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Structures of the Monohydrated (I) and Anhydrous (II) Forms of 2,2′-[Benzylidenemethylenebis(carbonylamino)]dibenzoic Acid, $C_{24}H_{18}N_2O_6.H_2O$ and $C_{24}H_{18}N_2O_6$

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Abstract. (I) $M_r = 448{\cdot}4$, triclinic, $P\bar{1}$, $a = 11{\cdot}687$ (4), $b = 10{\cdot}088$ (3), $c = 10{\cdot}519$ (5) Å, $\alpha = 105{\cdot}79$ (4), $\beta = 110{\cdot}25$ (4), $\gamma = 97{\cdot}83$ (3)°, $V = 1082{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}376$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}82$ mm^{-1}, $F(000) = 468$, $T = 293$ K, $R(F) = 0{\cdot}064$ for 2873 unique reflections with $F_o > 3\sigma(F_o)$. (II) $M_r = 430{\cdot}4$, monoclinic, $P2_1/a$, $a = 16{\cdot}469$ (3), $b = 11{\cdot}334$ (6), $c = 11{\cdot}312$ (3) Å, $\beta = 99{\cdot}49$ (2)°, $V = 2082{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}373$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}79$ mm^{-1}, $F(000) = 896$, $T = 293$ K, $R(F) = 0{\cdot}071$ for 2726 unique reflections with $F_o > 3\sigma(F_o)$. The molecular conformations of (I) and (II) are different [the main difference involves rotation about one of the central C(=O)—C bonds: torsion angle −166·8 (3)° for (I) and −29·9 (5)° for (II)]. N—H···O intramolecular hydrogen bonds are formed between the NH and COOH groups in both molecules. One of the NH groups of (I) forms a bifurcated intramolecular hydrogen bond.

Introduction. The crystal structures of the title compounds (I) and (II) are of current interest because of the unusual melting behavior of crystal (I). The monohydrate crystal (I) obtained from methanol–water solution showed an apparent increase of the melting point from 468 to 513 K resulting from the preceding press or granulation processing applied to the single crystal. From the differential thermal analysis of the pressed monohydrate crystal, the recrystallization of the anhydrous crystallites seems to occur in the melting process followed by dehydration during the temperature increase. The anhydrous crystals (II), however, were obtained from acetic acid solution, and their melting point was observed as 513 K. In the present paper, we describe the crystal structures of (I) and (II), and discuss the differences found between them.

Experimental. For (I) and (II): D_m not determined; Rigaku AFC-5RU diffractometer, graphite-monochromated Cu $K\alpha$ radiation; 2θ–ω mode, $2\theta_{\max} = 120°$; no significant intensity variation for three reflections monitored every 56 reflections; no absorption or extinction corrections; structures solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all H atoms located in difference Fourier maps; refinement by full-matrix least squares using modified version of *ORFLS* (Busing, Martin & Levy, 1962); non-H atoms anisotropic, H atoms isotropic; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/[\sigma^2(F) + (0{\cdot}023F)^2]$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). (I): crystal 0·18 × 0·20 × 0·27 mm, 2873 reflections, $-13 \le h \le 12$, $0 \le k \le 11$, $-11 \le l \le 10$, $R = 0{\cdot}064$, $wR = 0{\cdot}060$, $(\Delta/\sigma)_{\max} = 0{\cdot}77$, no peaks greater than 0·18 e Å^{-3} in final difference Fourier map. (II): crystal 0·10 × 0·17 × 0·20 mm, 2726 reflections, $-18 \le h \le 16$, $0 \le k \le 12$, $0 \le l \le 12$, $R = 0{\cdot}071$, $wR = 0{\cdot}069$, $(\Delta/\sigma)_{\max} = 0{\cdot}9$, no peaks greater than

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0·25 e Å^{-3} in final difference Fourier map. All computations on a FACOM M382 in the data-processing Center of Kyoto University.

