The versatility of formaldehyde in the synthesis of 1,3,5-triazinanes and bis(imidazolidinyl)methanes

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Table S1. Crystallographic data for compound ***3***.

Crystal data	
Chemical formula	$C_{24}H_{27}N_3$
M_r	357.48
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	18.0674 (7), 6.1252 (3), 19.8149 (9)
β (°)	108.863 (2)
V (Å^3)	2075.08 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Diffractometer	KappaCCD
Absorption correction	–
No. of measured, independent and observed reflections	7895, 4653, 1546 [$I > 2\sigma(I)$]
R_{int}	0.061
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.123, 0.429, 1.16
No. of reflections	4653
No. of parameters	272
No. of restraints	9
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.30

Table S2. Selected bond distances (Å) and bond angles (°) for the compound ***3***.

Bond lengths (Å)	
C2—N3 1.444 (5)	C11—C12 1.226 (8)
C2—N1 1.514 (6)	C21—C22 1.500 (7)
C181—C171 1.39	C12—C13 1.331 (8)
C4—N5 1.418 (6)	C22—C23 1.39
C4—N3 1.472 (6)	C22—C27 1.39
C6—N5 1.459 (6)	C141—N3 1.340 (9)

C6—N1 1.508 (7)	C23—C24 1.39
C7—N1 1.451 (6)	C141—C151 1.511 (10)
C7—C8 1.470 (8)	C24—C25 1.39
C19—C18 1.39	C151—C201 1.39
C8—C13 1.381 (7)	C25—C26 1.39
C8—C9 1.502 (8)	C151—C161 1.39
C17—C16 1.39	C201—C191 1.39
C9—C10 1.368 (9)	C26—C27 1.39
C10—C11 1.312 (10)	C191—C181 1.39
Bond angles (°)	
N3—C2—N1 111.3 (3)	C24—C23—C22 120
C171—C161—C151 120	C12—C13—C8 120.9 (6)
N3—C14—C15 112.4 (9)	C23—C24—C25 120
N5—C4—N3 113.9 (4)	N3—C141—C151 117.9 (8)
C19—C20—C15 120	C26—C25—C24 120
N5—C6—N1 113.0 (4)	C27—C26—C25 120
C20—C19—C18 120	C201—C151—C161 120
C17—C18—C19 120	C26—C27—C22 120
N1—C7—C8 112.2 (5)	C201—C151—C141 126.3 (14)
C16—C17—C18 120	C161—C151—C141 113.7 (14)
C17—C16—C15 120	C151—C201—C191 120
C13—C8—C7 127.9 (6)	C7—N1—C6 110.7 (4)
C16—C15—C20 120	C7—N1—C2 115.1 (4)
C13—C8—C9 114.4 (5)	C6—N1—C2 102.9 (5)
C16—C15—C14 112.7 (16)	C181—C191—C201 120
C7—C8—C9 117.8 (6)	C141—N3—C2 115.2 (5)
C20—C15—C14 127.3 (16)	C14—N3—C2 123.6 (5)
C10—C9—C8 116.6 (5)	C141—N3—C4 121.8 (5)
N5—C21—C22 116.4 (5)	C191—C181—C171 120
C11—C10—C9 121.0 (6)	C14—N3—C4 114.2 (5)
C12—C11—C10 123.4 (8)	C2—N3—C4 109.8 (4)
C23—C22—C27 120	C21—N5—C4 116.3 (4)
C23—C22—C21 118.6 (5)	C161—C171—C181 120
C27—C22—C21 121.4 (5)	C21—N5—C6 115.0 (5)
C11—C12—C13 123.6 (8)	C4—N5—C6 110.9 (4)

Table S3. Crystallographic data for compound ***4*** (orthorhombic polymorph).

Crystal data	
Chemical formula	$C_{17}H_{20}N_2S$
M_r	284.41
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, b, c (Å)	5.8326 (2), 16.3498 (5), 16.4816 (6)
V (Å^3)	1571.72 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20

Crystal size (mm)	0.25 × 0.13 × 0.08
Data collection	
Diffractometer	KappaCCD
Absorption correction	–
No. of measured, independent and observed reflections	12512, 3443, 1784 [$I > 2\sigma(I)$]
R_{int}	0.122
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.659
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.154, 0.93
No. of reflections	3443
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.30

Table S4. Selected bond distances (Å) and bond angles (°) for the compound ***4*** (orthorhombic polymorph).

Bond lengths (Å)	
C9—C11 1.385 (5)	N5—C6 1.439 (6)
C15—C14 1.366 (6)	N5—C4 1.455 (5)
C9—C12 1.389 (5)	N5—C7 1.467 (5)
C9—C8 1.516 (5)	C8—N3 1.463 (5)
C14—C13 1.379 (6)	S1—C6 1.837 (5)
C11—C13 1.380 (6)	S1—C2 1.834 (4)
C10—C17 1.369 (6)	N3—C2 1.442 (6)
C16—C19 1.388 (7)	C12—C15 1.376 (6)
C10—C16 1.373 (6)	N3—C4 1.460 (5)
C10—C7 1.515 (6)	C20—C19 1.373 (7)
C18—C17 1.379 (7)	C20—C18 1.374 (7)
Bond angles (°)	
C11—C9—C12 118.1 (4)	N3—C8—C9 111.7 (3)
C11—C9—C8 120.3 (3)	C6—S1—C2 93.3 (2)
C12—C9—C8 121.6 (4)	C2—N3—C4 111.3 (4)
C10—C16—C19 121.1 (5)	C2—N3—C8 113.4 (3)
C13—C11—C9 121.2 (4)	C4—N3—C8 115.1 (4)
C20—C18—C17 119.9 (5)	C15—C12—C9 120.6 (4)
C17—C10—C16 118.5 (4)	N3—C2—S1 113.9 (3)
C17—C10—C7 119.9 (4)	N5—C7—C10 111.8 (3)
C16—C10—C7 121.7 (4)	N3—C4—N5 118.5 (3)
C10—C17—C18 121.2 (5)	C19—C20—C18 119.6 (5)
C6—N5—C4 112.0 (4)	C14—C15—C12 120.7 (4)
C6—N5—C7 113.5 (3)	N5—C6—S1 114.0 (3)
C4—N5—C7 116.9 (4)	C15—C14—C13 119.8 (4)
C16—C19—C20 119.6 (5)	C14—C13—C11 119.6 (4)

