

chair conformations and are mutually inclined at 55.1°. The angles between the cyclohexyl rings and the adjacent urethane groups are 101.5 and 66.2°. The molecules are linked by four intermolecular C=O...H—N hydrogen bonds per monomer unit. Two hydrogen bonds are formed between neighbouring molecules similar to a dimerization. The two residual hydrogen bonds of a monomer unit are formed to different molecules. The structural analysis of the model compound allows the construction of the packing and conformation of the 1,4-butanediol-linked *trans,trans*-diisocyanatodicyclohexylmethane (*trans,trans*-HMDI) units in the hard domains of the corresponding polyurethane elastomers.

Introduction

Segmented polyurethane (PU) elastomers are multiblock copolymers (A–B)_n with an alternating sequence of hard (urethane) and soft (polyester or polyether) segments. The segmental incompatibility leads to microphase separation and, therefore, such materials show elastic properties (Noshay & McGrath, 1977; Eisenbach, Baumgartner & Günter, 1986; Meckel, Goyert & Wieder, 1987). At working temperature, the urethane segments form crystalline domains, which act as multifunctional thermoreversible crosslinks in the more or less liquid-soft segment phase. The morphology, and especially the hard domain structure, define the material properties of the thermoplastic PU elastomers.

PU elastomers with 1,4-butanediol-linked HMDI hard segments are known for their excellent optical clarity, light stability and hydrolysis resistancy, especially the elastomers based on isomeric pure *trans,trans*-HMDI which show superior physical and mechanical properties (Seneker, Born, Schmelzer, Eisenbach & Fischer, 1992). The structure of the methanol-capped isomeric pure *trans,trans*-HMDI (Me-*tt*HMDI-Me) has been determined as a model for the structure of the *trans,trans*-HMDI/1,4-butanediol polymer. The construction of polyurethane chains, making use of the structural analysis of model compounds, has been successfully demonstrated for hydrogen-bond forming (4,4'-diisocyanatodiphenylmethane/1,4-butanediol: Blackwell & Gardner, 1979; Born, Hespe, Crone & Wolf, 1982) and hydrogen-bond free (1,4-piperazine/1,4-butanediol: Enkelmann, Hayen, Eisenbach & Nefzger, 1994) polyurethanes.

Experimental

Synthesis of the title compound

5.0 g (19 mmol) of *trans,trans*-4,4'-diisocyanato dicyclohexylmethane (provided by Bayer AG; recrystal-

lized twice from *n*-hexane) in 200 ml of methanol was refluxed for 4 h under a dry nitrogen atmosphere. Upon cooling, white crystals of Me-*tt*HMDI-Me precipitated and were recrystallized from methanol; yield: 4.1 g, 66% of theory; m.p. 488 K. IR: 1695 [ν (C=O), s], 1545 (amide II, s) cm⁻¹. ¹H NMR: δ , 0.9–1.4 (*m*, 12 H, aliphatic H atoms), 1.72 (*m*, 4H, axial H atoms of C3/C3'), 1.96 (*m*, 4H, equatorial H atoms of C3/C3'), 3.38 (*m*, 2H, CH—NH), 3.63 (*s*, 6H, CH₃), 4.58 (*s*, 2H, NH). ¹³C NMR: δ , 32.0, 33.7 (C2/C2', C3/C3'), 33.4 (C1/C1'), 44.0 (bridge CH₂), 50.4 (C4/C4'), 51.8 (methoxy CH₃), 156.3 (urethane C=O). MS: *m/e* (relative intensity): 326 (*M*⁺, 20.0), 294 (5.6), 267 (10.4), 251 (14.9), 176 (20.4), 170 (40.7), 157 (60.7), 156 (8.2), 114 (100), 101 (5.8), 95 (12.2), 81 (14.0), 76 (26.0), 56 (7.9). Elemental analysis: (C₁₇H₃₀N₂O₄) calculated: C 62.55, H 9.26, N 8.58%. Found: C 62.18, H 9.25, N 8.58%.

