Packing Modes in Nitrobenzene Derivatives. I. The Single Stacks

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Abstract

The crystal packing modes of nitrobenzene derivatives, compounds classified as BCLASS = 15 by the Cambridge Structural Database (CSD), have been analysed. Several packing modes have been observed, although two of them, the so-called stacks and pseudo-herringbone, appear as the most populated ones. In 28.4% of the 169 structures that fulfilled the conditions of the search, the molecules are packed to form columns, with the aromatic planes almost parallel. Different ways of stacking within the columns and the way in which these columns pack together to give the whole crystal have been analysed.

1. Introduction

This work is aimed to analyse, characterize and attempt to parametrize the modes of packing of some molecular crystals in a similar way as was carried out previously for purines and pyrimidines (Motherwell & Isaacs, 1972; Motherwell, Riva di Sanseverino & Kennard, 1973). A small family was chosen in order to simplify the problem. The CSD offers a basic chemical classification, initially developed to aid chemical searches (CSD: Allen *et al.*, 1991); even if the classes proposed are very general and in spite of the fact that they suffer from some drawbacks, it appears to be an easy way to define the working subgroup. Class 15 of the CSD, corresponding to nitrobenzene-containing compounds, was chosen; however, it has to be remarked that this class appears incomplete since the CSD classification prioritizes the functional groups present in the compounds and does not classify a compound into several different classes.

It has often been reported in the literature that many planar or nearly planar molecules form columns with stacks of approximately parallel molecular planes separated by interplanar distances in the 3.3–3.6 Å range [the sum of the van der Waals radii of the two C atoms constituting the aromatic ring is 3.4 Å (Bondi, 1964)]; the successive partners forming the stacking may simply define a translation operation that sets a unit-cell axis corresponding to the shortest unit cell and having a value of approximately 4 Å; these structures may be called β structures (Schmidt, 1964; Desiraju, 1987, 1989; Gavezzotti & Desiraju, 1988). Another possibility is the formation of stacks of successive molecules giving

rise to symmetry operators distinct from translation (and then called non-β structures as opposite to the translation case and in spite of the translation length), as has been described by Sarma & Desiraju (1986). The partners may
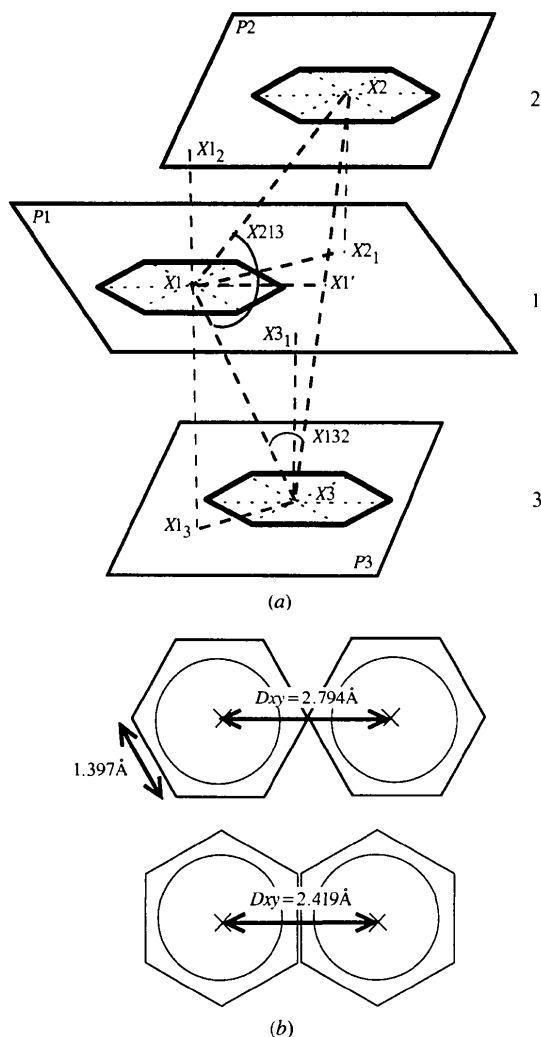

Fig. 1. (*a*) Stack parameter description. *X*: aromatic ring centroid; *Xij*: orthogonal projection of the aromatic ring centroid *i* on one adjacent aromatic ring plane *j*; *X1′*: intersection of the plane *P1* with the line *X2X3*; *P*: aromatic ring plane. (*b*) Down-the-stack view of the two limit cases of aromatic ring–aromatic ring overlap (values of phenyl C—C bond lengths taken from Allen *et al.*, 1987).

1- Are the two consecutive aromatic rings (1 and 2) of the stacking related by translation operations along the unit-cell axes?
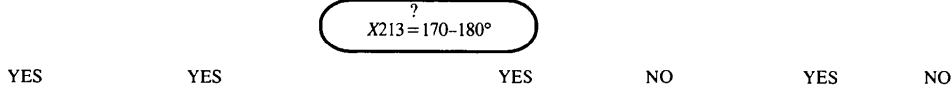
YES   NO

β-structures (B)   Non β-structures (N)

2- Is there any lateral translation ($X1X2_1$ and $X3X1_3$ distances non null) between the centroids of two consecutive rings 1 and 2 or 1 and 3?

$$X1X3 \overset{?}{\neq} X3P1$$
$$\text{or}$$
$$X1X2 \overset{?}{\neq} X1P2$$

NO   2/3   YES   NO   2/3   YES

1

B1   B2   N1   N2
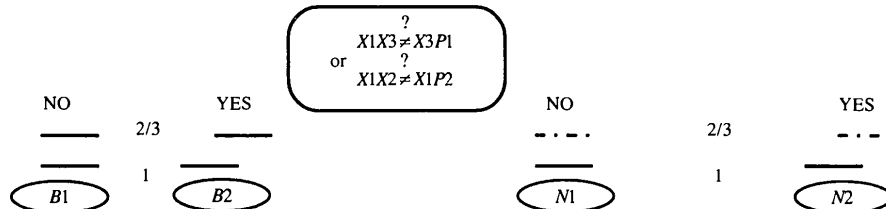
3- Is there any lateral translation of the centroids between aromatic rings 2 and 3?

$$X2X3 \overset{?}{\neq} X3P2$$

NO   2   YES   NO   2   NO   YES   YES

1   1

3   3

B1   B2   N1   N2a   N2b   N2c
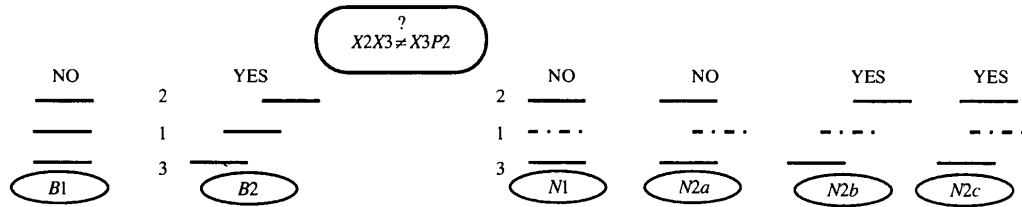
4- Are the three centroids $X1$, $X2$ and $X3$ aligned?

