Preparation and Hydrogen Bonding Studies of Phenylhydrazone Derivatives of Alloxan: Crystal and Molecular Structure of Pyrimidine-2(1*H*),4(3*H*),5,6-tetraone 5-(2-Nitrophenyl)hydrazone

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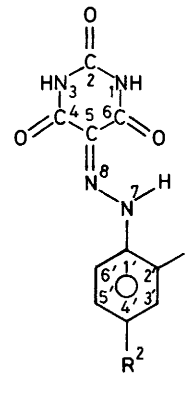
Eight phenylhydrazone derivatives of pyrimidine-2(1*H*),4(3*H*),5,6-tetraone, or 5-oxobarbituric acid (alloxan), are described. Spectroscopic pyrimidine (^{1}H n.m.r., i.r.) data indicate the presence of extensive hydrogen bonding which, as shown by *X*-ray crystallographic data for the title hydrazone, includes both intra- and inter-molecular interactions. The title hydrazone, $C_{10}H_7N_5O_5$, is monoclinic, space group $P2_1/a$, $a = 9.104(8)$, $b = 17.975(13)$, $c = 10.333(8)$ Å, $\beta = 113.5(1)°$, $Z = 4$. 2 145 Independent reflections have been measured on a diffractometer and the structure has been determined by direct methods and refined to *R* 0.074. There are four independent hydrogen bonds in the asymmetric unit: two intramolecular bonds which link N(7)–H(7) to an *o*-NO$_2$ group of the benzene ring and to a carbonyl group of the barbiturate ring and two intermolecular bonds which link NH sites of the barbiturate ring to a solvent *NN*-dimethylformamide oxygen atom and to a carbonyl oxygen atom of another barbiturate ring across a centre of symmetry.

Meldrum's Acid and dimedone readily form phenylhydrazone derivatives with extensive intramolecular $>C=O \cdots HN<$ hydrogen bonding. Structural data show that whereas the cyclohexane ring of the dimedone derivatives assumes an envelope conformation, the 1,3-dioxane-4,6-dione ring system of the Meldrum's Acid derivatives adopts a definite boat conformation.[1,2]

In this report we describe phenylhydrazone derivatives (**1**)—(**8**) of another related 4,6-dione, *viz.* pyrimidine-2(1*H*),4(3*H*),5,6-tetraone, or 5-oxobarbituric acid (alloxan), as approached from the same standpoint of spectral–structural elucidation. Satisfactory crystals for an *X*-ray structural determination were obtained for (**1**) with some difficulty from dimethylformamide (DMF) solutions. Of immediate interest are the nature and extent of the hydrogen bonding (intra or inter) present and the conformation of the barbiturate ring system. Compounds (**3**) and (**4**) have been reported previously (synthesis only).[3]

Experimental

The ^{1}H n.m.r. spectra were recorded on a Brüker WH90 instrument (90 MHz) using [$^2H_6$]DMSO solutions with tetramethylsilane as internal standard. I.r. spectra were recorded using a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls sandwiched between CsI plates. Mass spectrometeric studies were performed on a Kratos MS80 instrument by electron impact at 70 eV with an ion source temperature of 200 °C and using the direct inlet procedure. Microanalyses were obtained from BMAC Limited, Teddington. M.p.s are uncorrected. All compounds listed in Table 1 were obtained as yellow or orange solids following direct coupling of barbituric acid* with the appropriate benzenediazonium salt.



	R^1	R^2
(**1**)	NO_2	H
(**2**)	H	NO_2
(**3**)	H	H
(**4**)	H	Cl
(**5**)	H	CH_3
(**6**)	Cl	H
(**7**)	CH_3	H
(**8**)	NO_2	NO_2

Pyrimidine-2(1H),4(3H),5,6-*tetraone* 5-(2-*Nitrophenyl*)-*hydrazone*(**1**).—*o*-Nitroaniline (3.45 g) was dissolved in a mixture of concentrated HCl (25 cm^3) and H_2O (25 cm^3) following warming and stirring. The resulting solution was chilled to 0 °C and to it was added slowly an ice-cold aqueous solution of sodium nitrite (1.73 g in 20 cm^3) with subsequent stirring for 5 min at 0 °C. The solution of the resulting diazonium salt $C_6H_4(NO_2)N_2Cl$ was filtered rapidly and added to a stirred solution of barbituric acid (3.2 g) and sodium acetate (4.1 g) in methanol (50 cm^3) maintained at 0 °C. On warming to room temperature the *product* separated as a deep yellow solid which was collected, washed with ethanol (3 x 20 cm^3), and subsequently recrystallized from DMF (charcoal) as yellow

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* Pyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione.