Discussion. The final positional parameters and equivalent isotropic thermal parameters for the non-H atoms of (I) are listed in Table 1, and those for (II) are listed in Table 2.*

The resulting molecular structures of (I) and (II) are shown in Fig. 1. Bond distances and bond angles are listed in Table 3, and hydrogen-bond distances and angles in Table 4. In both molecules, all phenyl rings are planar within experimental error, as are the C=C groups. The dihedral angles between the C=C plane and the phenyl rings are 18·6 (2) [C(1) ring], 36·3 (1) [C(11)] and 26·5 (1)° [C(27)] for (I), and for (II) are 5·6 (2), 93·6 (1) and 20·5 (2)°, respectively. N—H···O intramolecular hydrogen bonds are formed between all NH and COOH groups. The N···O distances of 2·653 (6)–2·677 (6) Å are shorter than the mean distance of 2·755 (12) Å for 152 intramolecular N—H···O=C bonds given by Taylor, Kennard & Versichel (1984*a*). They are, however, close to those for the similar type of N—H···O hydrogen bonds in *ortho*-substituted aminobenzoic acid derivatives, *e.g.* 2·682 Å for anthranilic acid II (Boone, Derissen & Schoone, 1977). The main difference between the molecular conformations of (I) and (II) is found in the rotation about the C(21)—C(25) bond. The N(10)—C(21)—C(25)—C(26) torsion angles are −166·8 (3) for (I) and −29·9 (5)° for (II). The N(20)—C(23)—C(25)—C(26) torsion angles are −64·3 (4) for (I) and −70·0 (5)° for (II). H(10) in (I) approaches O(24) and

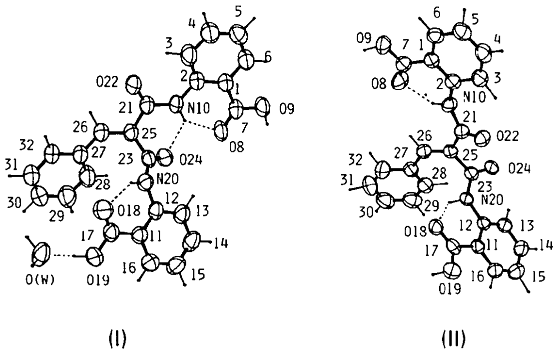

Fig. 1. Perspective view of molecules (I) and (II) showing the atom numbering and thermal ellipsoids (50% probability).

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (*Hamilton,* 1959) *with e.s.d.'s in parentheses for* (I)

	x	y	z	B_{eq}(Å^2)
C(1)	8392 (4)	2568 (4)	295 (4)	4·8 (1)
C(2)	7507 (4)	2550 (4)	922 (4)	4·9 (1)
C(3)	6941 (4)	3684 (5)	1067 (6)	6·8 (2)
C(4)	7250 (5)	4782 (5)	602 (6)	7·5 (2)
C(5)	8082 (5)	4791 (5)	−38 (6)	7·0 (2)
C(6)	8653 (4)	3686 (5)	−181 (5)	5·9 (2)
C(7)	9090 (4)	1442 (4)	155 (4)	5·3 (1)
O(8)	8990 (3)	472 (3)	621 (4)	6·6 (1)
O(9)	9851 (3)	1605 (3)	−490 (3)	6·5 (1)
N(10)	7209 (3)	1389 (3)	1361 (3)	4·9 (1)
C(11)	8941 (4)	−2148 (4)	5331 (4)	4·9 (1)
C(12)	8825 (3)	−1686 (4)	4165 (4)	4·8 (1)
C(13)	9595 (4)	−1973 (5)	3428 (4)	5·8 (2)
C(14)	10470 (4)	−2724 (6)	3852 (5)	6·7 (2)
C(15)	10594 (4)	−3199 (5)	4987 (5)	6·7 (2)
C(16)	9835 (4)	−2912 (5)	5724 (5)	5·9 (2)
C(17)	8166 (4)	−1803 (5)	6188 (4)	5·6 (2)
O(18)	7593 (3)	−888 (4)	6158 (3)	7·1 (1)
O(19)	8165 (3)	−2603 (4)	6992 (3)	7·1 (1)
N(20)	7919 (3)	−908 (4)	3757 (3)	5·0 (1)
C(21)	6336 (4)	1146 (5)	1887 (4)	5·3 (2)
O(22)	5645 (3)	1930 (4)	2043 (4)	8·0 (1)
C(23)	7282 (3)	−922 (4)	2429 (4)	4·7 (1)
O(24)	7510 (3)	−1462 (3)	1383 (3)	5·6 (1)
C(25)	6240 (4)	−155 (4)	2310 (4)	4·9 (1)
C(26)	5231 (4)	−598 (5)	2563 (4)	5·5 (2)
C(27)	4889 (4)	−1801 (5)	2976 (5)	5·5 (2)
C(28)	5292 (5)	−3052 (5)	2660 (6)	7·3 (2)
C(29)	4956 (5)	−4134 (5)	3125 (7)	8·5 (2)
C(30)	4218 (5)	−4000 (6)	3907 (6)	8·0 (2)
C(31)	3797 (4)	−2811 (6)	4202 (5)	7·0 (2)
C(32)	4118 (4)	−1715 (5)	3729 (5)	5·9 (2)
O(*W*)	6754 (3)	−2235 (4)	8408 (3)	7·8 (1)

