

Phase Transitions in Tris(3,5-dimethylpyrazol-1-yl)methane. The Structure of the High-Temperature Phase from X-ray Powder Diffraction

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Abstract

The crystal structure of the sublimated form (m.p. = 424 K) of tris(3,5-dimethylpyrazol-1-yl)methane has been solved by a Patterson search method from laboratory X-ray powder diffraction data. Crystal data: trigonal symmetry with the unit-cell parameters $a = 16.152(1)$ and $c = 5.353(1)$ Å, space group $P3$, $C_{16}H_{22}N_6$, $Z = 3$, 293 K. After indexing the powder pattern by two methods, the unit-cell parameters found were refined by a least-squares technique. A whole pattern-fitting program was used to extract the integrated intensities. The structure was solved taking a related compound as a search model and the final Rietveld refinement converged to $R_{wp} = 0.077$ and $R_p = 0.059$. This study is one of the first examples of Patterson search structure determination from an hemihedral space group using powder data. The complexity of the structural determination is increased by the presence of three molecules in the asymmetric unit.

1. Introduction

Over the last few years the conformations of bis-, tris- and tetrakis(pyrazol-1-yl)methane have been extensively investigated (Claramunt *et al.*, 1989, 1995). These compounds belong to a family of substances with considerable interest as metalloorganic ligands (references 1–9 in Claramunt *et al.*, 1995; Lorente, Etienne & Donnadieu, 1996). One of these compounds, the tris(3,5-dimethylpyrazol-1-yl)methane derivative, exists in two isolable isomers (*ABB* and *BBB*), whose interconversion by melting, crystallization and sublimation is summarized in Fig. 1 (Claramunt *et al.*, 1995). *A* and *B* denote, respectively, ring conformations with the N2 atoms on the same and on the opposite side as the C1–H1 bond (see Fig. 2), taking as a reference the plane which passes through the three N1 atoms bonded to the central C1 atom. In the present work the structural relationship between the two phases *BBB* and *ABB* of the tris(3,5-

dimethylpyrazol-1-yl)methane derivative has been studied. Inspection of Fig. 1 shows that by cooling the *BBB* melt, only crystals of the *ABB* isomer are formed.

Consequently, owing to the difficulty of obtaining single crystals of the *BBB* isomer, only fibrous samples, such as 'cotton-wool', obtained by sublimation were available. The structural study of the *BBB* isomer described in this paper constitutes a complex example of an organic structure solved from laboratory X-ray powder data. The principal experimental difficulties are the limited resolution of the powder diffraction pattern and the peak broadening due to the sample. There are also two additional difficulties which depend on the crystal structure: (a) the systematic peak overlap, as a consequence of the space-group symmetry ($P3$); (b) the presence of three molecules in the asymmetric unit, which increases the complexity of the structure solution and the number of structural parameters in the refinement. For most organic compounds containing rigid-body fragments, all these difficulties can be overcome using Patterson search methods. This methodology allows an accurate determination of the conformation and the molecular packing of the structure, which is the principal information needed for explaining the phase transition.

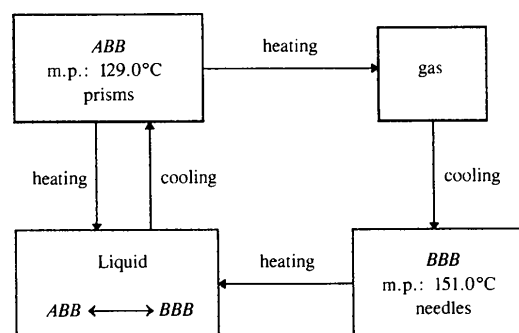


Fig. 1. Phase transitions scheme for tris(3,5-dimethylpyrazol-1-yl)methane (Claramunt *et al.*, 1995).

The only experimental evidence available concerning the structure of the unstable isomer came from ^{13}C NMR [CPMAS technique (Claramunt *et al.*, 1995)]. Comparison of the spectra of both polymorphs shows that the 'individual' molecules of the unstable polymorph must be more 'symmetrical' than those of the stable polymorph; this observation, coupled with semi-empirical calculations, pointed to the *BBB* conformation.

