH}_2)(\text{NFH}) \cdots \text{OH}_2$ complex. The positions of atoms and critical points are

Table 2. Geometry of the hydrogen bonds for **1** and **2** after neutron normalization for proton-donating bonds; symmetry: $-x$, $-y$, $-z$

Compound	D—H...A	$d(\text{D—H})$ (Å)	$d(\text{H...A})$ (Å)	$d(\text{D...A})$ (Å)	$\angle(\text{DHA})$ (°)
1	N1—H1...O1	1.009	2.039	2.915(2)	143.8
	N2—H2...O1	1.009	1.990	2.914(3)	151.0
2	N1—H1...O1	1.009	1.961	2.896(2)	153.1
	N2—H2...O1	1.009	1.989	2.910(2)	150.7

Table 3. Geometric and energetic parameters of the H-bonded systems considered: N—H proton donating bond length, H...O distance, N—H...O angle, H...H distance and H-bond or binding energy, E_{HB}

Substituents	Proton donors	N—H (Å)	H...O (Å)	N—H...O (°)	H...H (Å)	E_{HB} (kcal mol ⁻¹)
H,H (C=O) ^a	(NH ₂) ₂	1.011	2.225	143.9	2.263	-2.68
F,F (C=O) ^b	NHF	1.026	1.934	174.9	2.639	-7.05
Cl,Cl (C=O) ^a	(NHCl) ₂	1.016	2.109	143.5	2.137	-3.56
H,F (C=O) ^b	NHF	1.024	1.999	171.0	2.483	-5.70
H,Cl (C=O) ^c	NHCl	1.016	2.044	157.3	2.163	-5.95
	(NH ₂)	1.011	2.227	148.4		
F,Cl (C=O) ^b	NHCl	1.023	1.913	157.2	2.514	-7.23
H,H (C=S) ^a	(NH ₂) ₂	1.012	2.190	146.6	2.226	-3.06
F,F (C=S) ^b	NHF	1.027	1.917	172.7	2.656	-6.96
Cl,Cl (C=S) ^a	(NHCl) ₂	1.018	2.079	147.6	2.041	-3.61
H,F (C=S) ^b	NHF	1.026	1.965	168.4	2.454	-6.41
H,Cl (C=S) ^c	NHCl	1.019	1.959	187.4	2.175	-6.67
	(NH ₂)	1.013	2.441	124.8		
F,Cl (C=S) ^b	NHCl	1.026	1.880	158.0	2.600	-7.20

^a Bifurcated approximately symmetrical systems.^b Two-centre H-bonds.^c Bifurcated non-symmetrical systems.**Figure 3.** Molecular graph of O=C(NH₂)₂...OH₂ complex. The positions of attractors, bond critical points and the ring critical point are given. The bond paths are also included**Figure 4.** Molecular graph of S=C(NH₂)NHF...OH₂ complex. The positions of attractors, bond critical points and the ring critical point are given. The bond paths are included

presented within the graph. For this case the situation is more complicated. The water molecule behaves as a single proton acceptor and also a proton donor to one of the amino groups of thiourea. A similar situation is observed for other 'non-bifurcated' systems. In other words, for such systems the binding energies presented in Table 3 do not correspond directly to two-centre N—H...O H-bonds but they also contain the O(water)—H...N(urea or thiourea derivative) interactions.

The results mentioned above and presented in Table 3 indicate roughly the dependences known for typical conventional O—H...O bonds^{31,32} and also known for non-conventional C—H...X bonds.^{8,33} The stronger the H-bond the greater is the lengthening of the N—H

Table 4. Topological parameters of the H-bonded systems considered: electron density at N—H proton-donating bond, ρ_{NH} , electron density at H...O contact, $\rho_{\text{H...O}}$, and Laplacians of these densities, $\nabla^2\rho_{\text{NH}}$ and $\nabla^2\rho_{\text{H...O}}$, respectively (all values in au; substituents within amino groups are given in the first column; the order of N—H...O interactions is the same as for Table 3)

Substituents	ρ_{NH}	$\nabla^2\rho_{\text{NH}}$	$\rho_{\text{H...O}}$	$\nabla^2\rho_{\text{H...O}}$
H,H (C=O)	0.334	-1.690	0.014	0.052
F,F (C=O)	0.330	-1.832	0.026	0.096
Cl,Cl (C=O)	0.333	-1.747	0.018	0.067
H,F (C=O)	0.333	-1.815	0.023	0.084
H,Cl (C=O)	0.334	-1.747	0.020	0.076
	0.334	-1.691	0.014	0.051
F,Cl (C=O)	0.325	-1.771	0.027	0.099
H,H (C=S)	0.333	-1.699	0.015	0.055
F,F (C=S)	0.328	-1.826	0.027	0.099
Cl,Cl (C=S)	0.332	-1.741	0.019	0.072
H,F (C=S)	0.330	-1.815	0.025	0.090
H,Cl (C=S)	0.330	-1.765	0.024	0.091
	0.333	-1.653	0.010	0.035
F,Cl (C=S)	0.322	-1.770	0.029	0.105

