

The Crystal Structure of Terephthalamide

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The crystal structure of terephthalamide, $C_6H_4(CONH_2)_2$, has been investigated using three-dimensional X-ray data collected by means of a three-circle diffractometer in conjunction with a proportional counter. The space group is $P\bar{1}$ and there is one molecule in the unit cell. A full-matrix least-squares refinement of the positional and anisotropic thermal vibration parameters gave a final R value of 0.088. The molecules are linked together in sheets by hydrogen bonds with the plane of the amide group making an angle of 23° with the plane of the benzene ring. The bond lengths have been corrected for librational motion, and are C–C (amido) = 1.491 ± 0.005 , C–O = 1.247 ± 0.005 , C–N = 1.305 ± 0.005 , C–C = 1.409 ± 0.006 , C–C = 1.382 ± 0.006 and C–C = 1.380 ± 0.008 Å.

Introduction

The crystal structure of terephthalamide has been investigated as part of a series of studies of amides and similar hydrogen bonded structures. Apart from the hydrogen bonding network and the geometry of the amide group, the degree of planarity of the molecule as a whole was of interest.

Crystal data

Terephthalamide is insoluble in most common organic solvents and virtually insoluble in water. Crystals were obtained by dissolving a commercial sample in aqueous formic acid and allowing the solvent to evaporate slowly at a temperature of 30°C . The habit of the colourless crystals obtained suggested that terephthalamide is triclinic. Preliminary oscillation and Weissenberg photographs confirmed this.

Accurate cell dimensions were determined from θ measurements made on a three-circle diffractometer (Small & Travers, 1961) using an extrapolation method (Beagley & Small, 1964) to eliminate zero-error settings of the circles. The corrected interplanar spacings calculated for a number of sets of planes were used to give a best least-squares fit for the cell parameters. The density was measured by the flotation method using a mixture of carbon tetrachloride and chlorobenzene. Crystal data are shown in Table 1.

Table 1. *Crystal data*

$a = 5.027 \pm 0.001$ Å	$V = 183.88$ Å ³
$b = 5.355 \pm 0.001$	$Z = 1$
$c = 7.165 \pm 0.001$	$D_{\text{obs}} = 1.47$ g.cm ⁻³
$\alpha = 103.02 \pm 0.04^\circ$	$D_{\text{calc}} = 1.48$ g.cm ⁻³
$\beta = 100.90 \pm 0.03$	
$\gamma = 92.17 \pm 0.02$	

The space group was taken to be $P\bar{1}$ on the evidence of a centric distribution of the three-dimensional data (Howells, Phillips & Rogers, 1950).

Determination of the structure

Three-dimensional data were collected using the three-circle diffractometer. At room temperature, 796 integrated intensities, for which $\theta < 82^\circ$, were measured using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The intensities were corrected for absorption on the Chilton ATLAS computer using the program *ABSCOR*.

The structure was solved by interpretation of two-dimensional Patterson syntheses projected on (100) and (010). Refinement of the model obtained was carried out initially by two-dimensional least-squares calculations and subsequently by applying the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) to the three-dimensional data. The atomic scattering factors used throughout were those listed in *International Tables for X-ray Crystallography* (1962). Initially all reflexions were weighted equally but in the later cycles a weighting scheme was applied with $\sqrt{w} = 0.43/(J)$ where (J) takes the maximum value of the three functions, $0.008|F_o| - 0.15$, σ or 0.43 for a particular reflexion, where σ is the standard deviation of the structure amplitude based on counting statistics. Refinement of the carbon, nitrogen and oxygen parameters continued until R reached 0.124, when a weighted $F_o - F_c$ Fourier synthesis was computed to give the positions of the four hydrogen atoms of the asymmetric unit. These hydrogen atoms were given anisotropic thermal parameters equal to those of the atoms to which they were bonded and included in the next two cycles of least-squares refinement when R reached 0.099. The calculated structure amplitudes for the 011 and $1\bar{1}\bar{1}$ reflexions were considerably in excess of their observed magnitudes and, on the assumption that the difference was due to extinction, these reflexions were omitted from subsequent refinement cycles. In the last cycle the hydrogen atom positions were refined. The final R value was 0.088, the parameter shifts of the heavy atoms being less than one quarter of their estimated standard deviations.