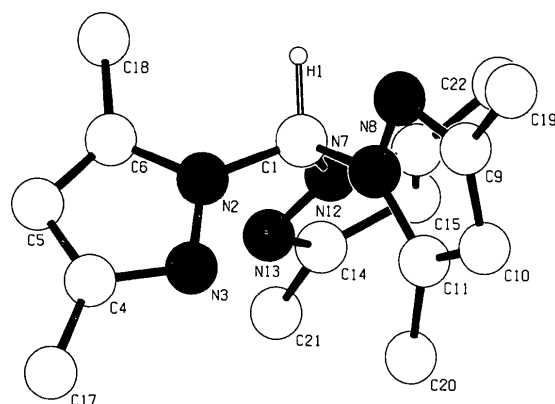
2. Experimental

The title compound was prepared by reacting trichloromethane with the 3,5-dimethylpyrazolate anion in phase-transfer conditions (Claramunt *et al.*, 1989). The compound, being obtained in solution, crystallizes in the m.p. 402 K polymorph (*ABB*). The sample used for this study was obtained by sublimation and its polymorphism checked out by ^{13}C CPMAS NMR (Claramunt *et al.*, 1995) and DSC (differential scanning calorimetry).

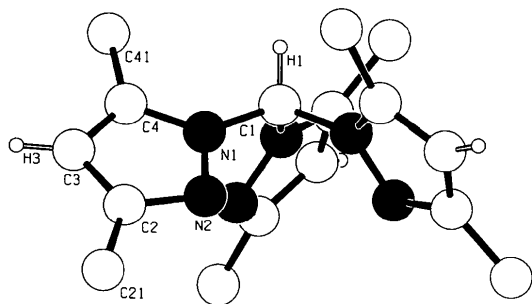
Two powder diffraction data sets were used for the study. For indexing purposes and also to have a reference material for calibration of the second instrument, data set (I) was collected with a high-resolution powder diffractometer (Siemens D500) using Bragg-Brentano geometry.

Pure $Cu K\alpha_1$ ($\lambda = 1.5405981 \text{ \AA}$) radiation was produced with an incident-beam curved-crystal Ge monochromator and asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm). The instrument resolution function has been described elsewhere (Louër & Langford, 1988) and the alignment of the diffractometer was checked with standard reference materials (Louër, 1986). To reduce peak displacements due to the effect of specimen transparency in reflection geometry, a thin layer of the powder was deposited on a silicon plate. The powder diffraction pattern was scanned in steps of 0.02° (2θ) with a fixed counting time of 89 s per step. Peak positions were obtained with the profile fitting program *PROFILE* from Socabim.

The second data set (II) was collected with an INEL cylindrical position-sensitive detector (CPS120), which allows for the simultaneous recording of a powder diffraction pattern over the range 120° . The detector consists of 4096 channels and the angular step is approximately 0.03° (2θ). It was used in a Debye-Scherrer geometry operating with monochromatic $Cu K\alpha_1$ radiation produced with an incident-beam curved quartz monochromator with asymmetric focusing (short focal distance 130 mm, long focal distance 510 mm). The geometrical arrangement has been described elsewhere (Fig. 1 in Louër, Louër & Touboul, 1992). A sample of tris(3,5-dimethylpyrazol-1-yl)methane was introduced in a 0.5 mm diameter Lindemann glass capillary and the data were collected for 60 000 s. During the experiment the sample was rotated around the θ axis to ensure correct averaging of the crystallites. To reduce the effect of the non-angular linearity of the detector, a segmented linear calibration was carried out from the data set (I) of the sample itself, as described in Louër, Louër & Touboul (1992). Diffraction details at angles greater than 45° (2θ) were very poor and, hence, not considered in the structure analysis.



(a)



(b)

Fig. 2. Comparison between (a) the *ABB* (Declercq & Van Meerssche, 1984) and (b) *BBB* (this work) ring conformations, with the corresponding atom labelling in each case.

