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Voronoi–Dirichlet tesselation as a tool for investigation of polymorphism in molecular crystals with $C_wH_xN_yO_z$ composition and photochromic properties

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The non-bonded interactions in five sets of polymorph substances with photochromic properties have been investigated within the Voronoi–Dirichlet approach. Twenty compounds with the general formula $C_wH_xN_yO_z$ were analyzed. Among ten possible types of non-bonded interactions at least five types are observed in the crystal structures of compounds under discussion. For all the structures the majority of interactions involve H atoms, namely London forces (H···H and H···C) and hydrogen bonds (H···O and H···N). A conformational polymorph was stated to be characterized by a unique set of inter- and intramolecular non-bonded interactions. It was quantitatively demonstrated that molecules in the same conformation can pack in a different way, and, *vice versa*, the change in conformation of a molecule does not prevent a substance from realising the same set of intermolecular contacts. In accordance with the data obtained for 2,4-dinitrobenzylpyridine derivatives, only conformational polymorphs with an intramolecular N···N interaction between a nitro group and a pyridine are photochromic.

1. Introduction

Conformational polymorphism is the phenomenon of different conformers of the same molecule occurring in different crystal forms (Nangia, 2008; Bernstein & Hagler, 1978). This group of substances has attracted increasing interest in recent decades (Nangia, 2008), because the discrepancies in their structures are caused only by weak non-bonded interactions. Thus, conformational polymorphs are perfect objects for an investigation devoted to the search for interrelationships between the structure and properties of a substance (Bernstein, 2002). Crystals of this group of polymorphs are able to change their color under irradiation (photochromism), stress (mechanochromism), pressure (piezochromism) and temperature change (thermochromism). In particular, there is the need for techniques that are able to compare the structures of conformers and to evaluate the differences in their structures quantitatively.

Recently a number of approaches have appeared that are able to test non-bonded interactions. Let us mention the *XPac* program and the similarity index of Gelbrich & Hursthouse (2005), and the *OPiX* program (Gavezzotti, 2005) used to calculate the distribution of molecule–molecule energies in the packing coordination sphere of a molecule, in combination with the more traditional crystallographic cell reductions and powder patterns. Significant progress in the analysis of non-bonded interactions has been reached due to the application of Hirshfeld's surfaces (Hirshfeld, 1977). The latter approach allows visualization of intermolecular interactions with a two-

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Table 1
The relative contribution (%) to the total area of the Hirshfeld surface (S_H; McKinnon, Fabbiani & Spackman, 2007) or the area of the molecular VDP (${}^0\Delta$; Serezhkin *et al.*, 2011) for the various intermolecular contacts in some molecular crystals.

The substance		H···H		C···C		C···H	
Chemical name	Refcode (Allen, 2002)	S_H	${}^0\Delta$	S_H	${}^0\Delta$	S_H	${}^0\Delta$
Benzene	BENZEN07[a]	64	61.3	0	0	36	38.7
Naphthalene	NAPHTA16[b]	54	50.2	1	0.3	45	49.5
Anthracene	ANTCEN10[c]	48	46.0	2	1.2	51	52.8
Paracetamol-I	HXACAN06[d]	45	46.6	†	2.0	22	24.2
Paracetamol-II	HXACAN21[e]	40	41.2	†	0.4	28	29.3

References: (*a*) Jeffrey *et al.* (1987), (*b*) Oddershede & Larsen (2004), (*c*) Brock & Dunitz (1990), (*d*) Wilson (1997), (*e*) Drebushchak & Boldyreva (2004). † The characteristics of the C···C contacts are not listed in the original work (McKinnon, Fabbiani & Spackman, 2007). In accordance with Serezhkin *et al.* (2011) paracetamol-I and paracetamol-II are characterized by seven and eight types of intermolecular contacts.

dimensional grid (McKinnon *et al.*, 2004; McKinnon, Fabbiani & Spackman, 2007; Spackman & Jayatilaka, 2009; McKinnon, Jayatilaka & Spackman, 2007) and can be used for the calculation of a similarity index between molecular structures (Parkin *et al.*, 2007). At the same time each approach has some restrictions, *e.g.* the latter method is handicapped in the case of multiatomic compounds (McKinnon, Jayatilaka & Spackman, 2007). Thus, we decided to analyze non-bonded interactions in the solid state with the stereoatomic model (Blatov & Serezhkin, 2000) based on descriptors of a Voronoi–Dirichlet polyhedron (VDP). In contrast with approaches dealing only with strong contacts, both the method of the Hirshfeld surfaces and the method of molecular VDPs take all the intermolecular interactions into account.

The molecular VDPs were firstly used in solid-state chemistry by Fischer & Koch (1979). Later the molecular VDPs were used to investigate a number of molecular crystals (Peresypkina & Blatov, 2000; Moggach *et al.*, 2008; Lozano-Casal *et al.*, 2005). Let us denote the method of representation of molecular crystals by Voronoi–Dirichlet tesselation as the method of the molecular Voronoi–Dirichlet polyhedra (MMVDP). In contrast with other approaches for the description of crystal space, the Voronoi–Dirichlet tesselation is not needed in van der Waals radii of atoms and is characterized by the absence of intermolecular voids. As a comparison, within the Hirshfeld surface approach $\simeq 5\%$ of crystal volume belongs to the voids (regions with low electron density), whilst within classical approaches, based on van der Waals radii and Kitaigorodskii's model, 20–35% of crystal volume belongs to the voids (McKinnon, Jayatilaka & Spackman, 2007). Although representation of a molecule with its Hirshfeld surface or molecular VDP are based on different principles and techniques, the resulting relative contributions of some types of non-bonded interactions to an area of molecular surface are in good accordance with each other (Table 1).