$$X213 \overset{?}{=} 170{-}180°$$

YES   YES   YES   NO   YES   NO

5- Is the environment similar on the two sides of the aromatic ring 1 (with rings 2 and 3 within the stack)?

$$\text{either} \quad X1X2 \overset{?}{=} X1X3$$
$$\text{or} \quad X1P2 \overset{?}{=} X3P1$$

YES   YES   YES   YES   YES   YES

2   2   2

1   1   1

3   3   3

B1   B2   N1/hom   N2a/hom   N2b/hom   N2c/hom

NO   NO   NO   NO

2   2   2   2

1   1   1   1

3   3   3   3
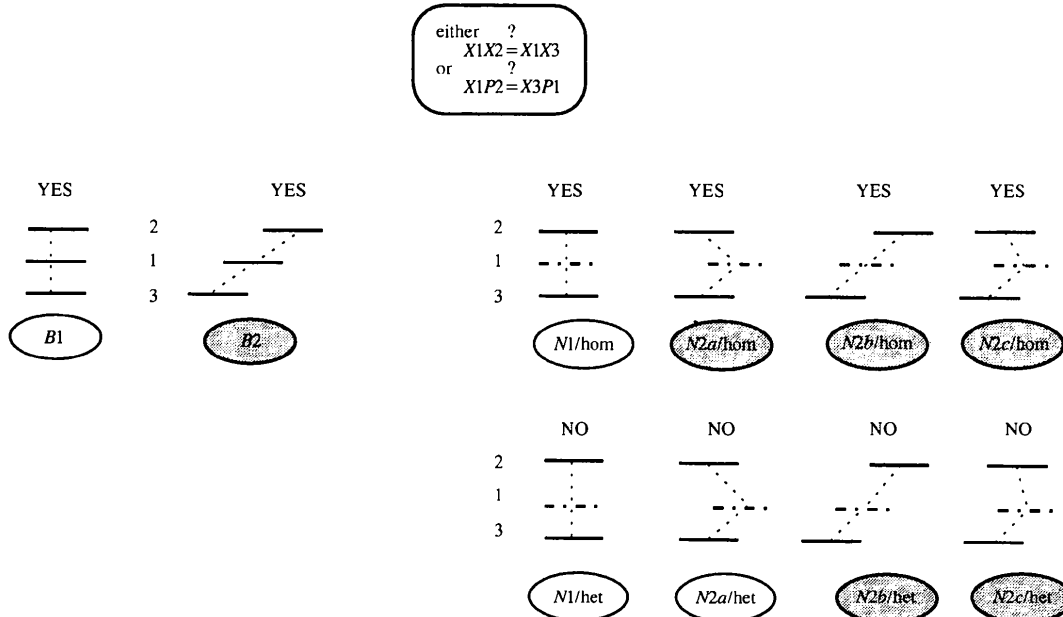
N1/het   N2a/het   N2b/het   N2c/het

Fig. 2. Procedure followed to distinguish different types of single stacks. [For clarity of the scheme, aromatic rings have been symbolized by parallel lines. Continuous lines symbolize molecules related by unit-cell translations and broken lines schematize molecules related to those indicated by continuous lines by symmetry operations different than translations. Numbers 1–3 correspond to the label of the aromatic rings described in Fig. 1(a). The quality of the tests means a difference of less than 0.01 Å.]

Table 1. *Geometrical parameters for homogeneous stacks*

Refcode	P1P2 (°) P1P3 (°)	X1X2 (Å) X1X3 (Å)	X1P2 (Å) X3P1 (Å)	X2X3 (Å)	X3P2 (Å)	X213 (°)	X132 (°)	Dxy (Å)	Overlap
B2 group									
JAZLAX	0.0	3.85	3.49	7.70	6.98	180.0	0.0	0.00	W
DUXSIY	0.0	4.04	3.50	8.08	7.01	180.0	0.0	0.00	W
GACGAS	0.0	4.04	3.66	8.08	7.32	180.0	0.0	0.00	W
QQQECG01	0.0	5.74	4.11	11.48	8.22	180.0	0.0	0.00	W
HIBWEU	0.0	3.87	3.45	7.74	6.90	180.0	0.0	0.00	W
PMNTBZ	0.0	5.37	3.78	10.74	7.56	180.0	0.0	0.00	W
HECDOI	0.0	5.42	4.09	10.84	8.18	180.0	0.0	0.00	W
YUYLEJ	0.0	4.84	3.35	9.68	6.70	180.0	0.0	0.00	W
N2a/hom									
SAZHAC†	0.0	4.34	3.96	7.93	7.93	131.8	24.1	1.77	AR/AR
	0.0	4.33	3.96	7.93	7.93	132.8	23.6	1.73	AR/AR
NOMESL	0.0	4.99	3.63	7.26	7.26	93.4	43.3	3.42	AR/S
JAVGAO	0.0	4.81	3.44	6.88	6.88	91.3	44.4	3.36	AR/S
N2b/hom									
ZZZFYW01	1.9	3.72	3.63	7.42	7.26	170.2	4.9	0.32	W
N2c/hom									
CIGGII	2.2	3.84	3.39	7.04	6.78	133.3	23.3	1.52	AR/AR
FALPEN	7.8	4.29	3.57	7.86	7.14	132.7	23.7	1.72	AR/AR
NACPON10‡	1.7	4.87	3.32	9.09	6.65	137.9	21.0	1.75	AR/AR
DOHCOS	4.8	5.04	4.12	9.23	8.24	132.5	23.7	2.03	AR/AR
HALJUZ	2.1	5.72	4.76	11.35	9.51	166.1	7.0	0.70	AR/AR
SEMTAF	3.2	3.82	3.54	7.15	7.08	138.9	20.6	1.34	AR/AR
YOHFAC	10.5	5.24	3.32	10.23	6.64	154.4	12.8	1.16	AR/AR

PiPj (*i,j* = 1,2,3) represents the angle between planes *i* and *j*, which are equal, *XiXj* the distance between centroids *i* and *j*, and *XiPj* the average distance between the centroid *Xi* and its orthogonal projection on *Pj* and the centroid *Xj* on *Pi*. *Xij*1 represents the angle between the vectors defined by the centroids **XjXi** and **XjX1**. *Dxy* represents the offset of the aromatic rings along the stack. The abbreviations used to define the overlap are W: whole aromatic ring overlap; AR/AR: aromatic ring–aromatic ring overlap; AR/S: overlap involving aromatic rings and substituents. † For the SAZHAC case, there are two different stacks in the packing, although equivalent within experimental error. ‡ Both homogeneous and heterogeneous stacks are found along two different directions of the NACPON10 structure.

