J Chem Crystallogr (2010) 40:397–401
DOI 10.1007/s10870-009-9667-0

ORIGINAL PAPER

Crystal and Molecular Structure of 4-Aminobenzohydrazide

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Received: 12 October 2009 / Accepted: 3 December 2009 / Published online: 13 December 2009

Abstract The molecule of 4-aminobenzohydrazide is essentially planar and geometric parameters conform to literature precedents. Supramolecular N–H···O and N–H···N interactions combine to link molecules of 4-aminobenzohydrazide into a three-dimensional network. Weaker N–H···N and N–H···π interactions consolidate the structure. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.411(2)$ Å, $b = 14.000(6)$ Å, $c = 9.894(4)$ Å, $\beta = 103.917(7)^\circ$, and $Z = 4$.

Keywords Hydrazide · Hydrogen bonding · N–H···π interaction

Introduction

High temperature resistive polymers have been the subject of considerable investigation in recent years owing to their ability to exhibit high thermo-oxidative stability, resistance to environmental degradation, and superior dielectric, thermal, adhesive, dimensional stability, and mechanical properties [1–7]. These properties are strongly influenced by their chemical structure, i.e. by both the chemical composition and molecular configuration. In particular, polymers containing aromatic rings in the main chain have received special attention as their presence makes these polymers more thermally resistant [8–10]. However, rigidity of the backbone renders them insoluble in most organic solvents and imparts high softening temperatures. These shortcomings make them generally difficult or too expensive to process, thus restricting their applications. Therefore, solubilization of high temperature polymers has been targeted by several means, such as by the incorporation of flexible linkages [8–10], bulky substituents [11–14], non-coplanar or alicyclic units [15, 16], or pendent flexible groups [17]. Hence, different classes of polymer such as polyimides, polyamides, poly(amide-hydrazide)s, poly(imide-hydrazide)s have been extensively studied.

In this connection, the introduction of hydrazide or amide plus hydrazide linkages into the backbone of the polymer chain is a viable alternative to improve the processability of high temperature resistive polymers. Further, the presence of hydrazide groups in the main chain can be exploited by converting them into the more chemically resistant and thermally stable oxadiazole structure by heating the polymer in the bulk or fiber form at elevated temperatures [18]. The title compound, 4-aminobenzohydrazide, was prepared as a part of an on-going research program aimed at the design and synthesis of structurally modified hydrazide for incorporation in high temperature polymers. Herein, the synthesis and crystal and molecular structures of 4-aminobenzohydrazide are reported.

Experimental

Materials and Physical Measurements

All reagents were of AR grade and were used without further purification. The precursor molecule, 1,4-bis(4-nitrobenzoyloxymethyl)benzene, was prepared using literature

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procedures [19, 20]. Elemental Analyses for C, H and N were performed on a Carlo Erba Corporation Model 1104 element analysis instrument.

Synthesis

A two neck 250 mL round bottom flask was charged with freshly synthesized 1,4-bis(4-nitrobenzoyloxymethyl)benzene (1.0 g, 2.29 mmol), hydrazine monohydrate (10 mL) and ethanol (80 mL). The resultant mixture was refluxed for 1 h. After the addition of 5% palladium on carbon (Pd/C, 0.2 g), the mixture was further refluxed for 15 h and filtered hot to remove Pd/C. The crude solid was recrystallized from ethanol to afford 4-aminobenzohydrazide (yield 73%, mp = 239 °C), which was then analyzed by single crystal techniques. Elemental analysis. Found: C = 55.09, H = 5.97, N = 27.80. $C_7H_9ON_3$ requires: C = 55.60, H = 5.96, N = 27.81 %. IR (KBr pellet) in cm^{-1}: 3450 υ(NH st), 3340, 3250 υ(NH_2 st), 1600 υ(C = O st). ^1H NMR (DMSO-d_6) in δ (ppm) and J (Hz): 9.29 (1H, s, C–N**H**–NH_2), 7.56 (8.4) (2H, d, a,a'), 6.54 (9.0) (2H, d, b,b'), 5.59 (2H, s, –N**H**$_2$), 4.31 (2H, s, NH–N**H**$_2$); see Scheme for atom labelling. ^{13}C NMR (DMSO-d_6) in δ (ppm) and J (Hz): 166.9 (**C** = O), 152.0 (H_2N–**C**), 120.4 (–**C**–C = O), 128.9 (a,a'), 113.1 (b,b').

