One-pot synthesis of novel 1,2,3,4,5a,7,8,8b-octaaza-acenaphthylenes

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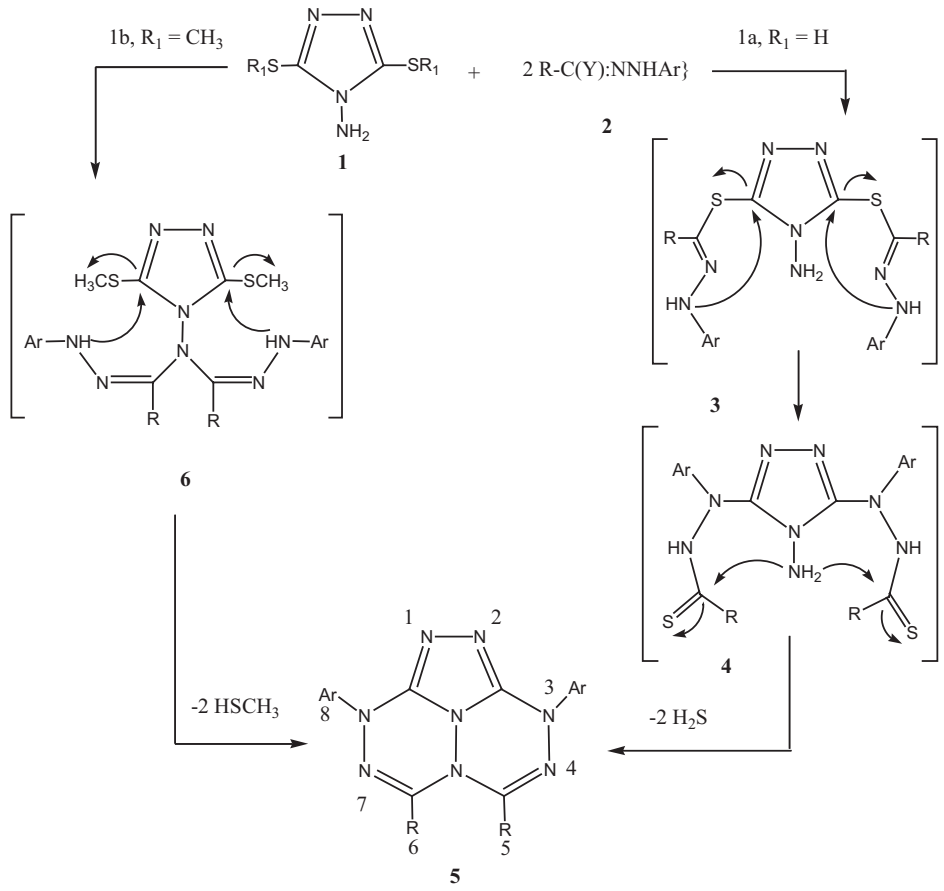
Reaction of 4-amino-4*H*-1,2,4-triazole-3,5-dithiol **1a** with hydrazonoyl halides **2** in ethanol in the presence of sodium ethoxide under reflux led to the formation of the title compounds **5.** The latter products can also obtained by reaction of 4-amino-3,5-di(methylthio)-4*H*-1,2,4-triazole **1b** with hydrazonoyl halides **2** in ethanol in the presence of sodium ethoxide by stirring over night at room temperature. The structures of the products were evidenced by spectral, elemental as well as X-ray diffraction analyses. The mechanism of the studied reactions was also discussed.

Keywords: hydrazonoyl halides, heterocycles, s-triazoles, heterocyclic thiols

In continuation of our previous work[1-9] dealing with the utility of hydrazonoyl halides as synthons for various fused heterocycles, we report here a facile one-pot synthesis of the title ring system by reaction of 4-amino-4*H*-1,2,4-triazole-3,5-dithiol **1a** or 4-amino-3,5-dimethylthio-4*H*-1,2,4-triazole **1b** with hydrazonoyl halides **2.** Such a ring system has not been reported hitherto. The title investigation forms a part of our program directed for synthesis of perifused heterocycles as studies on synthesis of such ring systems are rare.