Table 2. *Geometrical parameters for heterogeneous stacks*

Refcode	P1P2 (°) P1P3 (°)	X1X2 (Å)	X1X3 (Å)	X1P2 (Å)	X3P1 (Å)	X2X3 (Å)	X3P2 (Å)	X213 (°)	X132 (°)	Dxy (Å)	Overlap
N2b/het											
FULYEQ10	0.0	4.12	4.21	3.90	3.97	8.33	7.88	175.1	2.4	0.18	W
N2c/het											
NACPON10†	0.0	5.87	5.40	3.44	2.92	10.07	6.36	126.5	27.9	2.53	AR/S
BAFLEZ	0.0	4.96	4.10	3.42	3.72	8.47	7.15	138.3	22.9	1.72	AR/AR
VACBAC	0.0	4.98	4.50	3.81	4.07	8.88	7.89	138.8	21.7	1.71	AR/AR
ZIKTES	0.0	3.67	4.48	3.44	3.43	7.77	6.87	144.6	15.9	1.30	AR/AR
LEBGEE	0.0	5.90	3.67	3.24	3.46	8.28	6.70	117.8	39.1	2.72	AR/S
FABHOF	0.0	4.30	4.04	3.63	3.46	7.29	7.09	121.9	30.0	2.02	AR/AR + AR/S
TAFZAB	0.0	4.40	6.36	3.58	3.34	8.28	6.93	99.1	31.6	3.63	AR/S
SARXUE	0.0	5.45	6.66	3.03	3.23	9.30	6.26	99.9	35.3	3.90	AR/S

PiPj (*i,j* = 1,2,3) represents the angle between planes *i* and *j*, which are equal in most cases, *XiXj* the distance between centroids *i* and *j*, and *XiPj* the average distance between the centroid *Xi* and its orthogonal projection on *Pj* and the centroid *Xj* on *Pi*. *Xij*1 represents the angle between the vectors defined by the centroids **XjXi** and **XjX1**. *Dxy* represents the offset of the aromatic rings along the stack. The abbreviations used to define the overlap are W: whole aromatic ring overlap; AR/AR: aromatic ring–aromatic ring overlap; AR/S: overlap involving aromatic rings and substituents. † Both homogeneous and heterogeneous stacks are found along two different directions of the NACPON10 structure.

also be molecules of a different nature which are intercalated when forming binary complexes (Dahl, 1994). In the present case the possibility of complexes is eliminated by the criteria imposed on NRES of the CSD search, the number of chemical residues; therefore, the stackings would be either the *β* or non-*β* structures.

The interplanar distance within the stack is often used to evaluate the strength of the interactions involved, but some authors have remarked upon the lack of a systematic relationship between this parameter and the interactions (Prout & Kamenar, 1973); indeed, the interactions involved within the stacking may be of a

different nature, not only π–π (Burley & Petsko, 1985; Hunter & Sanders, 1990) or other attractive interactions, but also repulsive ones involving bulky substituents that could increase the interplanar distance (Dahl, 1994). Thus, we have enlarged the interaction range by taking into account stacks having interplanar and intercentroid

distances greater than those allowed by the π–π interactions; in the case of the stacks where the constituent molecules are defining a translation, we preserved the β structures nomenclature, but with the proviso in mind that the criteria of the 4 Å short axis (Schmidt, 1964; Desiraju, 1987, 1989; Gavezzotti &

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)
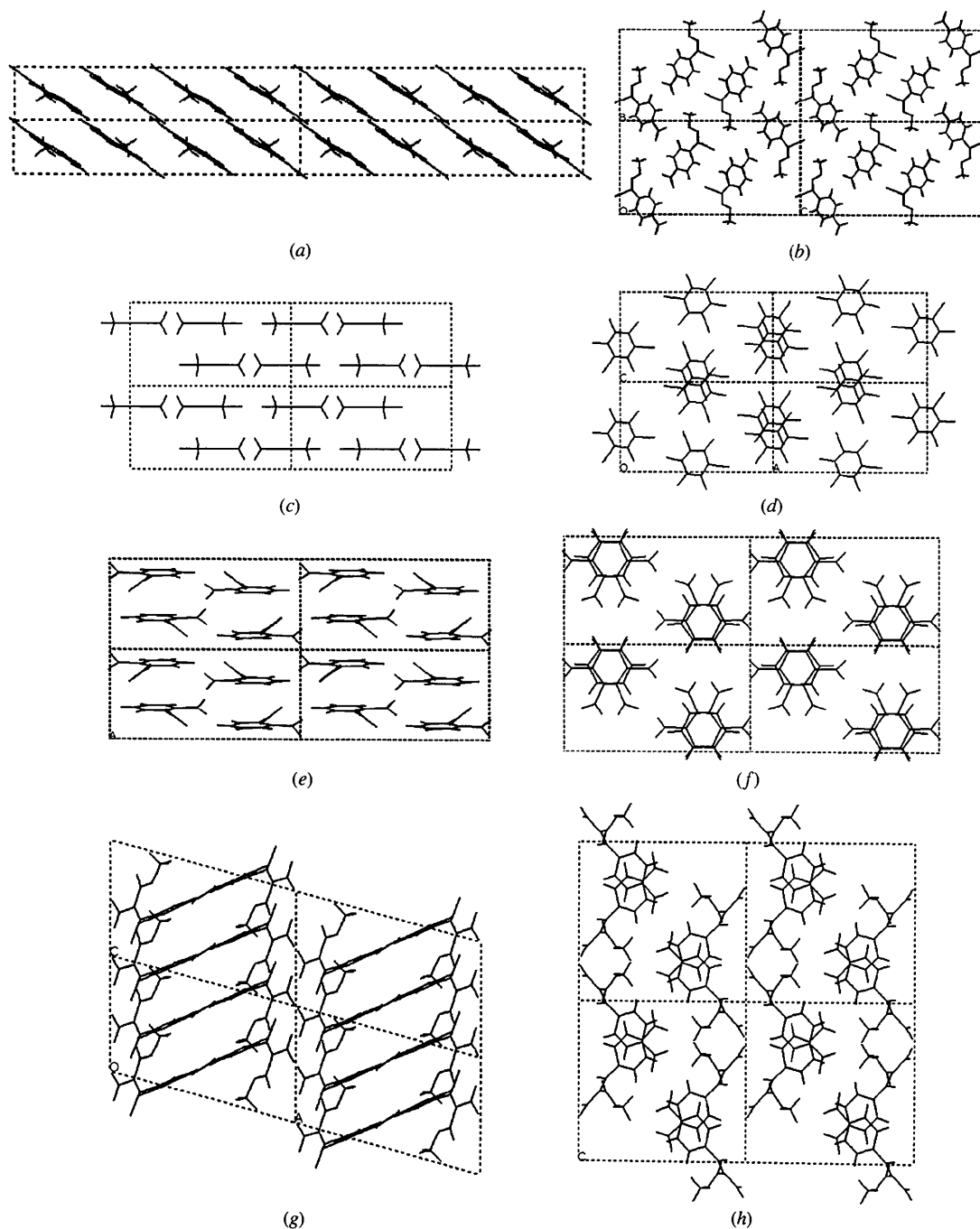
Fig. 3. Crystal packings for homogeneous stacks: view of the stacks perpendicular to the stack direction and view down the stack direction. (a) and (b) B2 type: DUXSIY [(E)-o-methyl-p-nitrobenzohydroximoyl]. (c) and (d) N2a/hom type: SAZHAC (m-dinitrotetramethylbenzene). (e) and (f) N2b/hom type: ZZZFYW01 (1,2-dinitrobenzene). (g) and (h) N2c/hom type: FALPEN [(E)-β-chloro-α-(methoxycarbonyl)-p-nitrocinnamaldehyde].