Table 2. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (*Hamilton,* 1959) *with e.s.d.'s in parentheses for* (II)

	x	y	z	B_{eq}(Å^2)
C(1)	5204 (3)	2410 (4)	3450 (4)	4·0 (2)
C(2)	5232 (3)	1467 (4)	2653 (4)	4·0 (2)
C(3)	4965 (3)	1653 (5)	1419 (4)	4·8 (2)
C(4)	4686 (3)	2764 (5)	1037 (4)	5·2 (2)
C(5)	4648 (3)	3679 (5)	1813 (4)	5·1 (2)
C(6)	4930 (3)	3512 (4)	3030 (4)	4·5 (2)
C(7)	5500 (3)	2246 (5)	4765 (4)	4·4 (2)
O(8)	5625 (2)	1307 (3)	5263 (3)	5·7 (2)
O(9)	5571 (2)	3256 (3)	5366 (3)	5·8 (2)
N(10)	5483 (2)	352 (3)	3097 (3)	4·2 (2)
C(11)	7881 (2)	−3937 (4)	1347 (3)	3·6 (2)
C(12)	7083 (2)	−3931 (4)	1641 (3)	3·5 (2)
C(13)	6538 (3)	−4830 (4)	1228 (4)	4·3 (2)
C(14)	6763 (3)	−5709 (5)	496 (5)	5·1 (2)
C(15)	7550 (3)	−5710 (5)	188 (5)	5·6 (2)
C(16)	8089 (3)	−4835 (5)	601 (4)	4·7 (2)
C(17)	8503 (2)	−3036 (4)	1807 (4)	3·9 (2)
O(18)	8409 (2)	−2244 (3)	2504 (2)	4·2 (1)
O(19)	9199 (2)	−3163 (3)	1379 (3)	5·5 (2)
N(20)	6871 (2)	−3002 (3)	2365 (3)	3·6 (1)
C(21)	5804 (2)	−545 (4)	2527 (4)	3·9 (2)
O(22)	5828 (2)	−562 (3)	1448 (2)	4·6 (1)
C(23)	6116 (2)	−2672 (4)	2557 (3)	3·7 (2)
O(24)	5470 (2)	−3186 (3)	2144 (3)	4·3 (1)
C(25)	6108 (2)	−1574 (4)	3286 (4)	3·6 (2)
C(26)	6414 (3)	−1504 (4)	4467 (4)	4·2 (2)
C(27)	6747 (3)	−2437 (5)	5299 (4)	4·5 (2)
C(28)	6609 (3)	−3639 (5)	5104 (4)	5·0 (2)
C(29)	6926 (3)	−4471 (5)	5942 (5)	6·0 (3)
C(30)	7395 (4)	−4131 (6)	7003 (5)	6·7 (3)
C(31)	7541 (4)	−2951 (7)	7216 (5)	8·4 (4)
C(32)	7226 (4)	−2099 (6)	6380 (5)	6·9 (3)

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* List of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42207 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and bond angles* (°) *for* (I) *and* (II)