The working capacity of the MMVDP has already been demonstrated by the analysis of non-bonded interactions in crystals of hydrocarbons (Serezhkin, Pushkin *et al.*, 2005; Serezhkin, Prokaeva, Pushkin, Serezhkina & Kudryashov, 2008; Serezhkin, Prokaeva, Pushkin, Serezhkina & Onuchak, 2008; Serezhkin, Serezhkina, Shevchenko & Pushkin, 2005), metal carbonyls and π-complexes (Serezhkin, Shevchenko & Serezhkina, 2005; Serezhkin, Shevchenko *et al.*, 2005), binary oxides and halogenides (Serezhkin *et al.*, 2009*a*,*b*) as well as some conformational polymorphs (Serezhkin *et al.*, 2010; Serezhkin *et al.*, 2011; Serezhkin & Serezhkina, 2012). It has been demonstrated that the differences in non-bonded interactions in the structures of conformational polymorphs can be characterized quantitatively based on the total number of non-bonded interactions, their distribution among inter- and intramolecular contacts and the identity of interacting atoms (the k–Φ criterion). The goal of the present paper was to verify the k–Φ criterion (Serezhkin & Serezhkina, 2012) for quantitative estimation of differences between molecular structures in crystals of conformational polymorphs based on the example of substances with the composition $C_wH_xN_yO_z$. The relationship between non-bonded interactions and photochromism of these substances was investigated within the method of molecular Voronoi–Dirichlet polyhedra.

2. Experimental

2.1. Investigation objects

All the reported compounds were taken from the Cambridge Structural Database (Allen, 2002) provided that:

(i) a substance consists only of molecules with $C_wH_xN_yO_z$ composition and exhibits polymorphism;

(ii) the crystal structures of at least two modifications of the substance were refined to $R < 0.08$;

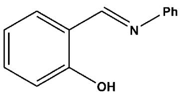
(iii) the coordinates of all atoms including H atoms are determined;

(iv) there is no disorder in the structure;

(v) the photo- or thermochromic properties of the crystal are mentioned in the CSD (Allen, 2002).

These conditions were met for five sets of compounds: 2-(phenyliminomethyl)phenol, $C_{13}H_{11}NO$ (1), 3-methyl-2-(2′,4′-dinitrobenzyl)pyridine (2), 6-(2′,4′-dinitrobenzyl)-2,2′-bipyridine (3), 4,4′-methylenebis(*N*-salicylidene-2,6-diisopropylaniline) (4) and 3-((2-hydroxy-3,5-di-*tert*-butylbenzylidene)amino)benzoic acid (5).

The structures of three, three, three, two and three modifications, respectively, have been determined to date. The majority of polymorphs of (1)–(5) were obtained by different authors and had no consistent notation. Thus, we labeled each structure by a digit and letter code [for example (2)-5*B*, Table 2], where the first digit varies from (1) to (5) and coincides with the number of the compound, and the second is the order number. The letter (*A*, *B* or *C*) in the last position points to the modification of the polymorph, which was determined by other authors (Arod *et al.*, 2005, 2007; Eichen *et al.*, 1997; Johmoto *et al.*, 2009; Naumov & Ohashi, 2004; Naumov & Sakurai, 2005; Scherl *et al.*, 1996; Schmidt *et al.*, 1999; Taneda *et al.*, 2004). Some structural information, the reference and code of the compound in the Cambridge Structural Database (CSD; Allen, 2002) are also listed in Table 2.



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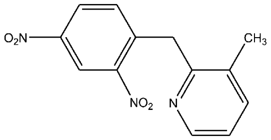

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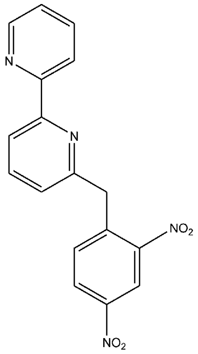

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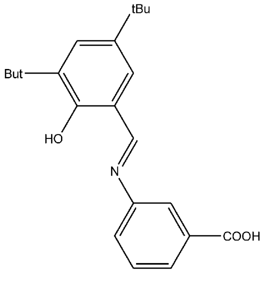

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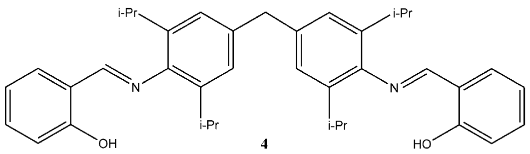

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2.2. The method of the molecular Voronoi–Dirichlet polyhedra

2.2.1. The molecular Voronoi–Dirichlet polyhedra and their descriptors. The Voronoi–Dirichlet polyhedron (VDP) of an A atom surrounded by $\{Y_i\}$ atoms is a convex polyhedron formed by planes that are drawn perpendicular to $A{-}Y_i$ contacts at their midpoints. The molecular VDP is constructed from VDPs of separate atoms. The VDPs of hydrogen atoms H6 and H11 as well as the molecular VDPs of polymorphs (1)-1*A* and (1)-2*B* are represented in Fig. 1 as an example.

