Phenylhydrazone Derivatives of Meldrum's Acid: Crystal and Molecular Structures of 2,2-Dimethyl-1,3-dioxan-4,5,6-trione 5-(2-Nitrophenylhydrazone) (1) and 2,2-dimethyl-1,3-dioxan-4,5,6-trione 5-(2-Chlorophenylhydrazone) (2)

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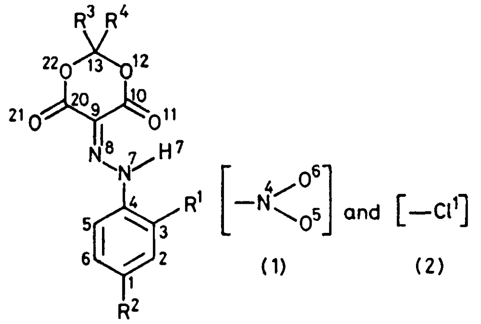
A series of phenylhydrazone derivatives of 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid) and of the corresponding 2-phenyl compound has been prepared. Their i.r. and ^{1}H n.m.r. spectra are discussed in terms of the extent of intramolecular hydrogen bonding. With *ortho*-nitro-group substituents on the aromatic ring, enhanced low-field chemical shifts of the order δ_{NH} *ca.* 15 imply a bifurcated hydrogen-bonding environment. Compound (1), $C_{12}H_{11}O_6N_3$, crystallises in the monoclinic space group $P2_1/a$ with a = 7.178(7), b = 13.976(12), c = 13.042(11) Å, β = 102.7(1)°, Z = 4. Compound (2), $C_{12}H_{11}ClO_4N_2$, crystallises in the orthorhombic space group $P2_12_12_1$ with a = 14.279(12), b = 18.950(15), c = 9.460(12) Å, Z = 8. Both structures were solved by the statistical method using the Shel-X 76 system of programs and refined using full-matrix least squares. The numbers of reflexions used in refinement and the final R values are (1), 1 369, 0.069 and (2), 1 490, 0.080, respectively. In (1) the $NO_2 \cdots HN$ and $C=O \cdots HN$ separations confirm the *ortho*-nitro-involvement in bifurcated intramolecular hydrogen bonding; in (2), though there is still substantial $C=O \cdots HN$ intramolecular hydrogen bonding the *ortho*-chloro atom is not involved. For (2) the ring fragment (I) is essentially planar but this is not so for (1). The 1,3-dioxan-4,6-dione cyclic system adopts a boat conformation in each structure. There is no intermolecular hydrogen bonding.

Two common characteristics have emerged from our current studies of various phenylhydrazones:[1-3] (a) the pronounced chemical shifts $\delta_{NH} > 12$ in those instances where strong intramolecular hydrogen bonding involving terminal † carbonyl groups and/or *ortho*-substituted nitro-groups is present; and (b) the inverse relationship between Ar–N(H) and N(H)–N bond lengths and the direct relationship between Ar–N(H) and $N=C\textless$ bond lengths within the $Ar-N(H)-N=C\textless$ skeleton. As a further investigation of these twin aspects of phenylhydrazones we present and discuss spectral (i.r. and ^{1}H n.m.r.) and structural data for an extensive series of derivatives (1)—(14) of 2,2-dimethyl-1,3-dioxan-4,6-dione, otherwise known as Meldrum's acid. A review of the general chemistry of Meldrum's acid has appeared recently.[4]



(1)-(7) $R^3 = R^4 = CH_3$
(8)-(14) $R^3 = H, R^4 = C_6H_5$
showing the crystallographic numbering