PACKING IN NITROBENZENES. I.

Table 3. *Pattern types for homogeneous stacks*

Refcode	Space group	d1 (Å) d4 (Å)	d (Å) d3 (Å)	α1 (°) α3 (°)	α2 (°)	α4 (°)	Pattern type
B2							
JAZLAX	$P2_1$	7.60	9.84	48.3	99.7	163.8	I(a)
HIBWEU	$P2_1/m$	6.91	10.52	41.3	81.1	163.7	I(a)
QQQECG01	C2/m	6.77	6.77	86.0	94.0	94.0	II
PMNTBZ	P1	8.96	11.68	105.3	74.7	74.7	III
HECDO1	P1	6.68	8.18	73.1	108.6	105.9	~III
DUXSIY	$P2_1/c$	7.20	18.00	112.0	35.7	100.3	I(b)
GACGAS	$P2_1/c$	7.73	19.33	113.3	35.2	98.3	I(b)
YUYLEJ	$P2_1/n$	12.10	9.58	101.4	89.5	67.8	I(b)
N2a/hom							
SAZHAC	$P2_1/m$	8.95	8.92	119.8	60.2	60.2	II
NOMESL	$Pna2_1$	8.66	8.66	58.1	121.9	121.9	II
JAVGAO	$P2_1/m$	9.59	14.44	79.9	100.1	100.1	III
N2b/hom							
ZZZFYW01	$P2_1/c$	7.99	7.29	62.5	126.1	108.7	~I(a)
N2c/hom							
CIGGII	$P2_1/c$	7.76	11.73	45.2	82.7	179.1	I(a)
YOHFAC	$P2_1/c$	6.78	9.34	80.2	78.7	121.3	~I(a)
FALPEN	$P2_1/c$	7.81	10.15	93.7	72.4	100.2	I(a)
NACPON10†	$P2_1/c$	6.48	6.74	99.3	78.8	82.6	I(a)
DOHCOS	$P2_1/a$	8.63	9.75	105.2	69.4	80.1	I(a)
HALJUZ	Ia	8.88	8.88	104.7	75.3	75.3	II
SEMTAF	Pbca	7.59	18.36	59.6	48.6	167.7	I(b)

† Both homogeneous and heterogeneous stacks are found along two different directions of the NACPON10 structure.
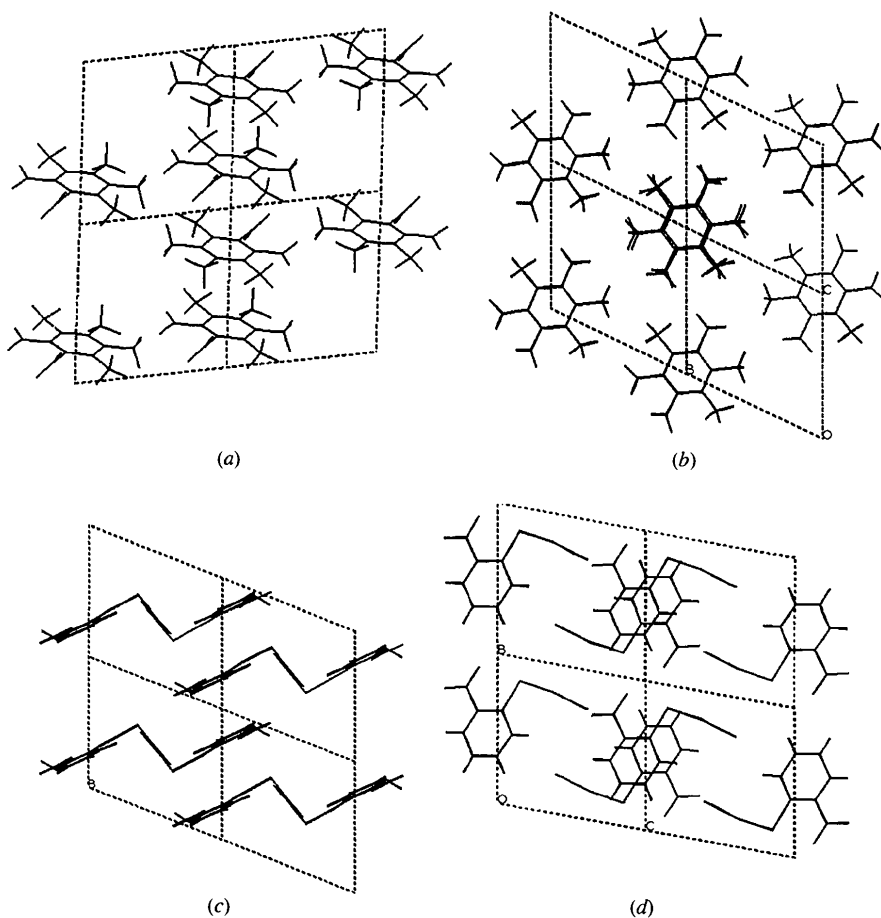

(a)

(b)

(c)

(d)

Fig. 4. Crystal packings for heterogeneous stacks: view of the stacks and view down the stacks. (a) and (b) *N2b*/het type: FULYEQ10 (o-dinitrotetramethylbenzene). (c) and (d) *N2c*/het type: ZIKTES (2-nitrobenzenesulfenyl thiocyanate).

Table 4. *Pattern types for heterogeneous stacks*

Refcode	Space group	$d1$ (Å) $d3$ (Å)	$d2$ (Å) $d4$ (Å)	$\alpha1$ (°) $\alpha3$ (°)	$\alpha2$ (°) $\alpha4$ (°)	Pattern type
N2b/het						
FULYEQ10	$P\bar{1}$	9.06	14.61	92.1	87.9	III
N2c/het						
NACPON10†	$P2_1/c$	6.24	6.24	93.5	86.5	II
FABHOF	$P2_1/c$	9.07	9.07	112.0	68.0	II
BAFLEZ	$P\bar{1}$	9.44	13.52	95.9	84.1	III
VACBAC	$P\bar{1}$	12.26	10.99	95.3	84.7	III
ZIKTES	$P\bar{1}$	9.51	12.55	91.5	88.5	III
LEBGEE	$P\bar{1}$	12.38	12.46	109.1	70.9	III
TAFZAB	$P\bar{1}$	13.15	8.07	93.4	86.6	III
SARXUE	$P\bar{1}$	12.12	10.77	93.5	86.5	III

† Both homogeneous and heterogeneous stacks are found along two different directions of the NACPON10 structure.