Results and discussion

The starting 4-amino-4*H*-1,2,4-triazole-3,5-dithiol **1a**[10] and its 3,5-dimethylthio derivative **1b**[11] and the hydrazonoyl halides **2**[12-22] used in this study were prepared as previously described. Reaction of 4-amino-4*H*-1,2,4-triazole-3,5-dithiol **1a** with hydrazonoyl halides **2** in 1:2 molar ratio in ethanol in the presence of sodium ethoxide under reflux yielded, in each case, a single product as evidenced by TLC analysis of the crude product. The structure of the isolated products **5** was elucidated on the basis of their spectral data (MS, IR, NMR) and microanalyses (see Experimental). All data were in full agreement with structure **5** (Scheme 1). For example, the mass spectral and elemental analysis data of the isolated products revealed that they were free of sulfur. The assigned structure for products **5** was also evidenced by IR, ^{13}C NMR and ^{1}NMR spectra. The IR spectra revealed in each case the absence of the absorption band corresponding to the amino group, and instead they exhibit the absorption bands corresponding to the



Scheme 1 Synthesis of 1,2,3,4,5a,7,8,8b-octaaza-acenaphthylenes.
Where Y = Cl, Br and Ar = C_6H_4X
2–5: R/X: **a**, Ph/H; **b**, Ph/4-NO_2; **c**, EtOCO/H; **d**, EtOCO/4-CH_3; **e**, EtOCO/4-Cl; **f**, EtOCO/4-NO_2; **g**, PhNHCO/H; **h**, PhNHCO/4-CH_3; **i**, PhNHCO/4-Cl; **j**, PhNHCO/4-NO_2; **k**, PhCO/H; **l**, PhCO/4-NO_2.

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substituents in the positions 3,5,6 and 8 in compounds **5**. Also, their ^{1}H NMR spectra revealed in each case the absence of the signal of the amino protons, and instead they showed signals corresponding to the protons of the substituents in position 3,5,6 and 8 in compound **5**. The signals that appeared in the ^{13}C NMR spectrum of **5e,** taken as a typical example of the series prepared, are shown together with their assignments in chart 1.

To account for the direct formation of the products **5** from reaction of compound **1a** with **2**, the mechanism outlined in Scheme 2 is proposed. According to this mechanism, the reaction starts with the formation of the thiohydrazonate intermediate which undergoes Smiles rearrangement,[23,24] to yield the thiohydrazide, which in turn undergoes *in situ* cyclisation *via* elimination of hydrogen sulfide to give the respective **5** as the end products (Scheme 1). In all cases examined, attempts to isolate the intermediates **3** and **4** failed, however. This finding indicates that such intermediates are consumed as soon as they are formed under the reaction conditions employed.

The assignment of structure **5** was further substantiated by an alternative synthesis. Thus, reaction of 4-amino-3,5-dimethylthio-4*H*-1,2,4-triazole 1b with hydrazonoyl halides **2** in ethanol in the presence of sodium ethoxide in 1:2 molar ratio by stirring overnight at room temperature, was found to give products that proved identical in all respects with products **5** obtained above. It is reasonable to assume that reaction of **1b** with **2** proceeds *via* the formation of the amidrazones **6**, which in turn, undergo cyclisation with concurrent elimination of methanethiol to give **5** as end products (Scheme 1).

To provide further evidence for the actual structure of the products **5** isolated from the studied reactions, we have turned to X-ray crystallographic analysis. The ORTEP plot of **5c** confirms that the structure of the products isolated from reactions of **1** with **2** is **5**. Selected bond distances and bond angles are depicted in Table 1.

Experimental

Melting points were determined on an electrothermal Gallenkamp apparatus and are uncorrected. The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide discs. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VXR-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in DMSO-d_6 and the chemical shifts were related to that of the solvent. The mass spectra were recorded on a GCMS-Q1000-EX Shimadzu and GCMS 5988-A HP spectrometers, the ionising voltage was 70 eV. Single-crystal X-ray diffraction analysis was recorded using Bruker nonius draft macscience.Jpn. Elemental analyses were carried out by the Microanalytical Centre of Cairo University, Giza, Egypt. The starting 4-amino-3,5-dithiol-4*H*-1,2,4-triazole **1a**,[10] 4-amino-3,5-bis(methylthio)-4*H*-1,2,4-triazole **1b**[11] and hydrazonoyl halides **2**[12-22] were all prepared according to literature methods.