DISCUSSION

It is clear from the i.r. data that $\textgreater C=O$ groups associated with the 1,3-dioxan-4,6-dione ring system are involved in intramolecular hydrogen bonding throughout the series (1)—(14). An intense ν(NH) band observed in the region 3 188—3 112 cm^{-1} (Table 1) is consistent with a major shift to lower energy on hydrogen-bond formation. No significant variation was detected between mull and solution spectra. The two intense bands in the carbonyl stretching region for Meldrum's acid, associated with in-phase ν_s of 1 786 cm^{-1} and out-of-phase ν_a of 1 769 cm^{-1} coupling of ν(C=O) vibrations,[5] appear at 25—30 cm^{-1} downfield in these phenylhydrazone derivatives. The ν(CN) stretching mode appears in the region 1 560—1 510 cm^{-1}. It is not possible to locate unequivocally the two bands at *ca.* 1 570—1 500 and *ca.* 1 370—1 300 cm^{-1} characteristic of ring-substituted nitro-groups from within the complex pattern of ring vibrations. The implied additional involvement of suitable *ortho*-substituents on the aromatic ring, *e.g.* $R^1 = NO_2$, to give a bifurcated hydrogen-bonding environment becomes evident, however, from the ^{1}H n.m.r. data (Table 1) where, as established previously,[1,3] variations in δ_{NH} can be more reliably correlated with the extent of hydrogen-bonding. Significantly each of the three compounds (1), (6), and (9) which feature an *ortho*-nitro group as ring substituent, shows a maximal δ_{NH} of *ca.* 15. On average this represents an enhanced downfield shift of *ca.* 1.2—1.5 p.p.m. with regard to other members of the series. In contrast the two compounds, (3) and (8), which show a minimal δ_{NH} of *ca.* 13.5 feature solely *para*-nitro-group substitutents. Methyl groups substituted on the aromatic ring (R^1R^2) give one sharp resonance, δ_{CH_3} 2.44—2.37. Methyl groups associated with the 1,3-dioxan-

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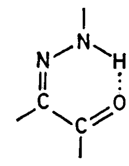
† Terminal groups are those attached to the imino-carbon atom of the skeleton.

TABLE 1

Compound	R^1	R^2	R^3	R^4	Empirical formula	M.p. (°C)	C $\frac{\text{calc}}{\text{obs}}$ (%)	H $\frac{\text{calc}}{\text{obs}}$ (%)	N $\frac{\text{calc}}{\text{obs}}$ (%)	δ_{NH}	δ_{CH_3} (R^3,R^4)	δ_{CH_3} (R^1,R^2)	ν (NH)/ cm^{-1}
(1)	NO_2	H	CH_3	CH_3	$C_{12}H_{11}N_3O_6$	164—165	49.2/49.0	3.8/3.8	14.3/14.1	14.93	1.85		3 152
(2)	Cl	H	CH_3	CH_3	$C_{12}H_{11}ClN_2O_4$	127—128	51.0/50.6	3.9/3.6	9.9/9.6	13.89	1.83		3 151
(3)	H	NO_2	CH_3	CH_3	$C_{12}H_{11}N_3O_6$	214—215	49.2/49.1	3.8/3.6	14.3/14.0	13.55	1.84		3 160
(4)	H	Cl	CH_3	CH_3	$C_{12}H_{11}ClN_2O_4$	165—166	51.0/50.7	3.9/3.7	9.9/9.8	13.61	1.81		3 140
(5)	H	CH_3	CH_3	CH_3	$C_{13}H_{14}N_2O_4$	155—156	59.5/59.0	5.4/5.1	10.7/10.7	13.70	1.80	2.37	3 115
(6)	NO_2	NO_2	CH_3	CH_3	$C_{12}H_{10}N_4O_8$	206—207	42.6/42.1	3.0/3.1	16.6/16.2	15.01	1.87		3 154
(7)	H	H	CH_3	CH_3	$C_{12}H_{12}N_2O_4$	171—172	58.1/57.8	4.9/4.7	11.3/11.1	13.65	1.81		3 139
(8)	H	NO_2	H	C_6H_5	$C_{16}H_{11}N_3O_6$	203—105	56.3/56.1	3.2/3.1	12.3/12.0	13.57			3 136
(9)	NO_2	H	H	C_6H_5	$C_{16}H_{11}N_3O_6$	197—198	56.3/56.2	3.2/3.2	12.3/12.1	14.94			3 154
(10)	H	Cl	H	C_6H_5	$C_{16}H_{11}ClN_2O_4$	223—224	58.1/58.0	3.4/3.0	8.5/8.2	13.63			3 128
(11)	Cl	H	H	C_6H_5	$C_{16}H_{11}ClN_2O_4$	194—195	58.1/57.8	3.4/3.1	8.5/8.2	13.90			3 148
(12)	CH_3	H	H	C_6H_5	$C_{17}H_{14}N_2O_4$	182—183	66.6/66.5	4.6/4.5	9.1/9.1	13.89		2.44	3 122
(13)	H	CH_3	H	C_6H_5	$C_{17}H_{14}N_2O_4$	199—200	66.6/66.3	4.6/4.7	9.1/9.0	13.70		2.38	3 112
(14)	H	H	H	C_6H_5	$C_{16}H_{12}N_2O_4$	196—198	64.9/64.6	4.1/4.0	9.5/9.2	13.64			3 132