Desiraju, 1988) is not fulfilled in all cases. Indeed, the short axis length has been shown to be an insufficient criterion in some cases to discriminate different modes of packings (Goddart, Haenel, Herndon, Krüger & Zander, 1995).

2. Methodology: database searches

The crystallographic information used was retrieved from the Cambridge Structural Database (CSD: Allen *et al.*, 1991). Searches were performed with the April 1996 Version 5.11, including the following *QUEST* and acceptance criteria: BCLASS = 15, corresponding to benzene nitro compounds, without disorder, RFAC (conventional R factor) $\leq$ 10%, ZPRIME (number of molecules per asymmetric unit) $\leq$ 1, RES (number of chemical residues) $\leq$ 1, ERROR-FREE coordinate sets.

Depicted refcodes were located, checked by hand and not included. The 3D (three-dimensional) geometrical searches were carried out with the help of the *QUEST3D* program (Cambridge Structural Database, 1992).†

The general search fragment with three rings that allowed us to describe the environment of one molecule within a single columnar stack is shown in Fig. 1(*a*). It seems necessary to establish parameters referred to a fragment common to all the structures, so the aromatic ring was taken as the reference to analyse the structures. Structures having intercentroid contacts, $XiXj$, with the following criteria were searched: $2 \leq X1X2 \leq 6$ Å; $2 \leq X1X3 \leq 8$ Å (different to distinguish asymmetric stacks) and $4 \leq X2X3 \leq 14$ Å.

A parameter (Dxy) was set, corresponding to the distance $X1X1'$, to describe the offset of the aromatic rings along the stack. By using limits for the Dxy values in the range 2.42–2.79 Å, according to the relative

† A list of CSD refcodes and figures corresponding to the different crystal packings have been deposited with the IUCr (Reference: BM0008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
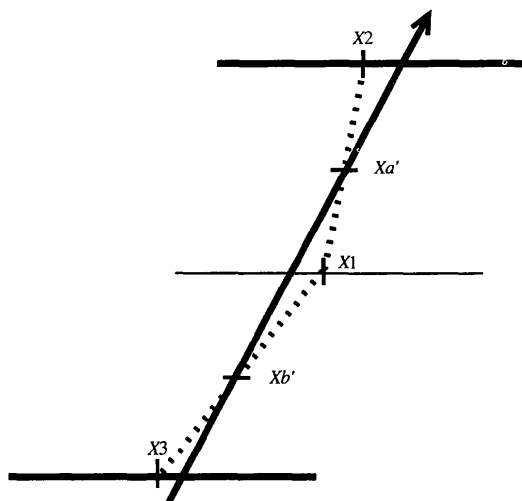

Fig. 5. Stack axis definition. (Parallel lines indicate schematically aromatic ring planes. Whereas aromatic rings drawn in bold are related by a translation operation, those indicated by thin lines can be related to the bold ones by another symmetry operation.) Xa',b': centroids of two adjacent aromatic rings ($X1$ and $X2$; $X1$ and $X3$, respectively).
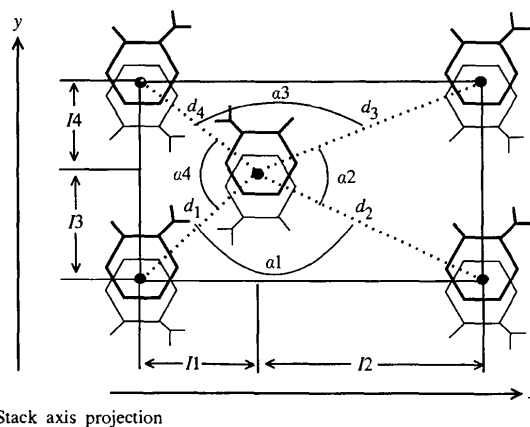

● Stack axis projection

Fig. 6. Projection of the stack axes on the perpendicular plane (x,y) to the column axes. (The orientation of the molecules is arbitrary.)

orientation of the aromatic rings within the stack (Fig. 1*b*), it is possible to distinguish the type of this offset between contiguous rings (rings 1 and 2 or rings 1 and 3) down the $X2X3$ line of the stack, that is, the overlap between aromatic rings from those involving the aromatic ring and substituent, of substituent–substituent. The distances between $X1$ and $X2_1$ and $X3$ and $X1_3$ (Xi_j being the orthogonal projection of Xi on Pj) describe the orthogonal slip between two consecutive aromatic rings within the stack. Other geometrical parameters describing the stack were calculated, such as the aromatic ring centroid distances ($X1X2$, $X1X3$, $X2X3$), the interplanar distances ($X1P2$, $X3P1$, $X3P2$), the interplanar angles ($P1P2$, $P1P3$) and the angles ($X213$ and $X132$) between vectors formed by the centroids.

3. Results and discussion

3.1. Single stack mode

As a result of the CSD search, 169 structures fulfilled the criteria given above. A preliminary estimate of the
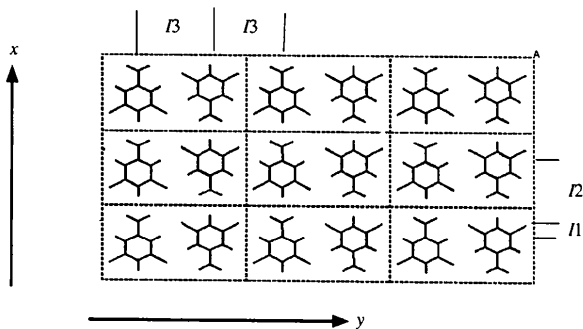

Fig. 7. An example of the crystal packings corresponding to type I(*a*) (only homogeneous stacks; HIBWEU, 3,5-dichloronitrobenzene). The separations between columns are represented as indicated in Fig. 6.

similarities in their 3D packing modes allowed a first classification: 27 structures were grouped as a first mode with common features, describing 'single stacks' composed of molecules having near-parallel aromatic rings (within 20°) within the stack, and forming angles smaller than 20° with the rings in the neighbour stacks. Another 21 structures, forming a similar stacking pattern, but with molecules bearing a second aromatic ring, which could form a second stack in some cases, were grouped in another mode. Another seven structures are classified as layered. Structures forming stacks but with interstack angles greater than 20° (a total of 56 structures) are described in the following article in this issue (André, Foces-Foces, Cano & Martinez-Ripoll, 1997), as well as the molecular packing of the remaining structures.

Within a single track, and in order to classify the different types observed using the geometrical parameters defined above, the procedure described in Fig. 2 has been followed. Thus:

The first test distinguishes the stacks containing only molecules related by translation (β structures) from those where the consecutive parallel molecules within the stack are generated by a symmetry operator other than translation (non-β structures).