Let us consider the main definitions of the MMVDP and molecular descriptors which are of importance for our discussion. To start with, each crystal space is partitioned with the Voronoi–Dirichlet tessellation taking the space group, cell parameters and atomic coordinates into account. An area (s_{ij}), rank (RC) and other characteristics (see supplementary material[1]) of any VDP face are calculated. The rank is the number of chemical bonds in the shortest chain connecting the A_i and A_j atoms in the crystal structure. Thus, all pair interactions can be automatically divided on valence bonds (RC = 1), intramolecular non-bonded interactions (RC > 1) and intermolecular non-bonded interactions (RC = 0). For example, in the case of the H6···H11 intramolecular interaction in (1) (Fig. 1), RC = 8. The molecular descriptors are calculated on atomic descriptors for all atoms of the molecule.

The surface of the molecular VDP is faceted by faces with RC = 0 and the number of intermolecular interactions (^0k) is calculated as the number of these faces. The total molecular area (^0S) for a given molecule is calculated as the sum of $^0s_{ij}$ (here and below the left superscripted number denotes the RC value for this contact) with the *InterMol* program (Serezhkin, Serezhkina, Shevchenko & Pushkin, 2005) included in the program package *TOPOS* (Blatov *et al.*, 2000). In particular, in the case of (1)-3*C* the molecular area ^0S is equal to $^0s_{\rm OO} + {^0s_{\rm NO}} + {^0s_{\rm CO}} + {^0s_{\rm HO}} + {^0s_{\rm NN}} + {^0s_{\rm CN}} + {^0s_{\rm HN}} + {^0s_{\rm CC}} + {^0s_{\rm HC}} + {^0s_{\rm HH}} = 0 + 0 + 1.8 + 25.2 + 0 + 0 + 11.2 + 1.5 + 118.0 + 135.9 = 293.6$ Å^2 (Table 2). It is also worth mentioning that either inter- (RC = 0) or intramolecular (RC > 1) non-bonded interactions can be quantitatively characterized within the MMVDP approach from a unified position; *e.g.* the area ($^{>1}S$) and the number ($^{>1}k$) of intramolecular non-bonded interactions can be calculated on the faces of atomic VDPs with RC > 1 for all atoms in a molecule.

The non-bonded interactions are herein denoted as A/Z, where the slash '/' indicates that the VDPs of the A and Z atoms share a face. The relative contribution of the total molecular area which goes to a given type of non-bonded intermolecular interaction ($^0\Delta_{AZ}$, %) is calculated as the ratio between the area of non-bonded intermolecular contacts of this type and ^0S. For example, for substances with a $\rm C_\mathit{w}H_\mathit{x}N_\mathit{y}O_\mathit{z}$ composition ten types of intermolecular contacts are possible and, generally, $^0\Delta_{\rm OO} + {^0\Delta_{\rm NO}} + {^0\Delta_{\rm CO}} + {^0\Delta_{\rm HO}} + {^0\Delta_{\rm NN}} + {^0\Delta_{\rm CN}} + {^0\Delta_{\rm HN}} + {^0\Delta_{\rm CC}} + {^0\Delta_{\rm HC}} + {^0\Delta_{\rm HH}} = 100$; the relative contributions of these types of contacts to the area of (1)-3*C* polymorph are 0, 0, 0.6, 8.6, 0, 0, 3.8, 0.5, 40.2 and 46.3%.

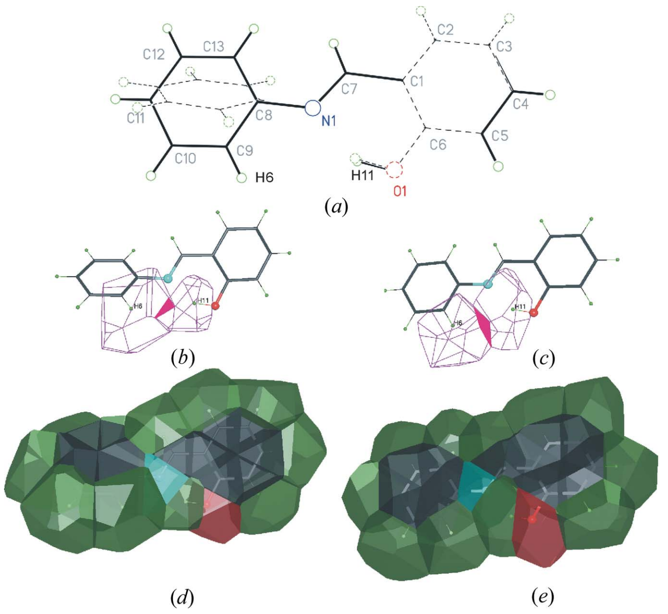

Figure 1
Two conformational polymorphs of 2-(phenyliminomethyl)phenol: ofitted structures of (1)-1*A* and (1)-2*B* (*a*), the C1–C6 ring is ofitted; the structure of (1)-1*A* is depicted with dashed lines; the VDPs of the H6 and H11 atoms in the crystals of (1)-1*A* (*b*) and (1)-2*B* (*c*); and the molecular VDPs in crystals of (1)-1*A* (*d*) and (1)-2*B* (*e*). The face corresponding to the H6···H11 interactions is marked with magenta and is characterized by Rank = 8 and an area equal to 0.22 and 0.78 Å^2 for (1)-1*A* and (1)-2*B*.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OG5056). Services for accessing these data are described at the back of the journal.