X-Ray Crystallography

Intensity data for a colorless block were collected at 98 K on a Rigaku AFC12/Saturn724 CCD fitted with Mo Kα radiation. The data set was reduced using standard methods [21]. The structure was solved by direct methods with SHELXS-97 [22] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-97 [22] with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.138P)^2 + 0.254P]$ where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were located in a difference Fourier map, including N–H hydrogen atoms, but were included in the final refinement in their calculated positions. For the N–H atoms, the positions were refined with the restraints N–H = 0.880 ± 0.001 Å or 0.910 ± 0.001 Å. Crystal data and refinement details are given in Table 1. Figure 1, showing the atom labeling scheme, was drawn with 50% displacement ellipsoids using ORTEP-3 [23] and the

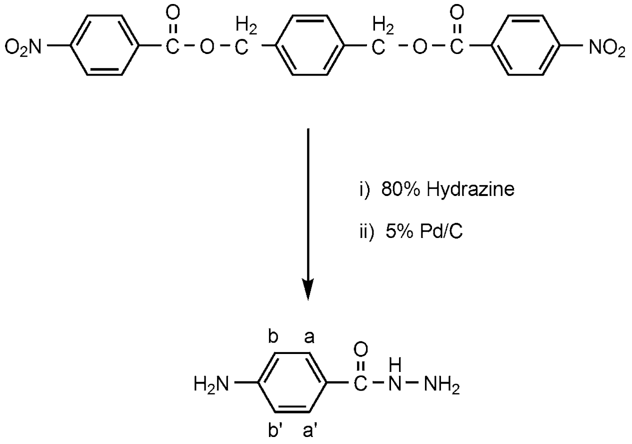
Table 1 Crystal data and refinement details for 4-aminobenzohydrazide

Empirical formula	$C_7H_9N_3O$	
Formula weight	151.17	
Crystal habit, color	Block, colorless	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
	a (Å)	5.411(2)
	b (Å)	14.000(6)
	c (Å)	9.894(4)
	β (°)	103.917(7)
Volume ($Å^3$)	727.5(5)	
Z		4
Density (calculated, g cm^{-3})	1.380	
Absorption coefficient (mm^{-1})	0.098	
$F(000)$	320	
Crystal size (mm)	0.11 × 0.18 × 0.46	
θ Range for data collection (°)	2.6–26.5	
Reflections collected	2977	
Independent reflections	1491	
R_{int}		0.019
Reflections with $I \geq 2\sigma(I)$	1435	
Number of parameters	115	
Goodness-of-fit on F^2	1.04	
a, b for weighting scheme	0.043, 0.345	
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.094$	
R indices (all data)	$R_1 = 0.039$, $wR_2 = 0.095$	
Largest difference peak and hole ($Å^{-3}$)	0.26, −0.22	
CCDC deposition no.	749935	

remaining figures were drawn with DIAMOND [24]. Data manipulation and interpretation were accomplished using WinGX [25] and PLATON [26].

Results and Discussion

The title 4-aminobenzohydrazide was prepared in accord with the following Scheme 1: and characterized spectroscopically (see Experimental). Full structural characterization was afforded by single crystal X-ray crystallography.



Scheme 1

The molecular structure of 4-aminobenzohydrazide with atom labeling is shown in Fig. 1. Excepting hydrazide hydrogens, the molecule is essentially planar as evidenced by the C3–C4–C7–O1, N3–N2–C7–C4, and N3–N2–C7–O1 torsion angles of −13.17(17), 175.32(9), and −4.05(17)°, respectively. Indeed, the maximum deviation from the least-squares plane through all non-hydrogen atoms is −0.212(1) Å for atom O1. The angles about the carbonyl-C7 atom range from a narrow 116.80(10)° for N2–C7–C4 to a wide 122.45(10)° for O1–C7–C4, consistent with significant carbonyl character in the C7=O1 bond (1.2408(14) Å). The N2–C7 bond distance is 1.3368(15) Å and N2–N3 is 1.4222(14) Å. These values are, respectively, equal within experimental error to those found in the crystal structure of benzhydrazide, i.e. 1.240(3), 1.338(5), and 1.415(4) Å [27]. In fact, a search in the CSD [28] shows that for 24 entries with the $H_2N–N(H)C(=O)C_6$ fragment in single component structures, the average C=O, N–C and N–N distances are 1.235, 1.332 and 1.416, respectively.