	(I)	(II)		(I)	(II)		(I)	(II)
C(1)–C(2)	1·407 (7)	1·404 (6)	C(21)–C(25)	1·498 (7)	1·485 (6)	C(14)–C(15)	1·374 (8)	1·396 (8)
C(1)–C(6)	1·391 (7)	1·385 (6)	C(25)–C(26)	1·341 (7)	1·350 (6)	C(15)–C(16)	1·377 (8)	1·361 (7)
C(1)–C(7)	1·491 (7)	1·499 (6)	C(27)–C(28)	1·403 (8)	1·393 (8)	C(17)–O(18)	1·213 (7)	1·221 (5)
C(2)–C(3)	1·397 (7)	1·409 (6)	C(28)–C(29)	1·375 (9)	1·377 (7)	C(17)–O(19)	1·319 (7)	1·324 (5)
C(2)–N(10)	1·415 (6)	1·397 (6)	C(29)–C(30)	1·379 (10)	1·371 (8)	N(20)–C(23)	1·331 (5)	1·350 (5)
C(3)–C(4)	1·380 (9)	1·385 (8)	C(11)–C(12)	1·398 (7)	1·408 (5)	C(23)–O(24)	1·223 (6)	1·235 (5)
C(4)–C(5)	1·361 (10)	1·367 (7)	C(11)–C(16)	1·397 (7)	1·400 (7)	C(23)–C(25)	1·517 (6)	1·494 (6)
C(5)–C(6)	1·375 (8)	1·391 (6)	C(11)–C(17)	1·495 (7)	1·479 (6)	C(26)–C(27)	1·448 (8)	1·461 (7)
C(7)–O(8)	1·217 (6)	1·206 (6)	C(12)–C(13)	1·388 (7)	1·387 (6)	C(27)–C(32)	1·387 (8)	1·395 (7)
C(7)–O(9)	1·310 (7)	1·327 (6)	C(12)–N(20)	1·420 (6)	1·413 (5)	C(32)–C(31)	1·388 (9)	1·391 (9)
N(10)–C(21)	1·343 (7)	1·357 (6)	C(13)–C(14)	1·378 (8)	1·384 (7)	C(31)–C(30)	1·357 (9)	1·373 (10)
C(21)–O(22)	1·225 (7)	1·228 (5)						
C(2)–C(1)–C(6)	119·4 (4)	120·6 (4)	O(22)–C(21)–C(25)	119·8 (5)	120·0 (4)	C(14)–C(15)–C(16)	119·4 (5)	119·6 (5)
C(2)–C(1)–C(7)	122·1 (4)	120·2 (4)	C(21)–C(25)–C(26)	118·5 (4)	124·1 (4)	C(11)–C(16)–C(15)	120·9 (5)	121·7 (5)
C(6)–C(1)–C(7)	118·5 (5)	119·1 (4)	C(21)–C(25)–C(23)	118·8 (4)	111·6 (4)	C(11)–C(17)–O(18)	124·3 (5)	125·5 (4)
C(1)–C(2)–C(3)	118·1 (5)	119·0 (4)	C(26)–C(27)–C(28)	123·8 (5)	124·9 (4)	C(11)–C(17)–O(19)	112·9 (4)	112·8 (4)
C(1)–C(2)–N(10)	119·4 (4)	119·8 (4)	C(27)–C(28)–C(29)	120·4 (6)	121·8 (4)	O(18)–C(17)–O(19)	122·9 (5)	121·7 (4)
C(3)–C(2)–N(10)	122·5 (5)	121·1 (4)	C(28)–C(29)–C(30)	120·3 (5)	120·3 (5)	C(12)–N(20)–C(23)	126·6 (4)	128·5 (3)
C(2)–C(3)–C(4)	120·3 (6)	118·6 (5)	C(29)–C(30)–C(31)	120·3 (6)	119·0 (6)	N(20)–C(23)–O(24)	124·7 (4)	124·6 (4)
C(3)–C(4)–C(5)	122·0 (5)	122·5 (4)	C(12)–C(11)–C(16)	118·6 (5)	118·5 (4)	N(20)–C(23)–C(25)	113·9 (4)	114·3 (3)
C(4)–C(5)–C(6)	118·4 (6)	119·3 (5)	C(12)–C(11)–C(17)	121·7 (4)	122·2 (4)	O(24)–C(23)–C(25)	121·4 (4)	121·1 (3)
C(1)–C(6)–C(5)	121·8 (5)	119·9 (4)	C(16)–C(11)–C(17)	119·7 (4)	119·3 (4)	C(23)–C(25)–C(26)	122·6 (4)	124·0 (4)
C(1)–C(7)–O(8)	123·6 (5)	125·1 (5)	C(11)–C(12)–C(13)	120·3 (4)	119·6 (4)	C(25)–C(26)–C(27)	130·6 (5)	129·4 (4)
C(1)–C(7)–O(9)	113·9 (4)	112·9 (4)	C(11)–C(12)–N(20)	119·1 (4)	118·0 (3)	C(26)–C(27)–C(32)	118·3 (5)	117·6 (5)
O(8)–C(7)–O(9)	122·5 (4)	121·9 (4)	C(13)–C(12)–N(20)	120·6 (4)	122·3 (4)	C(27)–C(32)–C(31)	120·9 (5)	119·9 (6)
C(2)–N(10)–C(21)	127·7 (4)	128·5 (4)	C(12)–C(13)–C(14)	119·4 (5)	120·5 (5)	C(30)–C(31)–C(32)	120·1 (6)	121·5 (5)
N(10)–C(21)–O(22)	123·5 (5)	124·3 (4)	C(13)–C(14)–C(15)	121·4 (5)	120·0 (5)	C(28)–C(27)–C(32)	117·9 (5)	117·5 (5)
N(10)–C(21)–C(25)	116·6 (4)	115·7 (4)						