3. Structure solution

The powder diffraction data [data set (I)] were indexed with the two programs *DICVOL91* (Boultif & Louër, 1991) and *TREOR90* (Werner, Eriksson & Westdahl, 1985). The same hexagonal unit cell, with high figures of merit $M_{20} = 145$ and $F_{20} = 232$ (0.0043, 20) for *DICVOL91* and $M_{20} = 173$ and $F_{20} = 334$ (0.0032, 20) for *TREOR90*, was obtained from both programs. (The greater figures of merit in the second case are due to an automatic correction for axial divergence effects of the position of the first three lines at low angles, on the basis of the positions of higher-reflection orders detected in the pattern.) After a least-squares reviewing of the data available of the pattern, the refined unit-cell parameters were: $a = 16.152(1)$ and $c = 5.353(1) \text{ \AA}$, $V = 1209.4(2) \text{ \AA}^3$. The final figures of merit are $M_{20} = 108$ and $F_{30} = 132$ (0.0060, 38) and the list of observed and

Table 1. *X-ray powder diffraction data of the high temperature phase of tris(3,5-dimethylpyrazol-1-yl)-methane*

<i>hkl</i>	$2\theta_{\text{obs}}$ (°)	$2\theta_{\text{calc}}$ (°)	d_{obs} (Å)	I_{obs}
100	6.299	6.314	14.02	<1
110	10.938	10.947	8.08	100
200	12.642	12.647	7.00	<1
001	16.538	16.547	5.36	1
210	16.748	16.756	5.29	6
101	17.717	17.727	5.00	2
300	19.014	19.019	4.664	33
111	19.880	19.883	4.463	2
201	20.876	20.881	4.252	<1
220	21.991	21.995	4.039	1
310	22.902	22.905	3.880	5
211	23.628	23.634	3.762	3
301	25.308	25.311	3.516	4
400	25.449	25.451	3.497	<1
221	27.650	27.650	3.224	<1
320	27.784	27.778	3.208	1
311	28.387	28.389	3.142	3
410	29.236	29.234	3.052	<1
401	30.497	30.510	2.929	<1
500	31.955	31.965	2.798	<1
321	32.504	32.505	2.752	1
330	33.248	33.255	2.693	<1
411	33.785	33.776	2.651	1
420	33.892	33.884	2.643	<1
510	35.705	35.711	2.513	<1
331	37.352	37.362	2.4056	<1
421	37.924	37.931	2.3706	<1
600	38.592	38.588	2.3311	<1
430	39.148	39.142	2.2992	<1
520	40.235	40.230	2.2396	<1
312	40.965	40.932	2.2014	<1
610	42.323	42.337	2.1338	<1
431	42.778	42.763	2.1122	<1
521	43.777	43.777	2.0662	<1
412	44.998	45.011	2.0130	<1
530	45.354	45.348	1.9980	<1
620	46.811	46.795	1.9391	<1

calculated peak positions is given in Table 1.† From the known volume of the molecule (418 Å³ obtained from Declercq & Van Meerssche, 1984, for the *ABB* isomer), the number of molecules, $Z = 3$, in the unit cell was deduced. Taking into account the value of Z , the short c parameter, the absence of systematic extinctions and the propeller-like geometry of the molecule, the most probable space group is $P3$.

12 unambiguously indexed and 92 systematically overlapped integrated intensities were extracted from data set (II) by means of the whole pattern fitting program *AJUST* (Rius *et al.*, 1996) in the range 6–45° (2θ). According to space group $P3$, and assuming a *BBB* conformation for the molecules, two more probable ways of accommodating the three molecules in the unit cell are: (a) with the centre of the molecule on a general position close to (1/3, 0, z), so that the three rings of one

Table 2. *Details of the rigid-body least-squares refinement from X-ray powder data of tris(3,5-dimethylpyrazol-1-yl)methane (isomer BBB)*

$\sigma(z)$ is the e.s.d. of the z coordinate of C1B and C1C, which are the pivot points for the molecular rotations. $\sigma(\phi)$, $\sigma(\psi)$ and $\sigma(\varphi)$ are the e.s.d.'s of the Euler angles describing each molecular rotation.