Table S5. Crystallographic data for compound ***4*** (monoclinic polymorph).

Crystal data

Chemical formula	$C_{17}H_{20}N_2S$
M_r	284.41
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	293
a, b, c (Å)	5.8447 (2), 16.3441 (5), 16.5135 (6)
β (°)	94.15
V (Å^3)	1573.33 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.25 × 0.13 × 0.08
Data collection	
Diffractometer	KappaCCD
Absorption correction	–
No. of measured, independent and observed reflections	5667, 5667, 3651 [$I > 2\sigma(I)$]
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.163, 1.08
No. of reflections	5667
No. of parameters	361
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.43

Table S6. Selected bond distances (Å) and bond angles (°) for the compound ***4*** (monoclinic polymorph).

Bond lengths (Å)	
S1—C35 1.840 (6)	N1—C27 1.495 (7)
S2—C32 1.793 (7)	C3—C4 1.368 (8)
S1—C33 1.889 (7)	C21—C22 1.388 (8)
S2—C31 1.834 (6)	C21—C20 1.418 (8)
C18—C19 1.388 (8)	C21—C28 1.505 (8)
C2—C1 1.355 (7)	N2—C32 1.419 (7)
C18—C17 1.419 (7)	N2—C30 1.455 (7)
C2—C3 1.384 (8)	N2—C26 1.526 (7)
C18—C29 1.526 (8)	N3—C28 1.413 (7)
C2—C27 1.509 (8)	N3—C33 1.454 (8)
N4—C29 1.430 (6)	N3—C34 1.459 (7)
C5—C4 1.351 (8)	C8—C9 1.340 (8)
N4—C35 1.463 (7)	C22—C23 1.397 (10)
C5—C6 1.366 (8)	C8—C7 1.360 (8)
N4—C34 1.488 (7)	C8—C26 1.523 (8)
C17—C16 1.392 (8)	C7—C13 1.399 (10)
C6—C1 1.369 (8)	C23—C24 1.401 (11)
C14—C19 1.399 (8)	C9—C10 1.391 (9)

C31—N1 1.425 (7)	C11—C13 1.331 (10)
C14—C15 1.407 (8)	C11—C10 1.359 (10)
C16—C15 1.370 (8)	C20—C25 1.376 (9)
N1—C30 1.443 (7)	C25—C24 1.394 (10)
Bond angles (°)	
C35—S1—C33 91.2 (3)	C32—N2—C30 110.4 (5)
C32—S2—C31 94.6 (3)	C32—N2—C26 115.0 (4)
C19—C18—C17 118.8 (5)	C30—N2—C26 117.6 (4)
C1—C2—C3 117.9 (5)	C28—N3—C33 112.5 (5)
C19—C18—C29 118.2 (5)	C5—C4—C3 118.7 (5)
C1—C2—C27 119.9 (5)	C28—N3—C34 115.9 (5)
C17—C18—C29 123.0 (5)	C33—N3—C34 113.3 (5)
C3—C2—C27 122.2 (5)	C21—C22—C23 119.0 (6)
C29—N4—C35 111.1 (4)	C2—C1—C6 118.9 (5)
C4—C5—C6 118.7 (5)	N4—C35—S1 116.0 (4)
C29—N4—C34 116.2 (5)	C9—C8—C7 117.3 (6)
C35—N4—C34 113.0 (5)	C9—C8—C26 119.1 (5)
C16—C17—C18 122.0 (5)	C7—C8—C26 123.6 (5)
C5—C6—C1 123.0 (5)	C8—C7—C13 123.2 (6)
C19—C14—C15 121.2 (5)	N3—C34—N4 116.7 (4)
N1—C31—S2 111.5 (4)	N1—C30—N2 119.9 (4)
C15—C16—C17 118.6 (5)	C22—C23—C24 120.5 (7)
C18—C19—C14 119.0 (5)	C8—C9—C10 120.1 (6)
C31—N1—C30 109.8 (5)	N3—C33—S1 116.2 (4)
C31—N1—C27 115.9 (4)	C8—C26—N2 112.4 (4)
C30—N1—C27 113.5 (4)	N3—C28—C21 110.5 (5)
C22—C21—C20 119.4 (6)	C13—C11—C10 119.2 (7)
C4—C3—C2 122.8 (5)	C11—C13—C7 118.5 (7)
C22—C21—C28 120.2 (5)	C25—C20—C21 122.1 (6)
C20—C21—C28 120.5 (5)	N2—C32—S2 112.6 (4)
C16—C15—C14 120.4 (5)	C20—C25—C24 117.8 (7)
N1—C27—C2 109.9 (4)	C25—C24—C23 121.2 (7)
N4—C29—C18 113.5 (4)	C11—C10—C9 121.7 (7)