Table 2
Some characteristics of non-bonded interactions in crystals of polymorphs (1)–(5) obtained within the MMVDP.

T_e – the temperature of the X-ray diffraction experiment, k – the number of inter- (^0k) and intramolecular ($^{>1}k$) contacts per one molecule. ^0S is the area of the molecule and $^{>1}S$ is the area of VDP faces which correspond to intramolecular non-bonded interactions per molecule.

Polymorph number	Reference	Reference code (Allen, 2002)	Space group	T (K)	Intermolecular interactions		Intramolecular interactions	
					^0k	^0S (Å^2)	$^{>1}k$	$^{>1}S$ (Å^2)
Polymorphs of $C_{13}H_{11}NO$ (1)								
(1)-1*A*	Arod *et al.* (2005)	SALCAN01	$P2_12_12_1$	120	268	281.5	49	100.3
(1)-2*B*	Arod *et al.* (2007)	SALCAN03	$Pbc2_1$	120	264	282.2	41	97.8
(1)-3*C* †	Arod *et al.* (2007)	SALCAN04	$P1$	120	258	293.6	53	103.8
Polymorphs of $C_{13}H_{11}N_3O_4$ (2)								
(2)-1*A*	Scherl *et al.* (1996)	RIGHUK01	$P2_1/c$	296	282	324.3	72	181.5
(2)-2*A*	Naumov & Sakurai (2005)	RIGHUK05	$P2_1/c$	316	284	325.0	71	185.4
(2)-3*A*	Naumov & Sakurai (2005)	RIGHUK06	$P2_1/c$	319.7	282	325.3	72	183.8
(2)-4*A*	Naumov & Sakurai (2005)	RIGHUK07	$P2_1/c$	324	282	324.9	72	185.4
(2)-5*B*	Naumov & Sakurai (2005)	RIGHUK08	$P2_1/c$	328.9	284	327.2	71	179.1
(2)-6*B*	Naumov & Sakurai (2005)	RIGHUK09	$P2_1/c$	337.5	284	329.5	72	180.9
(2)-7*B*	Eichen *et al.* (1997)	RIGHUK	$P2_1/c$	343	286	327.6	78	177.3
(2)-8*C*	Schmidt *et al.* (1999)	RIGHUK04	Cc	293	283	322.5	75	169.4
Polymorphs of $C_{17}H_{12}N_4O_4$ (3)								
(3)-1*A*	Naumov & Ohashi (2004)	ZOGQAN04	$Pna2_1$	78	358	387.1	87.5	171.8
(3)-2*A*	Scherl *et al.* (1996)	ZOGQAN02	$Pna2_1$	173	353	386.5	91.5	180.2
(3)-3*B*	Scherl *et al.* (1996)	ZOGQAN03	$P2_1/c$	173	374	387.9	80	173.8
(3)-4*C*	Naumov & Ohashi (2004)	ZOGQAN05	$P2_1/c$	78	346	379.8	90	176.1
Polymorphs of $C_{39}H_{46}N_2O_2$ (4)								
(4)-1*A*	Taneda *et al.* (2004)	ATIWOP	$P2_1/n$	296	596	409.8	300	750.0
(4)-2*B*	Taneda *et al.* (2004)	ATIWOP01	$C2/c$	296	628	408.2	293	621.6
Polymorphs of $C_{22}H_{27}NO_3$ (5)								
(5)-1*A*	Johmoto *et al.* (2009)	MOPNAH	$P2_1/n$	295	416	471.8	161	389.7
(5)-2*B*	Johmoto *et al.* (2009)	MOPNAH01	$P2_1/c$	293	406	488.4	166	405.3
(5)-3*C*	Johmoto *et al.* (2009)	MOPNAH02	$C2/c$	295	412	459.4	161.5	402.9

† The characteristics of non-bonded interactions are given for the major orientation of a molecule in a twinning crystal.

2.2.2. The k–Φ criterion. In our opinion (Serezhkin & Serezhkina, 2012) various conformations of chemically identical molecules can be distinguished among different modifications of a crystalline substance, provided that their molecular VDPs:

(i) have various numbers of contacts with RC > 1, or

(ii) have the same total $^{>1}k$, but vary in the sets of RC values, which correspond to at least one type of A/Z interaction.

The module of difference between the number of interactions ($^{>1}\varphi_{AZ}$) of a given A/Z type and RC value for two molecular VDPs is calculated. The sum of $^{>1}\varphi_{AZ}$ for all theoretically possible types of A/Z interactions ($^{>1}\varphi$) becomes the quantitative descriptor of discrepancies between various conformations. **Thus, the criterion of the same conformation of molecules (the k–Φ criterion) in the structures of various polymorph modifications is that the VDPs of molecules in these structures are characterized by (i) the same $^{>1}k$ value and (ii) $^{>1}\Phi = 0$**. In other words, rotations about single bonds of a substance are accompanied by the appearance/disappearance of intramolecular non-bonded contacts, hence two molecules can be considered as different conformers provided that they vary in the sets of intramolecular non-bonded interactions. The sets in turn may differ either in the number of contacts or in the identity of interacting atoms. Indeed, variation in the topology of observed intramolecular non-bonded interactions A/Z for compared molecular VDPs is accompanied by a change in $^{>1}k$ value. In this case $^{>1}\Phi$ is always positive and the higher the $^{>1}\Phi$ value, the more pronounced the discrepancies between conformational polymorphs. To finish with, let us mention $^0\varphi_{AZ}$ and $^0\Phi$, which are calculated in a similar way to $^{>1}\varphi_{AZ}$ and $^{>1}\Phi$, and characterize the discrepancies between the sets of intermolecular interactions for a given molecule in the structures of polymorphs.