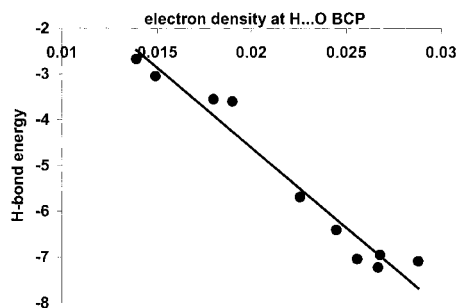


Figure 5. Relationship between H-bond energy (kcal mol^{-1}) and electron density at H...O BCP (in au)

donating bond and the shorter is the H...O intermolecular contact. Table 3 also shows the H...H intramolecular distances which are in agreement with the corresponding distances for the crystal structures presented above. For the crystal structures such contacts are 2.17 and 2.03 Å for **1** and **2**, respectively. For calculated systems these distances are in the range 2.04–2.26 Å for bifurcated systems and 2.45–2.66 Å for systems with two-centre H-bonds.

Table 4 presents the properties of the bond critical points (BCPs): the electron densities of BCPs of the N—H donors, ρ_{NH} , the electron densities of H...O BCPs, $\rho_{\text{H...O}}$, and their Laplacians, $\nabla^2\rho_{\text{NH}}$ and $\nabla^2\rho_{\text{H...O}}$, respectively. The topological parameters have been used previously for the description of the nature of bifurcated, three-centre hydrogen bonds.³⁴ Different compounds were chosen in the above-mentioned study and all the systems were optimized at the B3LYP/6–31G* level. The authors pointed out that for three-centre HBs there are two BCPs with similar characteristics of ρ and $\nabla^2\rho$; bifurcated H-bonds are energetically weaker than the typical hydrogen bonds.

It is well known that the electron density at H...Y BCP (Y is the acceptor of proton) correlates with H-bond energy.^{35–37} However, such a correlation is usually fulfilled for homogeneous samples of complexes.³⁸ Figure 5 shows the linear relationship between $\rho_{\text{H...O}}$

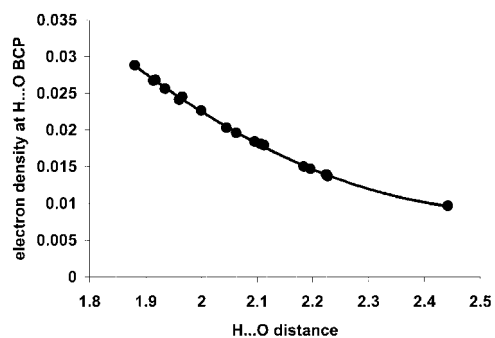


Figure 6. Dependence between H...O distance (in Å) within the N—H...O bond and the corresponding H-bond energy (kcal mol^{-1}) for the systems optimized here at the MP2/6–311 ++ G** level

and H-bond energy for the modelled systems investigated here; the correlation coefficient is 0.978. The non-symmetrical bifurcated systems were excluded from the sample of complexes here. This correlation is observed in spite of the fact that for some systems the binding energy also contains a slight energetic contribution of N...H—O interaction where the water molecule is a donor of proton (Fig. 4). We see that for the complexes investigated here the electron density at BCP is an even more convenient measure of H-bond strength since all intermolecular H...O contacts may be analysed separately. *Ab initio* or DFT results provide binding energies which represent the energies of single H-bonds if the bifurcated motif is symmetrical (contains equivalent H-bonds) and no other H-bonds within systems exist.

The proton...acceptor distance is often treated as a geometrical measure of the H-bond strength, especially for homogeneous samples of complexes.^{2,3,8} Figure 6 shows the correlation between the electron density at H...O BCP and H...O distance. The linear correlation coefficient is 0.984 and for the polynomial regression of the second degree the correlation coefficient is 1.000. The better polynomial correlation may be explained by the exponential or polynomial character of intermolecular interactions for which there is no linear dependence between the strength and the distance.

CONCLUSIONS

The crystal and molecular structures of *O,O*-diphenyl 1-(3-phenylthioureido)pentanephosphonate (**1**) and *O,O*-diphenyl 1-(3-phenylthioureido)butanephosphonate (**2**) were analysed, showing the existence of bifurcated (N—H)₂...O H-bonds with a bifurcated accepting oxygen atom. Such interactions are very important for the stabilization of crystal networks. It may be assumed that packing forces in the crystals are responsible for the existence of such patterns.

Ab initio calculations at the MP2/6–311 ++ G** level for the modelled systems show that the energy of single N—H...O interactions for symmetrical bifurcated systems is in the range -2.7 to $3.6 \text{ kcal mol}^{-1}$ ($1 \text{ kcal} = 4.184 \text{ kJ}$); the corresponding energies of non-symmetrical complexes are approximately two times greater (Table 3). This means that H-bond energies within R₂¹(6) motifs may be additive. This observation is supported by the results of topological calculations within the AIM scheme. The electron densities of BCPs for H...O contacts are almost two times greater for non-bifurcated than for bifurcated systems (Table 4).

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