Hydrogen bonds of the type O···H—C(CCl_3) have been reported to give rise to dimers with (*A*) 5,7-dichloro-6-methyl- and (*B*) 6-methyl-8-*N*,*N*-diacetylamino- derivatives of 2,4-bis(trichloromethyl)-1,3-benzodioxin (Irving & Irving, 1988*b*, 1989*b*, respectively). In both these compounds, as in the title compound, the dimers are formed by two molecules related by a centre of symmetry. [*A* is $P2_1/n$, $Z = 4$; *B* is $P\bar{1}$, $Z = 2$.] In *A* where the hydrogen bond is described by C(2)—H(21)···O (from the 6-methoxy group) some overlap of the aromatic rings in the dimer occurs giving H···O 2·44 (3) Å and the C—H···O angle 151 (2)°. In *B* no overlap of the aromatic rings is possible due to the presence of the bulky 8-substituent. Here the dimers are formed by hydrogen bonds between one of the carbonyl oxygen atoms of one molecule and both the atoms H(21) and H(41) in the other [H(21)···O 2·49 (3) Å, C(2)—H(21)···O 131 (2)°, H(41)···O 2·47 (3) Å, C(4)—H(41)···O 122 (2)°]. The new data support the claim that C···O distances for very weakly acidic C—H groups extend well beyond the 'conventional' van der Waals limit based on a survey of C—H···O interactions in chloroalkyl compounds (Desiraju, 1989).

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Structure of the High-Temperature-Melting Polymorph of 2,2′-Dipyridylamine

BY GLORIA J. PYRKA*

Department of Chemistry, Kent State University, Kent, OH 44242, *USA*

AND A. ALAN PINKERTON

Department of Chemistry, University of Toledo, Toledo, OH 43606, *USA*

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Abstract. $C_{10}H_9N_3$, $M_r = 171{\cdot}21$, triclinic, $P\bar{1}$, $a = 8{\cdot}229\ (2)$, $b = 10{\cdot}654\ (3)$, $c = 10{\cdot}668\ (2)$ Å, $\alpha = 92{\cdot}93\ (2)$, $\beta = 93{\cdot}01\ (2)$, $\gamma = 107{\cdot}5\ (2)°$, $V = 888{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 360$, $T = 296\ (1)$ K, $R = 0{\cdot}041$ for 1788 unique observed reflections. The structure consists of hydrogen-bonded dimeric molecules. The dihedral angles between the pyridyl rings in the two monomeric units are distinctly different [7·0 (5) and 28·8 (1)°].

Introduction. Dipyridylamine has received interest as a ligand due to the flexibility of the molecule at the amine N atom and its ability to stabilize five-coordinate copper(II) complexes without formation of a macrocycle (Johnson & Jacobson, 1973*a*; Jensen & Jacobson, 1981; Jacobson & Jensen, 1986). Much of the interesting chemistry of dipyridylamine is the

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* To whom correspondence should be addressed.

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result of the different possible geometries around the amine N atom and the increased acidity of the amine proton upon complexation. The structure of the low-melting polymorph of the free ligand (m.p. 357 K) was determined by Johnson & Jacobson (1973*b*). The structure of the higher-melting polymorph (m.p. 372 K) was undertaken to determine the interactions resulting in the higher-melting solid.

Experimental. Single crystals of 2,2′-dipyridylamine with a melting point of 372·0 (4) K were obtained by recrystallization from acetone. A colorless irregular plate with approximate dimensions 0·32 × 0·25 × 0·12 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Cell constants were determined from 25 reflections in the range $12 < \theta < 14°$. There were no systematic absences; the space group was determined to be $P\bar{1}$. The *hkl* data ranged from 0, −12, −13 to 9, 12, 12; $\sin\theta/\lambda_{\max} = 0{\cdot}62$ Å^{-1}. Three standard reflections collected every 50 min showed a decay of 5·8%. 3715 reflections were collected [ω–2θ scans, profile analysis (Blessing, Coppens & Becker, 1974)], of which 3457 were unique ($R_{\rm int}$ = 2·0%) and were corrected for Lorentz and polarization effects. The data were corrected for absorption (μ = 0·8 cm^{-1}, empirical correction, relative transmission coefficients 0·958 to 0·998) and anisotropic decay (0·941–1·108). The structure was solved by direct methods using *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). 1788 reflections having intensities greater than 3σ were used in the full-matrix least-squares refinement of 308 parameters (including a secondary-extinction coefficient = 4·9 × 10^{-6}), where $\sum w(|F_o| - |F_c|)^2$ was minimized with weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$. The refinement with all non-H atoms treated anisotropically and H atoms isotropically converged with R = 0·041 and wR = 0·051, S = 1·452, (Δ/σ) = 0·02; $(\Delta\rho)_{\max}$ = 0·15 (3), $(\Delta\rho)_{\min}$ = −0·08 (3) e Å^{-3}. The scattering factors were taken from Cromer & Waber (1974) and anomalous-dispersion coefficients were those of Cromer (1974). All calculations were performed on a VAXstation 3100 using *MOLEN* (Fair, 1989).