Table 1. Microanalytical and principal spectroscopic (^{1}H n.m.r. and i.r.) data for phenylhydrazone derivatives

			Analyses calc. (obs.) (%)				^{1}H n.m.r.‡				I.r.§	
Compd.	Formula	Mol. wt.	C	H	N	[*M*†]	NH			CH_3	ν(NH)/cm^{-1}	ν(C=O)/cm^{-1}
(1)	$C_{10}H_7N_5O_5$	277.196	43.3 (43.2)	2.5 (2.2)	25.3 (25.1)	277	15.27	11.77	11.54		3 187 (s), 3 086 (s)	1 759 (w), 1 738 (s), 1 713 (s), 1 674 (vs), 1 649 (vs), 1 610 (m)
(2)	$C_{10}H_7N_5O_5$	277.196	43.3 (43.1)	2.5 (2.1)	25.3 (25.3)	277	13.99	11.68	11.44		3 168 (s), 3 112 (sh), 3 068 (s)	1 789 (m), 1 733 (s), 1 678 (s), 1 655 (vs), 1 608 (s)
(3)	$C_{10}H_8N_4O_3$	232.199	51.7 (51.4)	3.5 (3.4)	24.1 (24.1)	232	14.16	11.45	11.22		3 263 (s), 3 172 (w), 3 096 (s), 3 068 (w)	1 783 (m), 1 756 (s), 1 711 (vs), 1 657 (vs), 1 619 (w)
(4)	$C_{10}H_7ClN_4O_3$	266.644	45.0 (44.8)	2.6 (2.4)	21.0 (21.0)	266	14.06	11.48	11.24		3 260 (s), 3 169 (w), 3 080 (s)	1 782 (m), 1 756 (s), 1 704 (vs), 1 651 (vs)
(5)	$C_{11}H_{10}N_4O_3$	246.226	53.7 (53.7)	4.1 (4.0)	22.8 (22.2)	246	14.20	11.46	11.23	2.32	3 260 (s), 3 175 (w), 3 091 (s), 3 040 (w)	1 784 (m), 1 758 (s), 1 710 (vs), 1 659 (vs)
(6)	$C_{10}H_7ClN_4O_3$	266.644	45.0 (44.6)	2.6 (2.4)	21.0 (20.7)	266	14.51	11.69	11.42		3 185 (s), 3 070 (s)	1 736 (vs), 1 698 (s), 1 672 (vs), 1 642 (vs)
(7)	$C_{11}H_{10}N_4O_3$	246.226	53.7 (53.6)	4.1 (4.0)	22.8 (22.6)	246	14.60	11.68	11.40	2.45	3 194 (s), 3 125 (w), 3 053 (s)	1 776 (w), 1 733 (vs), 1 691 (vs), 1 667 (vs), 1 641 (s), 1 610 (m)
(8)	$C_{10}H_6N_6O_7$	322.193	37.3 (37.0)	1.9 (1.8)	26.1 (25.9)	322	15.24	11.86	11.62		3 170 (s), 3 094 (s)	1 748 (s), 1 719 (s), 1 667 (vs), 1 616 (w), 1 607 (m)

† Mass spectrum *m/z*. ‡ δ For [$^2H_6$]DMSO solutions with tetramethylsilane as internal reference. § ν(cm^{-1}) as Nujol mull.

needles (3.7 g, 53%). Analytical data for this and the other compounds are listed in Table 1.

Crystal Data for (**1**).—$C_{10}H_7N_5O_5$, $M = 277.2$. Monoclinic, space group $P2_1/a$, $Z = 4$, $a = 9.104(8)$, $b = 17.975(13)$, $c = 10.333(8)$ Å, $\beta = 113.5(1)°$, $U = 1\,550.7$ Å^3, $F(000) = 1\,080$, $D_m = 1.18$, $D_c = 1.18$ g cm^{-3}, $\mu = 1.06$ cm^{-1}.