Range of 2θ (°)	6–45				
Space group, Z	$P3$, 3				
Unit-cell dimensions (Å)	$a = 16.152(1)$ $c = 5.353(1)$				
Volume (Å ³)	1209.4 (2)				
Temperature (K)	293				
Number of reflections	104				
Scale factor	1.28				
FWHM (°)	0.144				
B (Å ²)	7.39				
Mol. <i>A</i>		Mol. <i>B</i>		Mol. <i>C</i>	
$\sigma(z)$ (Å)	—	0.011		0.007	
$\sigma(\phi)$ (°)	0.47	0.66		0.49	
$\sigma(\psi)$ (°)	0.59	0.47		0.46	
$\sigma(\varphi)$ (°)	0.33	0.53		0.63	

Residuals†

R_p	0.059
R_{wp}	0.077
R_B	0.156
R_{exp}	0.021

† $R_p = (\sum |y_o(i) - y_c(i)|) / \sum y_o(i)$ (R pattern). $R_{wp} = ((\sum w(i)[y_o(i) - y_c(i)]^2) / \sum w(i)y_o(i)^2)^{1/2}$ with $w(i) = 1/y_o(i)$ (R weighted pattern). $R_B = [(\sum_j^{\text{ref}} |I_o(j) - I_c(j)|) / \sum_j^{\text{ref}} I_o(j)]$ (R Bragg factor). $R_{exp} = [(N - P) / \sum w(i)y_o(i)^2]^{1/2}$ (R expected factor).

molecule can have different orientations; (b) with the centre on each crystallographically non-equivalent three-fold axis, *i.e.* each molecule has ternary symmetry and a propeller-like conformation independent from the others. Note that if all the molecules were identical, a smaller unit cell would result as, for example, in the related compound tris(1-pyrazolyl)phosphine (Cobbledick & Einstein, 1975).

Patterson search methods have been widely used for solving crystal structures from powder data when, as in the present case, only low-resolution intensity data are available (Rius & Miravittles, 1987). Here, however, the power of these methods is weakened because most integrated intensities are systematically overlapped. Hence, only the orientation search has been performed. The molecular fragment used for the Patterson search was taken from the *ABB* isomer of tris(3,5-dimethylpyrazol-1-yl)methane (Declercq & Van Meerssche, 1984), which crystallizes in a monoclinic structure [$a = 17.573(11)$, $b = 23.000(10)$, $c = 18.105(8)$ Å, $\beta = 113.89(4)^\circ$, $V = 6691(6)$ Å³], space group $P2_1/n$, with four molecules in the asymmetrical unit ($Z = 16$).

The search model was oriented in the trigonal unit cell by the program *ROTS96* (Rius & Ochando, 1996) and placed according to the two checked above-mentioned possibilities. From the two possibilities, only the second one converged.

The subsequent rigid-body Rietveld refinement was performed with the program *RIBOLS* (Rius, 1989) using

† The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: NA0079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates for tris(3,5-dimethylpyrazol-1-yl)methane

	x	y	z
C1A	0	0	0.157 (0)
N1A	-0.065 (1)	0.031 (1)	0.245 (1)
N2A	-0.044 (1)	0.089 (1)	0.448 (3)
C2A	-0.123 (1)	0.096 (1)	0.481 (3)
C3A	-0.193 (2)	0.043 (1)	0.308 (1)
C4A	-0.156 (1)	0.001 (1)	0.160 (1)
C21A	-0.122 (1)	0.158 (1)	0.690 (5)
C41A	-0.197 (2)	-0.066 (1)	-0.062 (2)
C1B	0.667 (0)	0.333 (0)	0.385 (10)
N1B	0.617 (1)	0.384 (1)	0.461 (10)
N2B	0.547 (1)	0.347 (1)	0.636 (11)
C2B	0.515 (1)	0.410 (1)	0.644 (11)
C3B	0.562 (1)	0.483 (1)	0.474 (11)
C4B	0.626 (1)	0.465 (1)	0.355 (11)
C21B	0.438 (2)	0.391 (1)	0.825 (12)
C41B	0.698 (1)	0.518 (2)	0.151 (11)
C1C	0.333 (0)	0.667 (0)	0.411 (8)
N1C	0.303 (1)	0.731 (1)	0.512 (8)
N2C	0.349 (1)	0.789 (1)	0.708 (8)
C2C	0.298 (1)	0.832 (2)	0.757 (8)
C3C	0.219 (1)	0.800 (1)	0.602 (8)
C4C	0.223 (1)	0.734 (1)	0.448 (8)
C21C	0.331 (1)	0.904 (2)	0.963 (9)
C41C	0.157 (2)	0.673 (1)	0.238 (8)