An $F_o - F_c$ Fourier synthesis did not reveal any

further significant features. The final positional parameters are shown in Table 2 and the vibrational parameters of the heavier atoms in Table 3. Table 4 lists the final values of the observed and calculated structure amplitudes.

Table 2. Fractional atomic coordinates

The values of the fractional coordinates and the estimated standard deviations in parentheses are multiplied by 10⁴.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	57 (7)	7768 (6)	1999 (5)
C(2)	-2181 (7)	4577 (7)	3432 (5)
C(3)	2169 (7)	6722 (7)	5110 (5)
C(4)	9 (6)	6326 (6)	3544 (4)
O	2269 (5)	8642 (6)	1769 (4)
N	-2247 (6)	8063 (6)	932 (4)
H(1)	-2275 (81)	9106 (84)	-40 (65)
H(2)	-3931 (89)	7668 (83)	1344 (59)
H(3)	3712 (79)	8194 (79)	5313 (58)
H(4)	-3965 (83)	4375 (81)	2181 (60)

Table 3. Thermal vibrational parameters

The values of the vibration parameters and the estimated standard deviations in parentheses are multiplied by 10⁴. The temperature factor expression used is of the form

$$\exp \{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\}.$$

	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
C(1)	364 (14)	393 (15)	141 (7)	1 (11)	110 (8)	95 (8)
C(2)	381 (15)	470 (16)	138 (7)	-64 (12)	60 (8)	106 (9)
C(3)	331 (14)	435 (16)	149 (7)	-45 (12)	59 (8)	106 (9)
C(4)	319 (13)	368 (14)	133 (7)	-13 (11)	87 (7)	78 (8)
O	359 (12)	702 (16)	244 (7)	-36 (10)	130 (7)	239 (9)
N	366 (13)	506 (15)	183 (7)	-4 (11)	86 (8)	169 (8)