Precession photographs established the preliminary cell constants and space group. A crystal was mounted to rotate around the *a* axis on a Stoe STADI 2 diffractometer and data were collected from a variable width ω scan. Background counts were 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + 0.5 sinμ/tanθ). 2 145 Independent reflections with $2\theta < 50°$ were measured of which 1 389 having $I > 3\sigma(I)$ were used in subsequent refinement. The structure was solved by direct methods.[4] The oxygen, carbon, and nitrogen atoms were refined anisotropically. The hydrogen atoms were included in trigonal or tetrahedral positions; the positions of atoms bonded to nitrogen were refined, those bonded to carbon were not. Methyl hydrogen atoms were refined as rigid groups. Hydrogen atoms were given isotropic thermal parameters which were refined. The structure was refined using full-matrix least squares to R 0.074 ($R_w = 0.075$). In the final cycle of refinement no shift was greater than 0.1σ. There were no significant peaks in a final difference Fourier map. The weighting scheme chosen was $w = 1/[\sigma^2(F) + 0.003F^2]$ which gave similar values of $w\Delta^2$ over ranges of F_o and sinθ/λ. Calculations were carried out using SHELX 76[5] and local programs on the Amdahl V7 computer at the University of Reading. Atomic co-ordinates are given in Table 2. Details of interatomic distances and angles are listed in Table 3.

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	7 325(1)	1 803(7)	−6 706(10)
C(2)	7 313(10)	2 499(6)	−6 271(10)
C(3)	6 807(9)	2 646(5)	−5 177(9)
C(4)	6 326(9)	2 054(5)	−4 554(8)
C(5)	6 331(10)	1 347(6)	−5 052(9)
C(6)	6 859(11)	1 222(7)	−6 097(11)
N(1)	6 810(9)	3 389(5)	−4 754(9)
O(1)	6 396(10)	3 553(3)	−3 793(9)
O(2)	7 251(11)	3 886(4)	−5 328(9)
N(7)	5 872(8)	2 163(4)	−3 433(8)
N(8)	5 653(8)	1 579(4)	−2 780(7)
C(9)	5 174(9)	1 656(4)	−1 752(8)
C(10)	4 812(9)	2 373(4)	−1 276(8)
O(11)	4 984(7)	2 966(3)	−1 749(6)
N(12)	4 182(7)	2 332(4)	−274(7)
C(13)	3 973(10)	1 704(4)	356(9)
N(14)	4 461(8)	1 056(4)	−32(7)
O(15)	3 410(7)	1 710(3)	1 239(6)
C(16)	5 035(9)	962(5)	−1 073(8)
O(17)	5 274(8)	346(3)	−1 423(7)
O(100)	3 647(7)	3 651(3)	764(6)
C(102)	4 887(11)	4 007(5)	1 109(9)
N(103)	5 201(8)	4 662(4)	1 726(8)
C(104)	4 021(15)	5 027(6)	2 088(16)
C(105)	6 752(12)	5 011(7)	2 162(13)

Results and Discussion

Spectroscopic.—The i.r. spectra (mull) of the compounds show multiplet bands in the region 3 260—3 080 cm^{-1} assigned as ν(NH) stretching modes associated with both the N(1), N(3) and the N(7) centres. Their relative low energy position in the N–H stretching region reflects strong hydrogen bond involvement: (intermolecular) N(1) incorporating a solvent molecule of crystallization $>$NH $\cdots$ DMF, and N(3) as part of dimer formation $>$NH $\cdots$ O=C$<$ (see later); (intramolecular) N(7) is bonded to a $>$C=O group of the barbiturate ring and, specifically for compounds (**1**) and (**8**), additionally to an *o*-NO_2 group on the aromatic ring. Equally the C=O stretching region profile is complex, *e.g.* compound (**1**) typically shows bands at 1 759, 1 738, 1 713, 1 674, 1 649, and 1 610 cm^{-1} with no clear delineation between the various $\nu(CO)_{free}$ and $\nu(CO)_{H\text{-bonded}}$ stretching modes.[6]

The ^{1}H n.m.r. spectra show a three-peak (1:1:1) profile for the N–H protons; those associated with the barbiturate ring [N(1),N(3)] appearing within the range δ 11—12 with the phenylhydrazono [N(7)] signal shifted markedly downfield to