3. Results

The characteristics of the non-bonded interactions observed in crystals of (1)–(5) are listed in Table 2 and Table 1S of the supplementary material. Four of 20 crystal structures [(1)-3*C*, (2)-8*C*, (3)-1*A* and (3)-2*A*] include two symmetrically independent sorts of molecules. Thus, for these substances Tables 2–4 represent the average characteristics of the molecular VDPs. Relative contributions of non-bonded A/Z interactions in the structure of (2) are listed in Table 3, and those of polymorphs of (1), (3)–(5) are given as supplementary material (Table 2S). As seen from Table 3, polymorph modifications of (2) have similar sets of inter- and intramolecular contacts apart from an intermolecular contact between N

Table 3
Relative contributions of inter- ($^0\Delta$) and intramolecular ($^{>1}\Delta$) non-bonded contacts *A*/*Z* into the molecular surface area of $C_{13}H_{11}N_3O_4$ (2).

The values of $^0\Delta$ and $^{>1}\Delta$ are round to one decimal place. The absence of some type of intermolecular interactions in the crystal is denoted with hyphen.

Polymorph	Relative	Type of non-bonded interaction *A*/*Z*									
number	contribution (%)	O/O	N/O	C/O	H/O	N/N	C/N	H/N	C/C	H/C	H/H
(2)-1*A*	$^0\Delta$	2.3	2.2	5.6	39.6	–	0.2	6.6	1.6	19.0	23.0
	$^{>1}\Delta$	3.2	2.1	3.7	19.6	2.3	3.7	4.7	1.4	17.2	42.0
(2)-2*A*	$^0\Delta$	2.4	2.4	5.8	39.8	–	0.1	6.5	1.7	18.4	23.0
	$^{>1}\Delta$	2.6	2.1	3.8	19.3	2.3	3.6	4.6	1.3	16.5	43.8
(2)-3*A*	$^0\Delta$	2.3	2.3	5.8	39.7	–	0.2	6.5	1.7	18.5	23.0
	$^{>1}\Delta$	2.7	2.2	3.9	19.5	2.3	3.6	4.6	1.3	16.1	43.9
(2)-4*A*	$^0\Delta$	2.3	2.4	5.7	39.8	–	0.1	6.5	1.7	18.4	23.0
	$^{>1}\Delta$	2.6	2.1	3.8	19.4	2.3	3.6	4.5	1.2	16.3	44.0
(2)-5*B*	$^0\Delta$	2.0	2.9	5.9	40.6	–	1.4	5.7	2.5	14.3	24.6
	$^{>1}\Delta$	2.1	1.3	4.3	21.2	2.4	4.3	3.5	1.4	16.8	42.6
(2)-6*B*	$^0\Delta$	2.0	2.9	5.9	40.6	–	1.4	5.7	2.5	14.3	24.6
	$^{>1}\Delta$	2.1	1.3	4.3	21.3	2.4	4.3	3.4	1.4	16.8	42.6
(2)-7*B*	$^0\Delta$	2.2	3.0	6.2	40.0	–	1.4	5.4	2.7	14.3	24.7
	$^{>1}\Delta$	2.2	1.4	4.4	21.5	2.5	4.5	3.6	1.4	16.7	41.8
(2)-8*C*	$^0\Delta$	3.7	3.0	3.5	37.2	0.8	1.2	6.5	5.5	12.5	26.0
	$^{>1}\Delta$	3.2	0.5	5.7	19.6	0.5	4.3	3.2	1.9	18.4	42.6

Table 4
The number of intramolecular contacts in polymorphs of (2).

The polymorphs are listed with an increase of the $^{>1}k$ parameter (given in the last line of the table). Each number denotes the number of intramolecular contacts with a corresponding RC. The absence of some types of intermolecular interactions in the crystal is denoted with a hyphen. The ^{RC}k for the N/N, N/O and C/O interactions is given with bold underlined text provided that the ^{RC}k value differs from that in the structure of (2)-2*A*.