X-ray analysis

Single crystals were grown by slow evaporation from a chloroform solution at 293 K. A colourless crystal of dimensions 0.28 × 0.28 × 0.30 mm was selected for the structure determination. With the crystal cooled to 173 K, data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo *K*α radiation ($\lambda = 0.71073$ Å). Systematic absences of *h*0*l* ($h + l = 2n + 1$) and 0*k*0 ($k = 2n + 1$) determined the space group to be *P*2₁/*n*. 50 reflections in the range 28 < 2θ < 29° were used to refine the unit-cell dimensions from the Bragg angles (positioned by the diffractometer). From the unit-cell volume of 1840.3 Å³ and *Z* = 4, a density of 1.178 Mg m⁻³ can be calculated which agrees well with the observed density of 1.16 Mg m⁻³, measured by pycnometry in water. The intensity data for 4618 reflections in the range 2 < 2θ < 50° ($-15 \leq h \leq 21$, $-1 \leq k \leq 7$, $-21 \leq l \leq 19$) were collected using the ω -scan technique (scan width 1.2°, scan speed constantly at 2.0° min⁻¹, background measurements at both ends of the scan for a total time 25% of the scan time). The intensity of two check reflections monitored every 100 reflections remained constant during the data collection.

After Lorentz and polarization correction and merging (*R*_{int} = 0.021), the solution and refinement of the structure were carried out using the Siemens *SHELXTL-Plus* (Sheldrick, 1992) program system. The structure was solved by direct methods. In the least-squares refinement the function $\sum w (F_o - F_c)^2$ with $w = 1/\sigma^2(F_o)$ was minimized. The positions of the H atoms were calculated. The final full-matrix least-squares refinement with 3231 observed reflections [$F > 0\sigma(F_o)$, no reflections omitted] and 209 parameters converged at *R* = 0.059 and *wR* = 0.039. After the last cycle, the mean shift/ σ ratio was 0.000 (maximum shift/ σ : 0.001) and the residual electron density was 0.34 e Å⁻³.

Discussion

The final atomic coordinates of the non-H atoms and their equivalent isotropic U_{eq} values are listed in Table 1, while selected interatomic distances and bond angles are given in Table 2. A view of the molecule with atom numbering is shown in Fig. 1; the two halves of the molecule have been labelled *A* and *B*. The cyclohexyl rings have chair conformations, whilst the central methylene group and the respective urethane group occupy equatorial ring positions. The molecule is V-shaped with an angle of the central C—CH₂—C methylene unit of 116.1(2)°. The angle between the cyclohexyl planes is 55.1°; the plane of the rings is defined by the C atoms C(11), C(13) and C(15) for ring *A* and C(3), C(5) and C(7) for ring *B*.

Both urethane groups —O—C(=O)—NH— are planar and the C atoms of the adjacent terminal methoxy group also lie in the urethane plane. The inclinations of the urethanes [planes defined by N(2), C(16) and O(4) for ring *A* and N(1), C(2) and O(1) for ring *B*] to their respective cyclohexyl rings are 66.2 and 101.5°. The cyclohexane planes are given again by the atoms C(11), C(13), C(15) (ring *A*) and C(3), C(5), C(7) (ring *B*). The angle between the urethane planes is 109.1°. The torsion angles which define the sense of these rotations are listed in Table 3. The molecule is not symmetrical with respect to the central methylene group. The observed conformational asymmetry of the chemically symmetrical molecule seems to be necessary to optimize the hydrogen bonding. The packing of an array of molecules in the *b*-direction is shown in Fig. 2(a) and the *bc*-projection of the unit cell is shown in Fig. 2(b). The molecules are linked to each other by two types of intermolecular hydrogen bonds, so that each molecule forms four hydrogen bonds resulting in a three-dimensional hydrogen-bond network. Two hydrogen bonds with an N—H...O=C distance of 2.95 Å connect two neighbouring and point-symmetrical molecules with each other, similar to the formation of a dimer. In Fig. 2(b) the hydrogen bonds of such 'twins' are labelled 1 and 2. The two residual N—H...O=C hydrogen bonds of each twin (number 3, 4 and 3', 4', respectively; Fig. 2b) with distances of 2.88 Å are formed to different molecules.

The molecules are packed side-by-side along the *b*- and *c*-axes, and each molecule forms hydrogen bonds with three neighbours: one neighbour is the twin (two hydrogen bonds), and the two residual hydrogen bonds of each twin point in different directions (see Fig. 2b). The hydrogen-bonded 'layers' are stacked along the *a*-axis.