The second test (Fig. 2) differentiates the case where two consecutive rings within a stack are superposed exactly from where the molecules are laterally displaced. Recent studies based on *ab initio* calculations of benzene dimers show that for the stacking situation the most stable dimer corresponds to a displaced parallel one (Jorgenson & Severance, 1990; Tsuzuki, Tadafumi, Masuhiro & Tanebe, 1996); the distance between two adjacent centroids ($X1X2$ or $X1X3$) is then different from that between the two planes containing these two centroids ($X1P2$ or $X3P1$). No cases of exact superposition have been observed, probably for the reason given previously; moreover, this arrangement is unfa-
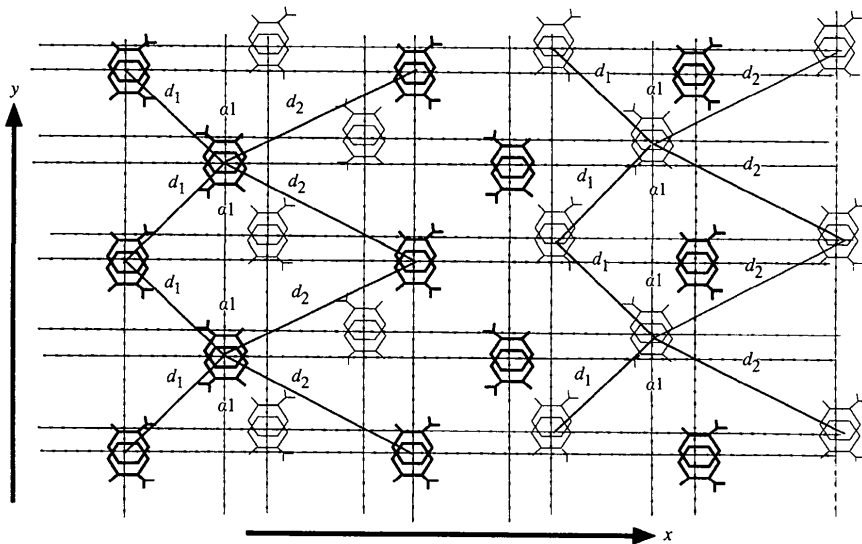

Fig. 8. Pattern type I(*b*) (the orientation of the molecules is arbitrary).

vourable with respect to the close-packing principle (Kitaigorodsky, 1973); because of the 'bumpiness' of aromatic rings, it has been shown that the optimum stacking involves packing the bumps of one ring into the depressions of the adjacent one (Desiraju, 1989; Wright, 1987).

The third test (Fig. 2) is similar to the second, but considers two non-adjacent molecules. In this case, the distance between two non-adjacent centroids ($X2X3$) is compared with that between the two planes containing these two centroids ($X3P2$).

The fourth test (Fig. 2) differentiates the stack patterns where the three consecutive centroids ($X2$, $X1$ and $X3$) are aligned and somehow overlapped, so the angle subtended at the central centroid ($X213$) has to be around 180° and the Dxy value quite low; it does not imply the exact superposition of the aromatic rings. This alignment is always accomplished by the β structures, where the translation relation implies a superposition of the molecules along its direction.

The fifth test (Fig. 2) distinguishes different stacks according to the interplanar separations within the stack or according to the centroid–centroid distances ($X1P2$ versus $X3P1$ or $X1X2$ versus $X1X3$); it is then possible to differentiate the stacks with homogeneous (hom) from

those with heterogeneous (het) intrastack separations. In the homogeneous case, the same repeat distance along the stack indicates the similarity of the interactions occurring between consecutive aromatic rings. The heterogeneous case indicates different interactions on the two sides of any aromatic ring, usually due to the presence of the substituents, favouring the formation of dimers.

Only six of the arrangements possible for the single stacking were observed in the CSD search of nitrobenzene derivatives (indicated in grey in the scheme of Fig. 2). The values of the geometrical parameters used for the analysis are presented in Tables 1 and 2, and an example of each type of single stacking shown in Figs. 3 and 4. Of the 27 examples classified as $B1$ stacks, $N1$/hom and $N1$/het have not been observed, probably for the reasons described above in the second test. No examples of the $N2a$/het type have been found and only one example of
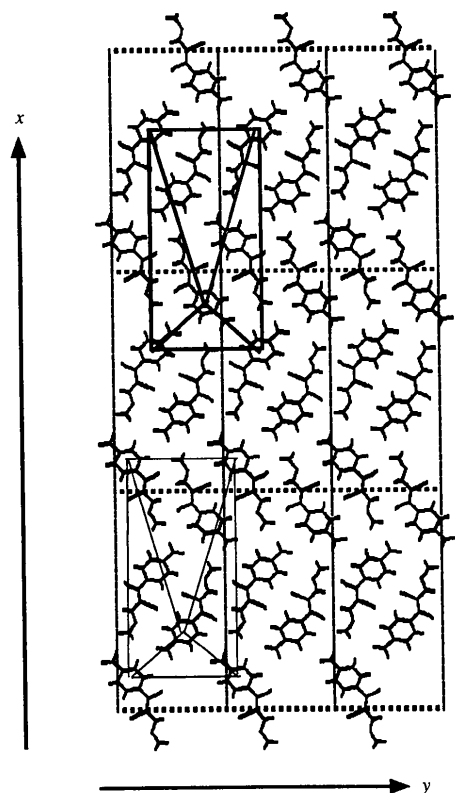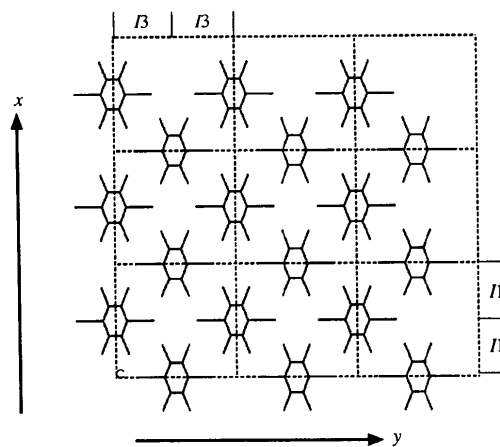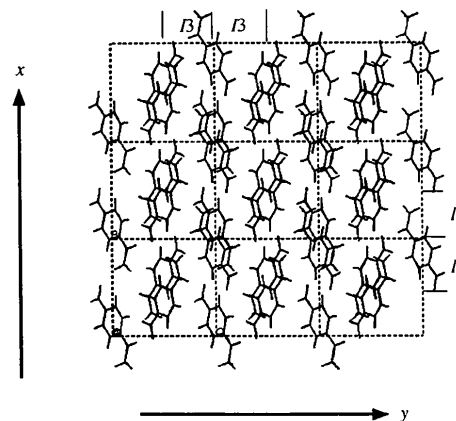
Fig. 9. An example of the crystal packings corresponding to type I(b) [only homogeneous stacks: GACGAS, methyl (Z)-α-cyano-β-hydroxy-p-nitrocinnamate]. A schematic representation analogous to that shown in Fig. 6 is superimposed to classify the type.