Type of contact	Rank	(2)-2*A*	(2)-5*B*	(2)-1*A*	(2)-3*A*	(2)-6*B*	(2)-8*C*	(2)-7*B*
O/O	2	2	2	2	2	2	2	2
N/O	6	2	2	2	2	2	**1**	2
C/O	2	4	4	4	4	4	**3.5**	4
	3	2	2	2	2	2	**2.5**	**1**
	4	1	1	1	1	1	1	1
	5	1	1	1	1	1	1	1
	6	–	**1**	–	–	**1**	**1**	**1**
	7	–	–	–	**1**	–	–	**1**
H/O	4	3	3	3	3	3	3	3
	5	1	1	1	1	1	1	1
	8	1	1	1	1	1	**1.5**	1
N/N	5	1	1	1	1	1	**0.5**	1
C/N	2	2	2	2	2	2	3	3
	3	2	2	2	2	2	1	2
	4	2	2	2	2	2	2.5	2
H/N	2	1	1	1	1	1	1	1
	3	3	3	3	3	3	2.5	4
	4	–	–	–	–	–	0.5	–
	5	–	–	–	–	–	0.5	–
C/C	2	7	8	7	7	8	7	7
	3	1	1	–	1	1	2.5	1
H/C	2	16	15	15	16	16	16	18
	3	4	4	7	4	4	7	7
	4	2	2	1	2	2	1	2
H/H	2	4	4	4	4	4	4	4
	3	3	3	3	3	3	3	3
	4	3	2	3	3	2	2.5	2
	5	3	3	4	3	3	3	3
Sum	–	71	71	72	72	72	75	78

atoms, which is observed only in the structure of the *C* modification.

The compounds under discussion contain almost 900 crystallographically different C, H, N or O atoms, and an atom is involved in 9(1) inter- and 5(1) intramolecular interactions on average. In the crystals of anils (1), (4) and (5) the number of types of non-bonded interactions varies from five to eight, and at least eight of ten possible types are observed in the crystals of heterocycles (2) and (3). For all the structures the majority of interactions go to H atoms. These are London forces (H/H and H/C) and hydrogen bonds (H/O and H/N), which cover from $\simeq 82\%$ [polymorphs of (2) and (3), Table 2] to 99% [(1), (4) and (5)] of the molecular area corresponding to non-bonded interactions (^0S and $^{>1}S$ in sum). This fact probably comes from the composition and structure of compounds (1)–(5), which are comprised of 32–52% of H atoms, and all of them are situated on the surface of a molecule. It is also worth mentioning that the total molecular area for each compound vary over a narrow range (Table 2).

4. Discussion

4.1. The *k*–Φ criterion in (1)–(5)

Taking the *k*–Φ criterion into account, one should conclude that all crystals of (1), (3), (4) or (5) are conformational polymorphs, since each pair of crystals vary in the total number of intramolecular interactions and the sets of interactions type, even in the case of the substances assigned to the same modifications [*e.g.* (3)-1*A* and (3)-2*A*]. The molecular VDPs obtained for the trimorphic (2) in some cases have the same number of intramolecular interactions [$^{>1}k$ values = 72 for (2)-1*A*, (2)-3*A*, (2)-4*A*, (2)-6*B*, Table 2]. Nevertheless, in accordance with the *k*–Φ criterion only the (2)-3*A* and (2)-4*A* pair is characterized by $^{>1}\Phi = 0$ and, hence, contains the molecules with identical conformations. All the remaining pairs of polymorphs with the same $^{>1}k$ are characterized by different sets of non-bonded intramolecular interactions. Let us cite the (2)-2*A* and (2)-5*B* pair of polymorphs as an example. The polymorphs have the same $^{>1}k = 71$, but in the latter case one additional C/O and one C/C interaction with RC = 6 and 2 appear, respectively, whilst H/C and H/H interactions with RC = 2 and 4 disappear (Table 4). Thus, $^{>1}\Phi = 4$ for this pair of polymorphs. In the same way, the (2)-3*A* and (2)-4*A* or (2)-6*B* and (2)-1*A* pairs are characterized by $^{>1}\Phi = 7$ or 10 (Table 4). The appearance and disappearance of intramolecular interactions between non-H atoms with RC = 5–7 is illustrated in Fig. 2. Hence, in accordance with the k–Φ criterion, eight structures of (2) contain molecules with seven different conformations.

All polymorphs of (1), (3), (4) or (5) are characterized by a different number of intermolecular contacts per molecule (Table 2), whilst in some crystals of anil (2) the same ^{0}k was obtained. Additional analysis revealed that only (2)-5*B* and (2)-6*B* are characterized by the same number ($^{0}k = 284$) and sets of types of intermolecular interactions ($^{0}\Phi = 0$). The molecule of anil (2)-2*A* in comparison to both (2)-5*B* and (2)-6*B* has the same ^{0}k but $^{0}\Phi = 60$. Three other polymorphs have $^{0}k = 282$ (Table 2), but also vary in the set of intermolecular non-bonded interactions: (2)-1*A* compared with (2)-3*A* or (2)-4*A* is characterized by $^{0}\Phi = 12$ or 16. Thus, from the example of 3-methyl-2-(2′,4′-dinitrobenzyl)pyridine (2) it was quantitatively demonstrated that molecules in the same conformation can pack in a different way [see the crystals of (2)-3*A* and (2)-4*A* with $^{>1}\Phi = 0$ and $^{0}\Phi > 0$], and, *vice versa*, different conformations of a molecule do not prevent a substance from realising the same set of intermolecular contacts [the (2)-5*B* and (2)-6*B* pair with $^{>1}\Phi > 0$ and $^{0}\Phi = 0$].

In accordance with the results obtained each conformational polymorph is characterized by a unique set of intra- and intermolecular contacts. In terms of thermodynamics, the appearance (or disappearance) of some theoretically possible types of non-bonded interactions have an affect on enthalpy, entropy and, finally, Gibbs free energy of a polymorph either for constant or varying conformations in a crystal structure. Thus, each polymorph is at a local minimum of free energy, which depends on the set of non-bonded intra- or intermolecular interactions. Concerning the crystal structure, the appearance (or disappearance) of some theoretically possible types of non-bonded interactions also influence the force field, which has an effect on the neighboring molecules and their energy in crystals of the polymorphs. Taking these facts into account, it is not surprising that even a tenuous change in conformation influences the energies of HOMO and LUMO and, finally, governs the physical properties of various polymorphs.