The meander-like hydrogen-bond network of the 'twins' is very different to the two-by-two and perpendicular hydrogen bonds of the 4,4'-di(methoxycarbonylimino)diphenylmethane (Me-MDI-Me) structure (Gardner & Blackwell, 1980). In the MDI compound,

Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients U_{eq} ($\text{\AA}^2 \times 10^2$) and their standard deviations for the non-H atoms

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	480 (8)	42172 (26)	85151 (9)	4.64 (6)
O(2)	2181 (8)	21033 (27)	95799 (9)	4.78 (7)
O(3)	71335 (8)	-22648 (25)	80344 (8)	4.12 (6)
O(4)	74786 (8)	-4257 (26)	92121 (8)	4.47 (6)
N(1)	12918 (9)	26953 (30)	93311 (9)	3.61 (7)
N(2)	63157 (9)	3425 (28)	80388 (9)	3.28 (6)
C(1)	-6515 (13)	24324 (47)	93776 (18)	6.32 (12)
C(2)	4880 (12)	31080 (34)	90899 (12)	3.36 (8)
C(3)	17702 (11)	36548 (34)	89455 (11)	3.31 (8)
C(4)	23425 (12)	54024 (35)	94786 (11)	3.63 (8)
C(5)	28856 (11)	63043 (34)	91039 (12)	3.37 (8)
C(6)	22688 (12)	19393 (34)	87755 (12)	3.46 (8)
C(7)	28227 (11)	28625 (34)	84112 (11)	3.33 (8)
C(8)	34073 (11)	45678 (32)	89608 (11)	2.88 (7)
C(9)	39733 (11)	55266 (33)	86193 (11)	3.09 (7)
C(10)	44496 (11)	39363 (31)	83490 (10)	2.76 (7)
C(11)	50197 (12)	50881 (32)	80602 (12)	3.26 (8)
C(12)	54673 (11)	35401 (33)	77431 (11)	3.24 (8)
C(13)	49669 (11)	23692 (33)	90230 (11)	3.14 (7)
C(14)	54172 (12)	7970 (32)	87219 (11)	3.24 (8)
C(15)	59615 (11)	18946 (32)	83902 (11)	2.95 (7)
C(16)	70083 (11)	-7409 (34)	84942 (11)	3.11 (8)
C(17)	78587 (14)	-35640 (44)	84489 (14)	5.54 (11)

Table 2. Selected bond lengths (Å) and angles (°) and their standard deviations

O(3)—C(17)	1.433 (3)	O(2)—C(1)	1.450 (3)
O(3)—C(16)	1.356 (3)	O(2)—C(2)	1.348 (3)
O(4)—C(16)	1.214 (2)	O(1)—C(2)	1.211 (2)
N(2)—C(16)	1.333 (2)	N(1)—C(2)	1.333 (3)
N(2)—C(15)	1.460 (3)	N(1)—C(3)	1.462 (3)
C(9)—C(10)	1.534 (3)	C(8)—C(9)	1.533 (3)
C(8)—C(9)—C(10)	1.161 (2)	C(1)—O(2)—C(2)	1.155 (2)
C(17)—O(3)—C(16)	1.161 (1)	O(2)—C(2)—N(1)	1.104 (2)
O(3)—C(16)—N(2)	1.101 (1)	O(2)—C(2)—O(1)	1.236 (2)
O(3)—C(16)—O(4)	1.235 (2)	O(1)—C(2)—N(1)	1.261 (2)
O(4)—C(16)—N(2)	1.263 (2)	C(2)—N(1)—C(3)	1.230 (2)
C(16)—N(2)—C(15)	1.225 (2)	N(1)—C(3)—C(4)	1.115 (2)
N(2)—C(15)—C(12)	1.094 (2)	N(1)—C(3)—C(6)	1.094 (2)
N(2)—C(15)—C(14)	1.107 (2)		

translational shifts within the hydrogen-bonded stacks can occur when crystallographically identical hydrogen bonds pointing in one direction only are broken, which is not possible in the *trans,trans*-HMDI structure; in the latter case, the disruption of all hydrogen bonds is required for molecular displacements.

We have used the packing and conformation determined for this compound to propose a model for the structure of hard segments of polyurethane

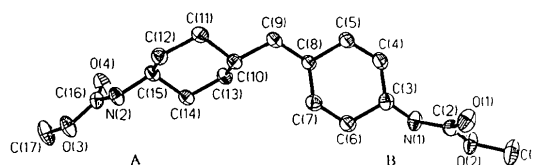


Fig. 1. Molecular structure of Me-*tt*HMDI-Me showing thermal ellipsoids and atomic numbering.

elastomers based on isomeric pure *trans,trans*-HMDI and 1,4-butanediol as a chain extender, using the principle of isomorphous substitution of the opposing methyl groups by a tetramethylene chain (Blackwell & Gardner, 1979); the two opposing methyl groups have been replaced by a tetramethylene chain connecting the two urethane groups without any displacement or conformational changes in the unit cell of the model compound, *i.e.* C(1) and C(4) of the tetramethylene bridge lie exactly on the positions of the methyl C atoms (Eisenbach, Steinlein & Milius, 1994). The conformation of the constructed polymer chain is in good agreement with the structural features of the bisurethane of 1,4-

Table 3. Selected torsion angles (°) of *trans,trans*-4,4'-di(methoxycarbonylimino)dicyclohexylmethane

E.s.d.'s are not greater than 0.3°.