Table 1. *Positional parameters with e.s.d.'s in parentheses*

$B_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*B*(Å^2)
N1*A*	0·8421 (2)	0·3429 (2)	0·0797 (2)	4·16 (4)
N2*A*	0·5826 (2)	0·2742 (2)	0·1597 (2)	4·08 (4)
N3*A*	0·4456 (2)	0·0814 (2)	0·2548 (2)	5·40 (5)
C1*A*	0·9669 (3)	0·3198 (2)	0·0166 (2)	4·84 (6)
C2*A*	0·9706 (3)	0·1970 (2)	−0·0222 (3)	5·46 (6)
C3*A*	0·8400 (3)	0·0911 (2)	0·0074 (2)	5·24 (6)
C4*A*	0·7102 (3)	0·1099 (2)	0·0735 (2)	4·52 (6)
C5*A*	0·7131 (3)	0·2391 (2)	0·1062 (2)	3·70 (5)
C6*A*	0·4438 (3)	0·1982 (2)	0·2165 (2)	3·98 (5)
C7*A*	0·3102 (3)	0·2484 (2)	0·2373 (3)	5·30 (6)
C8*A*	0·1773 (3)	0·1774 (3)	0·3003 (3)	6·84 (8)
C9*A*	0·1781 (4)	0·0579 (3)	0·3392 (3)	7·34 (8)
C10*A*	0·3119 (3)	0·0142 (2)	0·3140 (3)	6·67 (7)
H1*A*	1·055 (2)	0·397 (2)	−0·001 (2)	5·0 (5)*
H2*A*	1·063 (2)	0·187 (2)	−0·064 (2)	6·2 (5)*
H3*A*	0·846 (2)	0·002 (2)	−0·021 (2)	5·8 (5)*
H4*A*	0·620 (2)	0·041 (2)	0·101 (2)	5·6 (5)*
H5*A*	0·588 (2)	0·358 (2)	0·154 (2)	5·6 (5)*
H6*A*	0·323 (3)	0·335 (2)	0·208 (2)	7·0 (6)*
H7*A*	0·084 (3)	0·214 (2)	0·308 (2)	9·3 (7)*
H8*A*	0·092 (3)	0·010 (2)	0·375 (2)	7·7 (6)*
H9*A*	0·310 (3)	−0·075 (2)	0·341 (2)	7·7 (6)*
N1*B*	0·6262 (2)	0·5721 (2)	0·1702 (2)	4·36 (4)
N2*B*	0·8755 (2)	0·5768 (2)	0·2745 (2)	4·39 (4)
N3*B*	1·0567 (2)	0·7111 (2)	0·4375 (2)	5·32 (5)
C1*B*	0·5057 (3)	0·6284 (2)	0·1395 (2)	5·12 (6)
C2*B*	0·5019 (3)	0·7467 (2)	0·1908 (3)	5·92 (7)
C3*B*	0·6271 (3)	0·8108 (2)	0·2818 (3)	6·19 (7)
C4*B*	0·7529 (3)	0·7579 (2)	0·3166 (2)	5·22 (6)
C5*B*	0·7508 (3)	0·6385 (2)	0·2562 (2)	3·99 (5)
C6*B*	1·0209 (3)	0·6081 (2)	0·3540 (2)	4·22 (5)
C7*B*	1·1254 (3)	0·5267 (2)	0·3437 (2)	5·58 (6)
C8*B*	1·2702 (3)	0·5532 (3)	0·4206 (3)	7·04 (8)
C9*B*	1·3101 (3)	0·6596 (3)	0·5069 (3)	6·72 (8)
C10*B*	1·2030 (3)	0·7332 (3)	0·5122 (2)	6·40 (7)
H1*B*	0·841 (2)	0·798 (2)	0·388 (2)	6·2 (5)*
H2*B*	0·625 (3)	0·890 (2)	0·335 (2)	7·9 (6)*
H3*B*	0·418 (2)	0·775 (2)	0·166 (2)	6·8 (6)*
H4*B*	0·417 (2)	0·579 (2)	0·083 (2)	5·5 (5)*
H5*B*	0·862 (2)	0·510 (2)	0·218 (2)	4·8 (5)*
H6*B*	1·086 (2)	0·448 (2)	0·281 (2)	5·8 (5)*
H7*B*	1·355 (4)	0·492 (3)	0·414 (3)	14 (1)*
H8*B*	1·400 (3)	0·680 (2)	0·563 (2)	8·8 (7)*
H9*B*	1·214 (2)	0·803 (2)	0·568 (2)	5·9 (5)*