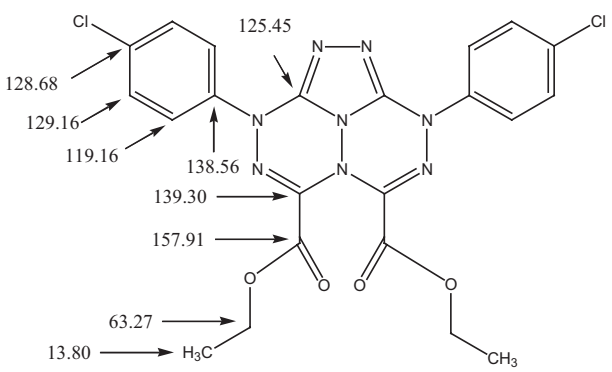

Chart 1

Table 1 Selected bond lengths and bond angles in the ORTEP of compound **5c** in the crystal; the crystallographic numbering does not reflect systematic numbering

Bond length/°A	Bond length/°A	Bond length/°A
N_{25}–N_{60} (1.36)	C_{40}–O_4 (1.25)	N_{20}–C_{24} (1.50)
N_{60}–C_{24} (1.24)	C_{40}–O_7 (1.36)	N_{20}–C_{33} (1.44)
C_{24}–N_8 (1.28)	O_7–C_{43} (1.46)	C_{33}–C_{41} (1.38)
N_8–N_{27} (1.38)	C_{43}–C_{51} (1.47)	C_{41}–C_{58} (1.34)
N_{27}–C_{31} (1.33)	C_{31}–N_9 (1.33)	C_{58}–C_{68} (1.32)
C_{31}–C_{40} (1.47)	N_9–N_{20} (1.44)	

Angle/ω	Angle/ω	Angle/ω
N_{25}–N_{60}–C_{24} (104.0)	N_{27}–C_{31}–C_{40} (127.0)	N_9–N_{20}–C_{24} (117.4)
N_{60}–C_{24}–N_{20} (129.4)	C_{31}–C_{40}–O_4 (122.0)	C_{24}–N_{20}–C_{33} (128.1)
N_{60}–C_{24}–N_8 (117.0)	C_{31}–C_{40}–O_7 (108.0)	C_{48}–C_{33}–C_{41} (118.0)
C_{24}–N_8–N_{27} (129.0)	C_{40}–O_7–C_{43} (112.0)	C_{33}–C_{41}–C_{58} (130.0)
N_8–N_{27}–C_{31} (115.2)	O_7–C_{43}–C_{51} (105.0)	C_{41}–C_{58}–C_{68} (113.0)
N_{27}–C_{31}–N_9 (123.0)	C_{31}–N_9–N_{20} (119.0)	

Synthesis of 1,2,3,4,5a,7,8,8b-octaaza-acenaphthylenes (**5a–l**) Method A: To a stirred sodium ethoxide solution, prepared from sodium metal (0.23 g, 10 mmole) and absolute ethanol (40 ml) was added compound **1a** (0.74 g, 5 mmole). After 10 min. the appropriate hydrazonoyl halide **2** (10 mmole) was added and the reaction mixture was refluxed for 6–7 h. The solid that precipitated was filtered off, washed with water, dried and finally crystallised from the appropriate solvent to give products **5**.

Method B: To a stirred sodium ethoxide solution, prepared from sodium metal (0.23 g, 10 mmole) and absolute ethanol (40 ml) was added compound **1b** (0.88 g, 5 mmole) and after 10 min. the appropriate hydrazonoyl halide **2** (10 mmole) was added. The reaction mixture was left overnight at room temperature, while being stirred. The solid that precipitated was filtered off, washed with water, dried and crystallised from the appropriate solvent to give the respective product **5**, which proved identical in all respects with that one obtaied from method A above. The physical constants together with the spectral data of products **5a–l** are listed below.