a Pearson-VII profile function with shape parameter $m = 1.6$. However, the Rietveld refinement of the structure only converged to $R_{wp} = 0.308$. All attempts to improve the refinement failed. Only when the chirality of one *BBB* molecule was reversed by rotating their rings in the opposite direction ($\sim 90^\circ$ around the C1—N1 bond) did the Rietveld refinement drop to $R_{wp} = 0.077$. This fact demonstrates that of the three independent molecules in the unit cell, one has different chirality than the others, but maintaining the *BBB* conformation according to the initially defined criterion, and also explains the existence of the larger unit cell. As shown in Table 2, the

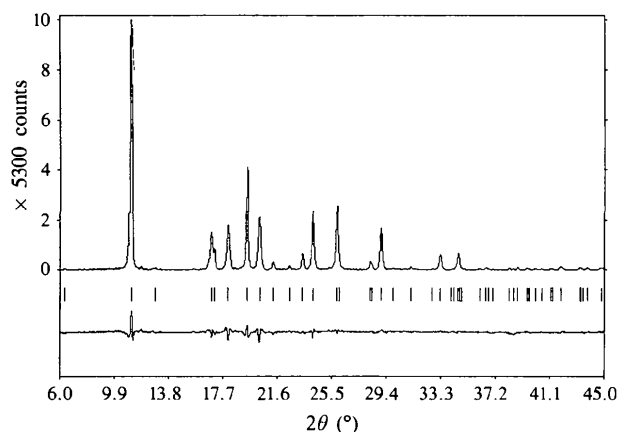


Fig. 3. Observed diffraction pattern and difference profile between observed and calculated patterns for tris(3,5-dimethylpyrazol-1-yl)methane (isomer *BBB*).

parameters refined are the z coordinates of two molecules and the angles describing the molecular orientations [total number of structural parameters = $2 + (3 \times 3) = 11$]. To be sure that this solution was the best, the z coordinates of two molecules were systematically changed by steps of $\Delta z = 0.10$ and the corresponding Rietveld refinements performed. The best result was the initial one. To complete the structure, the H atoms of the methyl groups were generated geometrically by the *SHELXL93* program (Sheldrick, 1993), since these atoms were not in the initial molecular fragment of the structure taken from Declercq & Van Meerssche (1984). The details of the final refinement are given in Table 2. The final coordinates for non-H atoms are listed in Table 3. The observed X-ray diffraction pattern and the difference profile between observed and calculated patterns are shown in Fig. 3. A projection of the unit cell with atom labelling and a stereoplot of the final crystal structure of the *BBB* isomer are represented in Figs. 4 and 5, respectively.

