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### $\alpha, \alpha'$ -Dimethyl- $\alpha, \alpha'$ -azinodi-*p*-cresol Monohydrate

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**Abstract.**  $C_{16}H_{16}N_2O_2 \cdot H_2O$ ,  $M_r = 286.33$ , monoclinic,  $P2_1/c$ ,  $a = 15.871$  (4),  $b = 8.300$  (2),  $c = 11.496$  (4) Å,  $\beta = 94.42$  (3)°,  $U = 1509.9$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.260$  Mg m<sup>-3</sup>, final  $R = 0.068$  for 1088 observed reflexions. Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). A torsional angle of 148 (1)° through the azine chain makes the molecule non-planar. No face-to-face close-packing of molecules occurs. The molecules are held together through hydrogen bonds of types O–H...O and O–H...N, involving a nitrogen atom of the azine chain, both molecular hydroxy groups and the water molecule.

**Introduction.** This analysis has been performed in connection with studies on nitrogen-containing aromatic compounds (Fayos, Martínez-Ripoll, García-Mina, Gonzalez-Martínez & Arrese, 1980; Meléndez & Serrano, 1982). The aim was to determine the dependence of structural features of these compounds, like molecular planarity and crystal packing, on solid-state properties such as thermochromism and photochromism.

A pale yellow prismatic single crystal was used to collect the intensities of 2041 independent reflexions up to  $\theta = 26^\circ$  using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) on a four-circle automatic

diffractometer. The data collection process used a rather fast  $\omega/2\theta$  scan, as an intensity decay of ~ 40% was observed after 30 h of experiment. After Lorentz-polarization and intensity-decay corrections, 1088 reflexions were tagged as observed with  $I > 3\sigma(I)$ .

The structure was solved by *MULTAN* (Main *et al.*, 1980) and successive Fourier syntheses. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). H atoms were located on a difference map calculated with those reflexions with  $\sin \theta/\lambda < 0.5$  Å<sup>-1</sup>. Refinement was performed by least-squares analysis using anisotropic thermal coefficients for non-H atoms and an isotropic fixed contribution for H atoms. A weighting scheme was chosen to obtain flat dependence of  $\langle w\Delta^2F \rangle$  vs  $\langle F_o \rangle$  and vs  $\langle \sin \theta/\lambda \rangle$  (Martínez-Ripoll & Cano, 1975). Final disagreement indices are  $R = 0.068$  and  $R_w = 0.087$ . Table 1 shows the final atomic parameters.\*