4,6-dione system (R^3 and R^4) are also characterised by one sharp singlet, δ_{CH_3} 1.81—1.87, *i.e.* there is no conformational preference in solution. For the parent Meldrum's acid a mixture of equal amounts of interconverting inversionally identical conformations gives rise to the averaged singlet, δ_{CH_3} 1.76.[6,7]

The choice of compounds for structural analysis was influenced partly by the suitability of crystals and partly by an awareness of the importance of R^1 *vis-à-vis* the strong intramolecular $R^1 \cdots$ NH and C=O $\cdots$ NH hydrogen bonding in the crystalline state which fashions the geometric and bond parameters within the ring backbone (I). Previous studies in these laboratories have established a correlation between the phenylhydrazone dimensions C(4)–N(7), N(7)–N(8), and N(8)–C(9) and the extent of hydrogen bonding present in the molecule. Selection of compounds (1) and (2) allows direct comparison in terms of the contributions of *ortho*-nitro *versus* *ortho*-chloro. Crystal data for (1) and (2) are given in Table 2.



(I)

Molecule (1) is shown in Figure 1 which is a projection onto the benzene ring plane. The N(7) atom is evidently hydrogen-bonded to two oxygens, namely O(6) at 2.64 Å and O(11) at 2.65 Å. This is concomitant with dimensions C(4)—N(7) 1.411(6), N(7)—N(8) 1.313(5), and N(8)—C(9) 1.318(6) Å. For comparison, dimethyl 2-(2,4-dinitrophenylhydrazone)propanedioate [numbered (4) in ref. 3] whose structure also embraces this type of bifurcated hydrogen bond shows these hydrazone dimensions as 1.380, 1.357, and 1.294 Å, respectively. The presence of a *para*-nitro-group in the latter may well be directly responsible for these overt variations. A further general feature of phenylhydrazones containing *ortho*-nitro-groups is that the C(3)–C(4)–N(7) angles are particularly large. This increase allows space for the formation of the $NO_2 \cdots$ HN bond with suitable geometry. Such an increase is found in (1) with the angle being 122.8(4)°. A direct off-shoot of this is an accompanying decrease in the C(5)–C(4)–N(7) angle at 119.6(4)°. The *ortho*-nitro group is not coplanar with the benzene ring; it is twisted at an angle of 13.4°. Similar rotation

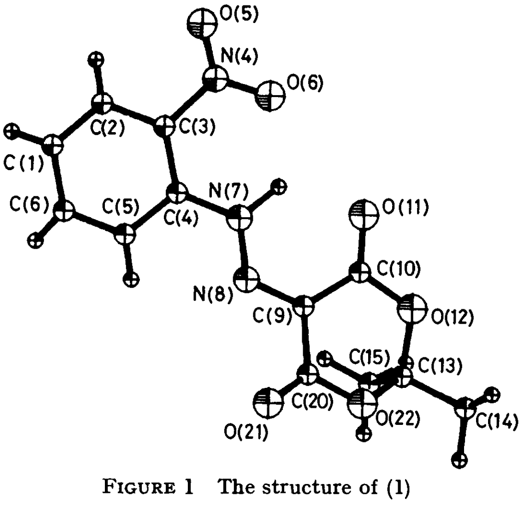


FIGURE 1 The structure of (1)