* Refined isotropically.

Discussion. Table 1* contains the final positional and isotropic thermal parameters. The bond lengths and angles with standard deviations are in Table 2. The structure of the 2,2′-dipyridylamine hydrogen-bonded dimer is shown in an *ORTEP* (Johnson, 1965) drawing with 30% thermal ellipsoids in Fig. 1; the packing in the unit cell is shown in Fig. 2. The structure consists of an asymmetric dimer of hydrogen-bonded dipyridylamine molecules.

The bond distances and angles in the individual molecules are similar to those observed in the low-melting polymorph. The asymmetry in the dimer is shown by the difference in the dihedral angles between the pyridyl rings [7·0 (5) and 28·8 (1)°, respectively]. This angle is 23° for the symmetric (twofold symmetry) dimer in the low-melting polymorph. The C5—N2—C6 angle is slightly larger for the more-planar dipyridylamine, 132·1 (2) compared to 129·9 (2)°, due to the same steric interactions which prevent the molecule from being planar. All bonds to the planar bridging N atoms are short, despite the large variations in dihedral angle. This implies that the π-orbital overlap is insensitive to the dihedral angle. The hydrogen bonds forming the dimer have H···N distances of 2·20 (2) and

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* Lists of structure factors and anisotropic thermal parameters, torsion angles, bond lengths and angles involving H atoms, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54355 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N1*A*	C1*A*	1·333 (3)	N1*B*	C1*B*	1·339 (3)
N1*A*	C5*A*	1·337 (2)	N1*B*	C5*B*	1·338 (2)
N2*A*	C5*A*	1·380 (3)	N2*B*	C5*B*	1·385 (3)
N2*A*	C6*A*	1·376 (3)	N2*B*	C6*B*	1·374 (3)
N3*A*	C6*A*	1·334 (3)	N3*B*	C6*B*	1·328 (3)
N3*A*	C10*A*	1·329 (3)	N3*B*	C10*B*	1·360 (3)
C1*A*	C2*A*	1·361 (3)	C1*B*	C2*B*	1·359 (3)
C2*A*	C3*A*	1·368 (3)	C2*B*	C3*B*	1·369 (3)
C3*A*	C4*A*	1·369 (4)	C3*B*	C4*B*	1·363 (4)
C4*A*	C5*A*	1·395 (3)	C4*B*	C5*B*	1·392 (3)
C6*A*	C7*A*	1·382 (4)	C6*B*	C7*B*	1·397 (4)
C7*A*	C8*A*	1·360 (4)	C7*B*	C8*B*	1·358 (4)
C8*A*	C9*A*	1·361 (4)	C8*B*	C9*B*	1·371 (4)
C9*A*	C10*A*	1·352 (4)	C9*B*	C10*B*	1·345 (5)
N1*A*	H5*B*	2·21 (2)	N1*B*	H5*A*	2·20 (2)