\* Lists of structure factors, anisotropic thermal parameters and atomic deviations from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36893 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub>/U<sub>iso</sub></i>
O(1)	1.1704 (2)	0.7444 (5)	0.9483 (4)	58 (2)
N(1)	0.7701 (2)	0.7091 (5)	0.8997 (4)	49 (2)
C(11)	0.9134 (2)	0.6472 (5)	0.8821 (5)	41 (2)
C(12)	0.9418 (3)	0.7510 (6)	0.9690 (6)	50 (2)
C(13)	1.0272 (3)	0.7872 (6)	0.9930 (5)	51 (2)
C(14)	1.0851 (2)	0.7154 (6)	0.9261 (5)	44 (2)
C(15)	1.0592 (3)	0.6113 (7)	0.8386 (6)	55 (2)
C(16)	0.9735 (3)	0.5775 (6)	0.8154 (5)	51 (2)
C(17)	0.8217 (3)	0.6086 (5)	0.8592 (5)	44 (2)
C(18)	0.7952 (3)	0.4622 (6)	0.7923 (6)	65 (3)
O(2)	0.2873 (2)	0.6031 (5)	0.8261 (4)	61 (2)
N(2)	0.6835 (2)	0.6729 (5)	0.8722 (4)	47 (2)
C(21)	0.5424 (2)	0.6882 (5)	0.9171 (5)	41 (2)
C(22)	0.5155 (2)	0.5930 (6)	0.8230 (5)	48 (2)
C(23)	0.4310 (3)	0.5658 (7)	0.7914 (6)	52 (2)
C(24)	0.3710 (2)	0.6355 (6)	0.8588 (6)	47 (2)
C(25)	0.3952 (3)	0.7274 (6)	0.9513 (6)	53 (2)
C(26)	0.4811 (3)	0.7541 (6)	0.9842 (6)	51 (2)
C(27)	0.6345 (2)	0.7164 (5)	0.9495 (5)	37 (2)
C(28)	0.6612 (3)	0.7910 (7)	1.0628 (6)	63 (2)
O(3)	0.7847 (2)	1.0452 (4)	0.8961 (4)	66 (2)
H(1)	1.185 (4)	0.857 (10)	0.992 (7)	63
H(2)	0.251 (4)	0.645 (8)	0.895 (6)	63
H(12)	0.901 (4)	0.790 (8)	1.024 (6)	63
H(13)	1.047 (4)	0.863 (8)	1.062 (6)	63
H(15)	1.097 (4)	0.566 (8)	0.788 (6)	63
H(16)	0.952 (4)	0.498 (9)	0.745 (6)	63
H(181)	0.807 (4)	0.348 (8)	0.822 (7)	63
H(182)	0.736 (4)	0.430 (8)	0.769 (6)	63
H(183)	0.813 (4)	0.430 (8)	0.716 (7)	63
H(22)	0.555 (4)	0.541 (9)	0.775 (6)	63
H(23)	0.412 (4)	0.503 (8)	0.713 (6)	63
H(25)	0.352 (4)	0.769 (8)	1.006 (7)	63
H(26)	0.499 (4)	0.838 (8)	1.049 (6)	63
H(281)	0.653 (4)	0.917 (8)	1.065 (6)	63
H(282)	0.715 (4)	0.801 (8)	1.074 (6)	63
H(283)	0.629 (4)	0.765 (8)	1.140 (6)	63
H(31)	0.786 (4)	0.934 (8)	0.903 (6)	63
H(32)	0.753 (4)	1.060 (8)	0.816 (7)	63

**Discussion.** The 50% probability thermal ellipsoids for the non-H atoms are shown in Fig. 1, which also gives the labelling of the atoms. The asymmetric unit contains a water molecule, labelled as O(3). Tables 2 and 3 list the bond lengths and bond angles, respectively. The aromatic C–C bond lengths deviate slightly, but in

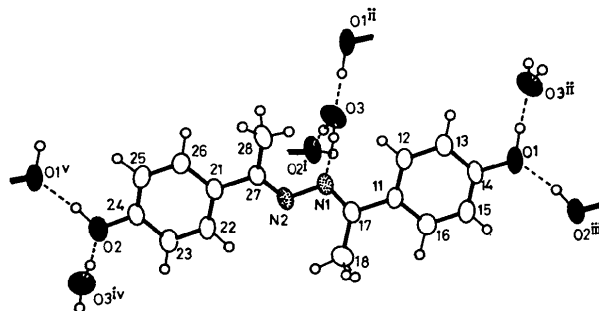


Fig. 1. Perspective drawing of the molecule and its nearest neighbours. Dashed lines represent hydrogen bonds. For symmetry code see Table 5.

Table 2. Bond lengths ( $\text{\AA}$ )

Average e.s.d.'s are 0.007  $\text{\AA}$  (0.07  $\text{\AA}$  when H atoms are involved).