Table 4. Observed and calculated structure amplitudes × 10²

<i>hkl</i>	<i>I</i> _o	<i>I</i> _c
001	85	85
010	65	65
011	15	15
012	10	10
013	12	12
014	8	8
015	5	5
020	25	25
021	18	18
022	12	12
023	10	10
024	8	8
025	6	6
030	35	35
031	25	25
032	18	18
033	12	12
034	10	10
035	8	8
040	45	45
041	35	35
042	25	25
043	18	18
044	12	12
045	10	10
050	55	55
051	45	45
052	35	35
053	25	25
054	18	18
055	12	12
100	100	100
101	100	100
102	100	100
103	100	100
104	100	100
105	100	100
110	150	150
111	150	150
112	150	150
113	150	150
114	150	150
115	150	150
120	200	200
121	200	200
122	200	200
123	200	200
124	200	200
125	200	200
130	250	250
131	250	250
132	250	250
133	250	250
134	250	250
135	250	250
140	300	300
141	300	300
142	300	300
143	300	300
144	300	300
145	300	300
150	350	350
151	350	350
152	350	350
153	350	350
154	350	350
155	350	350
200	400	400
201	400	400
202	400	400
203	400	400
204	400	400
205	400	400
210	450	450
211	450	450
212	450	450
213	450	450
214	450	450
215	450	450
220	500	500
221	500	500
222	500	500
223	500	500
224	500	500
225	500	500
230	550	550
231	550	550
232	550	550
233	550	550
234	550	550
235	550	550
240	600	600
241	600	600
242	600	600
243	600	600
244	600	600
245	600	600
250	650	650
251	650	650
252	650	650
253	650	650
254	650	650
255	650	650
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305	700	700
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333	850	850
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344	900	900
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350	950	950
351	950	950
352	950	950
353	950	950
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355	950	950
400	1000	1000
401	1000	1000
402	1000	1000
403	1000	1000
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415	1050	1050
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435	1150	1150
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442	1200	1200
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450	1250	1250
451	1250	1250
452	1250	1250
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454	1250	1250
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500	1300	1300
501	1300	1300
502	1300	1300
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523	1400	1400
524	1400	1400
525	1400	1400
530	1450	1450
531	1450	1450
532	1450	1450
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534	1450	1450
535	1450	1450
540	1500	1500
541	1500	1500
542	1500	1500
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544	1500	1500
545	1500	1500
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555	1550	1550
600	1600	1600
601	1600	1600
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605	1600	1600
610	1650	1650
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613	1650	1650
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615	1650	1650
620	1700	1700
621	1700	1700
622	1700	1700
623	1700	1700
624	1700	1700
625	1700	1700
630	1750	1750
631	1750	1750
632	1750	1750
633	1750	1750
634	1750	1750
635	1750	1750
640	1800	1800
641	1800	1800
642	1800	1800
643	1800	1800
644	1800	1800
645	1800	1800
650	1850	1850
651	1850	1850
652	1850	1850
653	1850	1850
654	1850	1850
655	1850	1850
700	1900	1900
701	1900	1900
702	1900	1900
703	1900	1900
704	1900	1900
705	1900	1900
710	1950	1950
711	1950	1950
712	1950	1950
713	1950	1950
714	1950	1950
715	1950	1950
720	2000	2000
721	2000	2000
722	2000	2000
723	2000	2000
724	2000	2000
725	2000	2000
730	2050	2050
731	2050	2050
732	2050	2050
733	2050	2050
734	2050	2050
735	2050	2050
740	2100	2100
741	2100	2100
742	2100	2100
743	2100	2100
744	2100	2100
745	2100	2100
750	2150	2150
751	2150	2150
752	2150	2150
753	2150	2150
754	2150	2150
755	2150	2150
800	2200	2200
801	2200	2200
802	2200	2200
803	2200	2200
804	2200	2200
805	2200	2200
810	2250	2250
811	2250	2250
812	2250	2250
813	2250	2250
814	2250	2250
815	2250	2250
820	2300	2300
821	2300	2300
822	2300	2300
823	2300	2300
824	2300	2300
825	2300	2300
830	2350	2350
831	2350	2350
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833	2350	2350
834	2350	2350
835	2350	2350
840	2400	2400
841	2400	2400
842	2400	2400
843	2400	2400
844	2400	2400
845	2400	2400
850	2450	2450
851	2450	2450
852	2450	2450
853	2450	2450
854	2450	2450
855	2450	2450
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902	2500	2500
903	2500	2500
904	2500	2500
905	2500	2500
910	2550	2550
911	2550	2550
912	2550	2550
913	2550	2550
914	2550	2550
915	2550	2550
920	2600	2600
921	2600	2600
922	2600	2600
923	2600	2600
924	2600	2600
925	2600	2600
930	2650	2650
931	2650	2650
932	2650	2650
933	2650	2650
934	2650	2650
935	2650	2650
940	2700	2700
941	2700	2700
942	2700	2700
943	2700	2700
944	2700	2700
945	2700	2700
950	2750	27

Table 5. Rigid-body thermal parameters referred to orthogonal axes a, b, c^*

Estimated standard deviations of the elements of the T and L tensors are given in parentheses.

$$\mathbf{T} = \begin{pmatrix} 330 (12) & -59 (10) & 126 (10) \\ & 458 (11) & 27 (10) \\ & & 269 (10) \end{pmatrix} \times 10^{-4} \text{ \AA}^2$$

$$\mathbf{L} = \begin{pmatrix} 17 (2) & & 0 (2) \\ & 6 (2) & \\ & 101 (7) & -97 (7) \\ & & 109 (8) \end{pmatrix} \times 10^{-4} \text{ rad}^2$$

Principal axes of T

R.m.s. amplitude (Å)	Direction cosines ($\times 10^3$)
0.220	-465 870 -163
0.203	-629 -454 -631
0.126	-623 -191 758

Principal axes of L

R.m.s. amplitude (rad)	Direction cosines ($\times 10^3$)
0.142	19 693 -720
0.043	930 252 267
0.025	364 -676 -641