3,5,6,8-Tetraphenyl-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5a)**: Yellow solid (EtOH), (0.94 g, 40%), m.p. 238°C, IR ν (cm^{-1}): 1643 (C=N), 1593 (C=C); ^{1}H NMR (DMSO-d_6) δ 7.2–8.0 (m, ArH); MS *m/z* (%) 470 (M^+ + 2,11), 469 (M^+ + 1, 31), 468 (M^+,100), 117 (33), 91 (27), 77 (30), 65 (33), 51 (13). Anal. Calcd. for $C_{28}H_{20}N_8$ (468): C, 71.78; H, 4.30; N, 23.92. Found: C, 71.89; H, 4.39; N, 24.00%.

5,6-Diphenyl-3,8-di(4-nitrophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5b)**: Pale brown solid (AcOH), (1.17 g, 42%), m.p. 306–308°C, IR ν (cm^{-1}) 1650 (C=N), 1592 (C=C); ^{1}H NMR (DMSO-d_6) δ 6.3–7.9 (m, 10H, ArH), 8.3 (d, *J* = 8 Hz, 4H, ArH), 8.4 (d, *J* = 8 Hz, 4H, ArH), MS *m/z* (%) 560 (M^+ + 2,5), 559 (M^+ + 1, 17), 558 (M^+,18), 117 (12), 103 (100), 90 (30), 76 (55), 64 (16), 50 (40). Anal. Calcd. for $C_{28}H_{18}N_{10}O_4$ (558): C, 60.21; H, 3.25; N, 25.08. Found: C, 60.13; H, 3.20; N, 24.85%.

5,6-Diethoxycarbonyl-3,8-diphenyl-1,2,3,4,5a,7,8,8b-octaaza-acena-phthylene **(5c)**: Yellow solid (EtOH), (1.03, g, 45%), m.p.190°C, IR ν (cm^{-1}) 1756 (C=O),1587 (C=N); ^{1}H NMR (DMSO-d_6) δ 1.3 (t, *J* = 7 Hz, 6H, 2 CH_3), 4.3 (q, *J* = 7 Hz, 4H, 2 CH_2), 7.2–7.9 (m, 10H, ArH); MS *m/z* (%) 461 (M^+ + 1, 13), 460 (M^+,38), 360 (38), 248 (5), 220 (11), 180 (4), 144 (16), 117 (51), 103 (38), 91 (33), 77 (100), 65 (45). Anal. Calcd.for $C_{22}H_{20}N_8O_4$ (488): C, 57.39; H, 4.38; N, 24.34. Found: C,57.20; H, 4.33; N, 24.13%.

5,6-Diethoxycarbonyl-3,8-di(4-methylphenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5d)**: Yellow solid (AcOH), (1.10 g, 45%), m.p. 246°C, IR ν (cm^{-1}) 1666 (C=O),1598 (C=N); ^{1}H NMR (DMSO-d_6) δ 1.3 (t, *J* = 7 Hz, 6H, 2 CH_3), 2.3 (s, 6H, 2 CH_3), 4.3 (q, *J* = 7 Hz, 4H, 2 CH_2), 7.3 (d, *J* = 8 Hz, 4H, ArH), 7.5 (d, *J* = 8 Hz, 4H, ArH), 7.3–7.7 (m, 8H, ArH); MS *m/z* (%) 489 (M^+ + 1, 13), 488 (M^+,26), 389 (19), 261 (25), 248 (14), 131 (68), 117 (23), 104 (20), 91 (100), 77 (22), 65 (30), 51 (6). Anal. Calcd. for $C_{24}H_{24}N_8O_4$ (488): C, 59.01; H, 4.95; N, 22.94. Found: C, 59.28; H, 5.01; N, 22.90%.