C(11)–C(12)	1.369	C(21)–C(22)	1.380
C(12)–C(13)	1.395	C(22)–C(23)	1.382
C(13)–C(14)	1.379	C(23)–C(24)	1.399
C(14)–C(15)	1.365	C(24)–C(25)	1.341
C(15)–C(16)	1.394	C(25)–C(26)	1.405
C(16)–C(11)	1.394	C(26)–C(21)	1.398
C(14)–O(1)	1.379	C(24)–O(2)	1.379
C(11)–C(17)	1.495	C(21)–C(27)	1.499
C(17)–C(18)	1.481	C(27)–C(28)	1.475
C(17)–N(1)	1.282	C(27)–N(2)	1.278
N(1)–N(2)	1.417		
C(12)–H(12)	0.99	C(22)–H(22)	0.97
C(13)–H(13)	1.04	C(23)–H(23)	1.06
C(15)–H(15)	0.95	C(25)–H(25)	1.02
C(16)–H(16)	1.08	C(26)–H(26)	1.04
C(18)–H(181)	1.02	C(28)–H(281)	1.06
C(18)–H(182)	1.00	C(28)–H(282)	0.86
C(18)–H(183)	0.99	C(28)–H(283)	1.08
O(1)–H(1)	1.08	O(2)–H(2)	1.07
O(3)–H(31)	0.92		
O(3)–H(32)	1.02		

Table 3. Bond angles ( $^\circ$ )

Average e.s.d.'s are 0.6 $^\circ$  (4 $^\circ$  for C–C–H and 6 $^\circ$  for H–C–H).

C(12)–C(11)–C(16)	117.5	C(22)–C(21)–C(26)	118.1
C(12)–C(11)–C(17)	121.7	C(22)–C(21)–C(27)	121.3
C(16)–C(11)–C(17)	120.8	C(26)–C(21)–C(27)	120.5
C(11)–C(12)–C(13)	122.8	C(21)–C(22)–C(23)	122.3
C(12)–C(13)–C(14)	118.4	C(22)–C(23)–C(24)	118.4
C(13)–C(14)–O(1)	120.5	C(23)–C(24)–O(2)	116.8
C(13)–C(14)–C(15)	120.6	C(23)–C(24)–C(25)	120.6
O(1)–C(14)–C(15)	118.9	O(2)–C(24)–C(25)	122.6
C(14)–C(15)–C(16)	120.2	C(24)–C(25)–C(26)	121.1
C(15)–C(16)–C(11)	120.6	C(25)–C(26)–C(21)	119.4
C(11)–C(17)–C(18)	120.1	C(21)–C(27)–C(28)	119.6
C(11)–C(17)–N(1)	116.0	C(21)–C(27)–N(2)	114.7
C(17)–N(1)–N(2)	114.6	C(27)–N(2)–N(1)	114.7
C(11)–C(12)–H(12)	118	C(21)–C(22)–H(22)	122
C(13)–C(12)–H(12)	118	C(23)–C(22)–H(22)	116
C(12)–C(13)–H(13)	121	C(22)–C(23)–H(23)	121
C(14)–C(13)–H(13)	121	C(24)–C(23)–H(23)	120
C(14)–O(1)–H(1)	114	C(24)–O(2)–H(2)	107
C(14)–C(15)–H(15)	122	C(24)–C(25)–H(25)	121
C(16)–C(15)–H(15)	118	C(26)–C(25)–H(25)	117
C(15)–C(16)–H(16)	121	C(25)–C(26)–H(26)	120
C(11)–C(16)–H(16)	118	C(21)–C(26)–H(26)	120
C(17)–C(18)–H(181)	123	C(27)–C(28)–H(281)	114
C(17)–C(18)–H(182)	126	C(27)–C(28)–H(282)	113
C(17)–C(18)–H(183)	127	C(27)–C(28)–H(283)	122
H(181)–C(18)–H(182)	89	H(281)–C(28)–H(282)	91
H(181)–C(18)–H(183)	89	H(281)–C(28)–H(283)	97
H(182)–C(18)–H(183)	91	H(282)–C(28)–H(283)	115
H(31)–O(3)–H(32)	102		

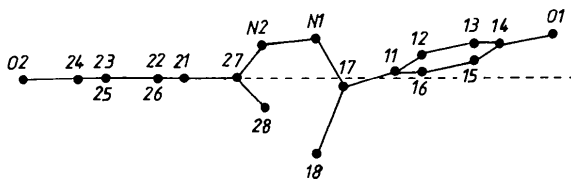


Fig. 2. Schematic drawing showing departures from planarity (vertical and horizontal displacements are on different scales).