TABLE 2

Crystal data and refinement details

Compound	(1)	(2)
Formula	$C_{12}H_{11}N_3O_6$	$C_{12}H_{11}N_2O_4Cl$
M	293.1	282.5
Crystal class	monoclinic	orthorhombic
Space group	$P2_1/a$	$P2_12_12_1$
Absences	$h0l,\ h = 2n + 1$ $0k0,\ k = 2n + 1$	$h00,\ h = 2n + 1$ $0k0,\ k = 2n + 1$ $00l,\ l = 2n + 1$
a(Å)	7.178(7)	14.279(12)
b(Å)	13.976(12)	18.950(15)
c(Å)	13.042(11)	9.460(12)
β(°)	102.7(1)	(90)
U(Å³)	1 276.1	2 559.7
F(000)	608	1 168
D_m (g cm^{-3})	1.52	1.46
D_c (g cm^{-3})	1.52	1.47
Z	4	8
μ(cm^{-1})	1.34	1.31
λ(Å)	0.7107	0.7107
Crystal size (mm)	0.3 × 0.5 × 0.5	0.4 × 0.4 × 0.4
Rotation axis	a	c
$2\theta_{max.}$(°)	50	50
No. of data measured	2 360	2 550
Criterion for data inclusion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of data used in refinement	1 369	1 490
Final *R* value	0.069	0.080

has been noted previously, *e.g.* the equivalent angle is 4.1° in compound (2) and 10.4° in compound (4) (see ref. 3).

In (2) there are two molecules (A and B) in the asymmetric unit. The geometries of the independent molecules (2A) and (2B) are very similar (A is shown in Figure 2). The hydrazone fragment for each has dimensions C(4)–N(7) 1.374(14), 1.414(13), N(7)–N(8) 1.295(12), 1.294 (12), and N(8)–C(9) 1.305(13), 1.298(12) Å. These are much as expected for a molecule in which the H(7) atom is singly hydrogen-bonded to just one oxygen with distances N(7) · · · O(11) at 2.65 Å in A and at 2.64 Å in B. Invariably the influence of geometry caused by the presence of such a terminal oxygen atom conjugated to the N(8)–C(9) bond far exceeds that provided by *ortho*-nitro- or *ortho*-chloro-groups. The chlorine atom is adjacent to H(7) leaving N(8) adjacent to H(5), presumably so that N(8) with its lone pair and Cl(1) can avoid intramolecular contact. The chlorine atom is similarly directed away from the imino-nitrogen in diethyl 2,4-bis-(*o*-chlorophenylhydrazono)-3-oxopentanedioate.[2] The absence of an *ortho*-nitro-group in (2) leaves C(3)–C(4)–N(7) and C(5)–C(4)–N(7) similar at 120.0(9), 124.1(9)° for A and 122.0 (9), 120.3(9)° for B. It is difficult to assess whether these differences between A and B are significant. In ref. 3 we established that there is a significant range of dimensions for this group even when the rest of the geometry is similar; the two structures in (2) might just reflect that range. What is clear is that the steric repulsions of the *ortho*-chloro-atom are considerably less than those associated with the *ortho*-nitro-group. Indeed, unlike the *ortho*-nitro-group, an *ortho*-chloro-atom cannot form a hydrogen bond with H(7) because the Cl · · · N distance is perforce too large.

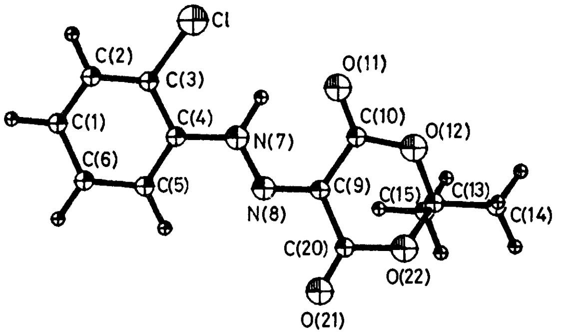


FIGURE 2 The structure of (2A). The structure of (2B) is equivalent

TABLE 3

Least squares planes

(a) Phenylhydrazone fragment. Plane 1 through C(n), n = 1—6

	(1)	(2A)	(2B)
C(1)	0.00	0.00	0.00
C(2)	—0.00	0.00	—0.01
C(3)	—0.00	—0.00	0.01
C(4)	—0.00	—0.00	0.00
C(5)	0.01	0.01	—0.01
C(6)	—0.01	—0.01	0.00
N(4)	—0.02		
O(5)	—0.26		
O(6)	0.23		
Cl(1)		0.05	0.03
N(7)	—0.00	—0.01	—0.05
N(8)	0.23	0.11	0.11
C(9)	0.11	0.13	0.19
C(10)	—0.32	0.07	0.00
C(20)	0.49	0.33	0.35

(b) Meldrum's acid fragment. Plane 2 through C(10), O(12), C(20), O(22)