C(1)—O(2)—C(2)—O(1)	0.1	C(17)—O(3)—C(16)—O(4)	1.3
C(17)—O(3)—C(16)—N(2)	-179.8	C(16)—N(2)—C(15)—C(12)	153.2
C(3)—N(1)—C(2)—O(1)	3.3	C(15)—N(2)—C(16)—O(4)	-9.3
C(2)—N(1)—C(3)—C(4)	104.4	N(1)—C(3)—C(4)—C(5)	-176.1
C(16)—N(2)—C(15)—C(14)	-84.0	N(1)—C(3)—C(6)—C(7)	-176.9
C(11)—C(12)—C(15)—N(2)	174.9	C(4)—C(5)—C(8)—C(9)	-177.7
C(13)—C(14)—C(15)—N(2)	-174.6	C(6)—C(7)—C(8)—C(9)	179.9
C(1)—O(2)—C(2)—N(1)	-180.0	C(5)—C(8)—C(9)—C(10)	-172.8
C(3)—N(1)—C(2)—O(2)	-176.6	C(7)—C(8)—C(9)—C(10)	-50.4
C(2)—N(1)—C(3)—C(6)	-133.0	C(8)—C(9)—C(10)—C(13)	-54.7
C(15)—N(2)—C(16)—O(3)	171.8	C(9)—C(10)—C(11)—C(12)	-177.0
C(8)—C(9)—C(10)—C(11)	-177.3		

butanediol with *trans*-4-isocyanatodicyclohexylmethane (Seneker, Born, Schmelzer, Eisenbach & Fischer, 1992; Born, Fischer & Eisenbach, 1994). The differences in the crystal structures of the dimethylurethanes of *trans,trans*-HMDI and MDI can explain the higher thermal and mechanical stability of *trans,trans*-HMDI-based polyurethanes compared with the MDI-analogous PU elastomers on a molecular level, as resulting from fundamentally different hydrogen-bond patterns in both model compounds (Eisenbach, Steinlein & Milius, 1994).

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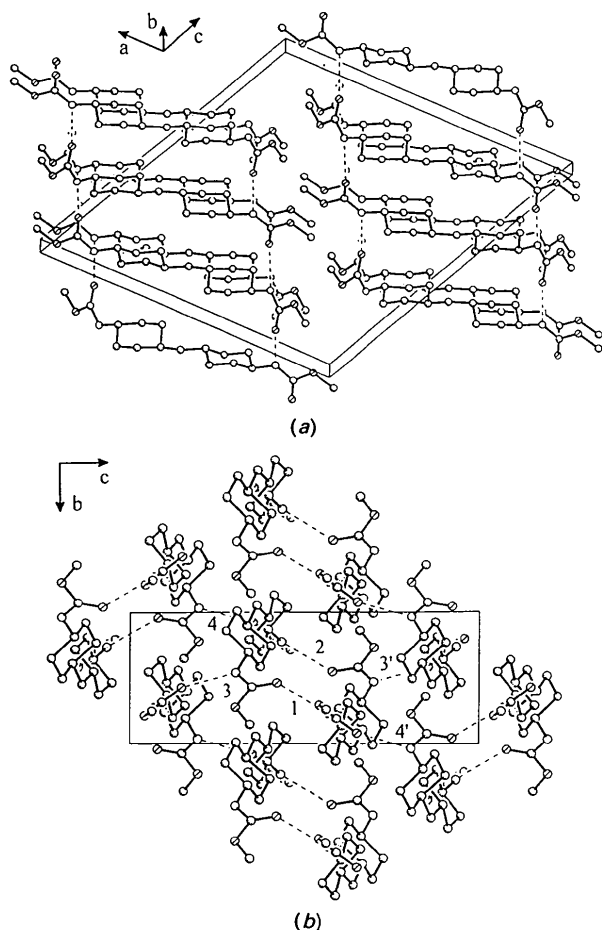


Fig. 2. (a) Projection of the crystal structure of Me-*tt*HMDI-Me in the *b*-direction; hydrogen bonds are indicated by dotted lines. (b) Crystal structure of Me-*tt*HMDI-Me (*bc*-projection); hydrogen bonds are indicated by dotted lines (for the meaning of the numbers, see text).