Table 4. Selected torsion angles ( $^{\circ}$ )

Average e.s.d.'s are $1^{\circ}$ .			
C(11)–C(12)–C(13)–C(14)	0	C(21)–C(22)–C(23)–C(24)	–1
C(12)–C(13)–C(14)–C(15)	0	C(22)–C(23)–C(24)–C(25)	1
C(13)–C(14)–C(15)–C(16)	1	C(23)–C(24)–C(25)–C(26)	–1
C(14)–C(15)–C(16)–C(11)	–1	C(24)–C(25)–C(26)–C(21)	2
C(15)–C(16)–C(11)–C(12)	1	C(25)–C(26)–C(21)–C(22)	–3
C(16)–C(11)–C(12)–C(13)	–1	C(26)–C(21)–C(22)–C(23)	2
C(12)–C(11)–C(17)–C(18)	–161	C(22)–C(21)–C(27)–C(28)	–168
C(12)–C(11)–C(17)–N(1)	20	C(22)–C(21)–C(27)–N(2)	13
C(16)–C(11)–C(17)–C(18)	19	C(26)–C(21)–C(27)–C(28)	10
C(11)–C(17)–N(1)–N(2)	177	C(21)–C(27)–N(2)–N(1)	176
C(17)–N(1)–N(2)–C(27)	148		

Table 5. Hydrogen bonds

E.s.d.'s are in parentheses.				
X–H...Y	X–H (Å)	X...Y (Å)	H...Y (Å)	$\angle$ X–H...Y ( $^{\circ}$ )
O(1)–H(1)...O(3 <sup>H</sup> )	1.08 (8)	2.561 (6)	1.57 (8)	151 (7)
O(2)–H(2)...O(1 <sup>H</sup> )	1.07 (7)	2.681 (5)	1.68 (7)	154 (6)
O(3)–H(31)...N(1)	0.92 (7)	2.800 (5)	1.89 (7)	170 (6)
O(3)–H(32)...O(2)	1.02 (7)	2.759 (6)	1.75 (7)	172 (6)

Symmetry code: (i)  $1 - x, 0.5 + y, 1.5 - z$ ; (ii)  $2 - x, 2 - y, 2 - z$ ; (iii)  $1 + x, y, z$ ; (iv)  $1 - x, -0.5 + y, 1.5 - z$ ; (v)  $-1 + x, y, z$ .

some cases significantly, from the value of 1.398 found in crystalline benzene (Bacon, Curry & Wilson, 1964). The values of C(11)–C(12), C(14)–C(15), C(21)–C(22) and C(24)–C(25) bond distances are 1.369 (7), 1.365 (7), 1.380 (7) and 1.341 (7) Å, respectively, and are lower than the other bond lengths in the rings. The exocyclic bond lengths indicate a structure which is predominantly  $>C=N-N=C<$ . In fact, the N–N bond length, 1.417 (7) Å, is somewhat less than the value of 1.449 Å generally accepted for a single bond between  $sp^3$ -hybridized nitrogen atoms (Morino, Iijima & Murata, 1960), but the difference can hardly be considered as indicative of double-bond character, since it corresponds to a shortening due to the change in hybridization. The C(17)–N(1) and C(27)–N(2) bond lengths of 1.282 (7) and 1.278 (7) Å are very near to the value of 1.27 Å given by Levine (1963) for the length of a pure C–N double bond.

As can be seen from the torsional angles given in Table 4, the molecule is not planar, mainly due to the

twisting around the bonds in the azine chain. These bend the molecule into a shallow *V* shape, as can be seen in Fig. 2.

The molecules are held together through hydrogen bonds of types O–H...O and O–H...N (dashed lines in Fig. 1). A nitrogen atom of the azine chain, both hydroxy groups of the molecule and a water molecule take part in the hydrogen bonding. Their geometrical features are given in Table 5. The face-to-face molecular packing observed in a similar compound (Fayos, Martínez-Ripoll, García-Mina, Gonzalez-Martínez & Arrese, 1980) does not occur in the present structure.

The calculations were done with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970).

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