	(1)	(2A)	(2B)
C(10)	0.00	—0.04	—0.00
O(12)	—0.00	0.04	0.00
C(20)	—0.00	0.04	0.00
O(22)	0.00	—0.04	0.00
C(9)	0.13	0.08	0.13
C(13)	0.58	0.56	0.58
O(11)	—0.11	—0.17	—0.15
O(21)	—0.22	—0.05	—0.11
C(14)	0.15	0.12	0.09
C(15)	2.06	2.05	2.06
Angle between Planes 1 and 2 (°)	22.3	7.6	11.9

Least-squares planes through the phenyl ring are given in Table 3. Interestingly, (2) is essentially planar in that N(7) and C(10) show small deviations from the least squares plane. The presence of the single hydrogen bond with formation of the six-membered ring N(7)-N(8)C(9)C(10)O(11)H(7) forces C(10) into the plane; C(20), however, lies somewhat outside this plane, 0.33 in A and 0.35 Å in B. In (1), and in sharp contrast, neither C(10), —0.32, nor O(6), 0.23 Å, lie in the plane of the phenyl ring. Clearly this is a consequence of the bifurcated hydrogen bond as very similar values (—0.28, 0.26 Å) are found in molecule (4) of ref. 3. Again C(20) lies well outside the plane (0.49 Å). It now remains to consider the dimensions of the 1,3-dioxan-4,6-dione fragment especially with respect to the exact ring conformation adopted in each case. The Cambridge Data Centre files [8] reveal three structures of derivatives of Meldrum's acid, none of which, however, involves a conjugated link at the 5-position, *viz.* (a) 5-phenyl,[9] (b) 5-ethyl,[9] and (c) 5-thienyl.[10] One other structure concerns (d) 12,12,18-trimethyl-10,14,17-trioxo-11,13-dioxa-1,4-dithiatrispiro[4.2.0.5.4.2]eicosane.[11] Ring conformations in (a)—(c) are identical in that C(10), O(12), C(20), and O(22) are planar (*n.b.* these are transposed to our crystallographic numbering system) and the atoms C(9), C(13), O(11), and O(21) are at the following distances from this plane: 0.50, 0.34, —0.28, —0.20 in (a); 0.49, 0.31, —0.26, —0.31 in (b); 0.48, 0.40, —0.31, —0.33 Å in (c). Thus these three derivatives show a boat structure with C(9) and (C13) the same side of the plane of four atoms. It is interesting though, in view of the cluttered nature of the molecule, not that surprising that (d) has very different deviations, *viz.* —0.51, 0.39, —0.25, —0.21 Å.

In the present structures the phenylhydrazone fragment of both (1) and (2) is conjugated to the 1,3-dioxan-4,6-dione system through N(8)=C(9) and whilst the geometry is still clearly a boat it is very shallow at the C(9) end. The deviations from the C(10)O(12)C(20)-O(22) plane are C(9) 0.13, 0.08, 0.13 Å and C(13) 0.58, 0.56, 0.58 Å in structures (1), (2A), and (2B), respectively.

By direct comparison C(13) is more puckered from the ring in these instances than is the same atom in (a)—(c). The extensive hydrogen-bond formation between O(11) and N(7) results in an angle non-equivalence, N(8)–C(9)–C(10) $>$ N(8)–C(9)–C(20), with values 124.3(4), 124.9(9), 124.4(8)° *versus* 115.9(4), 115.2(9), 116.9(8)° respectively for (1), (2A), and (2B). The least squares planes through the 1,3-dioxan-4,6-dione fragment (plane 2 in Table 3) show remarkable similarities, the only major difference being the angle made with the benzene ring, *viz.* 22.3° in (1), and 7.6 and 11.9 ° in (2). Doubtless the magnitude of the former is caused by the steric insistence of the *ortho*-nitro-groups which moves C(10) out of the plane of the aromatic ring.

In (1) there are several close intermolecular contacts of *ca.* 3.20 Å between molecules but no intermolecular hydrogen bonding. In (2) the two molecules in the asymmetric unit have very similar co-ordinates being related by x, $y + 0.31$, $z + 0.5$ for B $\longrightarrow$ A. The two benzene rings of the molecules A and B are thus essentially parallel with an angle of intersection of 7.0°. A packing diagram in the c projection which illustrates the arrangements of these two molecules is shown in Figure 3.