4. Results and discussion

There are three independent molecules in the unit cell placed on the threefold axes, two with similar conformations and the third with an enantiomeric one. Since the three molecules are symmetry-independent, the values of the N—C—N angle can be slightly different [110 (2), 112 (2) and 107 (2) $^\circ$]. These values are close to the ideal tetrahedral coordination (109.5 $^\circ$) and similar to the values found in related compounds as *e.g.* in the *ABB* isomer of tris(3,5-dimethylpyrazol-1-yl)methane [110, 111 and 111 $^\circ$ (Declercq & Van Meerssche, 1984)]; in the hydridotris(3,5-dimethylpyrazol-1-yl)borate anion, which possesses the *BBB* conformation and acts as a ligand of niobium [N—B—N angles vary between 108.2 and 110.6 $^\circ$ (Lorente, Etienne & Donnadieu, 1996)]; and in tetrakis(pyrazolyl)methane [N—C—N angles ranging

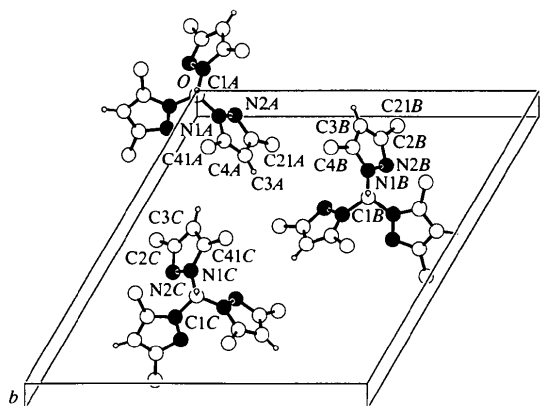


Fig. 4. Projection of the unit cell of the molecular structure of the *BBB* isomer with atom labelling (H atoms of the methyl groups have been omitted for clarity).

from 108.7 (2) to 110.4 (2) $^\circ$ (Claramunt *et al.*, 1989)]. It is interesting to compare these values with those found in trimesitylmethane, in which the presence of three methyl groups in positions 2, 4 and 6 of the benzene rings surely forces the molecule to adopt a more planar coordination [$C-C_{\text{central}}-C$ angle is 116 $^\circ$ (Blount & Mislou, 1975)].

The propeller-like conformation can be defined by the angle between the plane formed by C1, H1 and N1 and the mean plane through the pyrazolyl ring. The corresponding values for the three molecules of the *BBB* isomer are 42 (1), 45 (2) and 47 (2) $^\circ$. Due to the peculiar structure of this compound (threefold symmetry and three molecules in the unit cell), no structures could be found in the literature with strictly comparable propeller conformations. One example showing the variability of the conformation angle can be seen in the hydridotris(3,5-dimethylpyrazol-1-yl)borate anion (Loriente, Etienne & Donnadieu, 1996). Here, the anion acts as a ligand of the Nb atom and the propeller conformation angle is close to 0 $^\circ$, *i.e.* the pyrazolyl rings are almost perpendicular to the plane passing through the three N atoms directly bonded to the central B atom. Nevertheless, there are some compounds in which the molecules show propeller conformation angles in the same range as the *BBB* isomer, *e.g.* in the *ABB* isomer of tris(3,5-dimethylpyrazol-1-yl)methane [the corresponding values of each ring of one molecule are 29, 23 and 62 $^\circ$ as an average of the four molecules in the asymmetrical unit (Declercq & Van Meerssche, 1984)] and triphenylmethane [30, 34 and 53 $^\circ$, and 21, 38 and 47 $^\circ$ for each one of the two molecules in the asymmetrical unit (Riche & Pascard-Billy, 1974)]. Other compounds containing molecules with threefold symmetry have smaller values for the propeller conformation

angle, when compared with the average value (45 $^\circ$) found in *BBB*, *e.g.* in trimesitylmethane [38 $^\circ$ (Blount & Mislou, 1975)] and in tris-(1-pyrazolyl)phosphine [36 $^\circ$ (Cobbledick & Einstein, 1975)].

From the analysis of the structures of the *BBB* and *ABB* isomers, the two following similarities can be deduced: (a) both structures are formed by layers with all molecules within one layer pointing in the same direction; (b) the orientation of the molecular layers is preserved in the phase transition (Figs. 5 and 6), *i.e.* the normals to the layers are parallel to the *c* axis in *BBB* and to the *b* axis in *ABB*. The principal difference between the two phases is that *ABB* contains alternate layers related by an inversion centre, while in *BBB* all layers are identical. Consequently, adjacent layers in *ABB* have the molecules pointing in opposite directions.