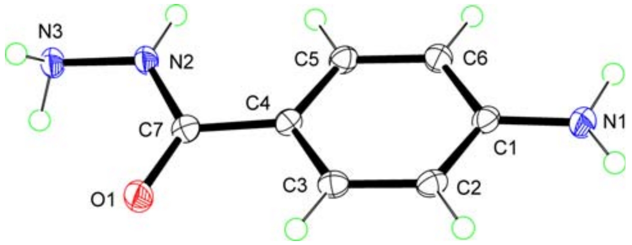


Fig. 1 Molecular structure of 4-aminobenzohydrazide. Displacement *ellipsoids* are drawn at the 50% probability level

Of particular interest is the crystal packing. Geometric parameters describing the most prominent intermolecular interactions are collected in Table 2. From Fig. 1 it is clear that there is a mismatch between acidic hydrogen atoms, i.e. there are five N–H atoms available to form hydrogen bonds, and three hydrogen bond acceptors, i.e. three: 1× oxygen and 2× nitrogen (N1 and N3). This disparity between donors and acceptors is partly compensated for by the carbonyl-O1 atom forming two N–H···O hydrogen bonds with symmetry related 4-amino–NH_2 hydrogen atoms. As illustrated in Fig. 2, this results in the formation of an eight-membered $\{O\cdots H–N–H\cdots\}_2$ synthon, $R_4^2(8)$, involving a total of four molecules. The next most prominent interaction, at least based on distance and angle considerations, occurs between centrosymmetrically related hyrazide-N3 and amide-N2–H atoms resulting in the formation of a six-membered $\{H\ldots N–H\}_2$ synthon, $R_2^2(6)$. These synthons serve to link the four molecule aggregates sustained by N–H···O hydrogen bonds into a supramolecular chain, with successive pairs of molecules virtually orthogonal to each other. Expanding these aggregates by further N–H···O and N–H···N hydrogen bonds orthogonal to the chain gives rise to a three-dimensional architecture as illustrated in projection in Fig. 3.

From the data included in Table 2, it is evident that the short and directional N–H···O and N–H···N hydrogen bonding interactions dictate the adoption of the observed

Table 2 Hydrogen bonding parameters (A–H···B; Å, °) for 4-aminobenzohydrazide

A	H	B	H···B	A···B	A–H···B	Symmetry operation
N1	H1n	O1	2.08	2.9846(19)	176	½ + *x*, ½ − *y*, ½ + *z*
N1	H2n	O1	2.08	2.9326(19)	156	1½ − *x*, ½ + *y*, ½ − *z*
N2	H3n	N3	2.12	2.9413(19)	154	−*x*, −*y*, 1 − *z*
N3	H4n	Cg(C1–C6)	2.82	3.4844(18)	131	1 − *x*, −*y*, 1 − *z*
N3	H5n	N1	2.42	3.286(2)	159	½ − *x*, −½ + *y*, ½ − *z*

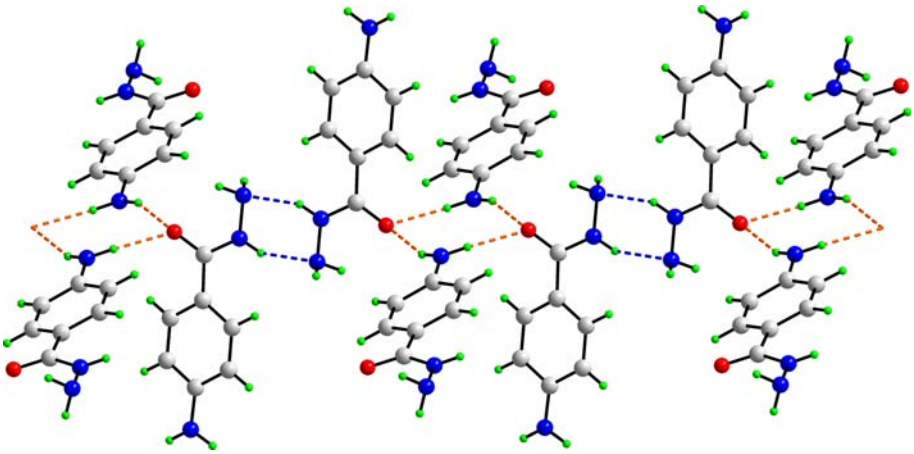


Fig. 2 Detail of the supramolecular association mediated by N–H···O (*orange dashed lines*) and N–H···N (*blue dashed lines*) hydrogen bonding in the crystal structure of 4-aminobenzohydrazide. The N–H···O and N–H···N hydrogen bonds extend in three dimensions to form a three-dimensional network. (Color figure online)