Fig. 10. An example of the crystal packings corresponding to type II. (a) Homogeneous stacks (QQQECG01, 1,2,4,5-tetrachloro-3,6-dinitrobenzene); (b) heterogeneous stacks (NACPON10, p-nitroacetophenone). $I1$ and $I3$ are defined in Fig. 6.

each of the N2b/het and N2b/hom types have been observed; N2a/hom is present in only three cases. The most frequently observed types of packing for the single stack mode are B2 (eight cases), N2c/hom (seven cases) and N2c/het (eight cases).

3.2. The single stack environment

In order to proceed further in the study of the single stack mode, a description of the relative position of a single column with respect to its neighbours was required. First, stack axes were defined as shown in Fig. 5, using the centroids Xa' and Xb' of two adjacent aromatic rings ($X1$ and $X2$, and $X1$ and $X3$, respectively). The environment of a single stack (i.e. four nearest neighbours related by translation along the two unit-cell axes) was then studied using the distances and angles defined in Fig. 6. Due to the complexity of the fragment necessary for this search and to the large CPU time required, the geometrical parameters were derived using *CERIUS*3.2 software (Molecular Simulations, 1993), running on a silicon Graphics Indigo workstation. The numerical values of these parameters are given in Tables 3 and 4, but they have been used in a qualitative manner: four general patterns are observed, allowing for a classification of the different crystal packings observed for the single stack mode.

Type I(a) is characterized by two adjacent equal distances ($d2 = d3$, $d1 = d4$ in Fig. 6) and two opposite equal angles ($\alpha1 = \alpha3$). An example of the crystal packing of the structures belonging to this type is plotted in Fig. 7. It can be observed that one of the angles formed between the stacks ($\alpha1$) is propagated along one direction (y) as well as the two distances $d1$ and $d2$. In the other direction (x), two alternative distinct intercolumnar

distances, $I1$ and $I2$, are observed, while in the y direction the same intercolumnar distance, $I3 = I4$, separates the stacks. In Fig. 7 it can be seen that the crystal packing contains layers of stacks, with alternating layers oriented in opposite directions.

Type I(b) involves the previous I(a) type, but with more stacks present in the unit cell; it corresponds in fact to two I(a) motifs, where one is translated with respect to the other (Fig. 8). Using the parameters established in the *Methodology*, only the mutual orientations of the aromatic rings are considered (Fig. 9).

Type II is characterized by $d1 = d2 = d3 = d4$, $\alpha1 = \alpha3$ and $\alpha2 = \alpha4$, but with $\alpha1 \neq \alpha2$ (Tables 3 and 4). These relationships have the effect that the same distances between layers of columns appear along each of the x and y directions, $I1$ in x and $I3$ in y (Fig. 10); thus, each stack is surrounded by four adjacent ones which are related to it by translation.

Type III is characterized by $d1 = d3$, $d2 = d4$, $\alpha1 = \alpha3$ and $\alpha2 = \alpha4$ (Fig. 11). Here any single column is surrounded by other columns which are related to the original one and among themselves by lattice translations; this arrangement is found in the $P\bar{1}$ space group (except for HECDOI, Fig. 12). The same pattern was also observed in type II and it produces an equal intercolumnar distance ($I1$ and $I3$) in each of the two directions x and y, respectively.

In Tables 3 and 4, all the structures have been differentiated firstly according to their single stack type and then by the arrangements of the stacks producing the packing; analysis of the intrastack interplanar distances revealed interesting features. It appears that all the structures presenting heterogeneous interactions on the two sides of aromatic rings correspond to stacks
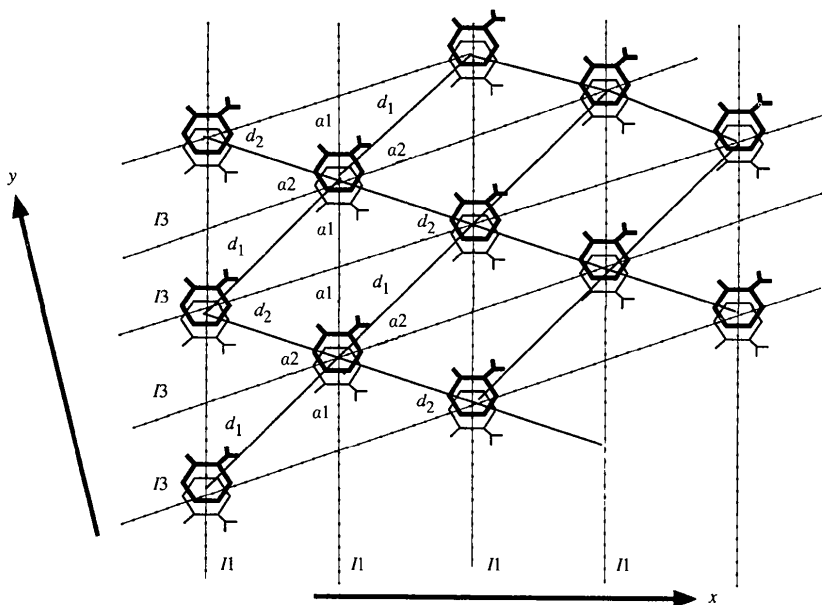

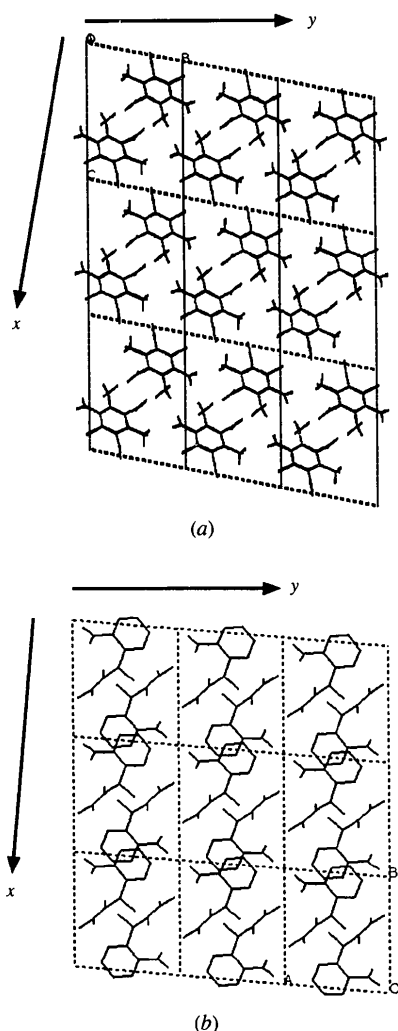Fig. 11. Pattern type III (the orientation of the molecules is arbitrary).

(a)

(b)

Fig. 12. An example of the crystal packings corresponding to type III. *(a)* Homogeneous stacks (HECDOI, 1-bromo-3,5-dimethyl-2,4,6-trinitrobenzene); *(b)* heterogeneous stacks [VACBAC, 3-amino-1-hydroxy-1-(2-nitrophenyl)but-2-ene-2-carbonitrile].

constituted by exactly parallel molecules ($P1P2 = P1P3 = 0°$ in Table 2) and related by two inversion centres, as indicated in Fig. 13(*a*); neighbouring molecules within one stack are arranged in an antiparallel manner. This produced a 'pseudo-symmetrically substituted' column with the same environment on both sides of the column (Fig. 13*b*). Thus, these stacks pack only in the types II and III; due to the 'pseudo-symmetry' of the stacks, no aggregation of the substituents of the same nature on one side of the column is observed and the intercolumnar distances (*I*1 and *I*2) are constant along the *x* and *y* directions.