C1*A*	N1*A*	C5*A*	117·8 (2)	C1*B*	N1*B*	C5*B*	117·2 (2)
C5*A*	N2*A*	C6*A*	129·9 (2)	C5*B*	N2*B*	C6*B*	132·1 (2)
C6*A*	N3*A*	C10*A*	116·9 (2)	C6*B*	N3*B*	C10*B*	115·6 (2)
N1*A*	C1*A*	C2*A*	123·9 (2)	N1*B*	C1*B*	C2*B*	124·1 (2)
C1*A*	C2*A*	C3*A*	118·0 (2)	C1*B*	C2*B*	C3*B*	117·7 (3)
C2*A*	C3*A*	C4*A*	120·2 (2)	C2*B*	C3*B*	C4*B*	120·5 (2)
C3*A*	C4*A*	C5*A*	118·2 (2)	C3*B*	C4*B*	C5*B*	118·1 (2)
N1*A*	C5*A*	N2*A*	113·1 (2)	N1*B*	C5*B*	N2*B*	112·7 (2)
N1*A*	C5*A*	C4*A*	121·8 (2)	N1*B*	C5*B*	C4*B*	122·2 (2)
N2*A*	C5*A*	C4*A*	124·9 (2)	N2*B*	C5*B*	C4*B*	125·1 (2)
N2*A*	C6*A*	N3*A*	119·1 (2)	N2*B*	C6*B*	N3*B*	120·2 (2)
N2*A*	C6*A*	C7*A*	118·7 (2)	N2*B*	C6*B*	C7*B*	117·3 (2)
N3*A*	C6*A*	C7*A*	122·1 (2)	N3*B*	C6*B*	C7*B*	122·5 (2)
C6*A*	C7*A*	C8*A*	119·1 (2)	C6*B*	C7*B*	C8*B*	119·5 (2)
C7*A*	C8*A*	C9*A*	119·1 (3)	C7*B*	C8*B*	C9*B*	118·9 (3)
C8*A*	C9*A*	C10*A*	118·5 (3)	C8*B*	C9*B*	C10*B*	118·4 (2)
N3*A*	C10*A*	C9*A*	124·3 (3)	N3*B*	C10*B*	C9*B*	125·1 (2)
N1*A*	H5*B*	N2*B*	177 (2)	N1*B*	H5*A*	N2*A*	171 (2)

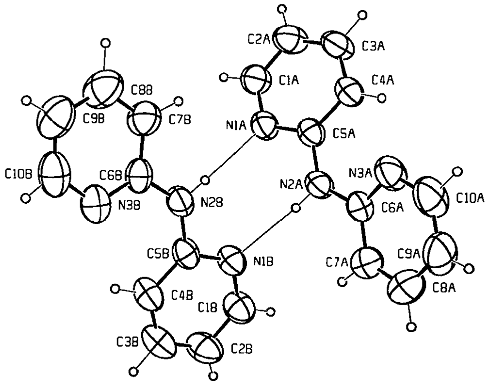

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the dipyridylamine dimer with 30% probability thermal ellipsoids.

2·21 (2) Å, with angles at hydrogen of 171 (2) and 177 (2)°.

A second difference between the two structure lies in the arrangement of the individual molecules within the hydrogen-bonded dimers. If we view the dimers down the bridge nitrogen–bridge nitrogen vector (Fig. 3) we see that the low-melting polymorph is a much flatter molecule. Further insight may be obtained from the dihedral angles between the best planes for the two halves of the dimeric units, 46° for the low-melting polymorph *versus* 72·6 (1)° in the present case. This leads to a major difference in the packing of the molecules in the unit cell. In the low-melting polymorph, the packing may be viewed as layers of 'planar' dimers with alternate layers rotated by 90°. In the high-melting-point structure, the packing is less efficient (density 1·28 *versus* 1·31 g cm^{-3}) as the dimers are no longer flat enough to form layers. We speculate that the difference in melting point is due to the ease of motion of layers with respect to each other in the

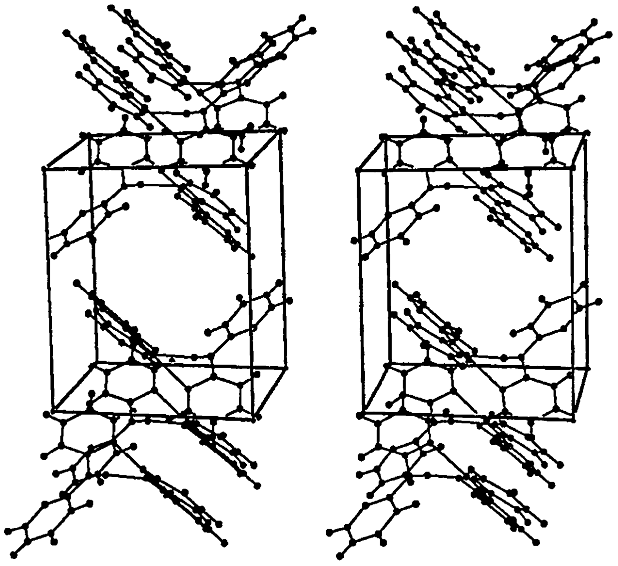

Fig. 2. Packing diagram for the high-temperature-melting polymorph of dipyridylamine.