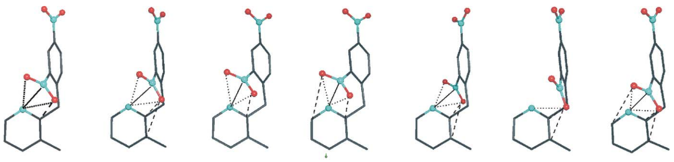
(2)-2*A* (2)-5*B* (2)-1*A* (2)-3*A* (2)-6*B* (2)-8*C* (2)-7*B*

Figure 2
The intramolecular interactions with RC = 5–7 in the structures of (2) between non-H atoms (see also Table 3). The N/N, N/O and C/O interactions are depicted with thin solid, dotted and dashed lines. H atoms are omitted for clarity.

4.2. Photochromic properties of (1)–(5)

The X-ray investigation of photochromic crystalline solids typically allows the initial state of the system, before reaction, to be obtained. Crystallographic determination of the structural changes accompanying the reversible phototransformation of an organic photochromic crystal is still limited by the investigation of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (Harada *et al.*, 1999). Nevertheless, information on the crystal structures of photochromic crystals is expected to extend our understanding of reaction mechanisms. Cohen & Schmidt (1964) postulated that ‘reaction in the solid state occurs with a minimum amount of atomic or molecular movement’. This means that interacting atoms should be close enough to each other in crystal space, or in terms of the MMVDP, that they are able to share a VDP face. Photochromism of (1), (4) and (5) comes from keto–enol tautomerization of the 2-hydroxybenzylideneamino group (Arod *et al.*, 2007; Taneda *et al.*, 2004; Johmoto *et al.*, 2009). It is generally accepted that an enol isomer with an intramolecular hydrogen bond between the hydroxyl group and the N atom undergoes an ultrafast H-atom transfer from the hydroxyl group to the N atom upon photo- or thermoexcitation. Thus, it is expected to be accompanied by the presence of a common H/N face between VDPs of the H atom of the hydroxy group and the N atom of the amino group. Indeed, such a face is observed in the crystal structures of all polymorphs of (1), (4) and (5). Besides, all *N*-salicylideneanilines are known to be photo- or thermochromic and intramolecular O—H···N bonds (and, as a result, H/N faces) are observed in their structures.

Photochromism of (2) and (3) is attributed to the intramolecular transfer of the benzylic proton to the pyridyl nitrogen (N*) *via* an aci–nitro intermediate (Eichen *et al.*, 1997; Naumov & Ohashi, 2004; Naumov & Sakurai, 2005; Scherl *et al.*, 1996; Schmidt *et al.*, 1999). Two of six polymorphs of (2) and (3), namely (2)-8*C* and (3)-3*B*, are photoinactive. Scherl *et al.* (1996) and Schmidt *et al.* (1999) propose a π–π interaction between pyridine and phenyl rings to be the reason for the photoinactivity. Besides some properties can be affected by a change in activation energy for proton elimination from the methylene moiety, which depends on the superposition of atoms in an active N*—C—CH$_2$—C—C—NO$_2$ moiety (Fig. 3*a*) including the CH$_2$ group, an oxygen of the NO$_2$ group and the N* (Scherl *et al.*, 1996). At last, Schmidt *et al.* (1999) suggested that (2)-8*C* and (3)-3*B* are photoinactive due to steric hindrance, which prevents the rotation of a nitro group involved in the formation of an intermediate.

In accordance with results of the MMVDP, (2)-8*C* and (3)-3*B* modifications contain intermolecular non-bonded interactions of the N/N type in their crystals (Tables 3 and 2S of the supplementary material). *Vice versa*, contacts of this type are not observed in photochromic (2) and (3). Each molecule of (2)-8*C* and (3)-3*B* is involved in four intermolecular interactions between an N atom of a nitro group and the N* atom with r(N···N) = 3.56–4.11 and 3.34–3.48 Å, respectively. At the same time, in the molecules of the photochromic (2) and (3) an intramolecular N/N contact is observed with r(N···N*) = 2.86–3.15 and 2.87–3.00 Å. Taking this contact into account, the $\mathrm{N^*{-}C{-}CH_2{-}C{-}C{-}NO_2}$ moiety should be represented as a six-membered ring (Fig. 3*a*). One may suggest that the appearance of this contact and, hence, a six-membered cycle is specific to the initial stage of a solid-state reaction of proton transfer by a nitro group from the C atom to the N atom of the pyridine cycle. Intermolecular N/N bonding between the same N atoms ($-\mathrm{NO_2}$ and N*), which is observed in crystals of (2)-8*C* and (3)-3*B* (Fig. 3*b*), prevents the formation of a favored initial stage and probably causes the formation of an alternative channel of energy dissipation and, hence, may lead to the disappearance of the photochromic effect. At the same time, additional analysis revealed that photoinactive polymorphs of (2), (3) and (5) are more involved in π–π interactions than their photochromic analogues. This fact is in good agreement with the assumption of Scherl *et al.* (1996) and Schmidt *et al.* (1999). As can be seen from Table 3 and Table 2S of the supplementary material, in the case of photoinactive anils (2)-8*C*, (3)-3*B* and salicylideneaniline (5)-3*C* the relative contributions of intermolecular C/C interactions (which can be assigned to stacking contacts) to the molecular surface area are 1.5–7 times larger than in their photochromic polymorphs. Hence, within the terms of the MMVDP two versions of photoinactivity of (2)-8*C*, (3)-3*B* and (5)-3*C* can be suggested.

