Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.
Megaw, H. D. (1968). *Acta Cryst.* A**24**, 583–588.
Megaw, H. D. (1970). *Acta Cryst.* A**26**, 235–244.
Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.
Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY system of crystallographic programs. Univ. of Maryland, College Park, Maryland.
Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

Acta Cryst. (1977). B**33**, 3609–3611

N,*N'*-(*p*-Phenylene)dibenzamide (PPDB)*

By S. Harkema and R. J. Gaymans

Chemical Physics Laboratory, Twente University of Technology, PO Box 217, Enschede, The Netherlands

(*Received* 11 *July* 1977; *accepted* 18 *July* 1977)

Abstract. $C_{20}N_2O_2H_{16}$, monoclinic, $P2_1/c$, a = 18·065 (1), b = 5·247 (1), c = 8·027 (1) Å, β = 93·99 (1)°, Z = 2. The crystal structure has been refined by least-squares techniques. R_w = 7·3%. The structure contains planar phenyl rings which are rotated with respect to the plane of the amide group owing to steric hindrance. The molecules are connected in one dimension by means of hydrogen bonds.

Introduction. Aromatic and mixed aliphatic–aromatic polyamides form a class of polymers having thermal and mechanical properties which are quite different from those of aliphatic polyamides. These exceptional properties are thought to be due to the fact that aromatic polyamides have a very high degree of crystallinity (Northolt & Van Aartsen, 1973). In order to obtain more insight into the structures of the crystalline phase of the polyamides a number of model compounds have been synthesized (Gaymans & Harkema, 1977). The melting behaviour of these compounds has been reported. To obtain detailed

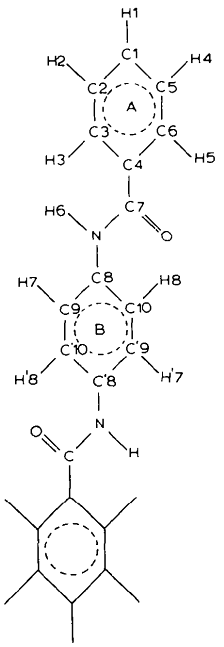

Fig. 1. Atomic arrangement of PPDB.

---

* The Crystal and Molecular Structure of Model Compounds of Aromatic and Aromatic–Aliphatic Polyamides. I.

Table 1. *Atomic positional parameters*

	x	y	z		x	y	z
C(1)	0·5791 (2)	−0·0447 (7)	0·1849 (4)	O	0·8176 (1)	0·3738 (4)	0·0694 (4)
C(2)	0·6358 (2)	−0·2050 (6)	0·2442 (4)	N	0·8506 (1)	−0·0444 (5)	0·0728 (3)
C(3)	0·7093 (2)	−0·1457 (6)	0·2121 (4)	H(1)	0·5255 (22)	−0·1042 (69)	0·2067 (48)
C(4)	0·7244 (1)	0·0689 (5)	0·1225 (4)	H(2)	0·6256 (19)	−0·3618 (68)	0·3084 (45)
C(5)	0·5941 (2)	0·1684 (7)	0·0955 (5)	H(3)	0·7480 (16)	−0·2647 (65)	0·2581 (40)
C(6)	0·6670 (2)	0·2299 (6)	0·0653 (4)	H(4)	0·5551 (14)	0·2817 (70)	0·0488 (44)
C(7)	0·8020 (2)	0·1494 (5)	0·0876 (4)	H(5)	0·6793 (17)	0·3900 (66)	0·0025 (42)
C(8)	0·9265 (1)	−0·0145 (5)	0·0360 (3)	H(6)	0·8322 (19)	−0·1988 (75)	0·0645 (45)
C(9)	0·9566 (2)	−0·2011 (5)	−0·0608 (4)	H(7)	0·9263 (16)	−0·3420 (54)	−0·1097 (36)
C(10)	0·9690 (2)	0·1854 (6)	0·0976 (4)	H(8)	0·9510 (16)	0·3191 (59)	0·1690 (38)

geometric information the crystal structures of some model compounds have been determined. This paper gives an account of the crystal structure of PPDB (Fig. 1).