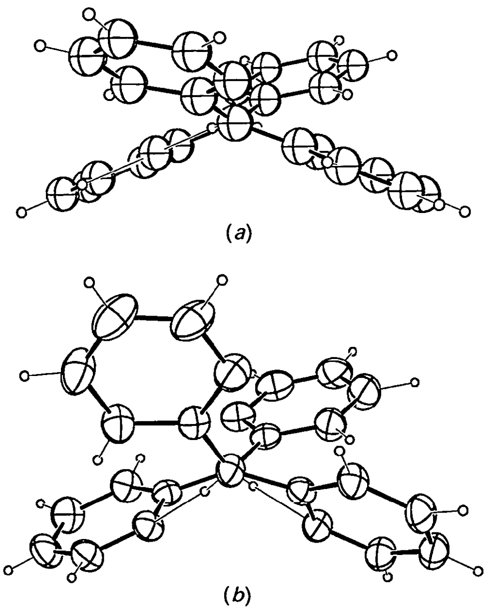

Fig. 3. *ORTEP* (Johnson, 1965) diagram of the dimer of (*a*) the low-temperature-melting polymorph and (*b*) the high-temperature-melting polymorph viewed down the direction of the bridge N atoms.

low-melting polymorph compared to the locking together of molecules in the high-melting form.

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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. XV. *N*,*N*′-Ditosyl-2,3,5,6-tetrahydro-1*H*,7*H*-4,1,7-benzoxadiazonine

BY A. STĘPIEŃ, E. WAJSMAN, A. M. BRZOZOWSKI AND M. J. GRABOWSKI

Department of Crystallography, Institute of Chemistry, University of Łódź, Nowotki 18, 91-416 *Łódź, Poland*

E. MIKICIUK-OLASIK

Institute of Chemistry and Technology of Drugs, School of Medicine, Narutowicza 120*a*, 90-145 *Łódź, Poland*

AND C. BAVOUX

Laboratoire de Minéralogie–Cristallographie, associé au CNRS (*UA* 805), *Université Claude Bernard Lyon* I, 43 *boulevard du* 11 *novembre* 1918, 69622 *Villeurbanne CEDEX, France*

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Abstract. $C_{24}H_{26}N_2O_5S_2$, $M_r = 486{\cdot}6$, monoclinic, $C2$, $a = 27{\cdot}869\,(5)$, $b = 8{\cdot}374\,(2)$, $c = 23{\cdot}058\,(6)$ Å, $\beta = 119{\cdot}14\,(3)^\circ$, $V = 4700\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}375\,(1)$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 22{\cdot}54$ cm^{-1}, $F(000) = 2048$, room temperature, $R = 0{\cdot}0455$ for 4141 reflections with $I > 3\sigma(I)$. There are two different molecules in the asymmetric unit. Molecule 1 exists in a chair-like conformation; molecule 2 occurs in two forms: a chair-like and a twist-chair conformation in a ratio of 0·63:0·37, respectively.

Introduction. Based on the expected pharmacological properties and complex-formation ability, a new class of benzoxadiazonine derivatives has been synthesized (Glinka, Mikiciuk-Olasik & Kotełko, 1977; Mikiciuk-Olasik & Kotełko, 1984). The possibility of using them as complexing agents for ^{99m}Tc, employed in medical diagnostics (Kapuściński, Liniecki, Durski & Mikiciuk-Olasik, 1986), seemed to be of special interest. The title compound was obtained by a condensation of *N*,*N*′-ditosyl-*o*-phenylenediamine with bis(2-chloroethyl) ether in presence of potassium *tert*-butanolate. The formula was confirmed by IR, ^{1}H NMR and MS analyses. The present X-ray structure determination was undertaken to provide the evidence for the structure of the molecule.

Experimental. Colourless thick-prismatic crystals of size 0·2 × 0·3 × 0·5 mm from ethanol at room temperature. Diffraction data measured on a CAD-4 diffractometer using the θ–2θ scan technique,

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