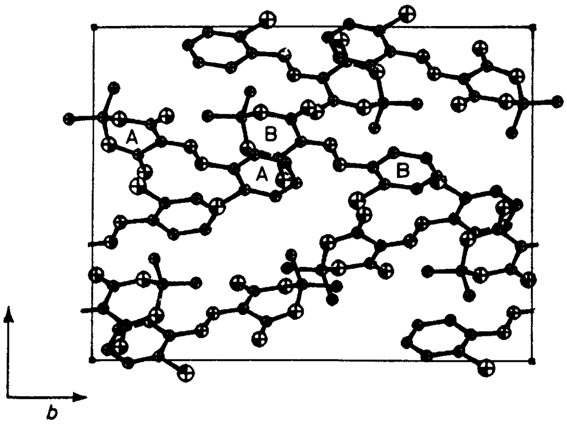


FIGURE 3 The unit cell of (2) in the c projection. Molecules A and B in the asymmetric unit are related by the transformation (x, $0.31 + y$, $0.5 + z$)

As in (1) there are no contacts less than the sum of van der Waals radii. Intermolecular distances in (1) and (2) $<$3.50 Å are given in Supplementary Publication No. SUP 23129 (21 pp.).*

EXPERIMENTAL

I.r. spectra were obtained using a Perkin-Elmer 580B spectrophotometer with samples either sandwiched as a mull (Nujol and hexachlorobutadiene) or as solutions (CCl_4) between caesium iodide plates. The n.m.r. spectra were recorded on a Bruker WH90 instrument (90 MHz) using $CDCl_3$ solutions with tetramethylsilane as an external standard.

The parent compound, Meldrum's acid, 2,2-dimethyl-1,3-dioxan-4,6-dione, was obtained following condensation of malonic acid with acetone in acetic anhydride in the presence of a trace amount of sulphuric acid.[12] The phenyl derivatives were similarly prepared using benzaldehyde.[13]

All the compounds listed in Table 1 were obtained as yellow, amber, or orange crystalline solids following direct coupling of Meldrum's acid, or phenyl derivative, with the

TABLE 4

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (1)

Atom	x	y	z
C(1)	4 655(8)	2 363(4)	5 929(4)
C(2)	3 817(7)	3 015(4)	5 178(4)
C(3)	2 757(7)	2 686(3)	4 219(3)
C(4)	2 505(7)	1 704(3)	4 005(3)
C(5)	3 377(7)	1 064(4)	4 788(4)
C(6)	4 395(8)	1 397(4)	5 733(4)
N(7)	1 437(6)	1 348(3)	3 042(3)
N(8)	1 548(5)	432(3)	2 840(3)
C(9)	428(7)	57(3)	1 998(3)
C(20)	771(7)	−961(3)	1 796(4)
O(22)	−522(5)	−1 385(2)	1 035(3)
C(13)	−2 387(7)	−961(3)	746(4)
O(12)	−2 207(5)	52(2)	523(2)
C(10)	−1 015(7)	581(3)	1 270(4)
O(21)	2 182(5)	−1 403(3)	2 199(3)
C(14)	−3 336(8)	−1 418(5)	−272(4)
C(15)	−3 386(8)	−1 086(4)	1 625(4)
O(11)	−1 213(5)	1 444(2)	1 271(3)
N(4)	1 901(6)	3 421(3)	3 456(3)
O(6)	677(6)	3 182(3)	2 686(3)
O(5)	2 446(7)	4 246(3)	3 603(3)

TABLE 5

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (2)