PPDB was prepared as described elsewhere (Gaymans & Harkema, 1977). Crystals suitable for X-ray structure determination were obtained by recrystallization from dimethylacetamide. A crystal with maximum dimension 0·5 mm was selected. Data were collected at 20°C with a computer-controlled single-crystal diffractometer (Philips PW 1100) using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1\cdot5405$ Å). Measurements were made up to $\theta = 60°$ with the ω–2θ scanning technique. The number of reflexions measured was 1326 of which 1186 had a net intensity greater than twice the standard deviation estimated from counting statistics. The latter reflexions have been used in the refinements.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The resulting E map showed the positions of all the heavy atoms. With two molecules in the unit cell and a fourfold general position the inversion centre of the molecule has to be on a crystallographic centre of symmetry. The weighting scheme used in the refinements is that normally used in our laboratory (de With, Harkema & van Hummel, 1976). The scattering factors used were those from *International Tables for X-ray Crystallography* (1974) for the heavier atoms. For H the scattering factors of Stewart, Davidson & Simpson (1965) were taken. The positions of all the H atoms were found from a difference synthesis calculated after refinement of the parameters of the heavy atoms. The parameters refined in the last cycles were the positional and isotropic thermal parameters for the H atoms and positional and anisotropic thermal parameters for the other atoms. A correction for isotropic secondary extinction (Larson, 1969) was applied. The final value of the weighted R index was 7·3%.*

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·383 (5)	C(8)–N	1·432 (4)
C(1)–C(5)	1·366 (5)	C(9)–C(10′)	1·399 (4)
C(2)–C(3)	1·405 (4)	C(1)–H(1)	1·06 (4)
C(3)–C(4)	1·374 (4)	C(2)–H(2)	0·95 (4)
C(4)–C(6)	1·391 (5)	C(3)–H(3)	0·99 (4)
C(4)–C(7)	1·510 (4)	C(5)–H(4)	0·98 (4)
C(5)–C(6)	1·394 (4)	C(6)–H(5)	1·02 (4)
C(7)–O	1·222 (4)	C(9)–H(7)	0·99 (4)
C(7)–N	1·355 (4)	C(10)–H(8)	0·97 (4)
C(8)–C(9)	1·386 (4)	N–H(6)	0·87 (4)
C(8)–C(10)	1·372 (4)		

Table 3. *Bond angles* (°)

C(5)–C(1)–C(2)	120·6 (5)	H(5)–C(6)–C(5)	121 (4)
H(1)–C(1)–C(5)	123 (4)	C(4)–C(7)–N	115·0 (4)
H(1)–C(1)–C(2)	116 (4)	C(4)–C(7)–O	121·2 (4)
C(1)–C(2)–C(3)	119·3 (4)	O–C(7)–N	123·8 (4)
H(2)–C(2)–C(1)	122 (4)	N–C(8)–C(9)	117·2 (4)
H(2)–C(2)–C(3)	119 (4)	N–C(8)–C(10)	122·0 (4)
C(2)–C(3)–C(4)	120·1 (4)	C(9)–C(8)–C(10)	120·7 (4)
H(3)–C(3)–C(2)	116 (4)	C(8)–C(9)–C(10′)	119·9 (4)
H(3)–C(3)–C(4)	123 (4)	C(8)–C(9)–H(7)	121 (4)
C(3)–C(4)–C(6)	120·0 (4)	H(7)–C(9)–C(10′)	119 (4)
C(3)–C(4)–C(7)	123·3 (4)	C(8)–C(10)–C(9′)	119·4 (4)
C(6)–C(4)–C(7)	116·7 (4)	C(8)–C(10)–H(8)	124 (4)
C(1)–C(5)–C(6)	120·4 (4)	H(8)–C(10)–C(9)	117 (4)
H(4)–C(5)–C(1)	122 (4)	C(7)–N–C(10)	124·9 (4)
H(4)–C(5)–C(6)	117 (4)	C(7)–N–H(6)	117 (4)
C(4)–C(6)–C(5)	119·6 (4)	H(6)–N–C(8)	117 (4)
H(5)–C(6)–C(4)	119 (4)		

Table 4. *Distances* (Å) *of the atoms to the different planes in the molecule*

Plane 1: plane fitted to the C atoms of phenyl ring *A* (see Fig. 1)

$$0\cdot45894x + 1\cdot78981y + 4\cdot40662z = 1\cdot00000$$

Plane 2: plane through the C(7), N and O atoms of the amide group

$$1\cdot00542x + 0\cdot09643y + 2\cdot04661z = 1\cdot00000$$

Plane 3: plane fitted to the C atoms of phenyl ring *B* (see Fig. 1)

$$1\cdot00000x - 0\cdot74099y + 1\cdot73022z = 1\cdot00000$$

	Plane 1	Plane 2	Plane 3		Plane 1	Plane 2	Plane 3
C(1)	0·001 (3)	–	–	O	–	0·000 (2)	–
C(2)	0·002 (3)	–	–	N	–	0·000 (2)	0·036 (2)
C(3)	0·000 (3)	–	–	H(1)	−0·05 (4)	–	–
C(4)	−0·005 (3)	−0·053 (3)	–	H(2)	−0·00 (4)	–	–
C(5)	−0·007 (3)	–	–	H(3)	0·11 (4)	–	–
C(6)	0·009 (3)	–	–	H(4)	−0·04 (4)	–	–
C(7)	0·034 (3)	0·000 (3)	–	H(5)	−0·03 (4)	–	–
C(8)	–	0·014 (3)	−0·002 (3)	H(6)	–	−0·19 (4)	–
C(9)	–	–	0·002 (3)	H(7)	–	–	−0·03 (4)
C(10)	–	–	0·002 (3)	H(8)	–	–	0·02 (4)