Table 3. Molecular dimensions (Å and °)

C(1)–C(2)	1.331(13)	N(8)–C(9)	1.306(9)
C(1)–C(6)	1.371(14)	C(9)–C(10)	1.463(11)
C(2)–C(3)	1.406(11)	C(9)–C(16)	1.461(10)
C(3)–C(4)	1.401(11)	C(10)–O(11)	1.208(8)
C(3)–N(1)	1.406(11)	C(10)–N(12)	1.371(9)
C(4)–C(5)	1.370(12)	N(12)–C(13)	1.354(10)
C(4)–N(7)	1.390(9)	C(13)–N(14)	1.364(10)
C(5)–C(6)	1.366(11)	C(13)–O(15)	1.212(9)
N(1)–O(1)	1.230(9)	N(14)–C(16)	1.381(9)
N(1)–O(2)	1.225(9)	C(16)–O(17)	1.212(9)
N(7)–N(8)	1.308(9)		
C(2)–C(1)–C(6)	121.1(8)	N(8)–C(9)–C(10)	124.1(7)
C(1)–C(2)–C(3)	119.8(9)	N(8)–C(9)–C(16)	114.8(6)
C(2)–C(3)–C(4)	119.4(9)	C(10)–C(9)–C(16)	121.1(6)
C(2)–C(3)–N(1)	117.9(8)	C(9)–C(10)–O(11)	124.0(6)
C(4)–C(3)–N(1)	122.7(7)	C(9)–C(10)–N(12)	115.1(7)
C(3)–C(4)–C(5)	118.8(7)	O(11)–C(10)–N(12)	120.8(7)
C(3)–C(4)–N(7)	121.7(8)	C(10)–N(12)–C(13)	126.1(7)
C(5)–C(4)–N(7)	119.4(7)	N(12)–C(13)–N(14)	116.5(7)
C(4)–C(5)–C(6)	120.3(9)	N(12)–C(13)–O(15)	122.5(8)
C(1)–C(6)–C(5)	120.5(10)	N(14)–C(13)–O(15)	120.9(7)
C(3)–N(1)–O(1)	121.0(7)	C(13)–N(14)–C(16)	127.0(7)
C(3)–N(1)–O(2)	120.2(8)	C(9)–C(16)–N(14)	113.7(7)
O(1)–N(1)–O(2)	118.8(9)	C(9)–C(16)–O(17)	125.3(6)
C(4)–N(7)–N(8)	118.2(7)	N(14)–C(16)–O(17)	120.8(7)
N(7)–N(8)–C(9)	120.2(6)		
Solvent DMF molecule			
O(100)–C(102)	1.221(10)	O(100)–C(102)–N(103)	127.4(7)
C(102)–N(103)	1.316(11)	C(102)–N(103)–C(104)	119.8(7)
N(103)–C(104)	1.430(11)	C(102)–N(103)–C(105)	122.4(8)
N(103)–C(105)	1.444(11)	C(104)–N(103)–C(105)	117.6(8)