Atom	x	y	z
Cl(1A)	−388(2)	2 149(2)	6 563(3)
C(1A)	330(9)	369(7)	8 486(16)
C(6A)	917(9)	612(7)	9 511(13)
C(5A)	1 108(9)	1 297(6)	9 652(13)
C(4A)	740(7)	1 791(5)	8 751(11)
C(3A)	136(8)	1 532(6)	7 696(11)
C(2A)	−76(8)	826(6)	7 553(13)
N(7A)	925(7)	2 501(5)	8 833(10)
N(8A)	1 402(6)	2 767(5)	9 868(9)
C(9A)	1 555(7)	3 445(5)	9 940(10)
C(10A)	1 191(8)	3 956(6)	8 970(11)
O(11A)	663(7)	3 819(4)	7 990(10)
O(12A)	1 470(5)	4 633(4)	9 104(7)
C(13A)	2 272(9)	4 778(5)	9 961(11)
C(14A)	2 240(11)	5 545(6)	10 335(14)
O(22A)	2 213(6)	4 394(4)	11 282(7)
C(20A)	2 081(9)	3 684(6)	11 209(11)
O(21A)	2 307(6)	3 323(4)	12 175(8)
C(15A)	3 151(9)	4 552(7)	9 210(12)
Cl(1B)	−205(2)	−1 030(2)	1 343(3)
C(1B)	551(8)	−2 825(6)	3 167(14)
C(6B)	1 073(9)	−2 582(6)	4 323(13)
C(5B)	1 192(8)	−1 881(6)	4 581(11)
C(4B)	791(7)	−1 385(5)	3 636(11)
C(3B)	286(8)	−1 643(6)	2 515(11)
C(2B)	164(9)	−2 347(6)	2 309(14)
N(7B)	877(6)	−653(4)	3 896(9)
N(8B)	1 447(5)	−415(4)	4 846(9)
C(9B)	1 582(7)	259(5)	4 969(9)
C(10B)	1 068(8)	803(6)	4 156(12)
O(11B)	413(6)	672(4)	3 398(9)
O(12B)	1 349(5)	1 472(3)	4 337(8)
C(13B)	2 280(7)	1 600(5)	4 869(12)
C(14B)	2 309(9)	2 352(5)	5 366(13)
C(20B)	2 229(8)	493(6)	6 093(11)
O(21B)	2 564(6)	94(4)	6 949(7)
O(22B)	2 422(5)	1 171(4)	6 144(7)
C(15B)	3 005(9)	1 410(6)	3 782(11)

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TABLE 6

Distances (Å) and angles (°)

Molecular dimensions	(1)	(2A)	(2B)
C(1)–C(2)	1.376(7)	1.366(18)	1.336(18)
C(1)–C(6)	1.379(7)	1.362(19)	1.402(18)
C(2)–C(3)	1.391(7)	1.379(16)	1.361(16)
C(3)–C(4)	1.405(6)	1.407(15)	1.371(14)
C(3)–X *	1.468(6)	1.754(12)	1.751(11)
C(4)–C(5)	1.397(7)	1.371(16)	1.418(15)
C(4)–N(7)	1.411(6)	1.374(14)	1.414(13)
C(5)–C(6)	1.369(7)	1.333(17)	1.360(17)
N(7)–N(8)	1.313(5)	1.295(12)	1.294(12)
N(8)–C(9)	1.318(6)	1.305(13)	1.298(12)
C(9)–C(10)	1.442(6)	1.430(15)	1.480(15)
C(9)–C(20)	1.478(6)	1.487(15)	1.476(14)
O(11)–C(10)	1.215(5)	1.242(15)	1.205(14)
O(12)–C(10)	1.364(5)	1.350(13)	1.340(12)
C(13)–O(12)	1.456(5)	1.429(13)	1.442(12)
C(13)–C(14)	1.496(7)	1.497(15)	1.502(15)
C(13)–C(15)	1.490(7)	1.505(15)	1.503(15)
C(20)–O(21)	1.203(6)	1.186(13)	1.207(13)
C(20)–O(22)	1.339(5)	1.360(14)	1.315(13)
O(22)–C(13)	1.436(6)	1.448(12)	1.469(13)
N(4)–O(6)	1.227(5)		
N(4)–O(5)	1.219(5)		
C(2)–C(1)–C(6)	119.7(5)	120.5(11)	118.1(10)
C(1)–C(2)–C(3)	119.3(4)	117.3(11)	121.7(12)
C(2)–C(3)–C(4)	121.5(4)	122.9(10)	121.8(10)
C(2)–C(3)–X *	116.3(4)	119.6(8)	120.5(9)
C(4)–C(3)–X *	122.2(4)	117.7(8)	117.5(8)
C(3)–C(4)–C(5)	117.6(4)	115.9(9)	117.6(9)
C(3)–C(4)–N(7)	122.8(4)	120.0(9)	122.0(9)
C(5)–C(4)–N(7)	119.6(4)	124.1(9)	120.3(9)
C(4)–C(5)–C(6)	120.3(4)	121.7(11)	118.9(10)
C(1)–C(6)–C(5)	121.5(5)	121.7(12)	121.8(10)
C(4)–N(7)–N(8)	118.5(3)	121.7(9)	121.2(8)
N(7)–N(8)–C(9)	120.1(4)	120.7(8)	120.0(8)
N(8)–C(9)–C(20)	115.9(4)	115.2(9)	116.9(8)
N(8)–C(9)–C(10)	124.3(4)	124.9(9)	124.4(8)
C(20)–C(9)–C(10)	119.7(4)	119.7(9)	118.4(9)
C(3)–N(4)–O(6)	118.8(3)		
C(3)–N(4)–O(5)	118.9(4)		
O(6)–N(4)–O(5)	122.3(4)		
C(9)–C(10)–O(12)	116.4(4)	118.3(9)	116.2(9)
C(9)–C(10)–O(11)	124.9(4)	124.4(9)	123.5(10)
O(12)–C(10)–O(11)	119.0(4)	117.0(9)	120.3(10)
C(13)–O(12)–C(10)	117.0(3)	118.2(8)	118.7(8)
O(22)–C(13)–O(12)	109.6(3)	110.2(8)	108.7(7)
O(22)–C(13)–C(14)	105.8(4)	106.4(8)	105.3(8)
O(12)–C(13)–C(14)	106.3(4)	107.2(9)	107.1(8)
O(22)–C(13)–C(15)	109.2(4)	108.2(9)	109.5(8)
O(12)–C(13)–C(15)	110.3(3)	110.2(8)	110.8(8)
C(14)–C(13)–C(15)	115.5(4)	114.5(10)	115.1(9)
C(9)–C(20)–O(22)	116.3(4)	114.3(9)	116.8(8)
C(9)–C(20)–O(21)	124.9(4)	125.7(10)	123.0(9)
O(22)–C(20)–O(21)	120.2(4)	119.6(9)	118.5(8)
C(20)–O(22)–C(13)	117.8(3)	117.5(7)	118.8(7)