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32867 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

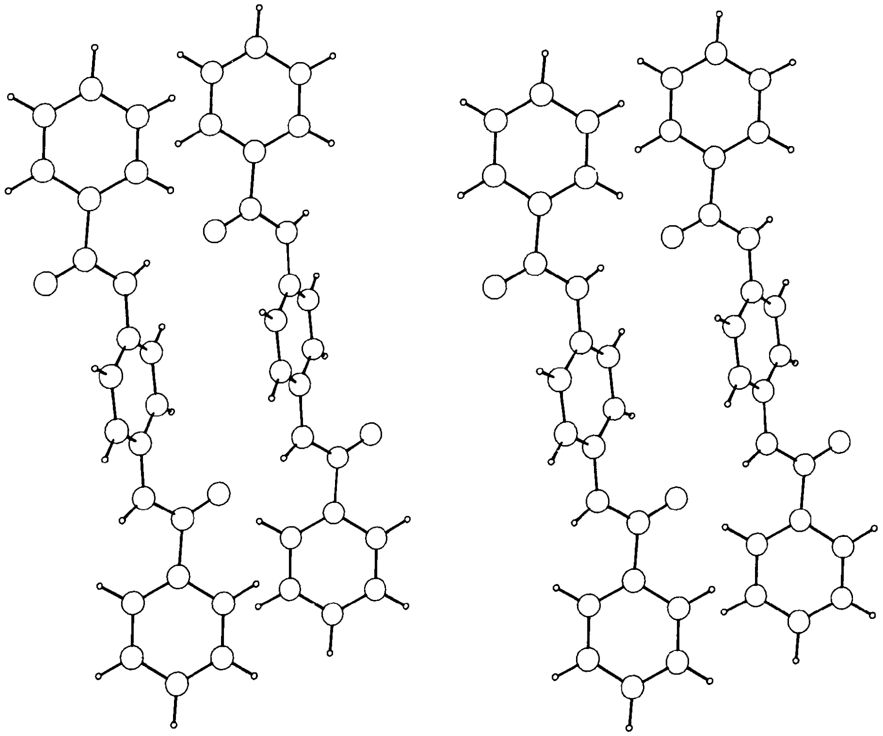

Fig. 2. Stereoscopic view of the crystal structure of PPDB.

Discussion. Final atomic positions are given in Table 1. The numbering of the atoms is depicted in Fig. 1. Bond lengths and angles are given in Tables 2 and 3. The molecule contains phenyl rings which are planar within experimental accuracy. Data pertaining to the best planes fitted to the C atoms of the phenyl rings are given in Table 4, from which it can be concluded that C(7) and the N atom attached to the phenyl rings have a significant deviation from the best planes. The H atom attached to the N atom is significantly out of the plane of the heavier atoms of the amide group. The angles between the different planes were also calculated. The angle between the planes of the amide group and phenyl group *A* is −29·1°. This is significantly different from the twist angle, 24·6°, found in benzamide (Blake & Small, 1972). The angle between the planes of the amide group and phenyl ring *B* is 35·9°, which is significantly different from the corresponding value, 17·6°, found in acetanilide (Brown, 1966). It should be noted that the values found are in good agreement with the angles estimated by Northolt & Van Aartsen (1973) for the polymer poly(p-phenyleneterephthalamide). As in benzamide and acetanilide, these twist angles are supposed to be due to steric hindrance between H(3) and H(6), and H(8) and O. The angles found support the view that in PPDB steric hindrance is even more important than in benzamide and acetanilide. The angle between the phenyl rings is 64·5°.

The angles found between the different planes prove that there is almost no conjugation between the different parts of the molecule.

The molecules are connected by N—H···O hydrogen bonds of length 3·111 (4) Å. A stereoscopic view of the molecule is given in Fig. 2.

References

Blake, C. C. F. & Small, R. W. H. (1972). *Acta Cryst.* B**28**, 2201–2206.

Brown, C. J. (1966). *Acta Cryst.* **21**, 442–445.

Gaymans, R. J. & Harkema, S. (1977). *J. Polym. Sci. Polym. Phys. Ed.* **15**, 587–590.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Larson, A. C. (1969). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 291–294. Copenhagen: Munksgaard.

Northolt, M. G. & Van Aartsen, J. J. (1973). *J. Polym. Sci. Polym. Lett. Ed.* **11**, 333–337.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

With, G. de, Harkema, S. & van Hummel, G. J. (1976). *Acta Cryst.* B**32**, 1980–1983.