Table 4. *Hydrogen-bonding schemes in* (I) *and* (II)

E.s.d.'s are in parentheses. *D*: donor, *A*: acceptor.

D–H···*A*	*D*···*A* (Å)	H···*A* (Å)	*D*–H···*A* (°)
Monohydrate (I)			
Intramolecular			
N(10)–H(10)···O(8)	2·655 (6)	1·86 (5)	138 (3)
N(10)–H(10)···O(24)	2·950 (5)	2·23 (4)	131 (3)
N(20)–H(20)···O(18)	2·677 (5)	1·93 (4)	141 (3)
Intermolecular			
O(9)–H(9)···O(8$^{\rm i}$)	2·644 (5)	1·69 (5)	179 (2)
O(19)–H(19)···O(*W*)	2·577 (6)	1·58 (5)	177 (2)
O(*W*)–H(*W*1)···O(22$^{\rm ii}$)	2·752 (5)	1·84 (4)	151 (3)
O(*W*)–H(*W*2)···O(24$^{\rm iii}$)	2·784 (5)	1·83 (4)	174 (2)
Anhydrous (II)			
Intramolecular			
N(10)–H(10)···O(8)	2·653 (5)	1·87 (4)	134 (2)
N(20)–H(20)···O(18)	2·655 (5)	1·89 (4)	138 (2)
Intermolecular			
O(9)–H(9)···O(18$^{\rm iv}$)	2·759 (4)	1·78 (4)	161 (2)
O(19)–H(19)···O(24$^{\rm v}$)	2·621 (5)	1·69 (4)	158 (2)

Symmetry code: (i) $2-x$, $2-y$, $-z$; (ii) x, y, $1+z$; (iii) $1-x$, $2-y$, $1-z$; (iv) $\frac{3}{2}-x$, $\frac{1}{2}+y$, $1-z$; (v) $\frac{1}{2}+x$, $\frac{3}{2}-y$, z.

forms an N—H···O bifurcated intramolecular hydrogen bond between O(8) and O(24); the H···O distances [1·86 (5) and 2·23 (4) Å] are asymmetric and the N—H···O angles [138 (3) and 131 (3)°] are small in comparison with those of the N—H···O=C bifurcated intramolecular hydrogen bonds observed hitherto (Taylor, Kennard & Versichel, 1984*b*). On the other hand, H(10) in (II) has a short intramolecular contact of 1·94 Å with H(26). The H(10)···H(26) non-bonding repulsion may cause the bond distortion around C(25); the C(21)—C(25)—C(26) angle of 124·1 (4)° is significantly larger than the corresponding angle of 118·5 (4)° in (I), and the C(21)—C(25)—C(23) angle of 111·6 (4)° is smaller than the 118·8 (4)° in (I). In addition to such intramolecular interactions, intermolecular crystalline forces may influence the molecular conformation. The water molecule in (I) forms three hydrogen bonds with O(19), O(22) and O(24) of neighboring molecules. All the OH and O=C groups form hydrogen bonds in both crystals, except for O(22) in (II) which does not. Short intermolecular nonbonding contacts are C(4)···C(28′) 3·452 (7) and C(7)···O(8′) 3·320 (6) Å for (I), and C(21)···C(30′) 3·336 (7) and C(21)···O(19′) 3·112 (5) Å for (II).

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