Discussion of the crystal and molecular structure

The crystal structure of terephthalamide consists of molecules held together by hydrogen bonding in sheets. Chains of molecules are hydrogen-bonded end-to-end across centres of symmetry, and adjacent chains are linked by hydrogen bonds approximately parallel to the a axis. The hydrogen-bonded distances (N...O) are 2.90 and 2.94 Å respectively and the N-H...O angles are 175.7 and 149.4°. There are no abnormal contact distances between atoms in adjacent sheets; the closest approach between heavy atoms is 3.43 Å for atoms C(2) and C(3). The crystal structure projected on to the (010) plane is illustrated in Fig. 1.

The bond lengths of the amide group and the benzene ring are comparable with those found in similar compounds. The carbon atoms of the benzene ring are coplanar within the limits of the experimental error, and the plane through the amide group makes an angle of 23° with this plane. The equations of these planes referred to the orthogonal axes a, b', c^* and the deviations of atoms from them are shown in Table 9. A similar twist, of magnitude 24.6°, has been found for benzamide (Blake & Small, 1972) in which the non-planarity is attributed to repulsion between an amide hydrogen atom and the *ortho* hydrogen atom rather than repulsion effects between adjacent hydrogen-bonded molecules. The same view is put forward for

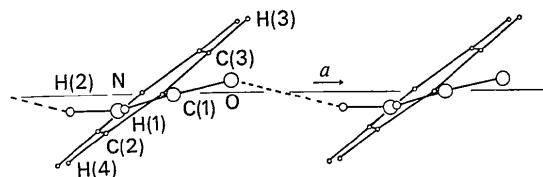


Fig. 2. Projection showing the side-to-side hydrogen bonding. For clarity only one of the amide groups is depicted.

the non-planarity of terephthalamide since the amide hydrogen atom, H(2), is involved in a close contact of 1.99 Å with the *ortho* hydrogen atom, H(4), whereas the closest approaches between adjacent molecules related by the a translation are 3.11 Å between atoms H(3) and H(4), 3.05 Å between atoms O and H(4) and 3.16 Å between atoms C(2) and H(3).

Table 7. Bond distances and their standard deviations

	Before libration correction	After libration correction
C(1)-C(4)	1.489 (5) Å	1.491 (5) Å
C(1)-O	1.244 (5)	1.247 (6)
C(1)-N	1.298 (5)	1.305 (6)
C(2)-C(4)	1.397 (6)	1.409 (6)
C(3)-C(4)	1.377 (5)	1.382 (6)
C(3)-C(2')	1.379 (8)	1.380 (8)
N-H(1)	0.98 (5)	
N-H(2)	0.98 (5)	
C(3)-H(3)	1.05 (4)	
C(2)-H(4)	1.12 (4)	

Table 8. Bond angles and their standard deviations

	Before libration correction	After libration correction
C(4)-C(1)-O	119.7 (7)°	119.6 (7)°
C(4)-C(1)-N	118.0 (7)	117.7 (7)
O-C(1)-N	122.3 (9)	122.7 (9)
C(1)-C(4)-C(2)	121.2 (7)	121.1 (7)
C(1)-C(4)-C(3)	119.3 (7)	119.2 (7)
C(2)-C(4)-C(3)	119.5 (7)	119.8 (7)
C(3')-C(2)-C(4)	119.8 (9)	119.4 (9)
C(2')-C(3)-C(4)	120.7 (9)	120.6 (9)
C(1)-N-H(1)	119 (2)	
H(1)-N-H(2)	120 (4)	
C(1)-N-H(2)	119 (2)	
H(3)-C(3)-C(2')	118 (2)	
C(4)-C(3)-H(3)	121 (2)	
C(4)-C(2)-H(4)	118 (2)	
H(4)-C(2)-C(3')	122 (2)	