5. Conclusions

Analysis of conformational polymorphs with $C_wH_xN_yO_z$ compositions combined with the data for polymorphs of ferrocene (Serezhkin, Shevchenko & Serezhkina, 2005) and $C_wS_uH_xN_yO_z$ (Serezhkin *et al.*, 2011; Serezhkin & Serezhkina, 2012; including seven structures of polymorphs of the well known ROY, 5-methyl-2-[(2-nitrophenyl) amino]-3-thiophenecarbonitrile {QAXMEH} Yu *et al.*, 2000; Chen *et al.*, 2005) within the method of the molecular Voronoi–Dirichlet polyhedra revealed that the change in conformation of a molecule is accompanied by the realisation of various sets of interatomic non-bonded interactions and can be evaluated quantitatively. The conformation and orientation of a molecule in a crystal correlate with each other and depend on the conditions of crystallization (pressure, temperature and the solvent). These are the key factors in polymorphism of molecular organic and metal-organic compounds. A number of examples have been obtained recently illustrating McCrone's opinion (McCrone *et al.*, 1965) 'that every compound has different polymorphic forms and that, in general, the number of forms known for each compound is proportional to the time and money spent in research on that compound'. Taking into account that the number of new modifications of substances is expected to increase, there is the need for approaches capable of analyzing a large number of substances to reveal the conformational polymorphs automatically and to measure the difference between conformations quantitatively. The method of the molecular VDPs and the k–Φ criterion proved to be useful in revealing polymorphs. Indeed, each structure is characterized by a unique and unambiguous Voronoi–Dirichlet tessellation. The method has no need for any van der Waals radii and measures the number and relative contributions of all types of non-bonded interactions to the area of the molecular surface, both inter- and intramolecular, quantitatively. Thus, in our opinion this approach would be helpful in the analysis of inter-

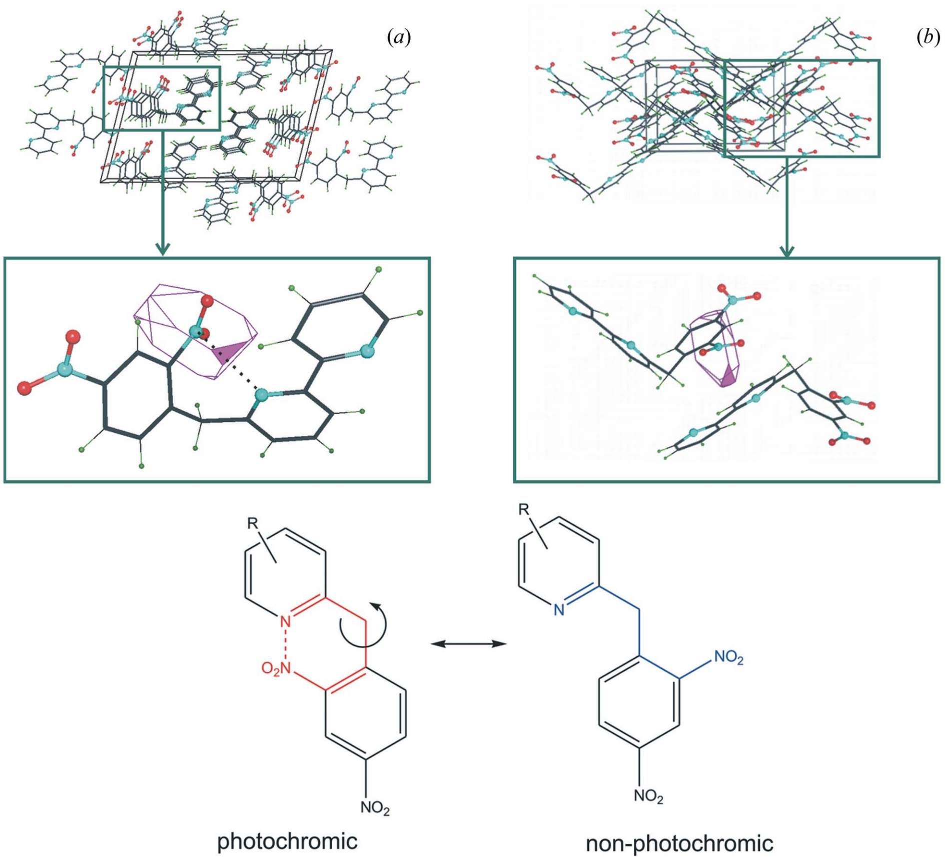

Figure 3
Fragment of crystal structures and observed N/N contacts in the structures of (*a*) (3)-1*A* and (*b*) (3)-3*B*. The VDP faces corresponding to the N/N interactions are marked with magenta.

relationships between the structure and properties of molecular polymorphic crystals.

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