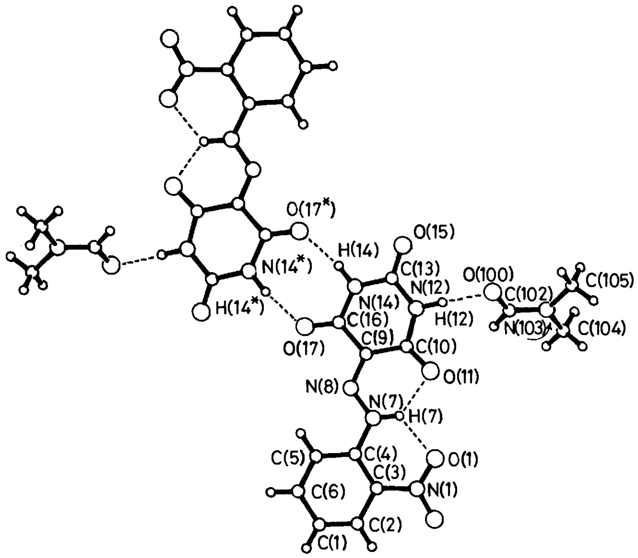
the δ 13—16 region. As discussed previously,[2,7] δ(NH) values have proved to be an extremely sensitive monitor of hydrogen bonding in phenylhydrazone derivatives. In this present series, compounds (**1**) and (**8**) which have an *o*-NO_2 group on the aromatic ring show maximal δ(NH) values of 15.27 and 15.24 respectively; compound (**2**) with a *p*-NO_2 group substituent shows a minimal δ(NH) 13.99. On average, compounds (**1**) and (**8**) show an enhanced downfield shift of 0.76—1.28 p.p.m. for NH with respect to those of the remaining compounds as a result of their unique bifurcated hydrogen bond $>C{=}O\cdots NH\cdots O_2N$. Variations in δ(NH) with changing *para*-substituents lie in the sequential order expected: electron-withdrawing (*p*-NO_2, δ 13.99; *p*-Cl, δ 14.06); inductive (*p*-CH_3, δ 14.20) compared with unsubstituted (*p*-H, δ 14.16). No such variation is observed for δ(NH) values [N(1),N(3)] which remain insensitive to *ortho- versus para*-substituents throughout the series. The methyl protons for (**5**) and (**7**) appear as singlets at δ 2.32 and 2.45, respectively: the phenyl ring protons appear as a multiplet in the region δ 7.63—7.25.

Preliminary investigations of the donor ability of these compounds indicate that there is no metal complex formation following direct addition of M^{II} salts (M = Co, Ni, Cu, and Zn). Typically, direct addition of $[Ni(DMSO)_6]^{2+}[ClO_4]_2^-$ to a $[^2H_6]$DMSO solution of (**3**) in an n.m.r. tube gave a clear yellow solution whose ^{1}H n.m.r. spectrum was identical to that of starting ligand but with startlingly improved resolution. The slight broadening of the NH signals in the original spectrum of (**3**) is most likely a reflection of fast proton exchange with OH protons introduced by 'wet' solvents during synthesis and recrystallization procedures [there is an extraneous signal at δ 3.4 (H_2O)]. In the absence of complex formation the $[Ni(DMSO)_6]^{2+}$ provides a convenient metal site for H_2O–DMSO exchange and acts as an effective scavenger for water molecules. Under a much slower exchange rate (or indeed absence of exchange) spectral resolution is thereby dramatically improved. Where complexes of transition and lanthanide metals with barbiturates have been structurally described,[8–11] they are of the general formula $M^{II}(barb)_2L_2$ and incorporate a substituted barbiturate anion (barb) and a strong nitrogen donor organic base (L) such as pyridine; in each case the barbiturate anion is bound to the metal solely through a deprotonated imine [N(3)] centre. We now find that prolonged treatment with M^{II} salts (M = Ni, Cu, and Zn) in the presence of strong base (NaOH) to facilitate amine deprotonation and excess of pyridine does give metal complexes.[12]

Table 4.

Hydrogen bonds	(Å) N···O	 H···O	(°) N–H···O
N(7)–H(7)···O(1)	2.59(1)	1.93(10)	122(8)
N(7)–H(7)···O(11)	2.62(1)	1.86(10)	130(8)
N(12)–H(12)···O(100)	2.72(1)	1.79(9)	171(6)
N(14)–H(14)···O(17*)	2.89(1)	1.83(8)	150(7)
	C···O	H···O	C–H···O
C(2)–H(2)···O(15†)	3.41(1)	2.59(8)	146(7)

* $1 - x, -y, 2 - z$. † Is $\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$.



Crystal Structure.—The asymmetric unit contains one molecule of (**1**) together with one molecule of solvent DMF. Two such units are held together by hydrogen bonds across a centre of symmetry as shown in the Figure, which also includes the crystallographic atomic numbering system. There are four independent hydrogen bonds shown as dotted lines in the Figure with dimensions listed in Table 4.