5,6-Diethoxycarbonyl-3,8-di(4-chlorophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5e)**: Yellow solid (AcOH), (1.32 g, 50%), m.p. 248°C, IR ν (cm^{-1}) 1730 (C=O),1592 (C=N); ^{1}H NMR (DMSO-d_6) δ 1.3 (t, *J* = 7 Hz, 6H, 2 CH_3), 4.3 (q, *J* = 7 Hz, 4H, 2 CH_2), 7.5 (d, *J* = 6 Hz, 4H, ArH), 8.2 (d, *J* = 8 Hz, 4H, ArH). ^{13}C NMR (DMSO-d_6) δ 13.80, 63.27, 119.16, 125.45, 128.68, 129.16, 138.56,

139.30, 157.91; MS *m/z* (%) 530 (M^+ + 2, 33), 529 (M^+ + 1, 14), 528 (M^+,42), 429 (11), 394 (48), 318 (13), 151 (87), 139 (48), 111 (100), 102 (23), 90 (14), 75 (51), 51 (13). Anal. Calcd. for $C_{22}H_{18}Cl_2N_8O_4$ (528): C, 49.92; H, 3.43; Cl, 13.40; N, 21.17. Found: C, 50.05; H, 3.64; Cl, 13.55; N, 21.22%.

5,6-Diethoxycarbonyl-3,8-di(4-nitrophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5f)**: Yellow solid (AcOH), (1.51, g, 55%), m.p.220°C, IR ν (cm^{-1}) 1731 (C=O),1591 (C=N); ^{1}H NMR (DMSO-d_6) δ 1.2 (t, *J* = 7 Hz, 6H, 2 CH_3), 4.2 (q, *J* = 7 Hz, 4H, 2 CH_2), 7.5 (d, *J* = 8 Hz, 4H, ArH), 8.2 (d, *J* = 8 Hz, 4H, ArH). MS *m/z* (%) 552 (M^+ + 2, 9), 551 (M^+ + 1, 22), 550 (M^+,29), 404 (11), 264 (11), 217 (20), 189 (20), 162 (23), 149 (24), 132 (24), 121 (41), 115 (18), 101 (30), 89 (100), 75 (75), 50 (58). Anal. Calcd. for $C_{22}H_{18}N_{10}O_8$ (550): C, 48.01; H, 3.30; N, (25.45. Found: C, 48.05; H, 3.43; N, 25.30%.

5,6-Diphenylcarbamoyl-3,8-diphenyl-1,2,3,4,5a,7,8,8b-octa-aza-a-cenaphthylene **(5g)**: Yellow solid (AcOH), (1.53 g, 55%), m.p. 240°C, IR ν (cm^{-1}) 3295 (NH),1660 (C=O),1595 (C=N); ^{1}H NMR (DMSO-d_6) δ 7.1–8.1 (m, 20H, ArH), 10.8 (s, 2H, 2 NH); MS *m/z* (%) 555 (M^+ + 1, 7), 554 (M^+,19), 408 (11), 288 (12), 220 (12), 144 (12), 119 (45), 91 (48), 77 (100), 65 (49), 51 (39). Anal. Calcd. for $C_{30}H_{22}N_{10}O_2$ (556): C, 64.97; H, 4.00; N, 25.26. Found: C, 64.80; H, 4.15; N, 25.09%.

5,6-Diphenylcarbamoyl-3,8-di(4-methylphenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5h)**: Yellow solid (AcOH), (1.75 g, 60%), m.p. 330°C, IR ν (cm^{-1}) 3282 (NH),1660 (C=O),1597 (C=N); ^{1}H NMR (DMSO-d_6) δ 2.3 (s, 6H, 2 CH_3), 7.1–7.3 (m, 10H, ArH), 7.6 (d, *J* = 8 Hz, 4H, ArH), 8.0 (d, *J* = 8 Hz, 4H, ArH), 10.8 (s, 2H, 2 NH); MS *m/z* (%) 583 (M^+ + 1, 3), 582 (M^+,7), 436 (5), 316 (6), 278 (6), 186 (7), 146 (11), 132 (38), 119 (72), 91 (100), 77 (26), 64 (45), 51 (32). Anal. Calcd. for $C_{32}H_{26}N_{10}O_2$ (582): C, 65.97; H, 4.50; N, 24.04, Found: C, 65.90; H, 4.75; N, 24.06%.