* X = Cl(1) in (2), X = N(4) in (1).

appropriate benzenediazonium salt. Compound (7) has been previously reported.[14,15]

2,2-*Dimethyl*-1,3-*dioxan*-4,5,6-*trione* 5-(2-*Nitrophenylhydrazone*) (1).—A mixture of *o*-nitroaniline (13.8 g) and concentrated HCl–H_2O (25 cm^3–25 cm^3) was warmed to give complete dissolution of the amine. The resulting solution was cooled (0 °C) and to it was added a chilled, aqueous solution of sodium nitrite (6.9 g in 15 cm^3). The solution of the resulting diazonium chloride $[C_6H_4(NO_2)N_2]^+Cl^-$ was filtered rapidly and added, with stirring, to a methanol (50 cm^3) solution of Meldrum's acid (14.4 g) and sodium acetate (16.4 g) maintained at an ice-cold temperature. The product separated as a brown solid which was collected and recrystallized from methanol–dichloromethane (charcoal) as amber needles, m.p. 164—165 °C.

Analytical and spectral data for this and other compounds are listed in Table 1.

Crystal Structure Determinations.—Both crystals were mounted on a Stoe STAD12 diffractometer and data was collected *via* variable width ω scan. Background counts were 20 s and the scan rate of 30 s degree^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. Absorption and extinction corrections were not applied. Both structures were solved without difficulty by the statistical method using Shel-X 76.[16] Both were then refined by full-matrix least squares with a weighting scheme that gave similar values of $w\Delta^2$ with ranges of F_o and $\sin\theta/\lambda$. For both structures this was $w = 1/(\sigma^2(F) + 0.003F^2)$ where $\sigma(F)$ was taken from counting statistics. Oxygen, nitrogen, and carbon atoms were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions. Those in methyl groups were refined as rigid groups; others were allowed to refine independently. Scattering factors were taken from ref 17. Calculations were made on the CDC 7600 computer at the University of London Computer Centre. Crystal data and refinement details are listed in Table 2. The least-squares planes calculations are given in Table 3. Atomic co-ordinates are given in Tables 4 and 5. Details of interatomic distances and angles are listed in Table 6. The anisotropic thermal parameters, observed and calculated structure factors, and hydrogen atom positions are given in SUP 23129.

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