In the homogeneous stacking case the molecules within the stack are not related by inversion centres, but either by a translation (Fig. 13*d*), a glide plane (Fig. 13*e*) or twofold screw axis (Fig. 13*f*). The homogeneous stacks constituted by molecules related by translation and glide operations are not 'pseudo-symmetrically substituted', except in the case where the molecule is pseudo-symmetrically substituted itself; this is observed for all the homogeneous stacks except in the N2*a*/hom case, where a twofold screw axis relates the molecules constituting the stack (SAZHAC, NOMESL, JAVGAO).

In summary, stacks having homogeneous intrastack interplanar distances are distributed over all the pattern types and no general tendency for an aggregation of the substituents is observed.

3.3. Other stacking modes

Another type of stacking mode has been observed for molecules which are more complex than those which form single stacks, in that they are composed at least of two aromatic rings (not necessarily two nitrobenzene rings). Stacks are formed by two rows of aromatic rings belonging to the same molecule, but these may be inclined at angles between 20 and 90°. The second row of aromatic rings may be involved in a second stack [TD1: two-dimensional stack case 1 (Fig. 14*a*)] or not, as in the
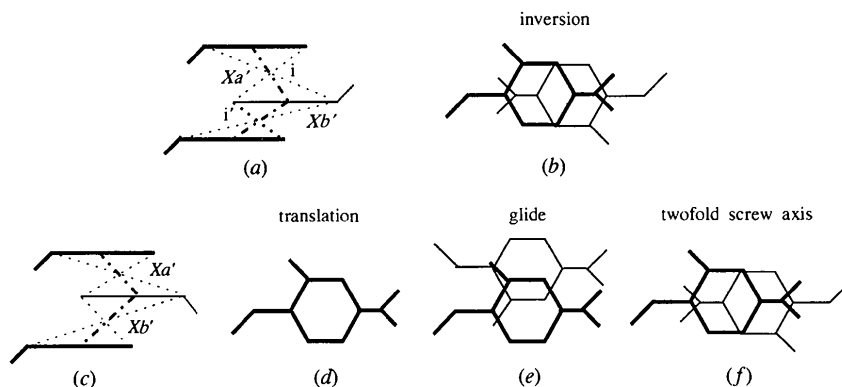

inversion

(a)   *(b)*

translation   glide   twofold screw axis

(c)   *(d)*   *(e)*   *(f)*

Fig. 13. *(a)* Scheme of an heterogeneous stack. *(b)* Schematic downview of an heterogeneous stack. *(c)* Scheme of an homogeneous stack. *(d)*, *(e)* and *(f)* Schematic downview of the different homogeneous stacks observed. [Molecules forming the stack are related by translation operation (*d*), or glide (*e*), or a twofold screw axis (*f*).] *i*, *i'*: inversion centres. *Xa'*,*b'*: centroid of two adjacent aromatic rings (*X*1 and *X*2; *X*1 and *X*3, respectively).

case of type TD2 (two-dimensional stack case 2, Fig. 14*b*).

3.3.1. *TD1 stacks*. This type corresponds to 2D single stacks. Stacks involving one part of the molecule (stack 1) appear segregated from other stacks (stack 2) involving another part of the molecule and oriented in a different direction. Several structures showing inter-planar angles within one stack of greater than 20° (VUKHIS, PNDPHS, DBPETY, HNIABZ11) have been considered, although these could also be considered as herringbone motives. In the case of DETGUE, one stack is constituted by four molecules.

3.3.2. *TD2 stacks*. In most cases the aromatic rings involved in the stack are nitrobenzene rather than any other aromatic rings. These stacks have been analysed in the same way as previously described for the single stacks. In the case of BUDDEJ, the stack is constituted by four molecules.
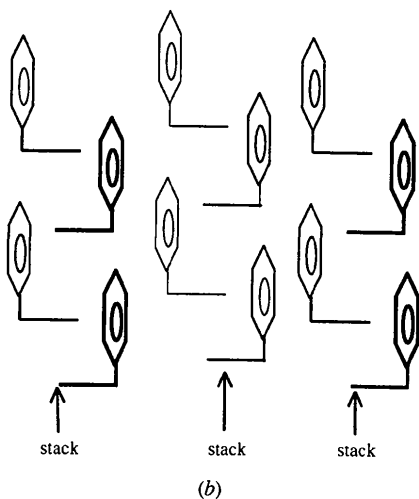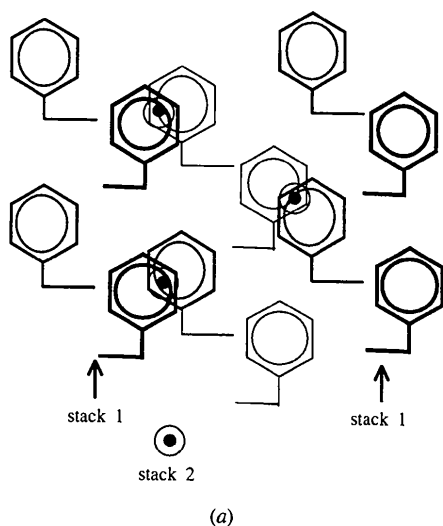

stack 1

stack 2

(a)

stack   stack   stack

(b)

Fig. 14. (*a*) Scheme of the TD1 stacks. (*b*) Scheme of the TD2 stacks.

4. Layers

The seven structures considered in this paragraph (4.1% of the total) do not form 'single stacks', such as those described for the CSD search of Fig. 1. In some cases, as in YOHDUU and SILTOW, the intercentroid distances were larger and in others, no overlap of aromatic rings was observed. For these reasons, these structures were considered as alternating layers. However, it can be remarked that similar layers might also be observed in some 'single stack' cases such as FULYEQ10, JAVGAO, NACPON10, NOMESL, SAZHAC, YOHDUU and ZIKTES.

5. Conclusions

Although the nitrobenzene derivatives studied are simple molecules, they pack in different modes; we have reported here the so-called stacks. Even within single stacks there appear to be ten types, according to the parameters described to characterize the stacks, although only three appear to be commonly populated: these are (*a*) the type with parallel molecules and aligned centroids ($X213 = 180°$); (*b*) the type with parallel molecules with $X213 < 180°$; (*c*) the type with neither parallel molecules nor aligned centroids. The way in which the stacks pack to give the whole crystal has also been described, giving rise to four types, two of them being more frequent. It seems, at least in the present cases, that $\pi \cdots \pi$ interactions are not of crucial importance, since the geometries have values well beyond the sum of the van der Waals radii.

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