With the *BBB* conformation of the polymorph obtained by sublimation (Fig. 1) having been established without ambiguity, it is now possible to try an interpretation of the phase diagram. According to MNDO (Claramunt *et al.*, 1995) calculations carried out on the isolated molecules, the *ABB* isomer is 6.7 kJ mol $^{-1}$ more stable than *BBB*, that is, 22.5 J g $^{-1}$, which is in good agreement with the differential scanning calorimetric determination of 21 J g $^{-1}$ (Claramunt *et al.*, 1995), showing that the packing energies should be similar for both polymorphs. Vaporization corresponds both to an increase in temperature and an isolation of individual molecules; its consequence is to shift the conformation equilibrium towards the *BBB* isomer which is trapped on the cold finger of the sublimation apparatus.

In conclusion, the *Patterson search* structure determination of tris(3,5-dimethylpyrazol-1-yl)methane from laboratory X-ray powder diffraction data has shown the effectiveness of this method in the structural and phase-transition investigations of organic compounds, when single crystal techniques cannot be applied.

APPENDIX A

There is another more detailed description of these propeller-like conformations based on the H—C—N—N torsion angles which differentiate between enantiomers. According to this last description, the two phases have the following conformations (assuming conformation α when the angle is negative and β when positive):

Phase *BBB*

	Mol. 1	Mol. 2	Mol. 3
H1—C1—N1—N2	-141 (2) $^\circ$	132 (5) $^\circ$	-137 (4) $^\circ$
Conformation	$\alpha\alpha\alpha$	$\beta\beta\beta$	$\alpha\alpha\alpha$

Phase *ABB* (Declercq & Van Meerssche, 1984)

	Mol. 1	Mol. 2	Mol. 3	Mol. 4
H1—C1—N7—N8	20 (1) $^\circ$	-28 (1) $^\circ$	-21 (1) $^\circ$	30 (1) $^\circ$
H1—C1—N12—N13	-118 (1) $^\circ$	111 (1) $^\circ$	121 (1) $^\circ$	-112 (1) $^\circ$
H1—C1—N2—N3	-149 (1) $^\circ$	158 (1) $^\circ$	147 (1) $^\circ$	-155 (1) $^\circ$
Conformation	$\beta\alpha\alpha$	$\alpha\beta\beta$	$\alpha\beta\beta$	$\beta\alpha\alpha$

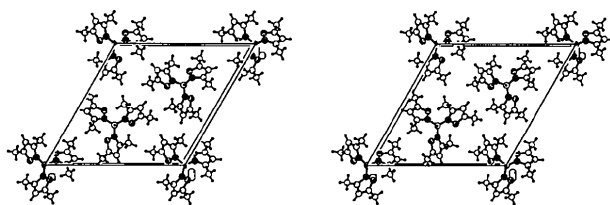


Fig. 5. Stereoplot of the crystal structure of tris(3,5-dimethylpyrazol-1-yl)methane (isomer *BBB*) along the *c* axis.

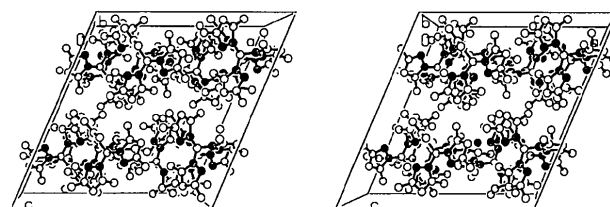


Fig. 6. Stereoplot of the crystal structure of tris(3,5-dimethylpyrazol-1-yl)methane (isomer *ABB*) along the *b* axis.

Multiplying by -1 (which corresponds to change the chirality of the propeller), $\alpha\alpha\alpha$ becomes $\beta\beta\beta$ and $\beta\alpha\alpha$ becomes $\alpha\beta\beta$, that is, to the *BBB* phase corresponds the $\beta\beta\beta$ conformation (or its enantiomer) and to the *ABB* phase corresponds the $\alpha\beta\beta$ conformation (or its enantiomer).

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