Table 6. Observed and calculated values of ($U_{ij} \times 10^4$) in Å²

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
C(1)	406	392	503	547	334	343	-84	-90	119	107	95	106
C(2)	469	439	604	560	326	346	-160	-153	32	34	118	108
C(3)	405	432	557	576	353	382	-130	-168	25	27	110	132
C(4)	365	345	482	479	314	285	-87	-66	84	121	69	46
O	403	428	836	791	577	563	-199	-173	96	65	303	324
N	432	444	607	635	434	419	-108	-117	51	52	208	187

Table 9. *Deviations of atoms from least-squares planes*

(a) Plane through the benzene-ring carbon atoms
Equation of the plane, referred to orthogonal axes a , b' , c^* is

$$-0.5879x + 0.6342y + 0.5022z = 3.3425.$$

C(2)	-0.001 Å	H(1)	0.516 Å
C(3)	-0.001	H(2)	0.939
C(4)	0.001	H(3)	0.124
C(1)	0.004	H(4)	0.058
O	-0.417		
N	0.450		

(b) Plane through atoms C(1), C(4), O and N

Equation of the plane, referred to orthogonal axes a , b' , c^* is

$$-0.2317x + 0.7189y + 0.6553z = 3.7368.$$

C(1)	0.000 Å	N	0.000 Å
C(4)	0.000	H(1)	0.060
O	0.000	H(2)	0.190

Another feature of interest is the degree of planarity of the hydrogen-bonding system, which is very similar to that reported for benzamide. The planes of the amide groups involved in hydrogen bonding across the centre of symmetry have a separation of 0.31 Å (0.37 Å in benzamide) and for the amide groups hydrogen-bonded side-to-side the separation is 1.16 Å (1.15 Å in benzamide). Fig. 2 shows the side-to-side

hydrogen-bonding network and illustrates the extent to which the 0.19 Å deviation of the amide hydrogen atom, H(2), from the amide plane places it further from the *ortho* hydrogen atom, H(4), and closer to a linear hydrogen-bonding direction.

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Kristall- und Molekülstruktur von 1-Hyoscyaminhydrobromid

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The crystal structure of 1-hyoscyamine hydrobromide ($C_{17}H_{24}O_3NBr$) has been investigated. The relationship between the molecular structure and the pharmacological mode of operation has been discussed with reference to the known properties of the acetylcholine receptor. Bonding to the receptor is achieved through the tertiary amino group with hydrogen bonds of 3.7 and 7.7 Å to the anionic site of the receptor.

Hyoscyamin ist ein Alkaloid der Atropingruppe, das sich in verschiedenen Pflanzen, z.B. *Atropa belladonna* (Tollkirsche) und *Hyoscyamus niger* (Bilsenkraut) findet. Es kommt in zwei optisch aktiven Formen vor, als (+)-Hyoscyamin und als (-)-Hyoscyamin. (-)-Hyoscyamin ist der Ester des Tropins und der (-)-Tropasäure. In der Natur findet man vorwiegend die linksdrehende Form. Seine pharmakologische Wirkung kommt dadurch zustande, dass Rezeptoren von Zellen, die auf Acetylcholin (ACh) ansprechen, für diese Transmittersubstanz unempfindlich gemacht werden. Die Wirkung von (-)-Hyoscyamin im peripheren Nervensystem ist allerdings beschränkt auf die glatte Muskulatur und die parasymphatisch innerierten Drüsen. An der quergestreiften Muskulatur und an den Ganglien wirkt Hyoscyamin nicht als

ACh-Antagonist. Die optischen Isomeren haben nicht dieselbe pharmakologische Wirksamkeit. (+)-Hyoscyamin beeinflusst das cholinerge periphere Nervensystem sehr viel weniger (Cushny, 1920), es kommt also bei der pharmakologischen Wirkung auf die räumliche Beziehung der Atomgruppen im Molekül an. Eine Aufklärung der Raumstruktur von Hyoscyamin und entsprechend wirkenden Verbindungen kann weitere Aufschlüsse über die Beziehungen zwischen chemischer Struktur und pharmakologischer Wirkung dieser Substanzen geben.

Material und Methode

Untersucht wurde das käufliche (-)-Hyoscyaminhydrobromid der Fa. Merck, Darmstadt.