Intramolecular. There are two intramolecular hydrogen bonds involving N(7)–H(7), one to O(1) belonging to the *o*-NO_2 group and the other to O(11) from a carbonyl group of the barbiturate ring. The two N···O distances are 2.59(1), 2.62(1) Å, respectively, and the two N–H···O angles are 122(8), 130(8)°, respectively. These values compare favourably with those found in similar 'bifurcated' phenylhydrazone derivatives, namely compound (**4**) in ref. 13, compound (**1**) in ref. 1, and compound (**1**) in ref. 14. The presence of such a bifurcated hydrogen bond clearly affects the geometry of the phenylhydrazono grouping though as far as the bond lengths are concerned our experience indicates that it is the carbonyl group rather than the nitro group which exerts the major influence;[13] we have found no correlation between the presence of a hydrogen bond from N(7)–H(7) to an *o*-NO_2 group and the phenylhydrazono dimensions. However, the presence of a terminal carbonyl group in conjugation with C(9)–N(8) markedly influences the bond dimensions of C(4)–N(7), N(7)–N(8), and N(8)–C(9), *viz.* a relative increase in N(7)–N(8) results *in a relative* decrease in the other two with mean distances of 1.400, 1.307, and 1.313 Å,[13] respectively. With no such carbonyl group present the mean distances are 1.36, 1.39, and 1.28 Å.[15] Compound (**1**) with dimensions 1.390(9), 1.308(9), and 1.306(9) Å clearly falls within the former category. Another common feature in structures containing a terminal carbonyl group is that the N(8)–C(9)–C(10) angle is considerably larger than that of N(8)–C(9)–C(16). In the present instance these angles are 124.1(7) and 114.8(6)°, respectively and, as previously argued,[15] such a difference, *ca.* 10°, is necessary to accommmodate the O(11) ••• N(7) hydrogen bond. Similarly we note that the C(3)–C(4)–N(7) angle [121.7(8)°] is larger than the C(5)–C(4)–N(7) angle [119.4(7)°] thereby facilitating the O(1) ••• N(7) hydrogen bond. That the 'distortion' around C(4) is much smaller than that around C(9) is seen as a measure of the inflexibility of the delocalized benzene ring with respect to the barbiturate ring. In structures without an *o*-NO_2 group present, C(3)–C(4)–N(7) is usually smaller than C(5)–C(4)–N(7). Least squares calculations show that the *o*-NO_2 group is coplanar with the benzene ring the angle of intersection being 1.1°. There is a pronounced deviation from hexagonal symmetry in the benzene ring; the most significant differences are in C(2)–C(3) and C(3)–C(4) which are lengthened quite considerably with respect to the other carbon–carbon ring distances. Such distortion may well be a direct off-shoot of the bifurcated intramolecular hydrogen bonding which involves the NO_2 group attached to C(3).[16] The barbiturate and benzene rings are not coplanar and the angle between them (15.4°) is unusual as it is caused by a fold as well as a twist about N(7)–N(8). Thus atoms C(16), N(14), O(17) are 0.67, 0.61, 0.88 Å from the benzene ring plane whereas C(10), O(11), N(12) on the 'opposite' side of the barbiturate ring are only displaced by 0.02, −0.19, and −0.09 Å, respectively.

Intermolecular. Each barbiturate ring is involved in three intermolecular hydrogen bonds. N(12) is hydrogen bonded to a solvent DMF molecule with N(12) ••• O(100) 2.72(1) Å; this is much shorter than the 2.96 Å observed in a recent structure of a phenylhydrazone:DMF complex[15] and reflects the greater polarization of H(12) in the barbiturate ring compared with H(7). The other N–H group of the barbiturate ring forms a hydrogen bond N(14)–H(14) ••• O(17*) 2.89(1) Å across a centre of symmetry (see Figure) which is the longest of the four hydrogen bonds featured in the unit cell. There is a possible further interaction involving the carbon atom C(2) of the benzene ring and a carbonyl atom of a barbiturate ring [C(2)–H ••• O=C<, 3.41(1) Å] but whether such an interaction is a 'true' hydrogen bond is a moot point.

The pattern of hydrogen bonding in the unit cell may well have affected the dimensions and conformation of the barbiturate ring. A least squares plane through the barbiturate ring atoms shows a pronounced puckering of the ring with deviations C(9) −0.04, C(10) 0.05, N(12) −0.01, C(13) −0.03, N(14) 0.04, and C(16) 0.2 Å. Distances from this plane of non-contributing atoms are N(8) −0.14, O(11) 0.10, O(15) −0.08, and O(17) −0.11 Å. These deviations follow no essential pattern and are probably the result of packing forces.

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