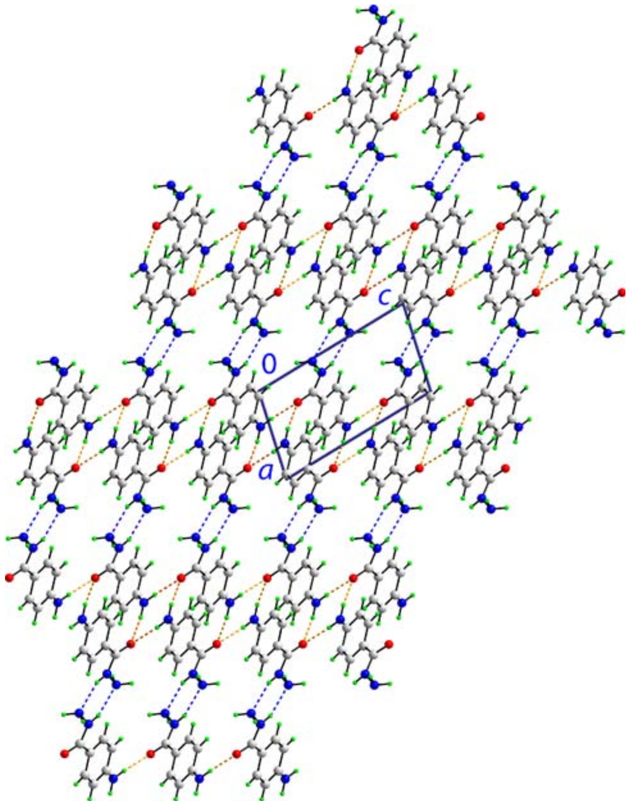


Fig. 3 Unit cell contents viewed in projection down the *b*-axis in the crystal structure of 4-aminobenzohydrazide

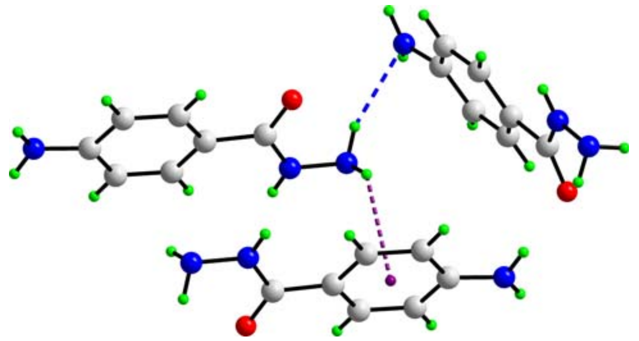


Fig. 4 Detail of the intermolecular interactions formed by the terminal –N(H)–NH_2 group in 4-aminobenzohydrazide. The weak N–H···N and N–H···π interactions are shown as *blue* and *purple dashed lines*, respectively, and cooperate to reinforce the N–H···O hydrogen bonds. (Color figure online)

network. However, this leaves two acidic hydrogen atoms, each bound to the hydrazide-N3 atom, yet to be accounted for. One of these, i.e. H5n, participates in a significantly weaker N–H···N interaction, compared to the aforementioned N–H···N hydrogen bonds, with the 4-amino–N1 atom, Table 2. The remaining H4n atom forms an N–H···π interaction where the π-system is defined by the C1–C6 aromatic ring. While this type of interaction is not common let alone fully understood [29–31], certainly not when compared with now well documented C–H···π contacts [32–34], there are several precedents for N–H···π interactions in the crystallographic literature [35–37]. The last two interactions, represented in Fig. 4, serve to provide additional stability to molecules bridged by the N–H···O hydrogen bonds.

In keeping with Etter's guidelines for hydrogen bond formation [38], the strongest donors and acceptors in 4-aminobenzohydrazide interact to form the framework of the crystal structure, leaving the hyrazide-N3 hydrogen atoms to participate in weak or non-conventional interactions.

Supplementary Material

CCDC-749935 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax +44(0)1223-336033; email: deposit@ccdc.ccam.ac.uk].

Acknowledgments The authors are grateful to the Department of Chemistry, Quaid-i-Azam University, for providing laboratory and analytical facilities. We are also grateful to the Higher Education Commission, Pakistan, for their financial support.

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