5,6-Diphenylcarbamoyl-3,8-di(4-chlorophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5i)**: Yellow solid (AcOH), (1.49 g, 45%), m.p. 302°C, IR ν (cm^{-1}) 3265 (NH),1668 (C=O),1596 (C=N); ^{1}H NMR (DMSO-d_6) δ 7.5–7.8 (m, 10H, ArH), 8.1 (d, *J* = 9 Hz, 4H, ArH), 8.2 (d, *J* = 8 Hz, 4H, ArH), 11.1 (s, 2H, 2 NH); MS *m/z* (%) 626 (M^+ + 2, 14), 625 (M^+ + 1, 9), 624 (M^+, 24), 441 (30), 322 (14), 299 (13), 206 (19), 151 (37), 119 (100), 91 (83), 77(60), 65 (62), 51 (39). Anal. Calcd. for $C_{30}H_{20}Cl_2N_{10}O_2$ (622): C, 57.80; H, 3.23; Cl, 11.37; N, 22.47. Found: C, 57.70; H, 3.30; Cl, 11.21; N, 22.26%.

5,6-Diphenylcarbamoyl-3,8-di(4-nitrophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5j)**: Yellow solid (AcOH), (1.71 g, 53%), m.p. 240°C, IR ν (cm^{-1}) 3424 (NH),1657 (C=O),1602 (C=N); ^{1}H NMR (DMSO-d_6) δ 7.3–7.8 (m, 10H, ArH), 8.1 (d, *J* = 8 Hz, 4H, ArH), 8.2 (d, *J* = 8 Hz, 4H, ArH),10.2 (s, 2H, 2 NH); MS *m/z* (%) 651 (M^+ + 7,1), 639 (1), 604 (1), 569 (1), 445 (1), 382 (1), 284 (3), 242 (2), 179 (8), 159 (6), 154 (4), 150 (4), 119 (36), 90 (31), 77 (15), 63 (100), 53 (40). Anal. (Calcd. for $C_{30}H_{20}N_{12}O_6$ (644): C, 55.90; H, 3.13; N, 26.08. Found: C, 55.80; H, 3.05; N, 26.15%.

5,6-Dibenzoyl-3,8-diphynyl-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5k)**: Yellow solid (AcOH), (1.00 g, 40%), m.p. 260°C, IR ν (cm^{-1}) 1669 (C=O),1599 (C=N); ^{1}H NMR (DMSO-d_6) δ 7.1–8.2 (m, ArH); MS *m/z* (%) 526 (M^+ + 2,17), 525 (M^+ + 1,22), 524 (M^+,1), 422 (9), 397 (4), 152 (39), 137 (69), 111 (52), 91 (56), 64 (55), 50 (45). Anal. Calcd. for $C_{30}H_{20}N_8O_2$ (524): C, 68.69; H, 3.84; N, 21.36. Found: C, 68.60; H, 3.72; N, 21.47%.

5,6-Dibenzoyl-3,8-di(4-nitrophenyl)-1,2,3,4,5a,7,8,8b-octaaza-acenaphthylene **(5l)**: Pale brown solid (AcOH), (1.23 g, 40%), m.p. 360°C, IR ν (cm^{-1}) 1661 (C=O),1594 (C=N); ^{1}H NMR (DMSO-d_6) δ 7.3–8.0 (m, 10H, ArH), 8.1 (d, *J* = 9 Hz, 4H, ArH), 8.3 (d, *J* = 9 Hz, 4H, ArH); MS *m/z* (%) 614 (M^+,7), 485 (3), 309 (4), 131 (11), 105 (100), 77 (34), 62 (5), 51 (17). Anal. Calcd. for $C_{30}H_{18}N_{10}O_6$ (614): C, 58.63; H, 2.95; N, 22.79. Found: C, 58.36; H, 3.07; N, 22.49%.

Crystal and molecular structure of compound **5c***:* All crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC – 666041. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan. The crystal system is triclinic and the space group is P1. Unit cell: *a* = 10.0002 (3)Å; *b* = 11.0762 (5)Å, *c* = 2.1798 (6)Å, α = 71.462 (2)°, β = 65.781 (2)°, γ = 63.179 (2)°, *V* = 1083.26 (8)Å^3, *Z* = 2. Crystallographic density, D_x = 1.412 Mg m^{-3} and λ = 0.71073. The R-factors are: R_{int} = 0.044, R(all) = 0.225, R(gt) = 0.154, wR(ref) = 0.341, wR(all) = 0.360 and wR(gt) = 0.342.

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